

R E V I E W

THEORY OF EQUALIZATION OF THERMAL AGEING
PROCESSES OF ELECTRICAL INSULATING MATERIALS
IN THERMAL ENDURANCE TESTS
I: REVIEW OF THEORETICAL BASIS OF TEST METHODS
AND CHEMICAL AND PHYSICAL ASPECTS OF AGEING

Paavo Paloniemi

Oy Strömberg Ab,
Helsinki, Finland

ABSTRACT

In this series of three papers, the theory of equalized ageing processes is presented, to provide a wider theoretical basis than the conventional methods for accelerated thermal endurance tests of electrical insulating materials.

In Paper I, the chemical and physical aspects of ageing are reviewed. The present methods for thermal endurance testing are critically assessed. Basic principles of the equalized ageing processes are presented and a comparison is made of its theory with that of the conventional methods.

Papers II and III, the detailed theory of equalized ageing processes is presented with practical application to ageing tests of materials. Comparative test results with critical evaluation of the equality of the ageing processes in the accelerated physical ageing tests completes this series of papers.

1. INTRODUCTION

Present methods for testing the long-term thermal endurance of electrical insulating materials sometimes suffer from lack of reliability. Reasons for this are twofold: partly the narrow theoretical basis of the conventional methods, and partly the large dispersion of test results. Additionally, the total testing time per material may be up to two years, being considered unacceptably long in the constant flow of new thermally stable candidates for electrical insulating materials.

The need for a deeper knowledge of the chemistry and physics behind the ageing phenomena has arisen. It is hoped that this route would lead to the development of more reliable and quicker test methods.

In this paper, the theoretical basis of the conventional methods is reviewed. Basic chemical and physi-

cal phenomena associated with ageing are briefly described which build a background for the presentation of the theory of equalized ageing processes (EAP). This theory is proposed to serve as a wider theoretical basis for accelerated thermal ageing tests of materials. In the subsequent papers, we will present the detailed theory of EAP with its application principles for ageing tests, together with comparative test results on several materials.

It follows directly from the way of application of the EAP principles that the reliability is increased both on theoretical and practical grounds. In spite of the shortened testing time, the EAP method is not to be compared to the usual rapid thermal analysis methods like differential thermal analysis (DTA) and thermogravimetric analysis (TGA), which in fact are not thermal endurance test methods at all.

2. THEORETICAL BASIS OF THE CONVENTIONAL METHOD

In 1930, using a large number of ageing test results of transformer insulations, Montsinger [1] observed that ageing was a continuous exponential function of temperature, contrary to the previous belief [2].

In the 1940's, Büssing [3] and Dakin [4] realized the connection between ageing phenomena and the Arrhenius law of chemical reaction rates. In the following, we repeat the results of Dakin in a generalized form.

Assume that a significant property value P depends on a significant concentration quantity c in the material (e.g. end-group concentration or inverse molecular mass), so that

$$P = f_1(c) \quad (1)$$

where $f_1(c)$ is a single-valued function of c .

In a fairly general form the concentration c changes in a chemical reaction following the equation

$$\frac{dc}{dt} = k f_2(c, c_1, c_2 \dots) \quad (2)$$

leading to deterioration of the material. Here, k is the reaction rate constant, t time, and c_1, c_2 , etc. other concentrations affecting the reaction of c , e.g. according to a reaction equation

$$aC + a_1C_1 + a_2C_2 + \dots = bB + b_1B_1 + \dots \quad (3)$$

Functions f_1 and f_2 need not be determined for our purposes. (According to the law of chemical reaction rates, Reaction (2)

$$f_2 = c^\alpha \cdot c_1^{\alpha_1} \cdot c_2^{\alpha_2} \dots)$$

is assumed to be homogeneous, i.e. not affected by diffusion phenomena, and essentially irreversible.

