

# **HISTORICAL REVIEW ON RESEARCH OF KINETICS IN THERMAL ANALYSIS AND THERMAL ENDURANCE OF ELECTRICAL INSULATING MATERIALS**

## **II. Thermal endurance evaluation by thermal analysis**

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### **Abstract**

Thermal analysis techniques, such as thermogravimetry, differential thermal analysis and evolved gas analysis, have been applied to thermal endurance evaluation of electrical insulating materials of high polymers, which are used for a long time at a relatively high operating temperature. Various attempts have been made to estimate the life time of the materials at the operating temperature by thermal analysis and a calorimetric method. These are critically described in this review paper.

**Keywords:** activation energy, DTA-TG, EGA, hydrolysis, reaction calorimetry, thermal decomposition, thermal endurance, thermal life, thermo-oxidative deterioration

### **Introduction**

Thermal endurance of electrical insulating materials is technically very important, because it has direct influence on life time of electrical machines, cables etc. These materials made of high polymers undergo thermal deterioration during a long use, for example for 10 years, since they are heated by heat evolved during operation due to electrical loss. Therefore, it has been an important problem to estimate the life time of these materials in practical application.

In the established test method [1, 2] it takes more than 5000 hours to evaluate their thermal endurance life. Therefore, it is needed to evaluate the life time in relatively short time. To establish a short-time test method, thermogravimetry (TG) and differential thermal analysis (DTA) have been applied in various ways, but not so satisfactorily. Evolved gas analysis (EGA) by stepwise heating and cooling was proposed later for this purpose and has been examined recently

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by a round robin test. A calorimetric method was proposed to observe the rate of thermo-oxidative degradation together with pyrolysis and hydrolysis separately.

In this series of papers the above-mentioned progress in a branch of thermal analysis is reviewed from historical viewpoint. In this part various attempts of thermal analysis application to the thermal endurance evaluation of electrical insulating materials are critically reviewed, while preceding researches to establish the conventional test method were described in the previous part, together with their relation to thermal analysis [3]. These are also useful for other industrial materials of high polymers, because the life time of these materials in practical operation is also an important problem.

### Conventional test method

In the conventional test method [1, 2], we utilize as principle that the logarithm of life time is in a linear relation with the reciprocal absolute temperature in accordance with Arrhenius law, provided that the deterioration proceeds by a single chemical reaction. This principle was first used by Kujirai and Akahira [3], and it was re-established by Dakin later [2], as described in the previous paper, part I of this series.

For the chemical reaction,

$$\frac{dx}{dt} = A \exp\left(-\frac{\Delta E}{RT}\right) g(x) \quad (1)$$

where  $x$ ,  $t$ ,  $A$ ,  $\Delta E$ ,  $R$  and  $T$  are respectively the amount of reacting chemical species, the time, the pre-exponential factor, the activation energy, the gas constant and the absolute temperature. We have the following equation by integration.

$$G(x) = A \int \exp\left(-\frac{\Delta E}{RT}\right) dt \quad (2)$$

where  $G(x)$  is equal to  $\int dx/g(x)$  and the integral on the right side is the reduced time [4]. When the process proceeds isothermally, it is equal to  $t \exp(-\Delta E/RT)$ .

Assuming that the practical characteristics  $P$ , such as mechanical and electrical properties, is dependent only on the chemical structure, i.e.,  $x$ , we have

$$p = f(x) \quad (3)$$

When the characteristics degrades to a certain limit,  $P_e$ , at which the materials can not be used furthermore in practical use, the chemical structure expressed by  $x$  changes to a certain extent,  $x_e$ , and hence  $G(x)$  also changes to a certain constant value,  $G(x_e)$  irrespective of the ageing temperature. Therefore,

$$\log t_e = \Delta E/RT + \text{constant} \quad (4)$$

where  $t_e$  is the life time. This is the principle of the conventional test method.

In this test method, the deterioration of the materials is carried out at relatively high temperatures under specified conditions similar to those in the practice, and the practical characteristics of the materials is measured intermittently until it is degraded beyond the limit,  $p_e$ . By applying the above principle Eq.(4), the life time thus observed is extrapolated to an operating temperature range, and the life time in practical application can be predicted. In another way the highest temperature at which the materials can be used for a guaranteed life is estimated.

### Classification of short-time methods

The various attempts to establish a short-time method can be classified into five schemes.

1) The most simple way is to apply TG at a constant heating rate under specified conditions and to use the thermal decomposition temperature for a given mass loss percentage as a measure of thermal endurance [5–7].

2) The second method was proposed based on the criticism of the above method, and it proposes to calculate the life time using kinetic parameters obtained by kinetic analysis of TG data [8].

