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APPLICATION OF STATIC AND DYNAMIC THERMOANALYTICAL METHODS TO ESTIMATE THE LIFETIME OF ELECTRICAL INSULATIONS

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Abstract

Different electrical insulations have been investigated by dynamic and static thermoanalytical methods. The kinetic parameters were evaluated with the aid of a fast calculation method. The results were discussed on the basis of the thermal stability and the lifetime curves thus obtained.

Keywords: electrical insulations, dynamic and static thermal methods, kinetics, lifetime estimation.

Introduction

Turbo-alternators (generators) are among the main elements of electrical energy industry. The increase in the power of the generators, technological development and efforts to improve reliability have had an important influence on the construction in recent years: the exploitation of structural materials has increased, materials of superior quality were developed and modern technologies were adapted.

Modern turbo-alternators are complex systems with all elements utmostly exploited since their ability for continuous operation has become a basic requirement.

Consequently, a systematic control of the state, diagnosis, and the subsequent measures are of utmost importance. Since deterioration of the working order and defects are most often resulting from the damage of the insulation of the stator winding, regular control and methods which allow reliable state estimation enjoy priority. The unexpected break-down of a generator, in addition to the costs of repair amounting to some 10 million entails even greater costs resulting from the power supply failure. The continuous control of generators over 50 MVA, about 40 in use is the most important task. These belong to seven thermal power stations and represent nearly 75 % of the entire capacity in Hungary. The insulation in the majority of the stator windings in these generators is a compound micafolium, in the minority it is synthetic resin. Compound insulations are composed essentially of mica splittings saturated with bitumen and layered on a carrier foil. This type of insulation is thermoplastic, is deformed under the joint action of heat and mechanical stress, plates of mica are shifted, the bitumen melts and the insulator becomes inhomogeneous, with gaseous inclusions. At higher temperatures bitumen becomes rigid as a result of ageing, and loses its binding ability, cannot fill cavities. Consequently, discharges occur in the cavities and the insulation deteriorates. The other problem is the oil and sometimes water vapour passing through the shaft seals partly dissolving, loosening bitumen, which causes a reduction in the voltage stability of the generator.

Owing to these difficulties, the production of stators with compound micafolium and asphalt mica was stopped in 1980. Nowadays new devices and replacement parts are made with Isotenax or Samicatherm, thermosetting epoxy based resin insulations. These insulations belong to class F in respect of thermal stability, they are practically insensitive to oil or water, with electrical and mechanical properties superior to the previous types. However, their long-term behaviour is not very well known, so studies in the field are welcome. So far 13 generators have been insulated by epoxy resin, and its use is expected to increase in the coming 10–15 years.

The thermal stability of polymers is important in respect of processing and production technology. This is especially true for electrical insulations, for which thermal load is one of the factors contributing to the ageing.

In the present work some thermal methods are presented which allow comparison of various materials and estimation of expected lifetime. The applicability of the methods is demonstrated by studies on some insulations used in Hungary. The authors express their thanks to the Electricity Generating Trust for approving of the publication of the results of a joint research project.

Methods, Kinetic Calculations

Thermoanalytical Studies

In thermal analysis changes of some properties of a sample are followed in the course of heating. Methods are generally grouped according to the property measured [1].

On the other hand, based on the nature of the temperature program applied, the methods are grouped as static (maintaining constant temperature, isothermal) and dynamic (with constant heating rate) techniques.

MEISEL's work [2] is referred to as a paper summarizing the principles and methods of thermal analysis.

In the present study both static and dynamic methods were used. In dealing with the insulations our previous research results have also been utilized [12–14].

Dynamic method

Dynamic studies were carried out using a Derivatograph, MOM Type OD-2 (Budapest, Hungary). The temperature was increased at a constant rate and the mass of sample (TG curve), the rate of mass change (DTG curve) and the enthalpy change (DTA curve) were simultaneously recorded. Measurements were made in air, at a heating rate of 5 °C/min, on 100 mg samples to characterize the thermal behaviour. For kinetic calculations the curves were recorded at heating rates of 1, 2, 5, and 10 °C/min, in nitrogen atmosphere on 50 mg samples. Before measurements the samples were cut into about 1 mm^3 cubes.

It should be mentioned that if the general thermal behaviour is studied it is justified to use air as the atmosphere in order to approach the conditions of practical use. In kinetic studies, however, nitrogen should be used to exclude thermo-oxidation processes and to allow purely thermal decomposition to be followed.

Static Method

In static studies the mass changes were recorded as function of the time at constant temperature using a specially modified balance, the so called 'thermobalance'. Constant temperature was ensured by a temperature controller, 'Programik', with an accuracy of ± 0.2 °C. Isothermal measurements were made on 0.25–0.5 g samples, generally for 24 hours.

Kinetic Calculation Methods

Kinetic evaluation of thermoanalytical curves has been in the forefront of research for decades. Since in the present work only thermogravimetric curves were processed to obtain kinetic data, only this aspect will be dealt with here in detail.

Kinetic evaluation of the results of static measurements

An isothermal thermogravimetric curve can be divided into two ranges. The initial, evaporation stage can be described by the following differential equation:

$$v_p = \frac{dN}{dt} = k_p N_0 = RTe^{\left(-\frac{\lambda_b}{RT}\right)}, \tag{1}$$

where

v_p — the rate of evaporation
N_0 — the number of particles evaporated from the equilibrium surface
k_p — the rate constant of evaporation
λ_b — the internal evaporation heat
T — the absolute temperature
R — the gas constant.

The initial evaporation range is followed by the range of thermal degradation:

$$v_d = -\frac{dx}{dt} = k_d f(x), \tag{2}$$

where

v_d — the rate of degradation
x — the reaction coordinate
k_d — the rate constant of degradation.

