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THE USE OF THERMAL ANALYSIS TO PREDICT THE THERMAL LIFE OF ORGANIC ELECTRICAL INSULATING MATERIALS

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Three different thermoanalytical methods are introduced as significant time-saving techniques in conventional life tests of some organic electrical insulating materials. DTA in cyclically alternated atmospheres of nitrogen and oxygen according to Randino and Andreotti, and TG analysis methods at different heating rates according to Flynn and Wall and to Broido were applied to two electrical insulations based on aromatic polyimide and epoxy resin. The activation energies obtained are compared with those derived from the slopes of the life-lines produced via conventional life tests. The assumptions necessary for applying the thermal analyses in these cases are discussed.

Electrical insulation can be subjected in service to many deteriorating factors simultaneously. These include oxidative atmospheres and elevated temperature, which cause deteriorating processes of thermal aging, degradation of mechanical and electrical properties, due to irreversible changes of chemical structure, and thus shortening of insulation service life.

The general equation characteristic of thermal life can be expressed [1] as

$$\log t_f = \frac{E}{2.303\,RT} + \log\left[\frac{g(P_f) - g(P_0)}{A}\right] \tag{1}$$

where t_f = time to failure, e.g. interval of observed physical property decay from initial value P_0 to failure criterion P_f,

E = activation energy of dominant chemical reaction,

R = universal gas constant,

T = absolute temperature, and

$g(P)$ = function of observed physical property, dependent on the reaction order.

Supposing a simple reaction degradation mechanism and the possibility of separation of the dominant degradation reaction, e.g. thermooxidation, $\log t_f$ vs. $\frac{1}{T}$ from (1) may be plotted as a straight line, whose slope is proportional to the activation energy E.

The conventional aging tests of insulating materials require long testing times and are too expensive. These tests are carried out by accelerated thermal aging at at least three elevated temperatures above the service temperature of the tested

insulating material. One measures a selected physical property, e.g. electrical breakdown strength, in selected time intervals until this property decreases during aging at different temperatures to the relevant failure criterion. By plotting the obtained data t_f *vs.* $\frac{1}{T}$ in semilogarithmic coordinates and applying regression analysis, we can obtain the linear life-line; and thus, through extrapolation from test temperatures down to the service temperature, we can predict the thermal life or endurance of the tested electrical insulation.

Significant acceleration of thermal life estimation can be achieved by using time-saving thermoanalytical techniques to determine, under specific simplifying conditions, the life-line slope $\frac{E}{2.303\,R}$ directly.

Randino and Andreotti [2] suggested a modified DTA method, which is suitable for organic insulations and allows the separation of the supposed dominant thermooxidative reaction of thermal aging when carried out over a sufficiently wide temperature range in cyclically alternated dynamic atmospheres of nitrogen and oxygen. During the cyclic injection of oxygen into the DTA cell there is a temporary increase in ΔT (thermooxidative peaks) over the nitrogen baseline, which is related to the internal chemical degradation. In the temperature range in which the thermooxidation progresses, the following equation is valid for the enthalpic changes:

$$\frac{\Delta H}{C_s} \cdot \frac{K \cdot m^n}{m_0} = \frac{\mathrm{d}(\Delta T)}{\mathrm{d}t} + C \cdot \Delta T \qquad (2)$$

where ΔH = total heat of reaction,
C_s = total heat capacity of sample holder and its content,
$K = A \cdot \exp\left(-\frac{E}{RT}\right)$ = Arrhenius reaction rate,
A = Arrhenius preexponential constant,
E = activation energy,
R = gas constant,
T = absolute temperature,
m = number of unchanged active moles during the thermooxidation,
m_0 = initial number of active moles,
n = order of reaction,
ΔT = amplitudes of thermooxidative peaks over the nitrogen baseline, and
C = constant.

At low heating rate $\frac{\mathrm{d}(\Delta T)}{\mathrm{d}t}$ may be neglected for sufficiently large ΔT and thus Eq (2) represents in log ΔT *vs.* $\frac{1}{T}$ coordinates a straight line with slope yielding the activation energy E.

Other methods, allowing essential shortening of thermal life tests, are derived

from the TG analysis technique. The checked physical property, characterizing the functionability of insulation, can also be a weight loss.

