Helena Latour-Słowikowska, Jerzy Słowikowski

CHANGES OF CHEMICAL REACTIONS AND THEIR INFLUENCE ON THE EVALUATION OF THERMAL ENDURANCE OF PAPER-OIL INSULATION SYSTEMS

1. Introduction

In current engineering it is accepted to express the relation between the life-time t_d of paper insulation and temperature by the following formula:

$$\lg t_{d,\Theta} = a - m\Theta \tag{1}$$

where: a, m - constants and Θ temperature in ^{o}C.

The characteristic quantity, easily determined from eq. (1), is the ageing temperature rise which brings about a twofold increase of the reaction velocity and in consequence a twofold reduction of the time t_d:

$$\Delta\Theta_R = \frac{\lg 2}{m} \tag{2}$$

It is well known $\Delta\Theta_R$ depends on the adopted criterion C_d of the end of life of the insulation: the more advanced ageing of the paper is admitted the smaller is the $\Delta\Theta_R$ value.

The studies of a sealed paper/oil system carried out at the LCIE [1] show that in the temperature range 100... 130°C, two ageing stages having different reaction velocity constants k_r appear. Moreover was stated the appearance of a reaction of a higher activation energy in the case of ageing at temperatures above 130°C, affecting the value $\Delta\Theta_R$, namely reducing it.

Dr. Helena Latour-Słowikowska - Electrotechnical Research Institute, Warsaw, Poland.
Ass. Prof. Jerzy Słowikowski - Research and Development Centre of Cable Industry "Energokabel", Ożarów Mazowiecki, Poland.

The studies carried out at the INSTYTUT ELEKTROTECHNIKI (IEL) alloved for a more precise determination of the character of reactions playing the main role in the ageing process. It was stated that the degradation process differs both from the aspect of its nature and its development in time, depending on the fact whether it takes place in amorphous cellulose regions or in quasi-ordered regions. The division of the ageing process into stages, recorded at the LCIE, has thus been physically confirmed. On the other hand, the appearance of simultaneous reactions which contribute to the ageing process more and more with the advancing degradation of cellulose and the temperature rise, has been stated.

The present report is an attempt to relate more closely the relation $\Delta\theta_R$ or rather the steepness of the paper life curve with the mechanism of the ageing process.

Let us remind that eq. (1) is an approximation of Bussing's formula:

$$lg\ t_{d,T} = A + \frac{B}{T} \tag{3}$$

where: A,B - constants,

T - absolute temperature in K, derived from Arrhenius law:

$$k_r = a_k\ exp - \frac{E_a}{RT} \tag{4}$$

where: k_r - reaction velocity constant,

a_k - constant,

E_a - activation energy,

R - gas constant, assuming that the ageing **process is the** consequence of the action of a single kind of reaction of a constant value E_a.

On the contrary to the characteristic (3) where E_a = const., the activation energy $E_{a,\theta}$ determined at different points of the curve (1) depends on temperature:

$$E_{a,\theta} = 2,3\ \frac{lg^2}{\Delta\theta_R\ .\ R}\ .\ \frac{1}{T^2} \tag{5}$$

It may be easily proved that $E_{a,\theta} = E_a$ only at $T = T_o$ in the neighbourhood of which the coefficients a and m of eq.(1) are determined by developing the function (3) into the Taylor's series.

2. Study of the nature of the reaction[x/]

The study was to determine the reactions decisive for the degradation
of mechanical features of the paper during the thermal ageing process.
Below are quoted the observations concerning the ageing of a sealed pa-
per/oil system:

- The reduction of the breaking resistance R_B of the paper takes pla-
ce, in the first place, owing to reactions appearing in quasi-ordered
cellulose regions, i.e. in intramicelar regions

- The reactions in quasi- ordered regions are preceded by the develop-
ment of radical reactions in amorphous (intramicelar) regions. This phe-
nomenon appears most distinctly in the ageing temperature range not ex-
ceeding $140^{o}C$. The consequence of the reactions taking in amorphous re-
gions is a relatively fargoing drop of the polymerisation degree d_p of
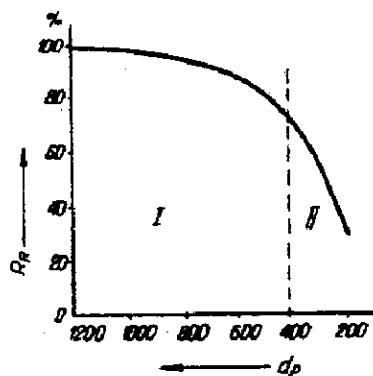the cellulose not followed by a fargoing change of R_B (see Fig.1).

