Life assessment of cable paper using slow thermal ramp methods

R.J. Heywood[a], G.C. Stevens[b,*], C. Ferguson[a], A.M. Emsley[b]

[a]*National Grid plc, Kelvin Avenue, Leatherhead, Surrey KT22 7ST, UK*
[b]*Polymer Research Centre, School of Physical Sciences, University of Surrey, Guildford, Surrey GU2 5XH, UK*

Abstract

Rapid thermal ramp techniques are widely used to assess the properties of polymers (e.g. DTA, TGA, etc.). For certain types of processes, slow thermal ramp methods can assist the process of assessing the longer term ageing and life prediction of a polymeric material in complex environments. We will illustrate this in relation to recent work on the ageing of Kraft electrical insulation paper in insulating oil in relation to the longer term ageing of oil-filled power cables. In this case the key indicators of degradation were the degree of polymerisation (DP) and the production of gases capable of dissolving in the oil and measured by dissolved gas in oil analysis (DGA).

Kinetic modelling of the change in the DP value was used to generate Arrhenius parameters and cable life prediction calculations were made for a range of potential cable operating temperatures. The DP decreases with age and increasing temperature in a complex chain scission reaction. In parallel, above 150°C there is a rapid exponential increase in the evolution of CO, CO_2, CH_4, C_2H_4 and C_2H_6 with increasing temperature. We found that the rate of degradation of the paper/oil system is dependent on the degree of containment of the ageing experiments. These results indicate that containment effects and resulting pressure effects exist in this type of accelerated non-isothermal ageing experiment and should be accounted for in practical ageing environments.

The estimated life of the paper can be calculated if we assume that the Arrhenius parameters are representative of the entire degradation process and if suitable end-of-life criteria can be defined. It is also possible to calculate the average operating temperature of an electrical cable over a fixed time period, knowing the starting and finishing DP. Some of the attractions, potential weaknesses and use of the slow thermal ramp method in complex environments are also discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Life assessment; Cable paper; Thermal ramp method

1. Introduction

Kraft insulation paper impregnated with dodecyl benzene (DDB) oil is used as an electrical insulation medium in high voltage power cables. Kraft paper is used in preference to other paper types due to its high purity. It is prepared for the electrical industry to a specific electrical resistivity by ensuring there are no metal ions present within the pulp. The combination of paper and DDB produces a high dielectric constant and higher electrical breakdown strength than either component alone and therefore acts as an extremely good insulator. Kraft paper ages in service due to degradative operating stresses and this ultimately governs the life of a power cable. The paper deteriorates due to a combination of thermal, oxidative and hydrolytic degradation mechanisms. It is important to understand the kinetics involved in the degradation of

*Corresponding author. Tel.: +44-1483-259599; fax: +44-1483-259555; e-mail: g.stevens@surrey.ac.uk

the paper if we wish to calculate the expected lifetime of the cable insulation systems.

A slow thermal ramp (STR) method has been used by Camino et al. [1] to investigate the thermal ageing behaviour of electrical transformer paper-in-oil insulation. The potential value of using this approach is that it can quickly provide indicative kinetic parameters that could be used to scope the ageing behaviour of insulating materials and allow conventional constant temperature accelerated ageing conditions to be established more rapidly prior to longer term testing. In the main, accelerated ageing of insulating materials has been done isothermally. Emsley and Stevens [2] have reviewed the kinetic mechanisms attributed to the degradation of insulating paper/oil media and Emsley et al. [3] have developed a novel kinetic model to follow the degradation of Kraft paper oil system using the degree of polymerisation (DP) as the monitoring technique. This study was initiated to obtain an initial assessment of the kinetic parameters of ageing insulation by the application of STR methods to cable paper/oil systems. The STR technique provides results in hours which models real behaviour in years.

The degree of polymerisation has been used historically as a measure of the degree of paper degradation. Paper degradation studies have been based on the work of Kuhn et al. [4] in 1930 and then extended by Ekenstam [5] in 1936. The kinetics of degradation assumed a random first order chain scission and showed a direct relationship of reciprocal DP and time by approximating to zero order. The converse logic is now often applied that if degradation follows a reciprocal DP relationship then it must involve a random process.