As in the degradation range the isotherm is nearly linear, the first order kinetic equation can be used:

$$v_d = -\frac{dx}{dt} = k_d(1-x). \tag{3}$$

The exact description of the degradation can be given by integrating *Eq.* (3). However, as the mass loss involved is very small, we can write:

$$\ln\frac{1}{1-x} \cong x = k_d t. \tag{4}$$

Thus, the rate constant is:

$$k_d = \frac{x_2 - x_1}{t_2 - t_1}, \tag{5}$$

or, the half lifetime is:

$$t_{1/2} = \frac{\ln 2}{k_d}. \tag{6}$$

The activation energy can be calculated from isotherms measured at different temperatures.

From the Arrhenius description the activation energy ΔH^* can be obtained:

$$\ln k_d = -\frac{\Delta H^*}{RT} + \ln A, \tag{7}$$

where

A — the pre-exponential factor.

From the ΔH^* the entropy ΔS^* and the free enthalpy ΔG^* can be obtained as follows:

$$\Delta S^* = 19.150(\lg k_d + \frac{\Delta H^*}{19.150T} - \lg 2.08 \cdot 10^{10} T), \tag{8}$$

$$\Delta G^T = \Delta H^* - T\Delta S^*. \tag{9}$$

Kinetic evaluation of the results of dynamic measurements

An important fraction of the thermoanalytical literature is devoted to the kinetic evaluation of curves recorded at a dynamic heating program [3]. By combining *Eqs.* (2) and (7) we get the n-th order kinetic equation:

$$-\frac{dx}{dt} = Ae^{\left(\frac{\Delta H^*}{RT}\right)} x^n. \tag{10}$$

Linear heating is defined by:

$$T = T_0 + \frac{dT}{dt} = T_0 + \beta t, \tag{11}$$

where

T_0 — the initial temperature [°C]

β — the rate of heating [°C/min].

The weight fraction of the residue (w) is considered as function of the reaction coordinate [4,5]:

$$w = w(x), \tag{12}$$

where $w = \frac{g_t - g_\infty}{g_0 - g_\infty}$,

g_t — the mass at time t[g]

g_0 — the mass at the beginning of decomposition [g]

g_∞ — the mass at the end of the decomposition [g].

Using *Eqs.* (11) and (12), *Eq.* (10) can be written in the following form:

$$\frac{dw}{dt} = -\frac{A}{\beta} e^{\left(\frac{\Delta H^*}{RT}\right)} w^n. \tag{13}$$

Most kinetic calculation methods start with *Eq.* (13). Some researchers attempted to determine kinetic parameters by further differentiating the differential equation [6,7]. Another possibility is the integration of *Eq.* (13). [5]:

$$\int\limits_0^w \frac{dw}{w^n} = \frac{1 - w^{1-n}}{1-n} = \frac{A\Delta H^*}{\beta R} \left\{ \frac{e^{-x}}{x} - \int\limits_x^\infty \frac{e^{-u}}{u} du \right\} \equiv \frac{A\Delta H^*}{\beta R} p(x), \tag{14}$$

where

$p(x)$ — the numeric integral $x \equiv \dfrac{\Delta H^*}{RT}$.

After some simplifications ΔH^* can be obtained [8]:

$$\log p(x) \cong -2.315 - 0.457 \frac{\Delta H^*}{RT}, \qquad \text{if} \quad \frac{\Delta H^*}{RT} \geq 20. \tag{15}$$

Thus *Eq.* (14) can be written as [9,10]:

$$\log \int\limits_0^w \frac{dw}{w^n} \cong \log \frac{A\Delta H^*}{R} - \log \beta - 2.315 - 0.457 \frac{\Delta H^*}{RT}. \tag{16}$$

Differentiating *Eq.* (16) we get:

$$\Delta H^* = -\frac{R}{0.457} \left(\frac{d \log \beta}{d(1/T)} \right). \tag{17}$$

The value of the derivative can be obtained by plotting the heating rate as function of $1/T$ for the same conversions.

The lifetime can be calculated using the following relationship [11]:

$$\ln t_l = \frac{\Delta H^*}{RT_f} + \ln \left[\frac{\Delta H^*}{\beta R} P \left(\frac{\Delta H^*}{RT_c} \right) \right], \tag{18}$$

where

t_l — the estimated lifetime [min]
T_f — the temperature of break-down — in general the operation temperature [K]
$P\left(\dfrac{\Delta H^*}{RT_c}\right)$ — numeric integral
T_c — critical temperature (for insulations generally the temperature belonging to 5 % mass loss) [K].

Results

Studies on Isotenax and Samicatherm Insulations
Dynamic thermoanalytical studies

The thermal decomposition curves of Isotenax and Samicatherm insulations are shown in *Figs. 1* and *2*. The shapes of the derivatograms are very similar. Appreciable decomposition starts above 260 °C. The TG and DTG curves show two decomposition steps. The temperature intervals, peak temperatures in the DTG curve and mass loss values for the two steps are summarized in *Table 1*.