The Arrhenius law gives expression to the reaction rate constant k as a function of temperature:

$$k = k_0 \exp(-E/RT) \quad (4)$$

with k_0 a constant, E the activation energy of the reaction in question, R the gas constant and T absolute temperature. As a consequence of Eqs. (1), (2), and (4), the time t_L to reach a certain property level P_L is

$$t_L = \frac{f_3(P_L, c_1, c_2 \dots)}{k} = t_0 \exp(E/RT) \quad (5)$$

with t_0 a constant during ageing, provided that the concentrations $c_1, c_2 \dots$ etc. and their reaction orders remain constant. Thus, on the conditions (1) and (2) the time to reach an end-point value (limit of serviceability) is also an exponential function of temperature, described by a straight line in the Arrhenius coordinates ($\log t, 1/T$). Equation (5) is valid for any order of reaction (2).

Based upon Eq. (5), a large amount of practical ageing testing work was performed in the 1950's and 1960's leading to standardization of the testing principles and test methods. The international IEC standard 216 [5] is here the basic document.

This is the theoretical basis of the conventional methods for testing the thermal endurance properties of electrical insulating materials today [5,6,22-25]. Already Büssing [3] and Dakin [4] were aware of the fact that if there is more than one significant reaction participating in the ageing process then Eq. (5) is no longer correct and the thermal endurance graph in Arrhenius coordinates is non-linear unless the activation energies of the reactions happen to be identical. Another cause for a non-linear behavior was found in diffusion-controlled reactions [6,7]. Non-linear behavior was frequently observed in practical testing work (e.g. [8,9]), making the extrapolation to lower temperatures for those materials uncertain.

Additionally, dispersion in the measurements of critical properties like breakdown voltage or in the determination of the time to reach the end-point value is often too large [10,11] to allow reliable extrapolation. Total testing time is unreasonably long, often taking from one to two years for a new material.

3. CHEMICAL BACKGROUND OF AGEING

The review of chemical ageing reactions presented here does not go very deeply in details. We refer to general presentations on the subject [13-16]. Our purpose is to describe the nature of ageing reactions to visualize the basis on which the theory of equalized ageing processes presented (in Section 5 and Papers II and III) is built.

Most chemical investigations on thermal deterioration processes of a material deal with thermal degradation reactions caused by temperature alone in vacuum or in an inert gas, with oxidative reactions caused by atmospheric oxygen (O_2) or ozone (O_3), or with hydrolytic reactions caused by water. Because most of the currently used solid electrical insulating materials are polymers, we confine ourselves to the degradation phenomena investigated in polymeric materials.

3.1 THERMAL DEGRADATION

High temperature alone may cause chemical changes in the material through thermal activation of reactions. These changes may be divided as

- depolymerization reactions which lead to breaking of the main chain
- crosslinking reactions between the chains
- reactions of the chain substituents

Usually, the reactions follow the free radical mechanism containing the following steps [15, p.567]. Initiation, at random, at chain ends or at a side group



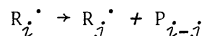
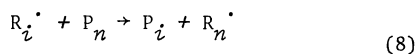
where P_n denotes the polymer molecule with n monomer units, and R_j a radical with j monomer units. Initiation is an important step in the reaction chain. Possible sources for initiation or radical formation can be heat, high energy radiation, UV radiation, mechanical stress, and some impurities which can act as chemical initiators [14, p. 427]. Radicals are very reactive species which continue the reaction path. Often there are weak links in the materials which are more susceptible to break and to form radicals than other bonds.

Initiation is followed by several types of reactions:

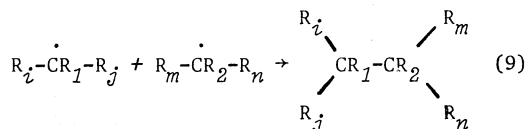
Radical preserving reactions, depropagation, being the reverse of polymerization,



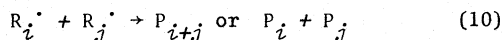
transfer reactions producing larger polymer fragments than monomer (P_1) and new radical types:



Termination reactions, crosslinking reactions



general radical recombinations



Possible combinations for thermal degradation reaction paths are numerous, because of the large number of

- ways of initiation producing different radicals,
- various bonds of different reactivities in the molecule,
- different ways of radical recombinations.

