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:

\[
\lg t_d, \Phi = a - m\Phi
\]  

where: \( a, m \) – constants and \( \Phi \) temperature in °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 \( t_d \):

\[
\Delta \Phi_R = \frac{\lg 2}{m}
\]  

It is well known \( \Delta \Phi_R \) 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 \( \Delta \Phi_R \) 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 \( k_\tau \) appear. Moreover, it 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 \( \Delta \Phi_R \), namely reducing it.
The studies carried out at the Institut Elektrotechniki (IIE) allowed 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 cel-
ulose regions or in quasi-ordered regions. The division of the ageing process into stages, recorded at the LCLA, has thus been physically con-
irmed. 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
$\Delta G_R$ 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:

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

where:
$A, B$ - constants,
$T$ - absolute temperature in K, derived from Arrhenius law:
$$k_T = k_0 \exp \left( \frac{E_a}{RT} \right)$$

where:
$k_T$ - reaction velocity constant,
$k_0$ - 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 con-
tant value $E_a$.

On the contrary to the characteristic (3) where $E_a = \text{const}$., the acti-
vation energy $E_{a,\Phi}$ determined at different points of the curve (1) de-
pend on temperature:

$$E_{a,\Phi} = 2,3 \frac{1}{\Delta \Phi_R \cdot R} \cdot \frac{1}{T^2}$$

It may be easily proved that $E_{a,\Phi} = E_a$ only at $T = T_0$ in the neigh-
bourhood 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

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 paper/oil system:

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

- The reactions in quasi-ordered regions are preceded by the development of radical reactions in amorphous (intramicellar) regions. This phenomenon appears most distinctly in the ageing temperature range not exceeding $140^\circ$C. The consequence of the reactions taking in amorphous regions is a relatively far-going drop of the polymerisation degree $d_p$ of the cellulose not followed by a far-going change of $R_B$ (see Fig.1).

![Diagram of tensile strength as a function of polymerization degree](image)

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.

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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 defended at INSTITUTE ELEKTROTECHNIKI in Warszawa in 1984.
taking place in amorphous regions and diffused from the latter region to intramicellar 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.

![Graph](image_url)

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 \( \rho \) 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 is displayed at the earlier stage of ageing if the ratio \( \rho \) 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-
Advanced ageing of the paper \((d_p\approx 100)\) the cellulose regions of the highest degree of order (crystallites) were not impaired (see Fig. 3).

\[
\begin{align*}
A_{1060}/A_{1170} & \quad \text{Characteristic of cellulose I} \\
A_{1005}/A_{1170} &
\end{align*}
\]

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 Bash 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 7.4 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 (1st 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, \(\gamma = \gamma(t)\) at 120 and 140°C using eq (3). Its value amounted to 22.4 kcal/mol, being close to the value \(E_a\) determined from Fabre's curves [4] for an ageing criterion \(d_p = 0.8\) \(d_p\) and at a

\[
\gamma = 1000 \left( \frac{1}{d_p} - \frac{1}{d_p'} \right) \text{ where } d_p \text{ - initial value, } d_p' \text{ - value after an ageing period } t.
\]

\(\gamma\) 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 ($\Delta \Theta_R = 9°C$) 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 $\varphi_{dp} = 0.6$ $\varphi_d$ is achieved. This is illustrated by the curve of the variation of the copper number $N_{Cu}$ versus $dp$ (Fig.4).

![Graph](image)

**Fig.4.** Changes of copper 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 $\varphi_d$ to 0.60 $\varphi_d$ the value $\Delta \Theta_R$ changes respectively from 9.2 to 8.4°C and the value $\varepsilon_a$ 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 $\varepsilon_a$ 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 successive reactions with different constants $a_x$ (see eq.(4)) and different values $\varepsilon_R$, the use of Büssing's formula looses its theoretical justification and the admittance, in this case, of $m = \Psi(C_d)$ becomes indispensable, the more that the reactions taking place in the region B are characterised by higher values $\varepsilon_a$ than those taking place in the region A (Fig.1).
The less severe is the admitted criterion of ageing $C_d$ (e.g. $C_d=0.1 \Delta p_{e}$) 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 $\Delta p_{e}=60^\circ C$ specified in the IEC Publication for transformer insulation, $E_a=35.4 \text{ kcal/mol at } 120^\circ C$, 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 $t_d = \gamma(T)$ in the system of coordinates $(\log t_d, \frac{1}{T})$ is of curvilinear nature $\chi$:

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

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

![Fig.5. Relation between tensile strength $R_b$ and $1/dp$ at various temperatures.](image)

$\chi$ The formula is derived assuming

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

where: C - concentration of reagent. $k_i$ - velocity constant of, i-reaction acting parallelly.
The curvature of the curve \( \lg t_d = \varphi \left( \frac{1}{T} \right) \) is distinct in the temperature range 120...160\(^\circ\)C and for a more severe ageing criteria, i.e. \( C_d = 0,5 R_n0 \) \((dp = 250)\). For instance, the values \( \Delta Q \) determined by the authors for a system having \( \rho = 0,08 \) amount for the range 120...140\(^\circ\)C = 8,2\(^\circ\)C and in the range 140...160\(^\circ\)C = 6,2\(^\circ\)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\(^\circ\)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 occurrence of these reactions may affect the relation \( R_n = \varphi(dp) \). In the temperature range 120...160\(^\circ\)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 \( \lg R_n = \varphi \left( \frac{1}{dp} \right) \) was observed (Fig.5). A well visible change of the curve \( R_n = \varphi(dp) \) was observed only at 170\(^\circ\)C.

The lifetime of paper as well as the inclination of the life curve are affected by the ratio \( \rho \) of the paper content to that of oil. At an ageing temperature of 120\(^\circ\)C and an ageing criterion \( C_d = 0,5 R_n0 \) adopted the rise of the value \( \rho \) from 0,08 to 0,13 caused a drop of \( t_d \) by about 25\% and a rise of \( \rho \) up to 0,28 - by about 70\%. The value \( \Delta Q \) in the range 120...140\(^\circ\)C was respectively: for \( \rho = 0,08 - 8,2^0\)C, for \( \rho = 0,13 - 8,6^0\)C and for \( \rho = 0,28 - 9,9^0\)C\(\times\).

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.

x/ In most transformers \( \rho \) 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 $0.7 \text{ mg KOH/g}$).

- 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.

References