3) The third attempt is to obtain the activation energy by TG or DTA, and to estimate the life time by extrapolating the life at a high ageing temperature measured by the conventional method and by using the activation energy obtained by TG or DTA [9, 10].

4) The fourth approach is application of EGA and the activation energy is estimated by measuring rate of gas evolution by stepwise heating and cooling. The life time is evaluated similarly to the third method [11].

5) The fifth one uses a calorimetric method to measure the rates of thermo-oxidative degradation, pyrolysis and hydrolysis by observing the heats of reaction under various specified atmospheres [12–14].

These five methods will be described in this order.

### Decomposition temperature as measure of heat resistance

For various insulating materials, TG was carried out at a given constant heating rate, and the decomposition temperatures at which the mass loss reaches 5% ( $T_d$ ) were measured [5], while the temperatures for a given life time (for example 20000 h), which is called temperature index,  $TI$ , were obtained by a conventional test. In Fig. 1,  $T_d$  and  $TI$  are plotted on the abscissa and the ordinate respectively [5]. It was stated that a single linear regression was found between the two types of temperature, while two regressions can also be ob-

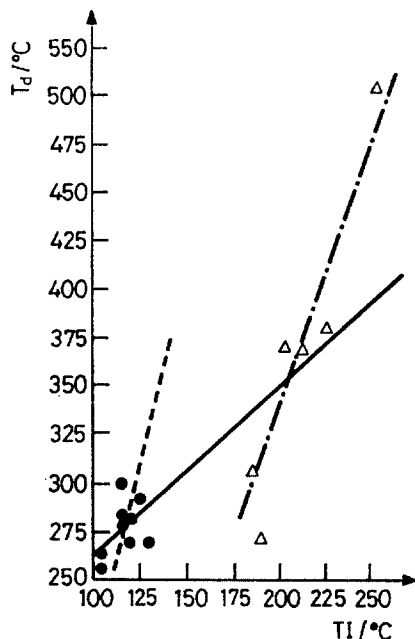


Fig. 1 Relation between  $T_d$  and  $TI$  for 20000 h life time [5]

served separately in a lower and in a higher temperature range [5]. Thus, the authors postulated that the decomposition temperature observed by TG can be used as a measure for long-term thermal endurance and that the highest temperature to guarantee a certain life time can be estimated by using these linear regression lines.

A similar but not so straightforward method for thermal endurance evaluation was established as an industrial standard [6]. In this standard test two temperatures are estimated and used; one is the temperature,  $A$ , at which a straight line connecting 20% mass loss and 50% mass loss intercepts the base line, i.e., the zero mass loss line, and the second temperature,  $B$ , is the temperature at 50% mass loss. Namely,

$$TGI = (A+B)/2 \quad (5)$$

where  $TGI$  is called the thermogravimetric temperature index as a measure of thermal endurance. Afterwards polyimide film was proposed for temperature calibration to minimize imprecision due to difference of the apparatus [7];

$$TGI = (A+B)/2K \quad (6)$$

where  $K$  is a correction factor, which is determined by using polyimide film as a standard material, and  $TGI$  for polyimide was defined to be 240°C. DiCerbo

[7] applied this method to enamelled wires, including overcoated ones. He postulated that the results by this method are in good agreement with those by the conventional test and that compatibility of two materials in the overcoated enamelled wires can be evaluated.

### Life estimation by kinetic analysis of TG data

The above simple method was criticized by Toop [8] from theoretical consideration of kinetics. This consideration can clearly be explained by using the reduced time [4] (Eq. (2)). When the extents of reaction or deterioration are equal to each other for a particular process under different temperature conditions, the reduced times are also equal to each other. Therefore, the reduced time for a given mass loss corresponding to the isothermal life in practical use is equal to the reduced time for the same mass loss by TG. Thus,

$$t_e \exp\left(-\frac{\Delta E}{RT_i}\right) = \frac{1}{\Phi} \int_0^{T_e} \exp\left(-\frac{\Delta E}{RT}\right) dT \quad (7)$$

where  $T_i$  and  $T_e$  are respectively the absolute temperatures for isothermal ageing and for TG at the heating rate of  $\Phi$ , at which the mass reaches to the given mass loss.

By investigating the mass loss percentage at a given life time for various materials, Toop found that the mass loss is approximately 50% for almost all materials. By using Eq. (7), Toop calculated  $T_e$  at a constant  $\Phi$  vs.  $\Delta E$  with  $T_i$  for the life of 20000 h as a parameter. The results are shown in Fig. 2. Therefore, observing by TG the temperature at which the mass reaches to 50% of the initial mass and estimating the activation energy, we can estimate the maximum temperature to guarantee the life by using this figure.