The basis of Kuhn's and Ekenstam's work is that the molecular weight distribution is monodisperse and that every bond within the polymer is identical. Therefore, every bond has the same probability of breaking. Under these conditions,

$$\frac{1}{\mathrm{DP}_t} - \frac{1}{\mathrm{DP}_0} = k^* t. \tag{1}$$

This relationship has been used by a number of workers to describe paper degradation such as Bouvier [6], Fung [7], Major [8], Shafizadeh and Bradbury [9] and Hill et al. [10]. Emsley and Stevens [2] have shown that it holds for the majority of the data
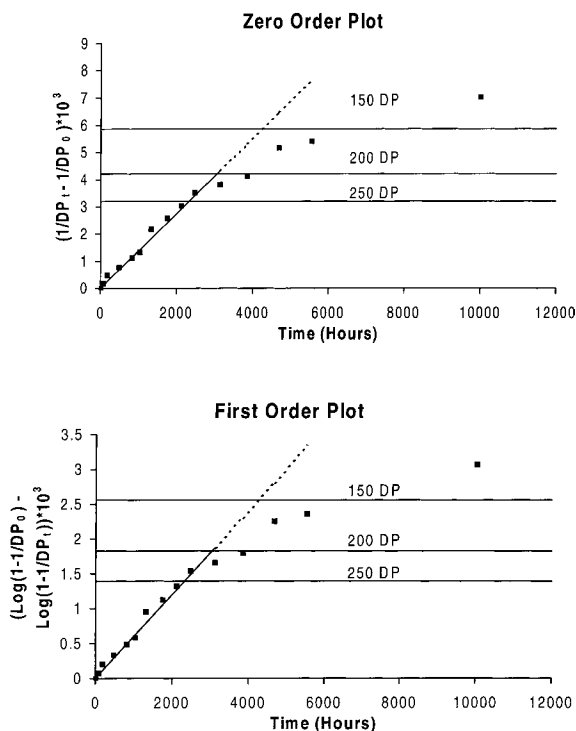

Fig. 1. The zero and first order kinetic plots of Kraft paper aged in air at 120°C. The broken lines are the projected zero and first order plots of the relationship held at low DPs.

available in the literature for degradation of Kraft paper under a variety of conditions.

However, work carried out by Heywood [11] shows that the first/zero order relationship does not hold at low DPs/high extent of reaction, see Fig. 1. It is at these low DPs that the strength of the paper becomes critical in calculating the remaining life and it is therefore important to be able to estimate them accurately. Emsley et al. [3] have developed a kinetic model that follows the DP/degradation relationship with more precision than either a first or zero order process. In this case,

$$\frac{\mathrm{d\,DP}}{\mathrm{d}t} = k_1 \mathrm{DP}^2, \tag{2}$$

$$\frac{\mathrm{d}k_1}{\mathrm{d}t} = k_1 k_2. \tag{3}$$

Combining and integrating these equations gives

$$\frac{1}{\mathrm{DP}_t} - \frac{1}{\mathrm{DP}_0} = \frac{k_{10}}{k_2} \left[1 - \mathrm{e}^{-k_2 t} \right], \tag{4}$$

where k_1 is the rate at which the DP degrades and k_2 is the rate at which k_1 changes, this allows the rate of degradation to change with time. The above equations can be used to describe the degradation process in terms of the reactivity of each inter-monomer bond. The first/zero order relationship assumes that each inter-monomer bond has the same probability of breaking (i.e. the same reactivity). In real terms a bond towards the end of the chain will experience different inter- and intra-molecular forces than one in the centre of the chain. Furthermore, physical hetero-geneity in the material means that not all the similar bonds experience the same degradative stresses. To back up this hypothesis high performance size exclusion chromatography of aged cotton paper [11] shows that the centre of the polymer chain breaks in preference to the chain ends. Fig. 1 shows how a first/zero order relationship deviates from the experimental DP data across the life of the paper compared to the Emsley/Heywood model.

2. Experimental conditions

Cable paper (Kraft paper from Tullis Russell Papermakers) was aged in the laboratory in dodecyl benzene (DDB) cable oil, provided by National Grid PLC.