Table 1

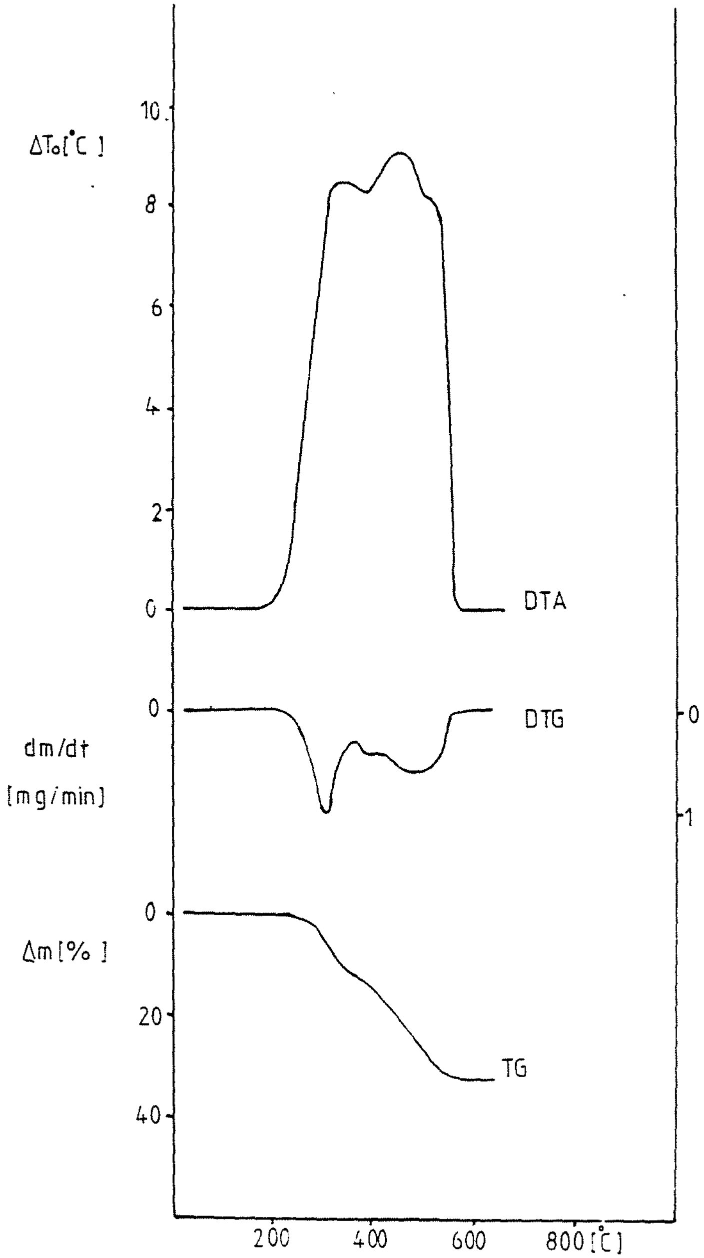
Name of the sample	Decomposition process	T_I [°C]	T_F [°C]	T_{DTG} [°C]	Δm [%]
Isotenax	1st step	260	350	305	11.0
	2nd step	350	560	500	21.0
Samicatherm	1st step	240	350	305	13.5
	2nd step	350	600	500	26.5

T_I — initial temperature of decomposition
T_F — final temperature of decomposition
T_{DTG} — peak temperature of the DTG curve
Δm — mass loss

Static thermoanalytical studies

Isothermal studies were carried out at temperatures (180, 200 and 220 °C) below the decomposition point selected based on the derivatograms (*Figs. 3* and *4*).

The mass losses measured for the two samples at different temperatures after 24 hours of heating do not differ remarkably, the actual values being slightly higher for the Samicatherm sample. This is in good agreement with the results of dynamic studies. The curves are similar in shape for the two samples, tending to a constant value.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DTA
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dm/dt
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Δm[%]
20
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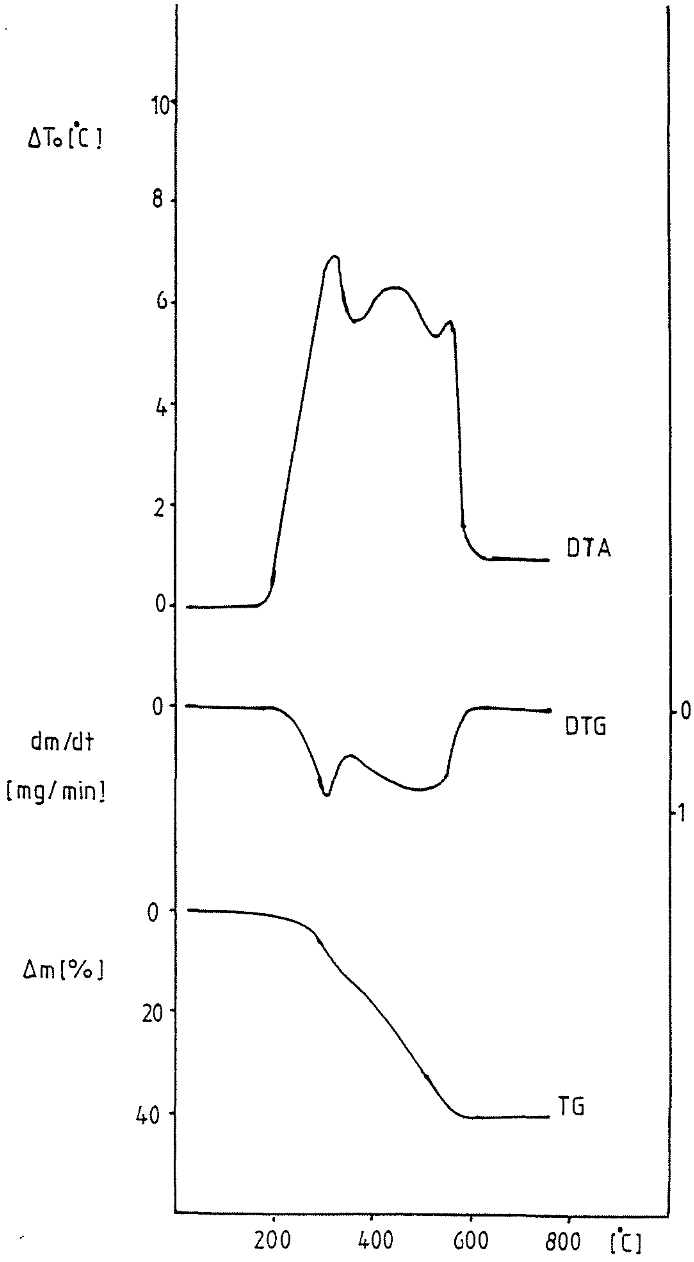
TG
200
400
600
800[°C]

Fig. 1.