In the figure TG results for polyvinylformal (FV in the figure), polyesterimide (PEI) and polyimide (PI) are shown together with the temperature to guarantee the life over 20000 h.

As clearly seen, the  $T_e$ 's for polyvinyl formal and polyamideimide are approximately equal to each other, but the  $T_i$ 's are quite different. This fact illustrates that  $T_e$  is not suitable as a measure for long-term thermal endurance. Thus the above mentioned first method is severely criticized. For evaluating long-term thermal endurance, at least two parameters, such as  $T_e$  (as in Fig. 2) or the reduced time and  $\Delta E$  are necessary, and this was also stated before [4].

The plot such as in Fig. 2 is, very useful for preliminary thermal endurance evaluation. When a new material is produced by modification of conventional materials, we should first made the TG of the materials and plot  $\Delta E$  vs.  $T_e$  estimated by some means from TG results. If the plot of the new material is shifted to right and upper directions, the modification is verified to be success-

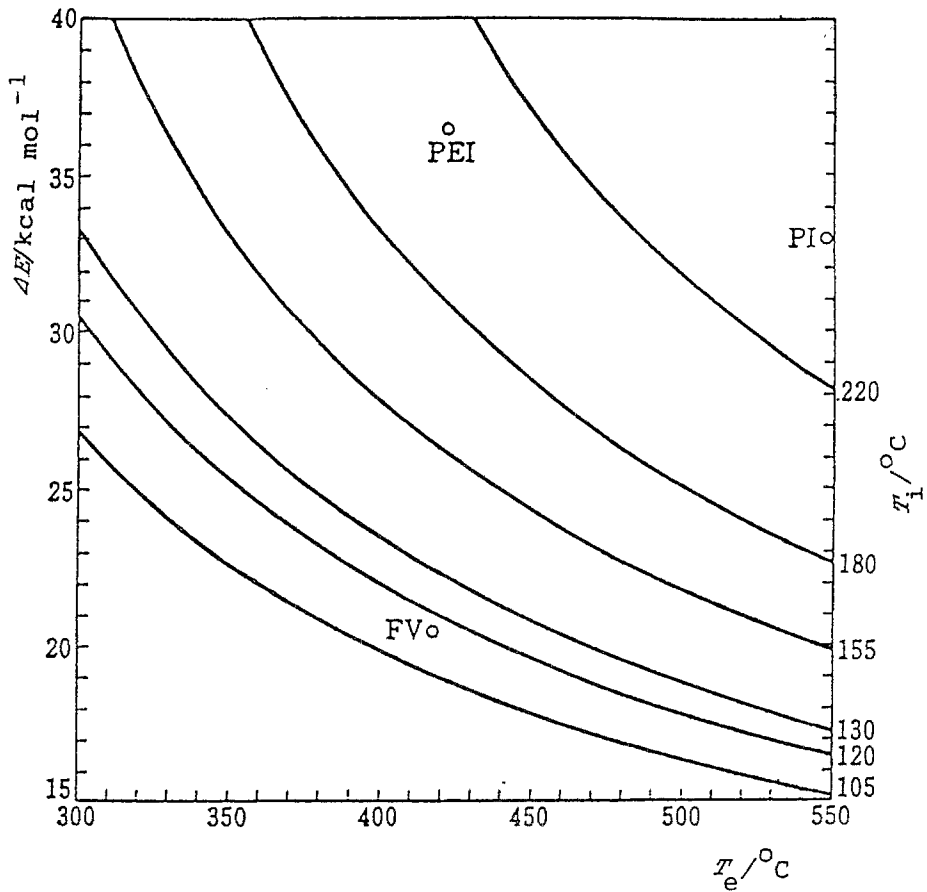


Fig. 2 Relation between  $T_e$  and  $\Delta E$  for indicated  $T_i$ 's for 20000 h life time as a parameter [8]. The heating rate for TG is of  $3.6^\circ\text{C min}^{-1}$ . [The unit kcal is equal to 4.18 kJ.]

ful. Otherwise it is not satisfactory. Toop postulated this analysis can be used at least as a preliminary test.