Before all ageing experiments the Kraft paper (3 g) was dried overnight under vacuum (105°C) and the oil was dried and degassed by bubbling nitrogen through it for at least 1 h. The paper and oil (60 ml) were added to glass ampoules in a nitrogen glove box. The concentration of oxygen in the oil was measured at 0.4% and the water content of the paper was <0.1%. The ampoules were vacuum-sealed in one case and in another arrangement a bubbler attachment was used to allow the pressure to vent during ageing. Loading a known amount of water (20 ppm) into the oil was carried out in a second bubbler experiment. The samples were placed in a temperature-programmed oven that was set to increase at 1°C an hour over the temperature range 60–230°C. Samples were periodically removed from the oven and the paper and oil analysed to assess the degree of degradation. The degree of polymerisation (DP) was obtained from a revised viscosity method [14], which is replacing existing standard methods [12,13]. Dissolved gas in oil analysis (DGA) was carried out using existing standard methods [15].

3. Experimental results

As the oil/paper system ages with time and temperature, gases are evolved and dissolve (partially) in
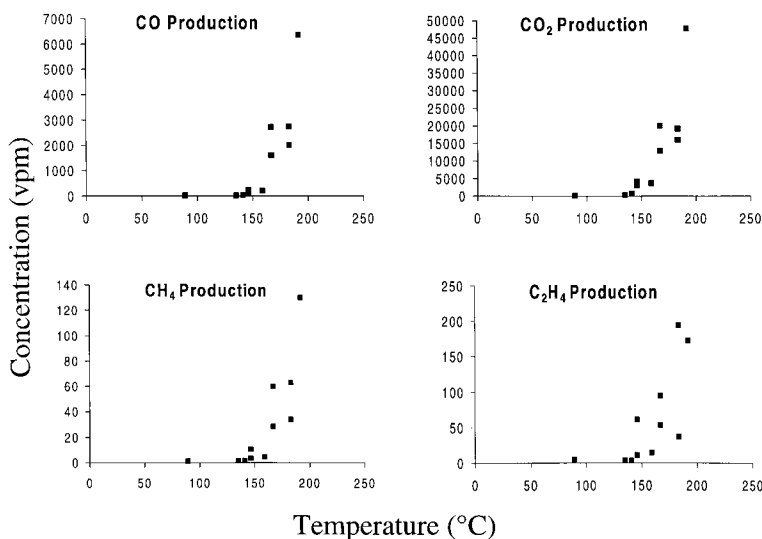

Fig. 2. Dissolved gas analysis of insulation oil from the ampoule experiment. As the temperature reaches 150°C there is a sharp increase in gas evolved during ageing.
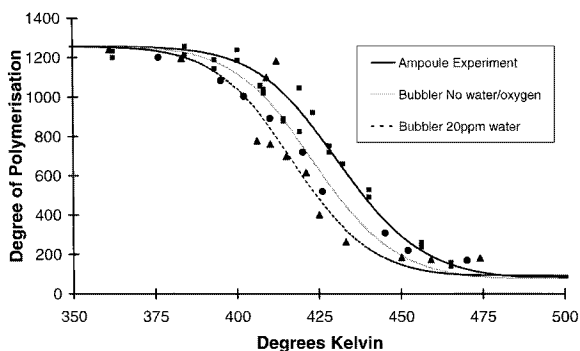
Fig. 3. The change in the degree of polymerisation with temperature. Black line is the ampoule experiment, the centre line is the dry bubbler experiment and the broken line is the water-loaded experiment.

the oil. Quantification of these gases (CO, CO_2, CH_4, C_2H_4 and C_2H_6) provides a measure of the oil/paper's thermal stability. DGA data was only available for the sealed ampoule experiment because the bubbler system used for other experiments allowed some of the gases to escape as degradation occurred. Fig. 2 shows the gas production for CO, CO_2, CH_4 and C_2H_4, illustrating a threshold temperature for gas production around 140–150°C.

Fig. 3 shows that the DP decreases during ageing, displaying an inverted sigmoid behaviour with increasing temperature in the STR technique. The DP decreases more rapidly for the water loaded experiment than the dry aged system and there appears to be a change in the degradation rate due to containment effects (i.e. between the ampoule and bubbler experiment).

4. Discussion

The DGA results indicate rapid degradation of the oil/paper system with the dominant evolved gases being CO_2 and CO. The DGA results from our first experiment show that there is a sharp increase in gas evolution as the temperature exceeds 140°C.