Flynn and Wall [3] proposed a method for obtaining the activation energy from more TG curves of the tested material through analysis carried out at different heating rates. They start with the supposition of the validity of the derived relationship:

$$\log t_f = \log \frac{E}{\beta R} + \log p\left(\frac{E}{RT_f}\right) + \frac{E}{2.303\, R} \cdot \frac{1}{T} \tag{3}$$

where β = heating rate,

T_f = absolute temperature of decreasing of initial weight ω_0 to failure criterion ω_f, and function

$$p\left(\frac{E}{RT}\right) = \frac{RT}{E} \cdot \exp\left(-\frac{E}{RT}\right) - \int_{E/RT}^{\infty} \frac{RT}{E} \cdot \exp\left(-\frac{E}{RT}\right) \mathrm{d}\left(\frac{E}{RT}\right). \tag{4}$$

Hence, by application of TG to the tested material at different heating rates it is possible, with a selected constant failure criterion (e.g. 5% of weight loss), to derive the respective values of E. From relation (3) it results that the $\log \beta$ *vs.* $\frac{1}{T}$ plot is linear, with a slope proportional to the activation energy. As was pointed out by Toop in [1], the heating rate β must be sufficiently low.

The value of the activation energy can be obtained from only one TG curve at one selected heating rate β. The method introduced by Broido [4] is based on the approximation that for weight losses up to 13% it is assumed that a first-order degradation reaction occurs and that the activation energy is independent of the heating rate. The general equation for the TG curve becomes according to Broido [4]:

$$\log \ln \frac{1}{\omega} = \log \frac{E \cdot A}{R \cdot \beta} + \log p\left(\frac{E}{RT}\right) \tag{5}$$

where ω = weight of tested insulation,

A = Arrhenius constant, and

$p\left(\frac{E}{RT}\right)$ = function defined by (4).

Since $\log p\left(\frac{E}{RT}\right)$ in the range of commonly-used activation energies and temperatures is nearly linear with $\frac{1}{T}$ [1], the relation (5) in $\log \ln \frac{1}{\omega}$ *vs.* $\frac{1}{T}$ coordinates gives a straight line with slope proportional to the activation energy.

Experimental

Thermoanalytical methods were carried out on test samples of two different insulating materials:

I. Kapton F*, an electrical wire insulation consisting of an aromatic polyimide based on a pyromellitic acid dianhydride and aromatic diamine and covered with sheets of Teflon FEP, a copolymer of tetrafluoroethylene with hexafluoropropylene;

II. Relanex**, a high-voltage insulation based on reconstructed mica paper, glass textile and modified epoxy resin.

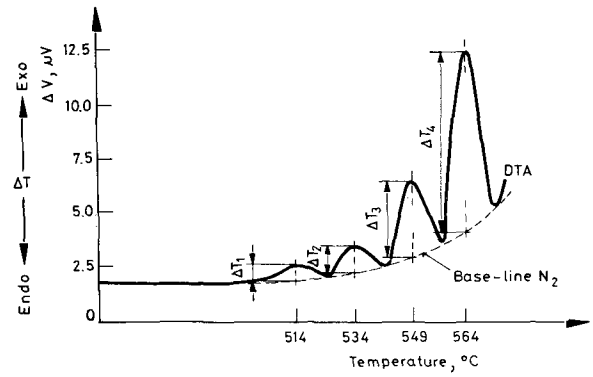

Fig. 1. DTA-curve of Kapton F (material I) in cyclically alternated atmospheres of nitrogen and oxygen

DTA and TG curves were obtained separately with a Stanton Redcroft*** modular thermoanalytical system consisting of a DTA 671 B low-temperature analyzer, a DTA 674 high-temperature analyzer and a TG 770 thermobalance with a Servoscribe 2S line recorder. DTA was carried out at a heating rate $\beta = 1°$/min in flowing nitrogen, then, starting from 500° (material I) and 180° (material II) cyclically alternated with oxygen injections in cycles of 3 min oxygen/7 min nitrogen. The flow rate for both media was 20 ml/min.

Test samples were in foil disc from in a platinum crucible (material I) and in powdered form, sieved to a granulation less than 160 mesh, in an aluminium crucible (material II). The reference material was Stanton Redcroft calcined alumina. The initial weight of both test samples was 10 mg. The DTA curves obtained are reported in Fig. 1 for material I and in Fig. 2 for material II.

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*** Stanton Redcroft, Copper Mill Lane, London, SW 17 OBN, England.