### Combination of thermal analysis with conventional test

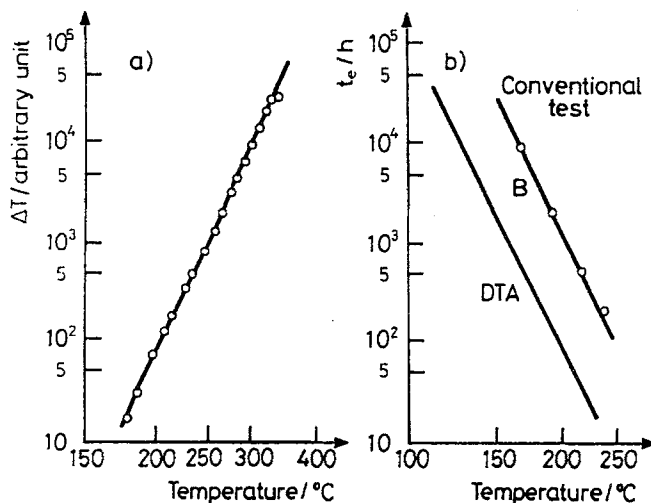
As seen above, two parameters are necessary for thermal endurance evaluation. Before Saito and his coworkers [15] selected the life time at a relatively high temperature and the activation energy. The life time at a relatively high temperature can be estimated in a short time by the conventional test, and the activation energy corresponding to the temperature dependence of the life [Eq. (4)] can be estimated by kinetic analysis.

They measured the rate of gas evolution from the sample subjected to isothermal deterioration. The gas evolved in a given time interval was completely

oxidized in the presence of platinum catalyst and the carbon dioxide formed was collected within a trap and measured by mass-spectrometry or gas chromatography. The activation energy was estimated from the temperature dependence of gas evolution rate (Arrhenius plot) [15]. This concept was successful.

Thermal analysis is used to estimate the activation energy instead of gas evolution. In a first method DTA was applied for this purpose [9]. DTA was carried out under a constant rate flow of nitrogen and a given amount of oxygen was injected intermittently into the nitrogen flow. Alternative exothermic peaks were observed in the DTA curve due to thermo-oxidative degradation by the injected oxygen. Because the peak height seems to be proportional to the rate constant of the thermo-oxidative degradation, the activation energy can be estimated by plotting the peak height vs. the reciprocal absolute temperature (Arrhenius plot). The activation energies thus estimated for glass cloth impregnated with polyester are compared with those obtained by the conventional test method and good agreement in the slope ( $-\Delta E/R$ ) was observed, as in Fig. 3.

Application of TG for this purpose was also suggested. Osuo [10] carried out TG's of virgin sample together with of partially deteriorated sample, and he compared the two TG curves with each other. Three-stage mass loss was observed for example for epoxide varnish, and differences between the two TG curves were found in the first stage. From this comparison, it was concluded that the reaction causing the thermal deterioration is the first stage, and he estimated the activation energy by kinetic analysis of the first stage mass loss of the TG curves. The comparison made by Osuo is very useful to detect the reaction to be assigned for estimation of the life time.



**Fig. 3** Temperature dependence of life observed by oxygen injection DTA (a) and comparison with data of the conventional test (b) for glass cloth impregnated polyester [9]. Although the temperature is shown, the abscissa of the both figures is the reciprocal absolute temperature

## Stepwise evolved gas analysis

The fourth method [11] is essentially the same concerning the fundamental concept as the method of Saito *et al.* [15], but it differs in the mode of estimating the activation energy from both the method by Saito *et al.* and the above third method.

One of the drawbacks of the third methods is the use of linear heating thermal analysis. The reaction observed by this type of thermal analysis is that at a relatively high temperature, whereas the reaction proceeding in practical use of the materials occurs in a relatively low operating temperature range. Another drawback is the control of the atmosphere, which also may differ from the actual atmosphere in electrical machines etc. Generally this drawback is clearly existed by the dependence of TG curves on the sample size and the shape of sample container. The above-mentioned drawbacks were confirmed by round robin tests [16–18].

In the fourth method [11] the rate of deterioration was observed from the operating temperature to the highest ageing temperature in the conventional test by using EGA by stepwise heating and cooling. Similarly to the work of Saito *et al.* [15], the sample is heated in the flow of air without carbon dioxide, and carbon dioxide gas evolved from the sample is analyzed, but the temperature of the sample is increased stepwisely and then decreased stepwisely or vice versa. When the rate of gas evolution in the heating mode is equal to that in the cooling mode at the same temperature, the deterioration in the respective cycle is negligibly small, and the rate is exactly proportional to the rate constant of the deterioration reaction. Then the Arrhenius plot can be drawn by using the observed rates.

In the method of Saito *et al.*, the sample was discarded after each isothermal measurement, and observation of the temperature dependence needed a long time. By stepwise EGA the temperature dependence can be observed using a single specimen and the time needed becomes short. Interaction of the specimen with the atmosphere can be kept constant and simulated to the practical atmosphere.

