DERIVATOGRAPHIC STUDY OF ELECTRICAL INSULATORS

By

G. LIPTAY,* P. DÁVID** and L. ERDEY*

*Department for General Chemistry, Polytechnical University of Budapest and

**Research Institute for Electrical Industry

(Received March 13, 1965)

Application of thermal analysis, and within it derivatography [1], for study of electrical insulators and insulating substances [2, 3], study of the effect of temperature on the insulating techniques and on the duration of life of the insulators is a very important objective.

Accordingly the two main objectives of thermal analysis in the present field are:

A. Study of changes which may or might play a role during production of the insulating material or insulator in the substance which undergoes various technological treatments.

B. Study of changes of the insulator caused by the effects which it suffers during use.

To the first group belong those thermoanalytical studies of technological nature which concern optimal (heat treating) production or processing technology of an insulating material or insulator. Also experiments of checking character have been intended to follow up kept or perhaps not allowed prescribed technological parameters of a certain production.

To the second group belong thermoanalytical experiments serving to compare thermal decomposition ability of various insulating materials and insulators, and experiments studying ageing properties of the same.

In the following potentialities of thermal analysis — and also derivatography — concerning this field are illustrated by two characteristic examples.

Earlier thermal studies — especially the differential thermoanalytical (DTA) ones — of thermoreactive materials have already shown [4] that extent of heat-treating, i.e. extent of polymerisation or condensation can be approached better, by discovery of deeper correlations by means of the thermal studies than on the basis of e.g. mechanical properties. Results of derivatography support this statement, by simultaneous measurement of enthalpy and weight changes [5, 6].

Similar conceptions were the result of the following experiment-series: derivatographic study of the common bakelite type pressing powder and that of shaped profiles pressed from it. It was expected that the different

condensation states of binding material produced in this way could be followed up on the basis of the corresponding derivatograms and this would give opportunity for the subsequent production testing and for checking of pressing time given by the prescribed technologies.

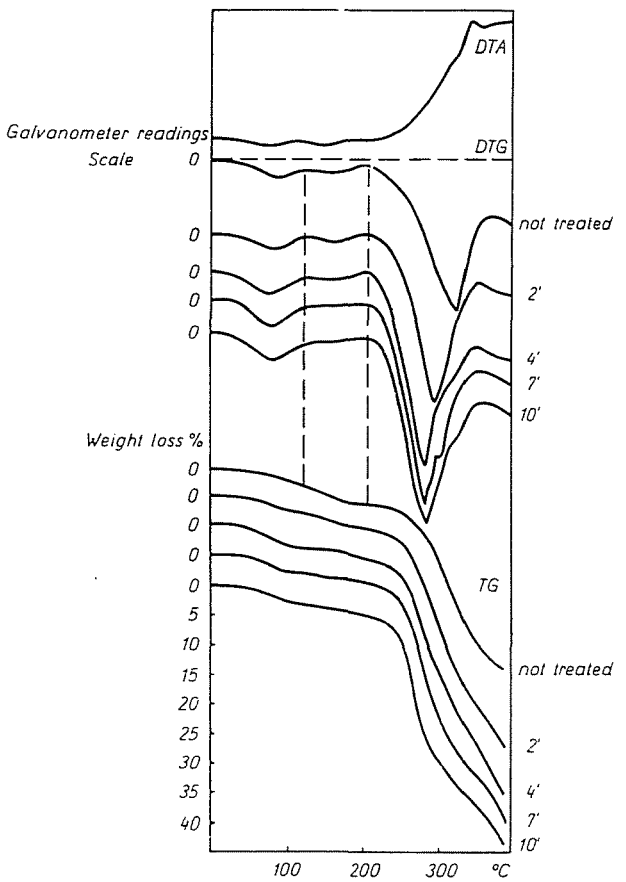

Fig. 1

The expectations could be proved by the obtained results. It is clear from Fig. 1 that process sections of the thermal decomposition proceeding at 100, 150 and 300°C show a tendency which can be brought into connection with the pressing time. First (I) process is the departure of moisture at about 100° C, the second one (II) at about 150°C is presumably the leaving of a free component, the third one (III) at about 300°C is a thermal decomposition process. Considering points marked out by projection of the derivative thermogravimetric (DTG) minima (which separate the process sections) on the thermogravimetric (TG) curve, weight decreases of the single sections can

Table I

Press'ng time m.nutes	Sectional process			Peak temperature
	I.	II.	III.	
0	3.5	2.8	25.4	330
2	3.4	2.2	29.2	300
4	4.0	1.8	31.0	280
7	3.3	1.7	31.5	280
10	3.7	1.5	32.0	280