ΔTo [°C]
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[°C]

Fig. 2.

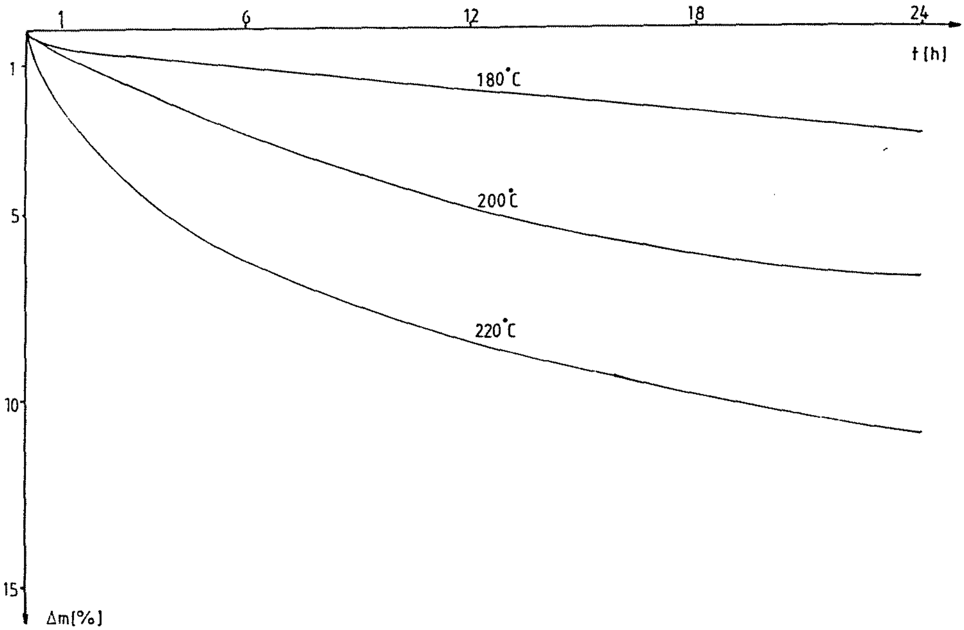


Fig. 3.

Results of kinetic calculations

TG curves obtained at different heating rates ($\beta = 1$, 2, 5 and 10 deg/min) during dynamic measurements and the derived isoconversion lines are shown in *Figs. 5* and *6* for Isotenax insulations. The activation enthalpies determined as described above are given in *Table 2*.

Table 2

Sample	ΔH^*[kJ/mol]
Samicatherm	57.38
Isotenax	98.34

Kinetic data determined from static measurements are summarized in *Table 3*.

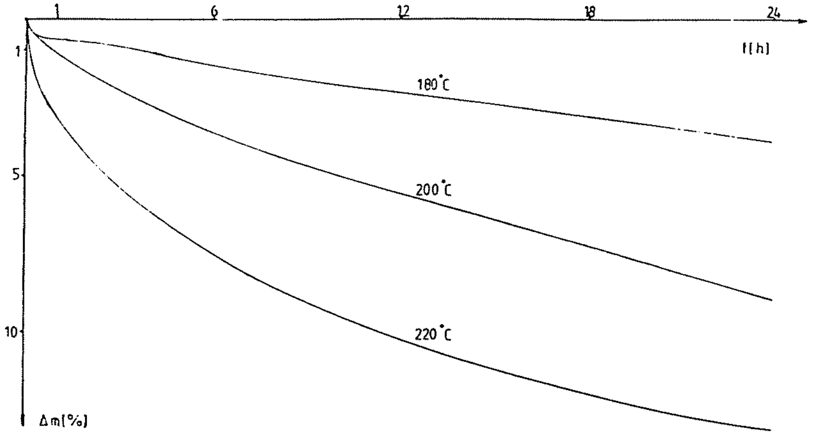
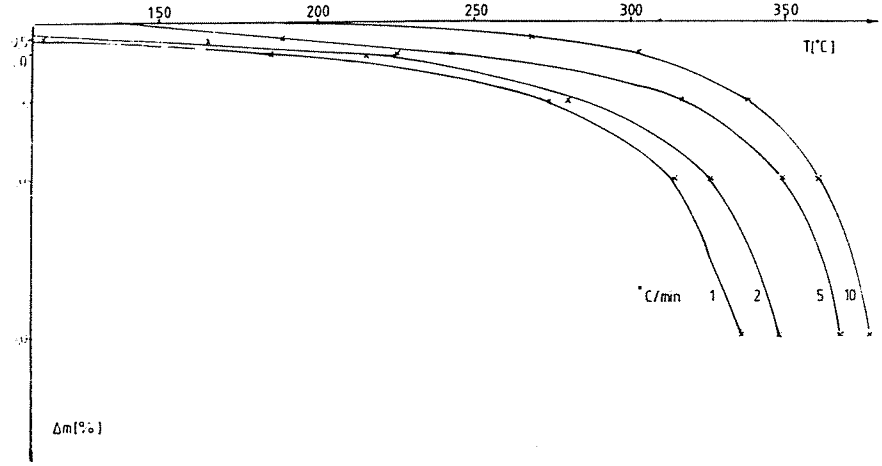

1
6
12
18
24
t[h]
1
5
10
Δm[%]
180°C
200°C
220°C

Fig. 4.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200
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300
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T[°C]
°C/min
1
2
5
10
Δm[%]

Fig. 5.