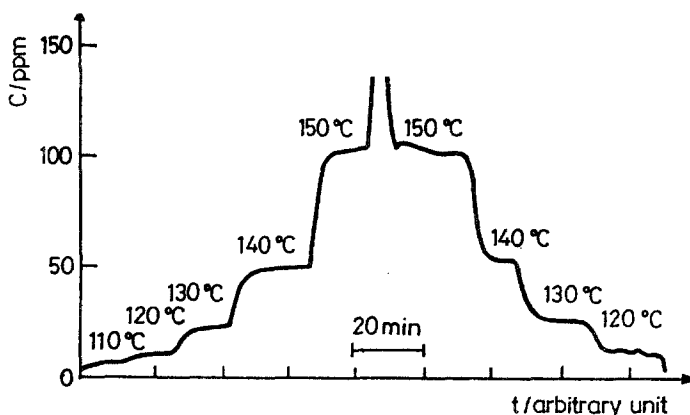
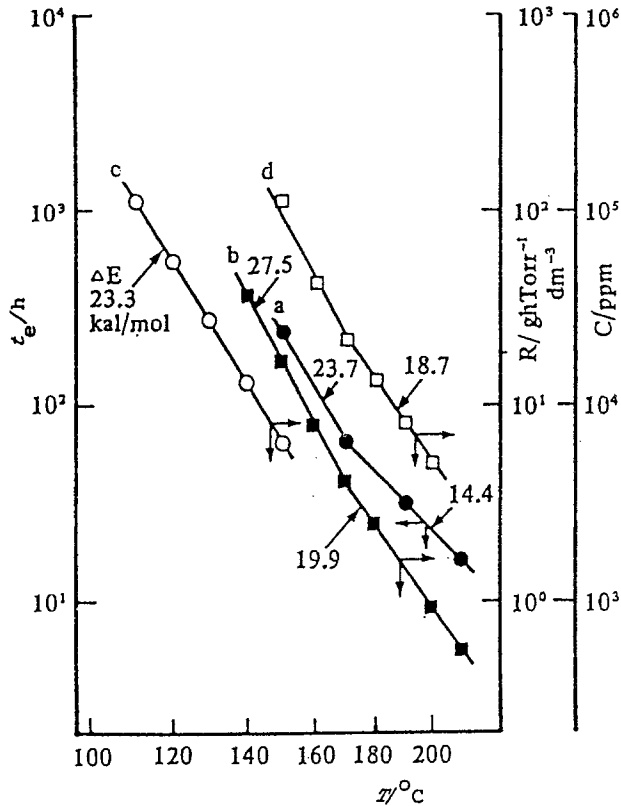


Fig. 4 Stepwise EGA curve for polyvinyl formal enamelled wire [11]. The symbol  $C$  represents the CO<sub>2</sub> concentration in the gas flow





**Fig. 5** Dependence of life time,  $t_e$  and deterioration rate on reciprocal absolute temperature for polyvinylformal enamelled wire [11]. The lines represent the results by a, the conventional test, b, isothermal evolved gas measurement and c and d, stepwise EGA, and  $R$  is the rate of gas evolution

One example of EGA curves for polyvinyl formal enamelled wire is reproduced in Fig. 4, and the temperature dependence of the gas evolution rate for this material is shown in Fig. 5 [11]. In the latter figure, the results obtained by the method of Saito *et al.* are also shown, together with the results of the conventional method.

Three points should be mentioned concerning this figure. The agreement between the slopes of the linear plots is fairly good for the results of the three methods, the stepwise EGA [11], the method of Saito *et al.* [15] and the conventional method. Similar agreement between stepwise EGA and the conventional method was observed for other materials [11]. These facts confirmed the reliability of stepwise EGA. In Fig. 5, breaking points are observed for all plots, which suggests that the mechanism and the activation energy of the thermal deterioration may change at this temperature. Similar change in the

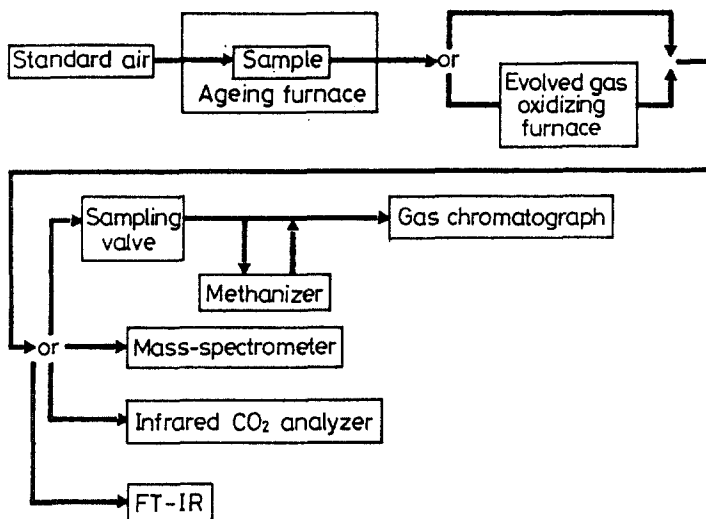


Fig. 6 Flow chart for the various stepwise EGA used in the round robin test

temperature dependence is sometimes observed also for other materials by the conventional test method. These results revealed the need to observe the temperature dependence down to the operating temperature for reliable extrapolation for the thermal endurance evaluation. It should be pointed out that the plot by stepwise EGA reaches to the operating temperature, so that reliability of extrapolation to the operating temperature is assured.