The investigations of thermal degradation mechanisms usually have been conducted at very high temperatures where the decomposition of the material is rapid (a matter of minutes), leading to a high percentage of volatile fractions. In such conditions some polymers depolymerize and mostly produce the monomer (e.g. polystyrene and polymethylmethacrylate), others degrade to fractions of higher molecular weight than the monomer (e.g. polyethylene). Crosslinking has also been observed, e.g. in polycarbonate [17]. A well-known example of the reactions of the substituents is the thermal degradation of polyvinylchloride where cleavage of HCl leads to double bond formation in the main chain and to material discoloration.

The several participating reactions in the thermal degradation are manifested in the large number of reaction products (even when the principal product is the monomer). Activation energies due to rate of evolution of different products may be similar or clearly different [16]. Therefore, it seems possible that at service temperatures quite different reactions may dominate than at ca. 200 K higher temperatures where the tests on degradation kinetics have been performed.

One conclusion can be drawn based on the reasoning presented above: if the thermal degradation reaction can be described with one activation energy at all, most probably it is valid for a narrow temperature range only and it should be determined just within that temperature range; this is a principle applied in the EAP method described later.

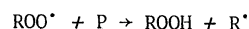
3.2 OXIDATIVE REACTIONS

The free radical reaction mechanism of oxidation was resolved only in the 1930's [15, p. 1055]. Oxidation actually "uses" the same free radicals as thermal degradation in the previous section, showing same type of reaction stages.

Initiation, as in Section 3.1

Propagation

Formation of peroxy radical and hydroperoxides



Thermal decomposition of hydroperoxides



We see that several new radicals are formed in consequence of one oxygen molecule being attached to a radical $R \cdot$. Oxidation reactions may therefore be autocatalytic, showing often an induction period with low oxidation rate (due to low initial number of peroxy radicals) until the autocatalytic process sets in. However, linear dependencies of hydroperoxide concentration on time and even autoretardant behavior also have been observed [14, p. 461].

Termination reactions, where the various types of radicals combine to form inert products, limit the hydroperoxide concentration to a stable value.

Like thermal degradation, oxidative reactions can lead to chain scissions and to crosslinking between chains, the net effect depending on which reactions dominate. Principal volatile products are water and carbon dioxide, but a large number of other oxygen-containing products have been observed [14, p. 458]. As in the previous section, it is to be expected that there are many reaction paths responsible for production of one or more compounds and oxidized groups. Even where oxidative reactions are concerned, it can be stated that if there is one dominating reaction, it may govern oxidation only in a narrow temperature range.

Oxidation may be catalyzed by several materials. Especially important for electrotechnology is that copper, or rather copper oxides, catalyze the oxidation [14, p. 476]. These effects are often ionic [14, p. 480].

One interesting feature in the oxidative reaction is that at sufficiently high oxygen concentration the reaction is of zero order, i.e. independent of oxygen concentration, whereas in the presence of low oxygen concentrations the rate of oxidation is a function of oxygen concentration [14, p. 476]. In the oxidation rate measurements performed in the author's laboratory [18,19], a dependence on oxygen concentration always was observed. This shows that under these conditions the oxygen concentration was in the "low" range. As a consequence it can be deduced that oxidation has not greatly reduced the concentration of radicals R^{\cdot} , i.e. thermal degradation reactions and oxidation can be taken to be independent of each other in those cases.

3.3 HYDROLYSIS

Water in a material may react with the material and cause degradation. This is called a hydrolysis reaction. Some amount of water is always present: in equilibrium with the surroundings the material contains absorbed water usually proportional to the relative humidity of the atmosphere and to the maximum water absorption of the material. Hydrolysis attacks mostly ester linkages ($R-CO-O-R'$ with R and R' parts of the polymer molecule). It is most important in condensation polymers like polyesters [15], polyamides, and polyimides [20].

Hydrolysis is a reversible reaction. However, in a solid material the reverse reaction may require diffusion of large molecules to a reaction site which may considerably slow the back esterification reaction [20,21].