The DP of the insulation paper decreases with increasing temperature. The isothermal kinetic model already developed [3] was modified for a thermal ramp experiment and a commercially available computer program was used to iterate the kinetic parameters (ModelMaker version 3.0.1, Cherwell
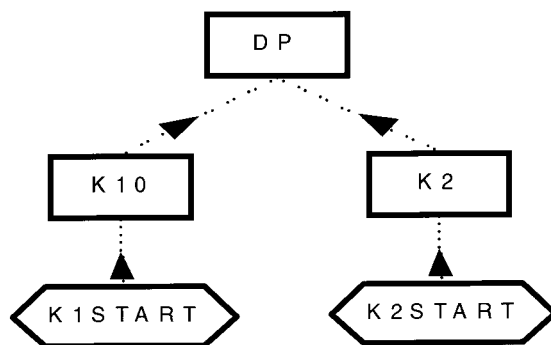

Fig. 4. The kinetic model set-up in ModelMaker.

Scientific) to determine the best fits to the experimental DP curves.

A flow chart illustrating the approach to the kinetic modelling is shown in Fig. 4. Each box contains a set of parameters and equations and the boxes are connected via "flows" to ensure that the mathematical calculations are linked. The procedure progressively increments the parameters in each kinetic process step to achieve the best overall fit to the experimental data for optimum values of k_{10} and k_2. The constants are influenced by temperature and therefore the Arrhenius equation is used to calculate activation energies for both k_{10} and k_2. The equations used in the simulation include the following.

Re-arranging Eq. (4), we can show that

$$k_1 = k_{10} - k_2 \left(\frac{DP_0 - DP_t}{DP_t DP_0} \right).$$

The rate of change of DP with temperature is required. Therefore,

$$\frac{d\,DP}{dT} = \frac{d\,DP}{dt}\frac{dt}{dT} = \frac{1}{\alpha}\frac{d\,DP}{dt},$$

where α is the heating rate. Using Eq. (2) and setting $\alpha = 1$ corresponding to 1°C per hour we obtain

$$\frac{d\,DP}{dt} = k_1 DP^2 \tag{5}$$

and using the rate constant expression for k_1 gives

$$\frac{d\,DP}{dT} = \frac{k_2(DP_0 - DP)DP}{DP_0} - k_{10}DP^2. \tag{6}$$

The rates k_1 and k_2 will change with time/temperature and boxes K1 and K2 (Fig. 4) account for this. There-

fore, box K1 and K2 contain, respectively,

$$\frac{dk_{10}}{dT} = \frac{k_{1_0} E_1 \cdot 1000}{R(T)^2}, \tag{7}$$

$$\frac{dk_{10}}{dT} = \frac{k_2 E_2 \cdot 1000}{R(T)^2}, \tag{8}$$

where E_1 and E_2 are the prescribed activation energies. The rates change with temperature and the starting value is dependent on the starting temperature of the experiment. Therefore using the Arrhenius equation one can derive a starting value of k_1 depending on the starting temperature of the experiment. Box K1START contains the following equation:

$$K1START = A_1 e^{-E_1/R(TSTART+273)}, \tag{9}$$

where A_1 is the temperature dependent pre-exponential factor (or frequency factor) and TSTART is in $°C$. The DP can therefore be modelled with respect to the change in temperature.

Table 1 summarises the calculated Arrhenius parameters, the activation energies were fixed at 113 and 111.5 kJ/mol for k_1 and k_2, respectively. These were calculated previously [11].

The kinetic data were used in conjunction with the DP data and possible end-of-life criteria to produce cable lifetime estimates for a range of potential cable operating temperatures. These are indicative lifetimes only and cannot be directly related to actual cable lifetimes because we do not know the precise failure mechanisms and how these may be related to the true end-of-life criteria for power cables. Similarly, the kinetic parameters have been calculated from data acquired largely above about 100°C and we have not yet established if they apply to the thermal ageing
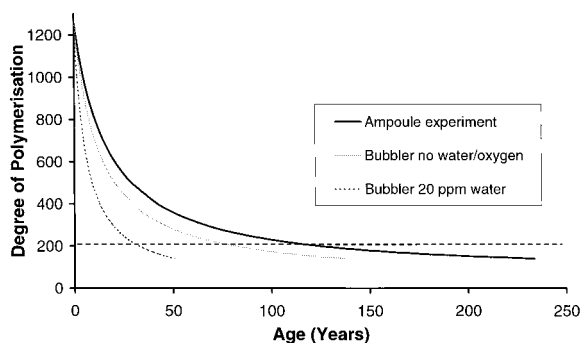