For observing the temperature dependence down to the operating temperature, analysis of evolved gas with high sensitivity and precision is needed together with high skilfulness, and various EGA's have been tried in the round robin test [19], as illustrated in Fig. 6. In some cases carbon dioxide in gas evolved from the sample under deterioration is analyzed directly, while in the other cases gas evolved from the sample is oxidized and total carbon dioxide formed by oxidation of carbonaceous products is analyzed. In infrared carbon dioxide analyzer, mass-spectrometer or FT-IR gas analyzer, carbon dioxide for-

Table 1 EGA apparatus used in round Robin Test

Participants	Type of EGA apparatus
A B C D E	Gas chromatograph (GC)*
F	GC + Evolved Gas Oxidizing Furnace (EGAOF)
G	Infrared CO <sub>2</sub> Gas Analyzer + EGAOF
H	FT-IR
I	Mass-spectrometer**

\* A methanizer and a flame ion detector are essential for gas chromatograph to improve sensitivity.

\*\*Thermal deterioration is analyzed in the flow of simulated air composed of helium and oxygen

Table 2 EGA round Robin Test results

Sample	Temperature range of test*/°C	Participants	Results $\Delta E_{obs}/\text{kJ mol}^{-1}$ **
Polyimide film	230-330	A B C D E F G H I	122.8+11.3
Polyvinyl formal wire	110-210	A C D E F G H I	107.0+5.1 <sup>+</sup>
Epoxide resin	170-270	A F H	120.6+4.8
100% Oileoresinous varnish	120-220	B C G I	93.4+7.7
Polyester-imide (PEI) wire	180-280	A D G	111.8+11.8
Phenol-alkyd varnish	140-230	A B C D E F G H I	87.2+9.8 <sup>++</sup>
Polyamide-imide (PAI) wire	230-330	D E G	113.8+63.0
PEI wire overcoated with PAI	210-310	A B C E	90.5+11.0 <sup>++</sup>
Aramid paper	240-340	A F H	151.9+31.1 <sup>++</sup>

\* The temperature range is generally from the assumed temperature index minus 10°C to the assumed temperature index plus 90°C.

\*\* The overall average and the range at 95% confidence are shown.

+ The linearity of the plots was obtained only above 160°C.

++ Some participants observed a breaking point or nonlinearity in the plots, while the other did not find it.

mation is measured continuously, but in gas chromatograph a given amount of the gas is collected intermittently from the gas flow with a sampling valve and subsequently analyzed. In the round robin test 9 participants used EGA with the above-mentioned various types of apparatus, and as listed in Table 1, and 11 different samples were tested. The samples and the test results concerning the activation energies obtained by the participants are tabulated in Table 2.

The method can not be applied to ethylene propylene rubber and polyester sheets, because detectable gas was not evolved from these materials. Presumably mainly oxygen absorption occurred in the thermal deterioration of ethylene propylene rubber. For polyester sheets partial melting occurred and the surface area decreased during test. Therefore, reliable results were not obtained for these materials.

For the other samples detectable  $\text{CO}_2$  gas evolution was observed and the temperature dependence of the life was obtained. Typical plots of gas evolution rate vs. the reciprocal absolute temperature are reproduced in Fig. 7. As it is