Fig.1. Tensile strength as a function of polymerization degree

The reactions taking place in quasiordered regions are of composite
nature. Hydrolysis reactions and reactions known under the general term
of secondary reactions can be discerned. The hydrolysis reactions are
initiated by moisture particles formed in consequence of radical reactions

x/ The results of H.Latour-Słowikowska's doctor's thesis "Analysis of the
   thermal ageing process of electroinsulating papers in paper/oil systems
   with the use of the infrared spectroscopy. The thesis was defenced at
   INSTYTUT ELEKTROTECHNIKI in Warszawa in 1984.

taking place in amorphous regions and diffused from the latter region to intramicelar spaces. At temperatures up to and including 140°C the initiation of the hydrolysis reaction is preceded by a period during which the moisture particles, owing to their polar nature, build into the intermolecular lattice. This phenomenon reaches its maximum (see Figs 2a and b) following which the hydrolysis reaction is initiated.
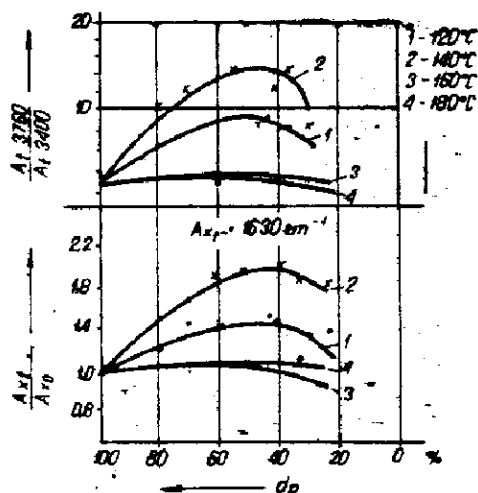

Fig.2. Changes in spectrum of cellulose II in the O - H stretching region (a) and of water band (b)

Above 140°C, the ageing temperature rise (records have been made at 160, 170 and 180°C) is accompanied with a decay of the formation of transient forms of bound water. The secondary reactions result in the formation of decomposition products of pyrolytic nature and of oxidation products. These reactions at temperatures up to and including 140°C and at a paper mass ratio ρ to the mass of oil not exceeding 0,08 appear when the degradation of the paper is far advanced.

Their contribution in the ageing process increases above 140°C. The action of the latter reactions in displayed at the earlier stage of ageing if the ratio ρ is increased and in the case of aged oil (the acid number N_A exceeding 0,1 mg KOH/g).

In the temperature range up to 180°C, even at the stage of a very ad-

vanced ageing of the paper ($d_p \approx 100$) the cellulose regions of the highest degree of order (crystallites) were not impaired (see Fig.3).
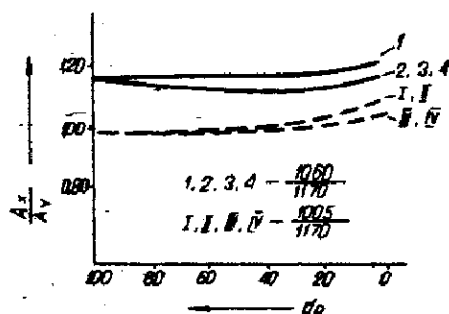

Fig.3. Absorbance Ratio
1 - A_{1060}/A_{1170}, 2 - A_{1005}/A_{1170}. Characteristic of cellulose I

3. Effect of the particular ageing stages on the lifetime characteristics

The discrimination of three regions of morphologic structure of cellulose: A - amorphous, B - quasi-ordered and C - ordered, was confirmed in the studies of Baah and Levin [2] as well as of Murphy [3]. They stated the reactions taking place in the particular regions differ essentially from the aspect at activation energy, namely: in the region A the value E_a does not exceed 34 kcal/mol, in the region B - 39 kcal/mol and in the region C it reaches about 60 kcal/mol.