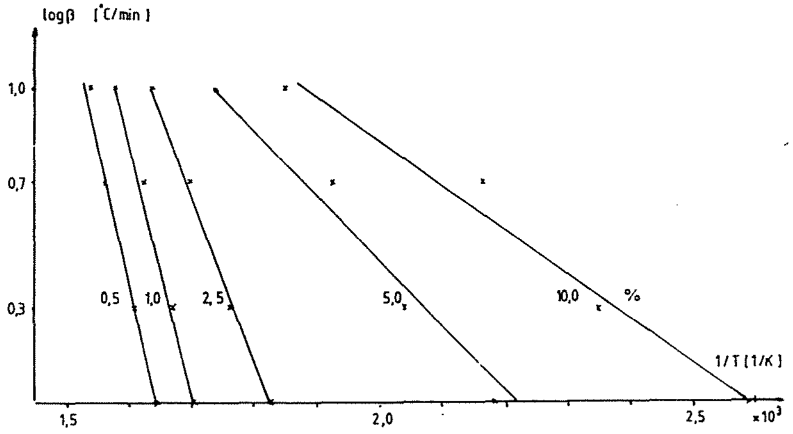


Fig. 6.

Table 3

Sample	T[° C]	180	200	220
Isotenax	k[1/min]×10^3	2.00	6.49	18.25
	$t_{1/2}$[min]	346.6	106.8	38.0
Samicatherm	k[1/min]×10^3	3.00	6.75	10.50
	$t_{1/2}$[min]	231.0	102.7	66.0

The Arrhenius lines derived from the kinetic data are presented in *Fig. 7*, the thermodynamic constants determined from the lines are given in *Table 4*.

The comparison of data obtained based on static and dynamic measurements showed a good agreement for both samples studied.

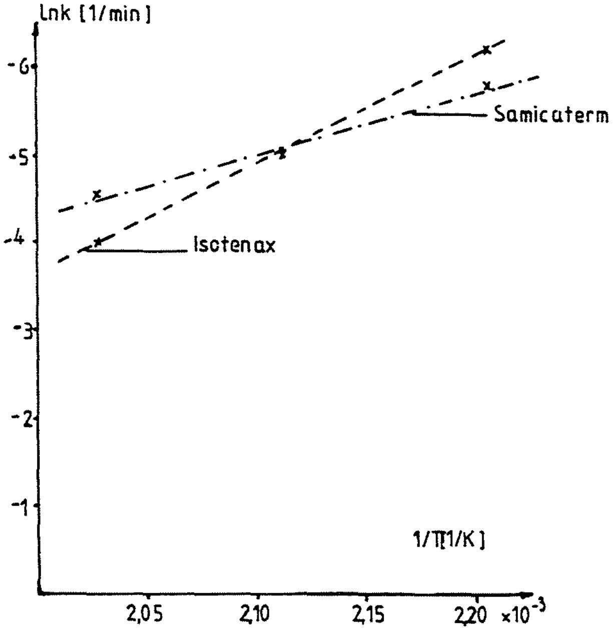


Fig. 7.

Table 4

Sample	ΔH^*[kJ/mol]	ΔS^*[kJ/molK]	ΔG^*[kJ/mol]
Isotenax	106.82	–64.94	137.55
Samicatherm	58.69	–48.09	81.44

Investigation of Asphalt and Shellack Insulations

Dynamic thermoanalytical studies

The derivatogram of a new asphalt sample is presented in *Fig. 8*. The sample contained about 1 % water adsorbed at the surface. Decomposition started above 200 °C as an exothermal process.

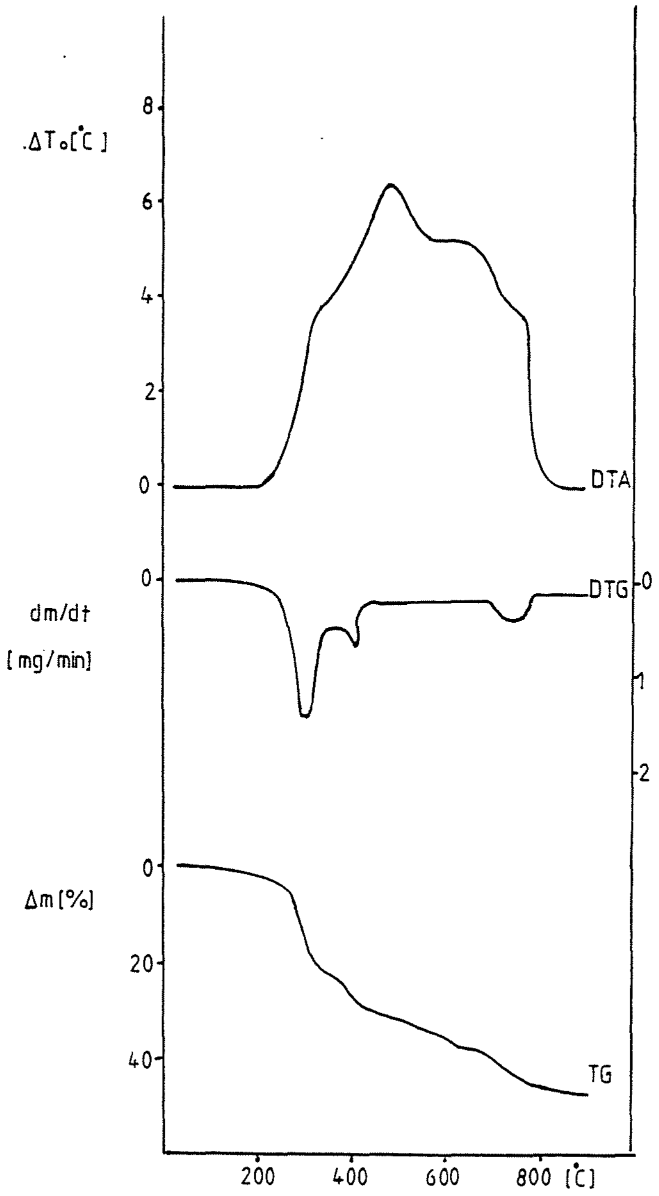


Fig. 8.