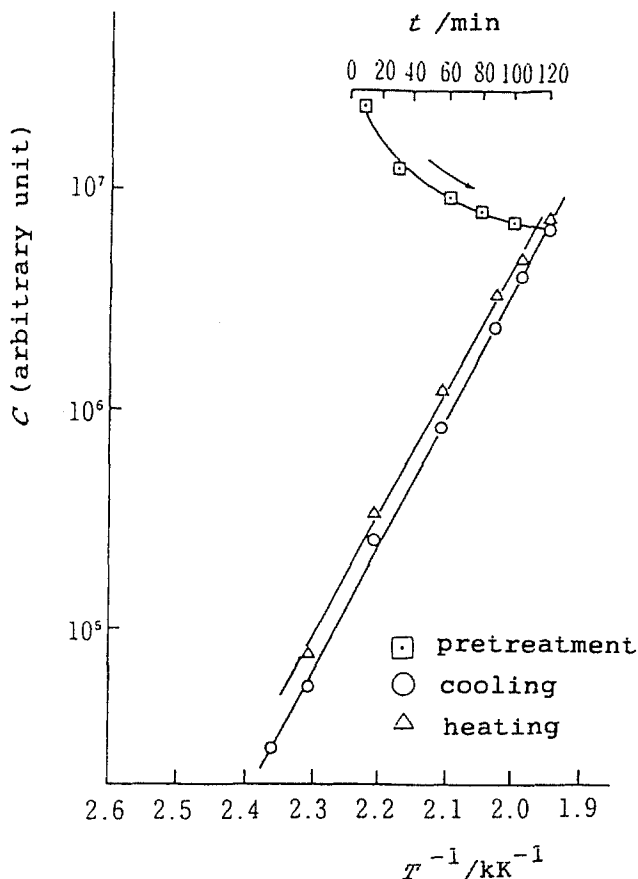


Fig. 7 A typical plot of gas evolution rate  $C$  vs. reciprocal absolute temperature

seen in this figure, the sample was heated to the highest testing temperature, where the pretreatment of the sample was continued till the rate of gas evolution became constant. This procedure of pretreatment is essential for obtaining satisfactory results, because undesirable ingredients such as residual solvent and unreacted monomer are eliminated by this procedure. Because the minimum concentration of  $\text{CO}_2$  is the order of 1 ppm, the background noise is very serious, and thus only gas concentration data which are threefold larger than the background noise were accepted. To increase the S/N ratio, increase in the sample size and decrease in the gas flow are effective, and contamination of  $\text{CO}_2$  from ambient atmosphere through tube joints etc, and evolution of  $\text{CO}_2$  by heating of the tubes etc, are strictly examined.

Very good results were obtained for polyimide films, and their scattering of the estimated activation energy values is small as seen in Fig. 8. Other materials, for which similar very good agreements were observed, are epoxide resin, polyester-imide enamelled wire and 100% oileresinous varnish. For polyvinylformal enamelled wire, phenol-alkyd resin varnish and polyester-imide enamelled wire overcoated with polyamide-imide, fairly good agreements among the participants were obtained, but not so good as for polyamide-imid enamelled wire and aramid paper. Reasons for these discrepancies were not found. These are shown in Table 2. However, discrepancies due to difference in the type of EGA apparatus were not found, and all types of the apparatus used are thus suitable for the purpose.

It should be noted that the stepwise EGA was applied to insulating systems, which are composites used in practical electrical machines, such as epoxide resin and mica [20, 21]. The results were compared with those by conventional motorette test [22] using a miniaturized magnet coil in motors, and good agreement was observed [20, 21]. Thus it was clearly shown that the stepwise EGA method is applicable not only to single component materials, but also to composite materials, such as practical insulating systems.

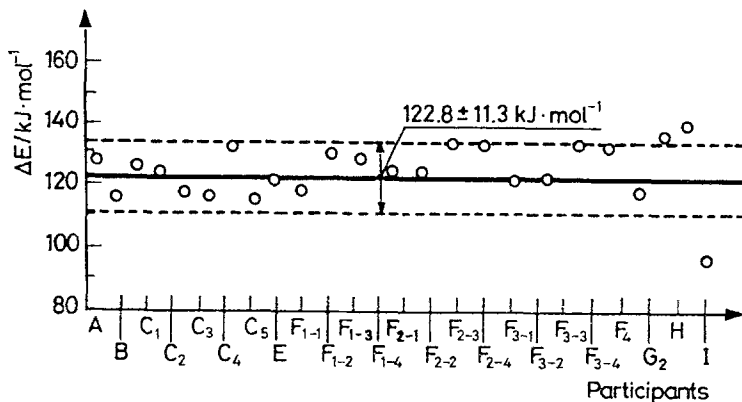


Fig. 8 Activation energy for polyimide film deterioration. Some participants of the round robin test made multiple runs

## Calorimetric method

Possibility of concurrent parallel reactions in thermal deterioration was postulated by Toop, but he did not propose any method in which these parallel reactions are taken into account [23]. For this purpose a method was proposed by Paloniemi, and an isothermal conduction calorimeter is used to detect the heat of reactions due to thermo-oxidative deterioration, thermal decomposition and hydrolysis [12–14].