Hydrolysis is an ion reaction, caused by hydrogen ions H^+ in neutral and acid conditions. It has been shown that in polyethylene terephthalate (PET) the rate of hydrolysis is proportional to $[H^+]\cdot[H_2O]$, the square brackets denoting concentrations of the corresponding groups [15, p. 556]. Because $[H^+]$ depends on the concentration of the acidic end groups $-COOH$ in PET, the hydrolysis rate is autocatalytic to some extent.

In linear polymers like PET, hydrolysis causes random scission of the polymer chain leading to rapid decrease of molecular mass. In a network polymer, e.g. anhydride cured epoxide resin which also contains a large number of ester links, splitting some of them has no overall observable effect on properties; this explains the well-known higher resistance to hydrolysis of these polymers.

4. PHYSICAL AGEING PHENOMENA

Physical phenomena which may be connected with thermal ageing are changes in molecular order, evaporation of some constituents (e.g. plasticizers) and diffusion of active gases into the material or of reaction products out of the material.

Changes in molecular order may have some effect on the ageing process in semi-crystalline and oriented polymers like PET, since reactions where some active gas participates (oxidation, hydrolysis) proceed at different rates in ordered and in amorphous regions; the reaction in the crystalline phase being usually much slower than in the amorphous one [15, p. 70].

When accelerated ageing tests are performed, the crystalline structure of the material should resemble that at service temperatures. Because the thermodynamic equilibrium between crystalline and amorphous phases depends on temperature, ageing tests of partially crystalline materials should be performed as near to the service temperatures as possible.

Evaporation of some constituent, e.g. plasticizer, is a straightforward phenomenon which similarly should be taken into account in the ageing tests.

Diffusion of active gases into the material is sometimes the rate-controlling factor in the ageing reaction [6]. When the reaction is diffusion-controlled, it is no longer homogeneous in the material and ageing proceeds at different rates at different distances from the surface of the material. If the ageing process is to be accurately reproduced in an ageing test, then even the dependence of the reaction rate on the distance from the surface of the material should be taken into account. This is not possible in the conventional ageing test methods, whereas in the EAP method it is possible for one diffusion-controlled reaction, as will be described in Paper II.

The effect of diffusion of the reaction products has not been investigated in connection with ageing tests. When the reversibility of thermal degradation and hydrolytic reactions are considered, then even these diffusion effects seem to be possible.

5. THE EQUALIZED AGEING PROCESS METHOD (EAP)

The considerations presented in Sections 3 and 4 describing the numerous possible paths of degradation reactions have shown that an exact reproduction of an ageing process in an accelerated ageing test is probably never possible. The simple theory of Dakin [4] described in Section 2 can be seen to be a crude first approximation, despite its success in testing many materials.

The theory of equalized ageing processes along with its practical implementation moves us a step closer to reproduction of the true ageing process. It will be shown that accurate reproduction is possible, if the activation energies of all reactions in the ageing process are known, if the reactions are sufficiently independent of each other and if by some means the acceleration factors of each reaction can be regulated to be identical.

For a sufficiently good approximation of the EAP, it has to be assumed that one of the thermal degradation reactions, one of the oxidation reactions and one of the hydrolytic reactions dominates the respective group of reactions. Then, a good reproduction of the service ageing process can be realized. The rates of oxidation and hydrolytic reactions can be regulated by appropriately changing the respective

gas concentrations in the atmosphere; in this way the acceleration factors of all three principal ageing reactions can be equalized. This process is visualized in Fig. 1. In a similar way, reactions caused by other possible active gases in the atmosphere (SO_2 , etc.) could be taken into account, provided that the corresponding reaction rates could be determined.