Fig. 5. Calculated isothermal ageing of cable paper at 60°C degree of polymerisation vs. time. Black line is the ampoule experiment, the centre line is the dry bubbler experiment and the broken line is the water-loaded experiment.

of paper insulation at cable operating temperatures, so the results should not be used at this stage to draw engineering conclusions.

The projected life of cable paper in a closed environment can be assessed from the DP ageing time plots shown in Figs. 5 and 6 for 60°C and 80°C isothermal ageing, respectively. For an end-of-life DP value of 200, the lifetime is estimated to be 125 years at a constant temperature of 60°C and 13 years at 80°C from thermal ramp experiments. The lifetimes increase significantly with lower end-of-life DP values. Fig. 7 shows, from the kinetic parameters modelled, how the DP would decrease for the three experiments if they were run isothermally at 60°C. The data can also be represented as a linear plot as shown in Fig. 7, and one can determine the life of the

Table 1
Summary of the calculated Arrhenius parameters

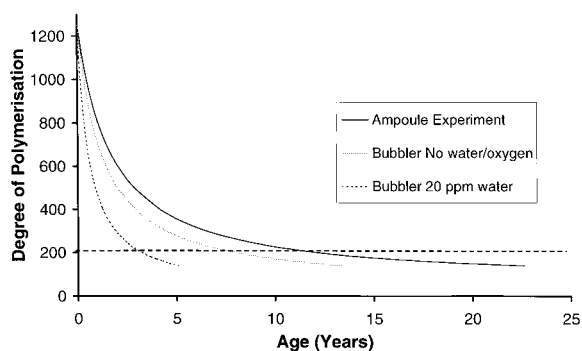| Experiment	Rate constant	Pre-exponential factor (A)
Sealed ampoule	k_1	2.673E+09
	k_2	1.639E+11
Bubbler no water/oxygen	k_1	3.723E+09
	k_2	1.621E+11
Bubbler 20 ppm water	k_1	8.215E+09
	k_2	5.704E+11

Fig. 6. Calculated isothermal ageing of cable paper at 80°C degree of polymerisation vs. time. Black line is the ampoule experiment, the centre line is the dry bubbler experiment and the broken line is the water-loaded experiment.
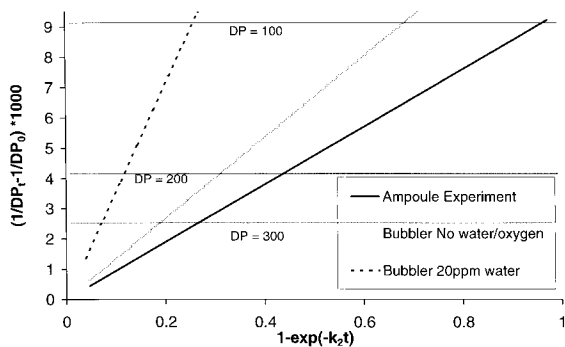
Fig. 7. Calculated isothermal ageing of cable paper at 60°C, linear relationship of DP with time. Black line is the ampoule experiment, the centre line is the dry bubbler experiment and the broken line is the water-loaded experiment.

paper depending on the end of life point chosen. For example if the cable paper aged (ampoule experiment) isothermally at 60°C, then the life would be approximately 65 years if 300 DP was used as the end of point criteria or the life would be greater than 250 years if 100 DP is used.

Figs. 3, 5, 6 and Table 1 show that the fully sealed ampoule experiment produces lower degradation rate constants. This could arise from the build-up of gas pressure as degradation proceeds or it could be due to more effective containment and exclusion of oxygen. Further work is planned to investigate pressure effects.