The above three potential reactions may proceed concurrently in thermal deterioration of the materials. Thus the kinetic equations are as follows.

$$\frac{dx}{dt} = A_1 \exp\left(-\frac{\Delta E_1}{RT}\right) g_1(x) \quad (8)$$

$$\frac{dx}{dt} = A_2 \exp\left(-\frac{\Delta E_2}{RT}\right) g_2(x) [\text{O}_2]^m \quad (9)$$

and

$$\frac{dx}{dt} = A_3 \exp\left(-\frac{\Delta E_3}{RT}\right) g_3(x) [\text{H}_2\text{O}]^n \quad (10)$$

where  $[\text{O}_2]$ ,  $[\text{H}_2\text{O}]$ ,  $m$  and  $n$  are the partial pressure of oxygen, that of water vapor, the reaction order of oxygen in the thermo-oxidative reaction and that of water vapor in the hydrolysis, respectively, and the subscripts denote the respective reaction.

For the case that only a single reaction proceeds, acceleration of the thermal deterioration can be realized only by increasing the temperature and keeping the partial pressure constant. However in the case of multiple concurrent reactions, the ratio of acceleration by increasing the temperature is different for the three reaction processes, because of differences in the activation energies. We must thus accelerate the reactions in the same manner, otherwise the process of thermal deterioration is changed by the acceleration, as pointed out by Toop [20]. Thus, first we should evaluate the reaction orders,  $m$  and  $n$ , by changing the partial pressures. By adjusting the latter the ratio of acceleration of each reaction becomes the same, so that the deterioration proceeds identical to the actual deterioration during operation.

One of the results in which the above three reactions were detected is shown in Fig. 9 [12]. In the figure the heats of reactions under various atmosphere are shown. The changes of the evolved heats are due to the effect of the atmosphere and they are the evidence for the multiple reactions causing the deterioration. By adjusting the partial pressure, the rate of acceleration could be adjusted [14].

Similarly the effect of the atmosphere was detected by stepwise EGA [11]. This method seems also to be applicable to evidence multiple concurrent reac-

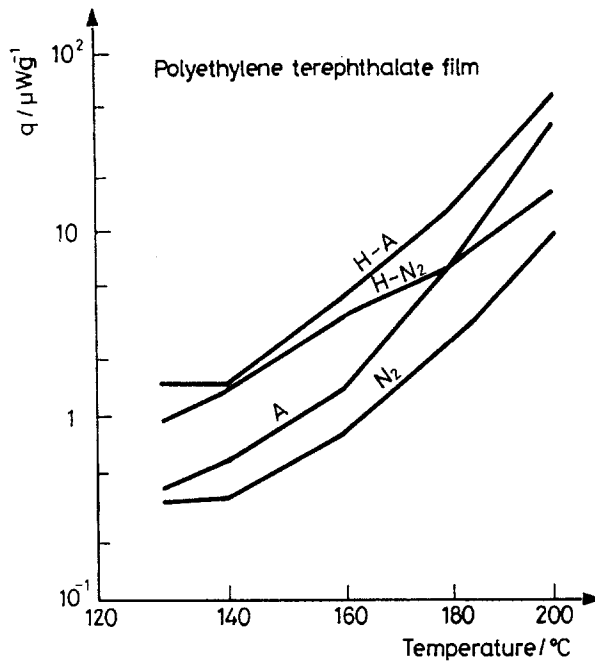


Fig. 9 Evidence of occurrence of concurrent reactions by calorimetry [12]. The symbols A, H and N<sub>2</sub> are respectively air, water vapor and nitrogen, and  $q$  is the rate of heat evolution per unit mass

tions. However, EGA can only be applied to reactions evolving carbonaceous gases, while the calorimetric method can be applied to any reaction accompanied by heat evolution or absorption.

### Concluding remarks

An accelerated test method for electrical insulating materials of high polymers was established, as described in the part I, but it needs a long time. However, short-time test methods have not yet been established.

As seen above, however, various attempts have been made and useful results have been obtained for thermal endurance evaluation. These are very useful to evaluate thermal endurance of other industrial materials, especially for evaluation of long-term thermal endurance. Some methods are not satisfactory because of incorrect theoretical background, as criticized by Toop. Applicability of thermal analysis at constant heating rate is limited for estimating long-term thermal life, because the process proceeding in usual thermal analysis conditions tends to differ from those in the actual operating temperature range. In other word, the temperatures in usual thermal analysis are too high for

extrapolating the results to a lower temperature range, and the atmosphere tends to differ from that in practical use.

In the stepwise EGA and the isothermal calorimetric method, the temperature where accelerated processes are observed is almost the same as in the conventional test and not so high as in usual thermal analysis. It can also be ascertained that the observed processes are the same as the actual processes at the operating temperature, so that there is little danger of too long extrapolation, but high sensitivity, precision and skill are needed by the same reason. When these are realized, these methods are most reliable for long-term thermal endurance evaluation by extrapolation.

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