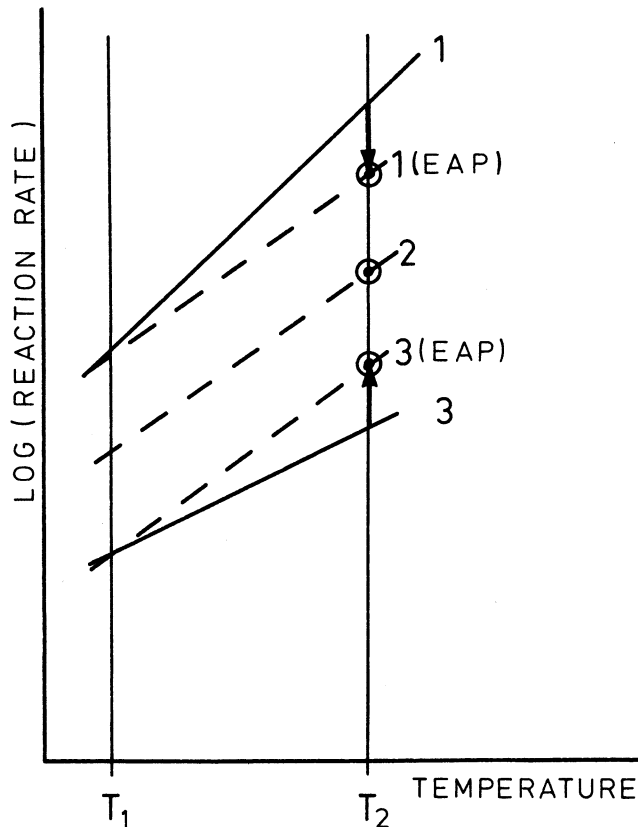


Fig. 1: Visualization of the principle of an equalized ageing process.

1. Rate of oxidation
 2. Rate of thermal degradation
 3. Rate of hydrolysis
- 1(EAP) and 3(EAP): Respective equalized reaction rates

The practical application of the EAP method consists of two different parts: Firstly, reaction rate measurements at temperatures ranging from expected service temperatures to suitable temperatures for accelerated physical ageing tests. Secondly, an accelerated physical ageing test at a temperature where the time to reach the serviceability limit is in the order of 300 to 3000 hours. This ageing test must be performed using a gas composition in the atmosphere such that the conditions for EAP are fulfilled. The ageing test result can be simply transferred to a lower reference temperature by multiplying the observed time to serviceability limit by the common acceleration factor of the ageing reactions (since all the ageing reactions are equally accelerated, there is only one acceleration factor applicable).

6. CONCLUSIONS

The ageing phenomena described in Section 3 show clearly the effects of various chemical ageing reactions and of diffusion (Section 4) on the ageing processes of materials. We can therefore conclude: Ageing processes consist of several chemical reactions (instead of one) which may have different activation energies and which all may have some effects on physical properties. Some reactions may additionally be diffusion-controlled. Obviously the shape of the physical life curve in Arrhenius coordinates obtained in the conventional ageing tests may correspond to none of the possible activation energies of the ageing reactions, and there is no reason to expect it to be linear. Thus, in the general case, Eq. (5) is not valid.

As an obvious consequence, the linear extrapolation of the life curve resulting from conventional ageing tests from test temperatures to lower temperatures will often be uncertain. Because of the lack of known mathematical relationship between life and temperature, a statistical estimation of confidence limits at lower temperatures is not possible.

The basic principles of the equalized ageing process method presented here and further treated in subsequent parts are based on a wider theoretical basis than the conventional thermal endurance test methods. However, the critical evaluation of the chemical ageing reactions shows that even when the EAP method is applied in practice, some limiting conditions must be fulfilled. Therefore, the EAP method should be considered as a further approximation towards the exact reproduction of the service ageing processes of electrical insulating materials.