In the case of paper aged in a sealed system and at temperatures up to 140°C the period of activity of radical reactions (I-st ageing stage - Fig.1) may be rather easily discerned. Assuming for simplicity reasons that during this period a single kind of reaction prevails, E_a was determined from the curve, $\gamma = \Upsilon(t)^{x/}$ at 120 and 140°C using eq (3). Its value amounted to 22,4 kcal/mol$^{xx/}$ being close to the value E_a determined from Fabre's curves [4] for an ageing criterion $dp_d = 0,8\ dp_o$ and at a

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x/ γ = 1000 ($\frac{1}{dp_o} - \frac{1}{dp_t}$) where dp_o - initial value, dp_t - value after an ageing period t.

xx/ The ratio of the mass of paper to that of oil is 0,08; the initial moisture content in paper was 0,5% per weight.

temperature of 120°C which amounts to about 23,5 kcal/mol ($\Delta\Theta_R = 9^{\circ}$C) and to the value quoted in other LCIE reports - 20 kcal/mol.

In the range up to and including 140°C it may be admitted that the first ageing stage lasts up to the moment $dp_t = 0,6\ dp_o$ is achieved. This is illustrated by the curve of the variation of the copper number N_{Cu} versus dp (Fig.4).
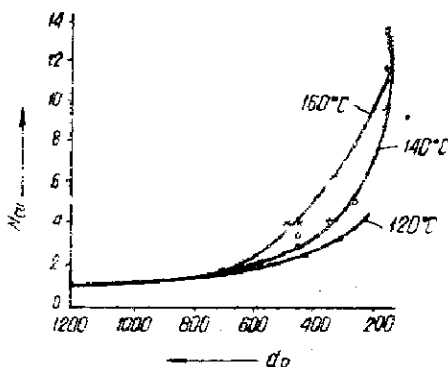

Fig.4. Changes of cupper number as a function of dp by different ageing temperatures

According to Fabre [4],if the ageing criterion C_d is changed from 0,95 dp_o to 0,60 dp_o the value $\Delta\Theta_R$ changes respectively from 9,2 to 8,4°C and the value E_a determined from eq (5) for 120°C from 23,1 to 25,3 kcal/mol, i.e. only by 10%.

In consequence, if a constant value E_a is admitted over the first ageing stage it does not give rise to a large error, though the appearance of reactions, proven e.g. by a small change of N_{Cu} (see Fig.4) cannot be excluded.

At an ageing criterion C_d admitting a high paper degradation degree ($C_d = 0,5\ R_{Ro}$ and below) due to at least two succesive reactions with different constants a_k (see eq.(4)) and different values E_a, the use of Büssing's formula looser its theorecital justification and the admittance, in this case, of $m = \Psi(C_d)$ becomes indispensible, the more that the reactions taking place in the region B are characterised by higher values E_a than those taking place in the region A (Fig.1).

The less severe is the admitted criterion of ageing C_d (e.g. $C_d = 0,1$ dp_o) the more important will become the role of in the degradation of cellulose of reactions taking place in the region B and the closer must be the value of E_a determined from eq. (3) or eq. (5) to the actual value E_a corresponding to the latter reactions. It is easy to prove that, for $\Delta\theta_R = 6^{\circ}C$ specified in the IEC Publication... for transformer insulation, $E_{ae} = 35,4$ kcal/mol at $120^{\circ}C$, hence, it is close to the energy ascribed to region B by the above quoted authors [2,3].