TG analyses were carried out in a platinum crucible in a dynamic oxygen atmosphere with a flow rate of 50 ml/min at heating rates $\beta = 1, 2, 3$ and $5°$/min. Initial sample weights were 6 and 10 mg for materials I and II, respectively. In Fig. 3 there is an example of a TG curve for material I, and in Fig. 4 for material II at a heating rate $\beta = 2°$/min until the weight loss was 20%.

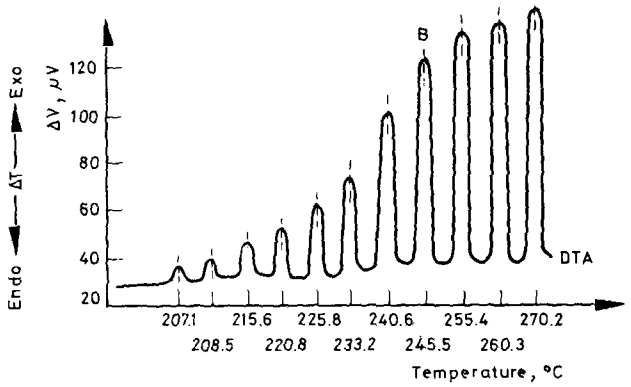

Fig. 2. DTA-curve of Relanex (material II) in cyclically alternated atmospheres of nitrogen and oxygen

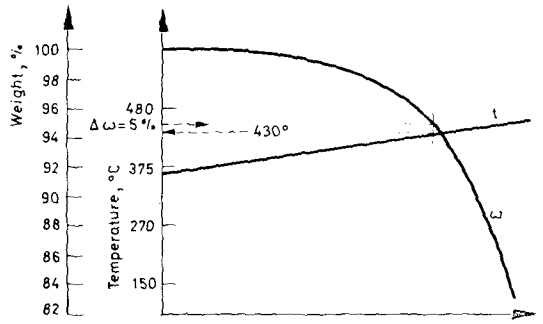

Fig. 3. TG-curve of Kapton F (I)

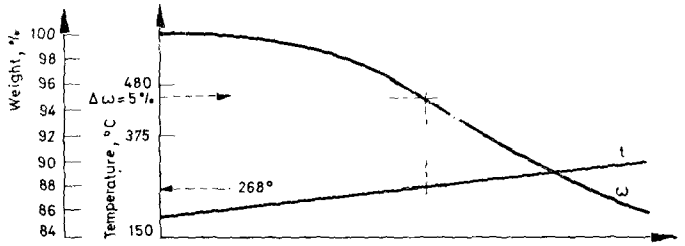

Fig. 4. TG-curve of Relanex (II)

Results and discussion

The log ΔT plot from DTA analysis, log β *vs.* $\frac{1}{T}$ for the constant failure criterion weight loss $\Delta\omega = 5\%$, and the log ln $\frac{1}{\omega}$ plot *vs.* $\frac{1}{T}$ until the weight loss $\Delta\omega = 16\%$ from TG analysis data of material I are reported in Fig. 5. The reciprocal scale of absolute temperature T is plotted reversally and calibrated in degree^{-1}. In Fig. 6 there are analogous plots for material II.

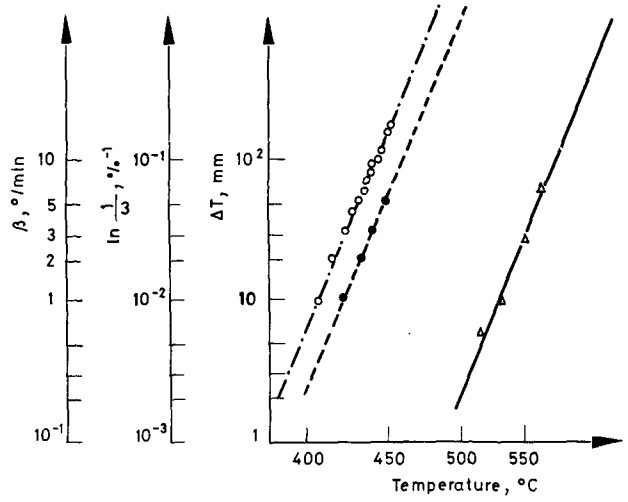

Fig. 5. log ΔT, log β and log ln $\frac{1}{\omega}$ versus $\frac{1}{T}$ plots of Kapton F (I) —·— ln $\frac{1}{\omega}$ (TG), — — — β (TG), ——— ΔT (DTA)