REFERENCES

- [1] V. M. Montsinger, "Loading transformers by temperature," AIEE Transactions, Vol. 49, pp. 776-792, April 1930.
- [2] C. P. Steinmetz, B. G. Lamme, "Temperature and electrical insulation", AIEE Transactions, Vol. 32, pp. 79-89, 1913.
- [3] W. Büssing, Beiträge zum Lebensdauergesetz elektrischer Maschinen, Archiv für Elektrotechnik, Vol. 36, pp. 333-361, Nr. 6, 1942.
- [4] T. W. Dakin, "Electrical insulation deterioration treated as a chemical rate phenomenon", AIEE Transactions, Vol. 67, pp. 113-118, 1948.
- [5] IEC-Publ. 216, Guide for the deterioration of thermal endurance properties of electrical insulating materials.
Part 1(1974): General procedures for the determination of thermal endurance properties, temperature indices and thermal endurance profiles
Part 2(1974): List of materials and available tests.
- [6] T. Hino, "Accelerated thermal deterioration test of insulators in air and test results on enamelled wires," 1973 Annual Report, Conference on Electrical Insulation and Dielectric Phenomena, pp. 12-20.
- [7] F. Lebok, Die Dauerwärmebeständigkeit von Isolierlacken als reaktionkinetisches Problem, Deutsche Farben-Zeitschrift, Vol. 15, pp. 378-385, Nr. 9, 1961.
- [8] K. H. Wechsler, "Thermal endurance of rigid electrical insulation," IEEE Winter Power Meeting, New York 1964.
- [9] E. Moriame, "L'endurance thermique des isolants et systèmes d'isolation 2. Indice de température. Contrôle du vieillissement thermique de différents matériaux isolant. R.G.E., Vol. 83, pp. 452-466, No. 7/8, July/August, 1974.
- [10] H. Goldenberg, "Thermal endurance of polyester enamelled wires using twisted wire specimens," Progress report on statistical analysis of results, ERA-Report, No. 5016, 1963.
- [11] A. G. Day, "The Reliability of tests for the thermal evaluation of insulation," Conference on Electrical Insulation, Lancaster 1970.
- [12] E. L. Brancato, L. M. Johnson, "Thermal aging problems in electrical insulation, past, present, and future," Proc. of the 8th Electrical Insulation Conference, Los Angeles 1968, pp. 56-60.
- [13] Conley, "Thermal stability of polymers," Dekker, New York, 1970.
- [14] C. H. Bamford, C. F. H. Tipper, "Degradation of polymers," Vol. 14, Comprehensive Chemical Kinetics, New York 1975.
- [15] E. M. Fettes, "Chemical reactions in polymers," New York 1964.
- [16] S. L. Madorsky, "Thermal degradation of organic polymers," New York 1964.
- [17] A. Davis, J. H. Golden, "Competition between scission and crosslinking processes in the thermal degradation of a polycarbonate," Nature 206, 397 (1965).
- [18] P. Paloniemi, "Normalizing the experimental ageing process of an insulating material by changing the test atmosphere, 1973 Annual Report, Conference on Electrical Insulation and Dielectric Phenomena, pp. 3-11.
- [19] P. Paloniemi, P. Linström, "Application of the equalized ageing process method on thermal endurance testing of polyhydantoin film," IEEE Transactions on Electrical Insulation, Vol. EI-12, pp. 67-74, Febr. 1977.
- [20] N. A. Adrova, M. I. Bessonov, L. A. Laius, A. P. Rudakov, "Polyimides, a new class of heat-resistant polymers," Jerusalem 1969.
- [21] P. Paloniemi, "Thermal endurance tests on insulating materials in controlled atmosphere applying Isothermal Differential Calorimetry, Proc. of the Nordic Insulation Conference NORD-IS 72, Trondheim 1972.
- [22] Y. Saito, T. Hino, "A study of thermal deterioration of kraft pulps using a Mass Spectrometer," AIEE Trans. on Power App. and Syst., Vol. 78, pp. 602-606, 1959.
- [23] Y. Saito, T. Hino, "Study of thermal deterioration of enamelled wires by the mass spectrometer method," AIEE Trans. on Power App. and Syst., Vol. 71, pp. 653-657, Oct. 1960.
- [24] J. P. Randino, J. R. Andreotti, "Differential thermal analysis as applied to the deterioration of electrical insulation, Insulation, pp. 24-32, May 1963.
- [25] R. Blahnik, B. Hranickova, Z. Vavrinkova, M. Vlkova, "Kontrolle der Konstanz des Degradationsmechanisms in Abhängigkeit von der Intensität der einwirkenden Faktoren," Proc. of the 4th international symposium on "Modelling of Environmental Effects on Electrical and General Engineering Equipment", Liblice 1975, pp. 82-95.

Manuscript was received 5 October 1979, in revised form 22 August 1980.