The thermoanalytical curves of a used asphalt sample studied are presented in *Fig. 9*. The curves are similar in shape to those of the new sample, but the characteristic temperature intervals of the decomposition processes and the actual values of the mass loss are different (see *Table 5*).

This indicates that during use ageing processes take place in the asphalt insulation which are manifested in changes in the thermal properties, hence the ageing process can be followed by thermal methods of analysis. A sample of used asphalt insulation contaminated with oil during use was also studied. The first decomposition step increased remarkably (39 %), the second one accompanied by a mass loss became smaller (5 %), while the third one remained practically unchanged (14.5 %) compared with the new and used asphalt samples.

The derivatogram of a shellack sample is similar to that of the asphalt. At the beginning of decomposition volatile components are released (see *Table 6*), then the decomposition is similar to that of the asphalt samples.

Based on the results of dynamic studies, the isotherms were measured at 160, 180 and 200 °C. The isotherms of the asphalt insulations tend to a limiting value, while with shellack after a fast initial section the rate becomes constant. The mass losses observed after 24 hours of heat treatment are summarized in *Table 7*.

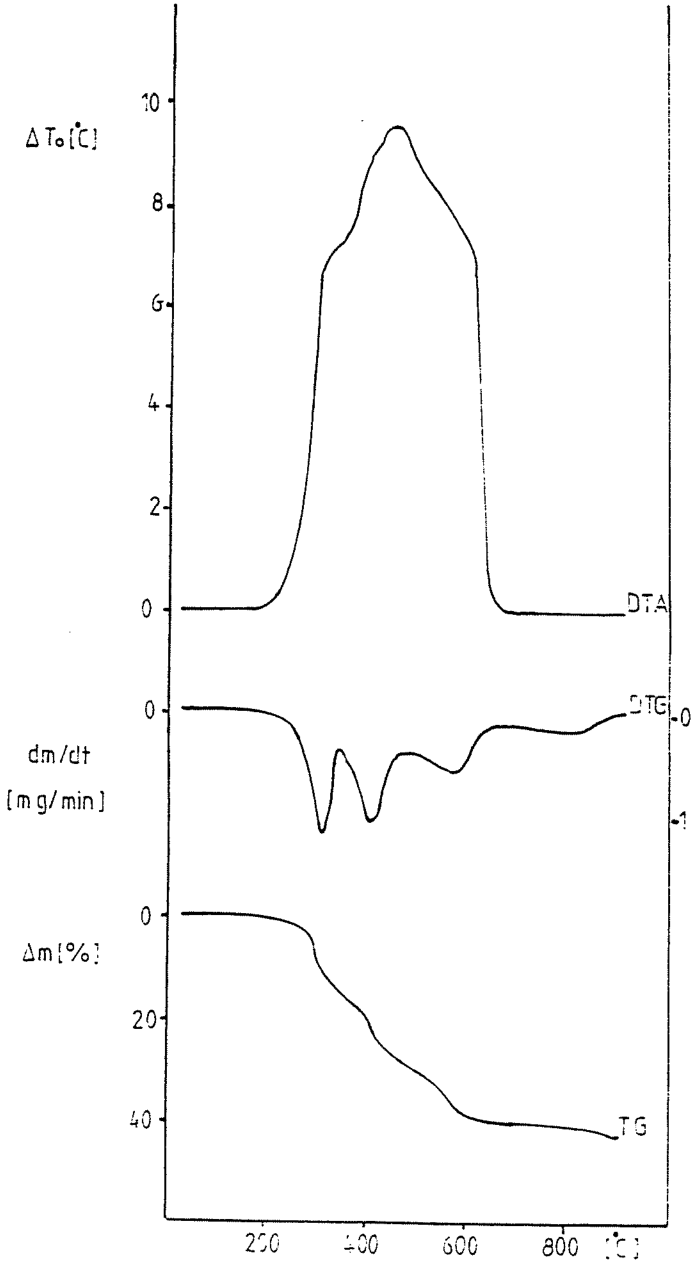
Results of kinetic calculations

The kinetic data calculated from the results of static thermoanalytical studies on new and used asphalt insulations are presented in *Table 8*.

As in the case of the asphalt sample contaminated with oil the initial process of thermal decomposition was connected with the evaporation of oil components, the thermal curves were not evaluated kinetically, since the data were not characteristic of the insulator itself. The thermodynamic constants calculated from the dependence of the rate constant (k) on temperature are given in *Table 9*.

For the asphalt insulations dynamic studies were carried out at different heating rates, and the activation enthalpy was determined as described earlier in this paper (see *Table 10*).

The activation enthalpies calculated from the results of static and dynamic measurements show a good agreement, so they can be accepted as realistic values.


ΔT₀ [°C]
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DTA
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dm/dt
[mg/min]
DTG
0
1
0
Δm [%]
20
40
TG
200
400
600
800
[°C]

Fig. 9.

Table 5

Name of the sample	Decomposition process	T_I [°C]	T_F [°C]	T_{DTG} [°C]	Δm [%]
New asphalt	1st step	200	350	300	20
	2nd step	350	460	410	8.5
	3rd step	460	800	720	15
Used asphalt	1st step	200	340	310	14
	2nd step	340	450	410	13
	3rd step	450	640	610	15

Table 6

Name of the sample	Decomposition process	T_I [°C]	T_F [°C]	T_{DTG} [°C]	Δm [%]
Shellack	1st step	50	250	100	3.5
	2nd step	250	360	325	23.0
	3rd step	360	480	410	11.0
	4th step	480	800	—	7.5

Discussion

Comparison of Isotenax and Samicatherm Insulations

Thermoanalytical studies have revealed that the decomposition of the two insulation types proceeds similarly. The fractions undergoing thermal decomposition are 32 and 40 % for Isotenax and Samicatherm, respectively. The fraction remaining unchanged above 600 °C indicates the presence of inorganic constituents. The kinetic evaluation of thermoanalytical results allowed the lifetime of insulations to be estimated (see *Fig. 10*).