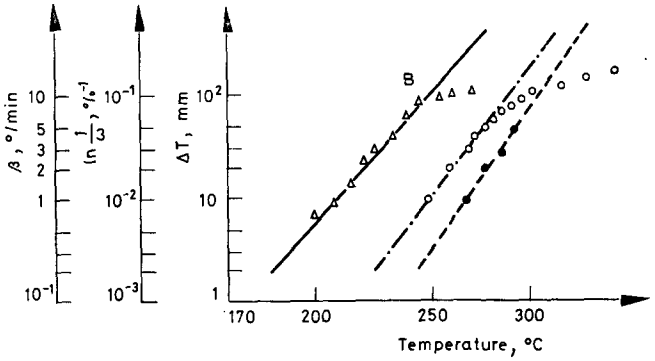

Fig. 6. log ΔT, log β and log ln $\frac{1}{\omega}$ versus $\frac{1}{T}$ plots of Relanex (II) —·— ln $\frac{1}{\omega}$ (TG), — — — β (TG), ——— ΔT (DTA)

The assumptions of possible substitution of plots of log ΔT, log $\Delta\beta$ and log $\ln\frac{1}{\omega}$ *vs.* $\frac{1}{T}$ by regression straight lines with slopes proportional to the activation energy are particularly linear life-lines, a simple first-order reaction mechanism and, in the case of DTA in cyclical flowing atmospheres, assumed degradation by a pre-

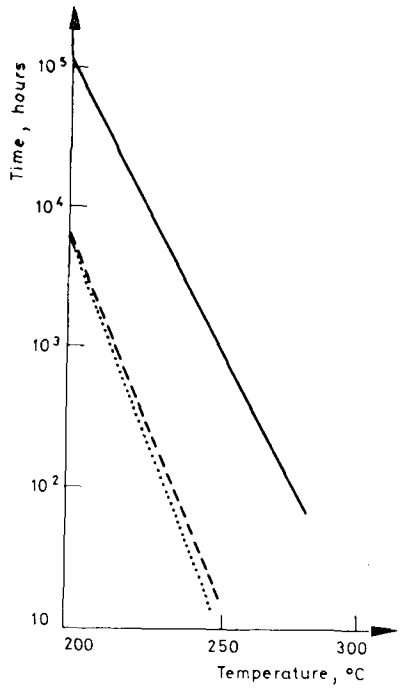

Fig. 7. The comparison of slopes of regression lines obtained by thermal analysis and by conventional ageing tests for Kapton F (I) ——— V_b(T), — — — β (TG) $\equiv \ln\frac{1}{\omega}$ (TG), · · · · ΔT (DTA)

dominant thermooxidative reaction. Material I, as results from the practically identical slopes of plots in Fig. 5, fulfils these conditions. In contrast, material II, an insulating system with epoxy resin as organic component, which mainly undergoes thermal aging, obviously exhibits a more complex degradation mechanism. As results, for example, from the plot log $\ln\frac{1}{\omega}$ *vs.* $\frac{1}{T}$ in Fig. 6, characteristic deviations from a linear plot start from a weight loss $\Delta\omega \doteq 5\%$. The shape of this plot justifies the assumption of involving a second reaction order in the degradation mechanism [5]. This is confirmed by the smaller slope and thus by a smaller activa-

tion energy, obtained with DTA of material II in the cyclically alternated atmospheres of nitrogen and oxygen (see Fig. 6). Thermooxidation thus obviously contributes only partially to the total degradation of material II. The deviation of the log ΔT plot from a straight line (see points B in Figs 2 and 6) corresponds to the thermooxidative reaction.

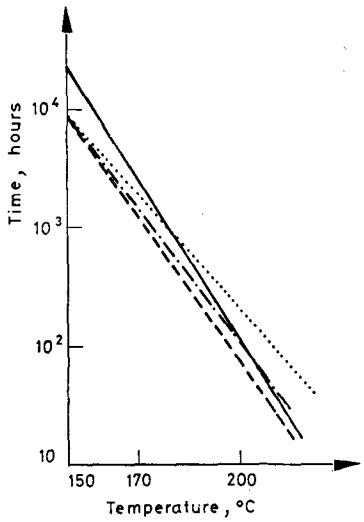

Fig. 8. The comparison of slopes of regression lines obtained by thermal analysis and by conventional ageing tests for Relanex (II). —— V_b (II); —·— $\ln\frac{1}{\omega}$ (TG); — — — β (TG); ····· ΔT (DTA)