Alternatively, knowing the Arrhenius parameters, the starting DP of the paper and aged DP value from viscometry, one can calculate the isothermal or average operating temperature of a particular cable. Fig. 8
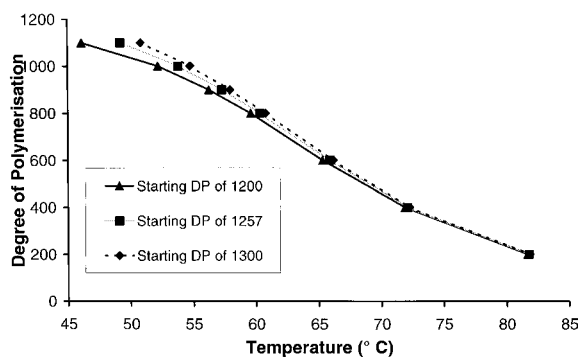

Fig. 8. The effect of cable operating temperature on the degree of polymerisation.

shows such a plot where a decrease in the aged DP value confers a higher operating temperature or power loading for the cable. If one assumes that the cable paper has a DP of 900 after 30 years and the initial DP is 1257, the constant operating temperature would be approximately 57°C; for a DP value of 200 it would be around 82°C.

5. Conclusions

The principal benefit of the slow thermal ramp (STR) method is that it provides relatively rapid insight into the ageing behaviour of complex ageing environments such as cable insulation ageing. We have shown that,

- Degradation of a cable paper/oil electrical insulation system can be monitored using degree of polymerisation (DP) of the paper determined by viscometry.
- The DP decreases with age and increasing the temperature increases the rate of degradation.
- Water accelerates the degradation rate of the paper/oil system in common with the trends observed for the ageing of paper insulation in power transformers [2,3].
- STR experiments in sealed and vented vessels suggest that a pressure effect may exist with increasing pressure slowing the rate of degradation.
- There is a rapid increase in gas evolution as the temperature of degradation exceeds 150°C in the slow thermal ramp experiment.
- The quantity of CO, CO_2, CH_4, C_2H_4 and C_2H_6 measured by dissolved gas analysis increases exponentially with increasing temperature above 150°C. We have not attempted to relate this to any potential cable failure criteria in the current work as the concentrations appropriate to either dielectric failure or mechanical failure are not well established. However, with further work, it may be possible to use DGA as an additional failure criterion in temperature regimes where gas evolution is rapid enough to cause local saturation of the oil. Under this condition, the formation of gas bubbles capable of supporting electrical discharges under the local fields available within the cable would be the first stage in dielectric failure of the cable.

Acknowledgements

The research was supported through a sub-contract with the National Grid PLC.

References

[1] G. Camino, S. Levchik, J. Schiers, W. Tumiatti, M. Avidano, On analytical and applied pyrolysis, Proceedings of the Conference on 12th International Symposium, Venice, 14–18 October 1996.
[2] A.M. Emsley, G.C. Stevens, Cellulose 1 (1994) 25–56.
[3] A.E. Emsley, R.J. Heywood, M. Ali, C.M. Eley, Cellulose 4(1) (1997) 1–5.
[4] W. Kuhn, K. Fruedenberg, W. Durr, F. Bolz, G. Steinbrunn, Ber. 63 (1930) 1510.
[5] A. Ekenstam, Ber. 69 (1936) 553.
[6] B. Bouvier, Rev. Gen. Elect. 79(6) (1970) 489–496.
[7] D.P.C. Fung, TAPPI 52 (1969) 319.
[8] W.D. Major, TAPPI 41 (1958) 530.
[9] F. Shafizadeh, A.G.W. Bradbury, J. Appl. Polym. Sci. 23 (1979) 1431.
[10] D.J.T. Hill, T.T. Le, M. Darveniza, T. Saha, Polym. Degn. Stab. 49 (1995) 429–435.
[11] R.J. Heywood, The degradation models of cellulosic transformer insulation, Ph.D. Thesis, 1997.
[12] ASTM 4243-86, Measurement of the average viscometric degree of polymerisation of new and aged electrical papers.
[13] IEC 450, Measurement of the average viscometric degree of polymerisation of new and aged electrical papers.
[14] A. Wilson, M. Ali, R.J. Heywood, DOBLE Conference, Boston, USA, April 1996.
[15] BS 61181/IEC 1181, Impregnated insulating materials. Application of dissolved gas analysis (DGA) to factory tests on electrical equipment, 1993.