The mathematical model of the course of the reaction versus time and temperature becomes more and more complicated with the proceeding of the ageing process; account must be taken of the simultaneity of several reactions. The simplest mathematical model leads to a formula in which the function $t_d = f(T)$ in the system of coordinates ($\lg t_d$, $\frac{1}{T}$) is of curvilinear nature[x/]:

$$\lg t_d = A_c + \frac{E_1}{RT} - \ln\left[1 + \sum_{i=2}^{n} \frac{a_{ki}}{a_{k1}} \exp\left(-\frac{E_i - E_1}{RT}\right)\right] \qquad (6)$$

where: A_c - constant, $a_{k1}...a_{kn}$ - constants, $E_1...E_n$ - activation energies of particular reactions ordered from minimum to maximum values
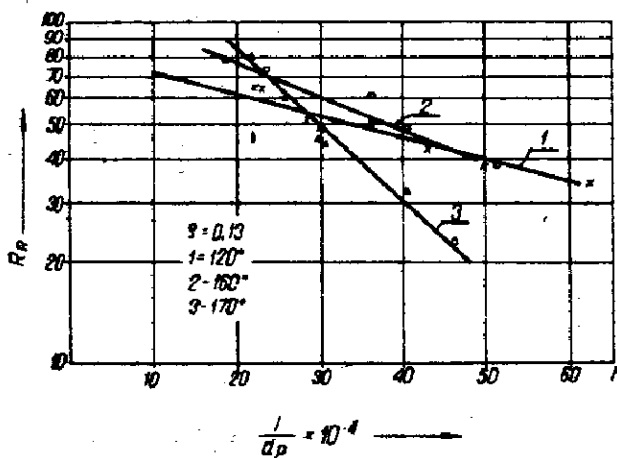

Fig.5. Relation between tensile strength (R_R) and $1/dp$ at various temperatures.

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x/ The formula is derived assuming

$$\frac{dc}{dt} = C \sum_{i=t}^{R} k_i$$

where: C-concentration of reagent. k_i-velocity constant of, i-reaction acting parallelly.

The curvature of the curve $\lg t_d = \varphi(\frac{1}{T})$ is distinct in the temperature range 120...160°C and for a more severe ageing criteria, i.e. $C_d = 0,5\ R_{Ro}$ (dp = 250). For instance, the values $\Delta\Theta_R$ determined by the authors for a system having $\rho = 0,08$ amount for the range 120...140°C - 8,2°C and in the range 140...160°C - 6,2°C.

The test results quoted in Chapter 2 display an ever more complicated paper degradation process when the ageing temperature is raised. For instance, above 140°C the contribution of oxidation reactions grows . This is displayed by changes of the IR band intensities at 1700...1720 cm^{-1} which can be ascribed to the formation of aldols [5].

The occurence of these reactions may affect the relation $R_R = \varphi(dp)$. In the temperature range 120...160°C and at $\rho = 0,08$ the authors did not record essential changes of the latter relation, though, a tendency to an increase of the inclination of the curve $\lg R_R = \varphi(\frac{1}{dp})$ was observed . (Fig.5). A well visible change of the curve $R_R = \varphi(dp)$ was observed only at 170°C.

The lifetime of paper as well as the inclination of the life curve are affected by the ratio ρ of the paper content to that of oil. At an ageing temperature of 120°C and an ageing criterion $C_d = 0,5\ R_{Ro}$ adopted the rise of the value ρ from 0,08 to 0,13 caused a drop of t_d by about 25% and a rise of ρ up to 0,28 - by about 70%. The value $\Delta\Theta_R$ in the range 120... 140°C was respectively: for $\rho = 0,08 - 8,2°C$, for $\rho = 0,13 - 8,8°C$ and for $\rho = 0,28 - 9,9°C^{x/}$.

4. Conclusions

- The degradation process of paper in a sealed system is due to several reactions having different velocity constants k_i - and different activation energies. The proceeding degradation as well as the raising of the ageing temperature are accompanied by an increased contribution of reactions characterised by larger activation energies.

- The dependence of m on the ageing criterion C_d is due to the change of activation energies and of velocity constants k_i of the reactions in course of the ageing process.

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x/ In most transformers ρ does not exceed 0,08.

The dependence of the inclination of the life curve on the ageing temperature, recorded by the authors in the proximity of $140^{\circ}C$, is to be ascribed to the simultaneous appearance of several reactions.

- The value of the coefficient m is affected by the relationship of the content of the mass of paper to that of oil. The ageing process of cellulose is accelerated in effect of the ageing of oil (acid number N_A exceeding 0,1 mg KOH/g).

- The important contribution of radical reactions in the initiation of the degradation of cellulose as well as the role played by amorphous regions display the effect on the life of paper which may be exerted by its morphologic structure and impurities.

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