Figures 7 and 8 compare the slopes of the regression lines of the plots in Figs 5 and 6, obtained by thermal analysis and plotted from an arbitrarily chosen point, with the slopes of life-lines for materials I and II obtained with conventional aging tests with a selected failure criterion of 50% loss of electrical breakdown voltage V_f. The life-line I in Fig. 7 is taken from reference [6]. Life-line II in Fig 8. was determined by conventional life tests on statistical sets of test samples – insulated test bars with insulating tape II up to 2 mm thickness, processed under current technological conditions and altered at 4 different temperatures, 155, 170, 185 and 200°. As follows from Fig. 7, activation energies obtained by thermal analysis of material I approach the activation energy value derived from the slope of the life-line. This confirms the corectness of the selection and correlation of the failure criteria of 50% electrical breakdown voltage and 5% weight loss, recommended by the IEC Publication [7].

In the case of material II (see Fig. 8) the activation energy value derived from the slope of the life-line is greater than the activation energies found by thermal analysis methods (Fig. 6).

It is necessary to emphasize that the life-line in Fig. 8 also covers up the influence of the technology of processing of the insulation system. It is questionable if the selected values of the failure criteria are justified. There exist no international recommendations in this case.

From the distribution of the life characteristic points, it can be deduced that the life-line is nonlinear. This confirms the assumption of a more complex degradation mechanism of epoxy resins.

Conclusion

The application of thermal analysis in thermal endurance and life tests represents a significant time-saving technique in justified cases of some organic insulating materials under conditions when the above-presented assumptions are fulfilled. The time necessary for evaluation of the thermal life is thus limited by the necessity of determination of the life-line intercept and of obtaining one point by a conventional aging test at the highest possible test temperature.

It must be emphasized here that, due to the insufficient resolution of the applied thermoanalytical methods, it is possible to obtain activation energies of assumed degradation reactions in higher temperature ranges than relate to the service temperature range of the insulations checked. Thus, one takes the risk of analyzing a completely different degradation mechanism in the different temperature ranges.

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RÉSUMÉ — On présente trois méthodes thermoanalytiques différentes qui permettent de réaliser un gain de temps important lors de l'examen conventionnel de la durée de vie de quelques isolants électriques organiques. L'analyse termique différentielle en atmosphères cycliquement alternées d'azote et d'oxygène, suivant Randino et Andreotti, et la thermogravimétrie avec différentes vitesses de chauffage, suivant Flynn et Wall et Broido, ont été appliquées à deux isolants électriques à base de polyimide aromatique et de résine époxy. Les énergies d'activation obtenues sont comparées à celles déduites de la pente des lignes de vie, obtenues par des examens conventionnels de durée de vie. Les approximations nécessaires pour appliquer l'analyse thermique à ces différents cas sont discutées.

ZUSAMMENFASSUNG — Drei verschiedene thermoanalytische Methoden werden als wesentlich zeitsparende Techniken bei der üblichen Prüfung der Lebensdauer einiger organischer elektrischer Isoliermaterialien beschrieben. DTA in zyklisch wechselnden Atmosphären von Stickstoff und Sauerstoff nach Randino und Andreotti und Methoden der TG-Analyse bei verschiedenen Aufheizgeschwindigkeiten nach Flynn und Wall und Broido wurden bei zwei elektrischen Isolierstoffen auf aromatischer Polyimid und Epoxyd-Harz Basis eingesetzt. Die erhaltenen Aktivierungsenergien werden mit den aus der Neigung der an Hand konventioneller Lebensdauertests erhaltenen Lebenslinien verglichen. Die nötigen Voraussetzungen zur Anwendung der Thermoanalyse in diesen Fällen werden erörtert.

Резюме — Введены три различных термоаналитических метода существенно ускоряющие обычную проверку продолжительности жизни некоторых органических электроизоляционных материалов. К двум электроизоляторам, на основе ароматического полиимида и эпоксисмолы, были применены ДТА в циклически чередующихся атмосферах азота и кислорода, согласно Рандино и Андреотти, а также ТГ методы анализа при различной скорости нагрева, согласно Флинна и Валла, а также Броидо. Полученные энергии активации сопоставлены с теми, что были получены обычными тестами продолжительности жизни из наклонов линий продолжительности жизни. Обсуждены необходимые допущения для применения термического анализа в таких случаях.