Table 7

Sample	Mass loss after 24 hours Δm[%]		
	160°C	180°C	200°C
New asphalt	3.8	6.7	11.8
Used asphalt	7.9	10.5	14.7
Oil-cont. asph.	13.8	18.0	32.5
Shellack	4.4	5.9	15.6

Table 8

Sample	T[° C]	160	180	200
New asphalt	k[1/min]$\times 10^3$	1.33	3.33	12.88
	$t_{1/2}$[min]	520	208	53.8
Used asphalt	k[1/min]$\times 10^3$	5.18	8.17	23.51
	$t_{1/2}$[min]	133.7	84.9	29.5
Shellack	k[1/min]$\times 10^3$	1.00	3.67	8.18
	$t_{1/2}$[min]	693.1	189	84.8

Table 9

Sample	ΔH^*[kJ/mol]	ΔS^*[kJ/molK]	ΔG^*[kJ/mol]
New asphalt	100.77	–73.50	143.07
Used asphalt	43.76	–191.88	130.71
Shellack	90.55	–95.28	133.72

Table 10

Sample	ΔH^*[kJ/mol]
New asphalt	93.29
Used asphalt	39.12

The lifetime line obtained for Isotenax seemed to be realistic while the stability found for Samicatherm appeared to be too low. The reason for this may be the relatively high proportion of adsorbed substances at the surface of Samicatherm insulations. The lifetime line is less steep for Samicatherm insulations which means that it is less sensitive to temperature changes, thermal shocks.

Comparison of Asphalt Insulations

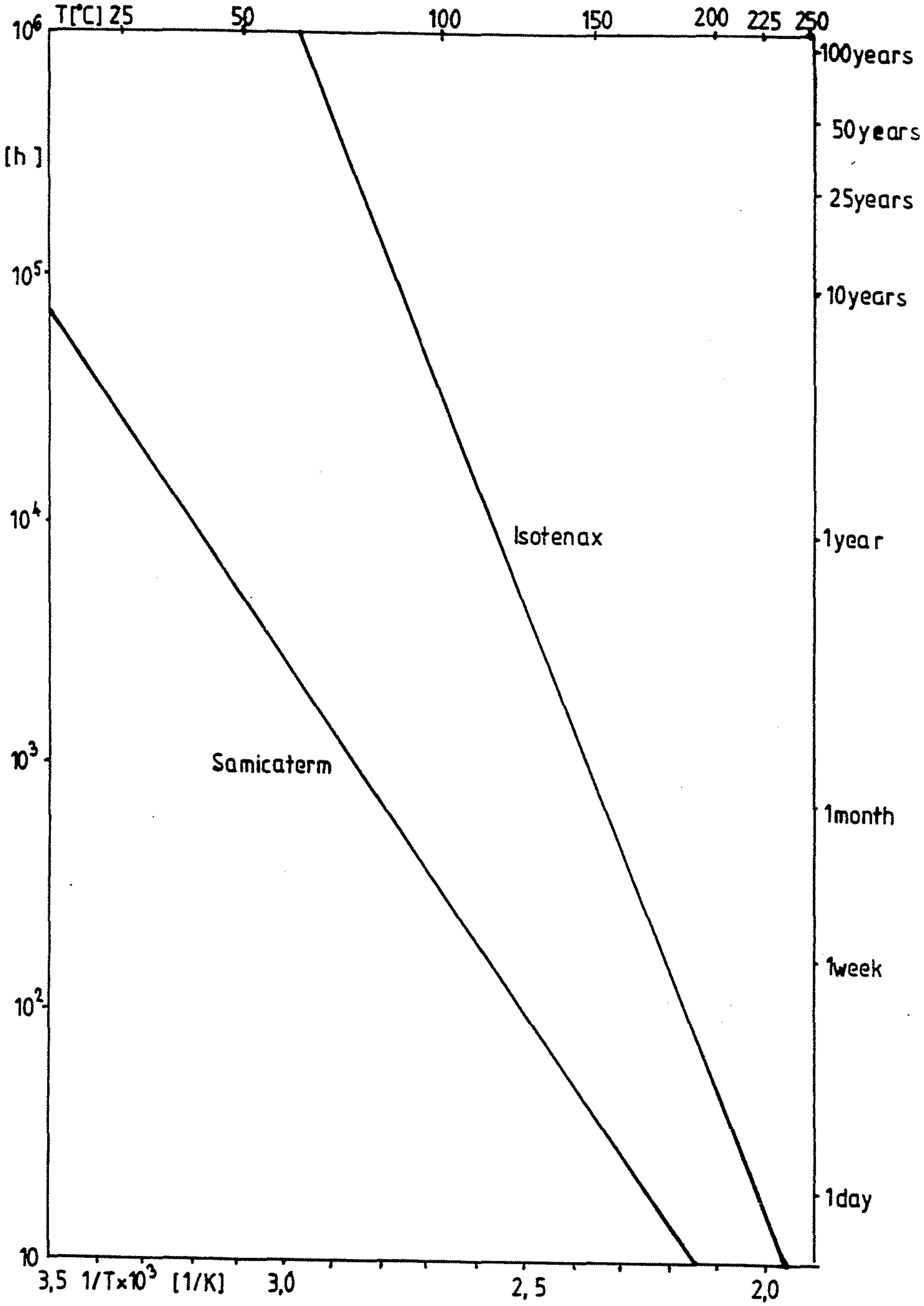
The investigations have shown that changes during the use and those due to contamination with oil of asphalt samples can be followed by thermal methods of analysis.

The exothermal process at 300 °C was ascribed to the decomposition of cellulose. The extent of this process is greater for new samples than for used ones, which suggests a degradation of the insulation during use.

The kinetic evaluation of the experimental results has also revealed that the stability characteristics of the sample deteriorate during use. Contamination with oil drastically reduces the thermal stability of asphalt samples. This may only partly be ascribed to the mass loss due to the evaporation of the oil. It seems probable that the oil dissolves some components which are essential in ensuring the stability of asphalt insulations.

The lifetime lines for new and used asphalt samples are shown in *Fig. 11*.

At low temperatures a lower stability is suggested for new samples by the elimination of volatile components. At the working temperature the stability was found to be similar, whereas on exposure to high temperatures for prolonged time or thermal shock, used and oil-contaminated samples tended to break down, whereas new samples showed a higher stability.


T[°C] 25
50
100
150
200
225
250
10⁶
[h]
10⁵
10⁴
10³
10²
10
100years
50years
25years
10years
1year
1month
1week
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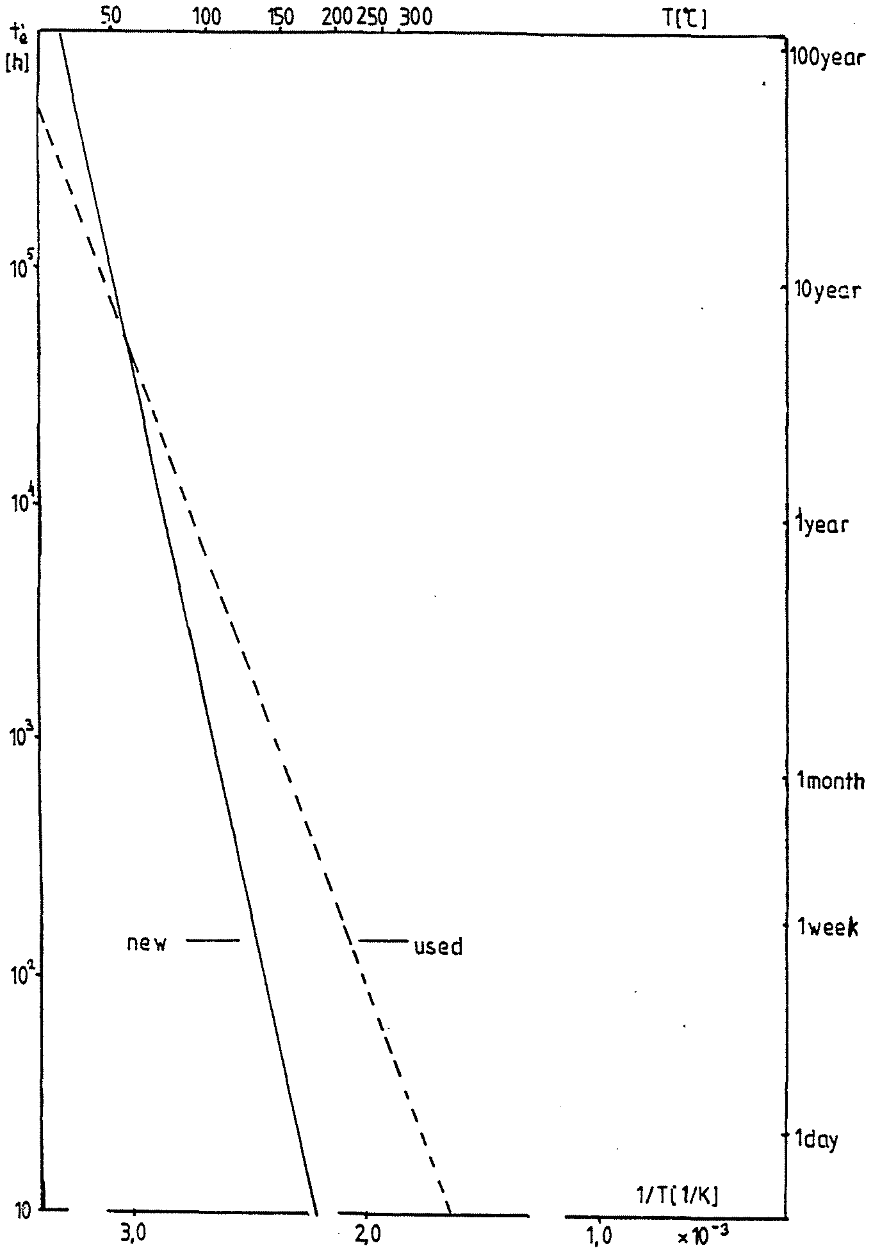
Isotenax
Samicaterm
3,5 1/T×10³ [1/K] 3,0
2, 5
2,0

Fig. 10.


50
100
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T[℃]
t_e^i [h]
10^5
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10year
1year
1month
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new
used
1/T[1/K]
3,0
2,0
1,0
$\times 10^{-3}$

Fig. 11.

Comparison of Asphalt and Shellack Insulations

Static thermoanalytical studies have shown that the samples behave similarly at low temperatures. As the temperature rises, the properties of shellack get worse, so this material may only be used at places where low thermal load is expected.

Summary

Various thermoanalytical methods have been used to classify and compare electrical insulators. In addition to the time consuming and tedious isothermal measurement technique that has so far been used almost exclusively in insulation technique, a rapid and convenient dynamic method has been used. The stability characteristics calculated using different measurement and calculation methods showed good agreement. Thermodynamic parameters and the lifetime can be estimated reliably based on dynamic thermoanalytical measurements.

It should be emphasized that the methods and calculations used are based on formal kinetic considerations, and the data obtained, e. g. the rate constants can be taken as overall values. It has not been proved that the chemical changes are due only to a single reaction. Nevertheless, the overall values obtained are acceptable in absolute value and lifetime estimates can serve as basis for comparison of insulators of similar type.

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