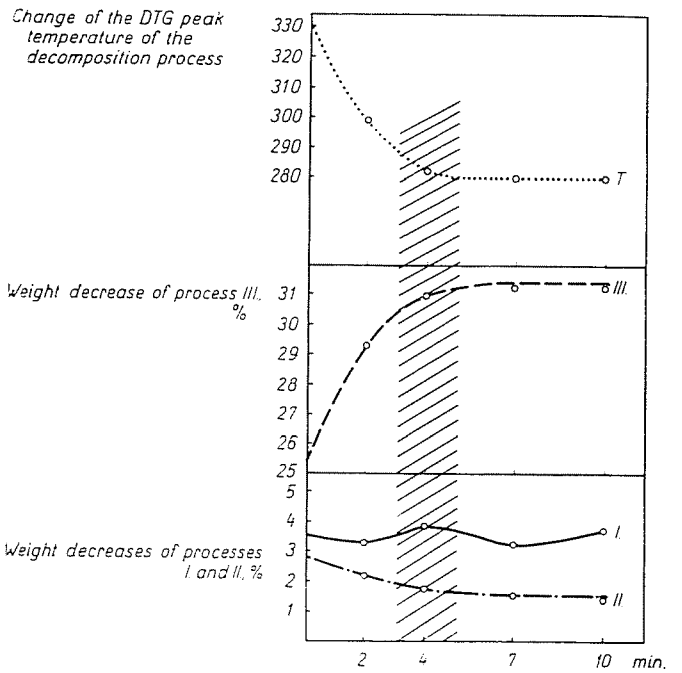

Fig. 2

be obtained. These values and the temperature corresponding to the DTG, — or rate — maximum of the third process are contained in Table I as function of the pressing time, values of which are demonstrated in Fig. 2.

The figure shows that process I does not show any appreciable tendency. The reason for this is that the moisture content depends on the conditions (storing, moisture content of the air, etc.). The other characteristics however show a definite tendency: amount of substance leaving in process II decreases, while the amount of substance leaving in process III increases. That is: this is a product of the pressing and heat-treating process. Temperatures of DTG maxima of process III are of decreasing character. The changes give very characteristic curves, the most interesting common property of which is that

they show the greatest change of direction in the range at about the 4 minutes pressing time (hatched section). As is obvious from Fig. 2 that at a longer than 4 minutes pressing time these properties of the substance do not change as quickly as in the case of a shorter than 4 minutes pressing time. Thus also Fig. 2 shows the pressing time of about 4 minutes as a critical point in the shape of the curves, which agrees well with the technologically prescribed 4 minutes, as pressing time, obtained in a quite different manner.

The example of heat-treating technology mentioned above undoubtedly shows that derivatography can be applied for the following up of a production of this type, or the subsequent control of the products. This success is chiefly due to the fact that all DTA, TG and DTG curves were taken simultaneously and on one and the same sample, which is the greatest advantage of the derivatography compared with other thermal methods [7].

Thus all heat-treating technologies in which besides enthalpy changes, marked weight changes occur, can be more advantageously studied by the derivatographic than by the DTA method.

So *e.g.* stoving conditions of varnished wires must be characterized by the weight change as a function of the temperature too, besides the enthalpy change. Departure of solvents present in the laquer and stoving of the varnish are processes proceeding in time, which have a necessary and optimal overlapping, this optimum cannot be approached without measuring the weight change.

The characteristic property of the thermal analysis (and within it especially of derivatography) that it describes thermal decomposition of one and the same substance broken down to more sectional processes, and makes it possible to evaluate changes caused by mechanical effects or irradiation, not only by the usual methods yielding only the resultant *(e.g.* tensile strength), but also to study correlation of the effects with the single sectional processes, to draw from the derivatographic results deeper, more material conclusions for the mechanism of the changes.

Furthermore, the second most important aspect of derivatography is — as was already mentioned in the introduction — investigation of the ageing process and by it more material evaluation of concept of the duration of life [8].

As it has been already shown, picture of thermal decomposition produced by the thermal analysis as a sum of sectional processes reflects the past of the studied substance well, and in this way the effects obtained during the processing, *e.g.* heat treating etc., can be evaluated or measured by means of studying these sectional processes separately. But in the same way, obviously sectional processes of thermal decomposition of the substance are in different correlation to the ageing of the substance, proceeding at a given temperature, *e.g.* also with time of ageing. A possible ageing process also belongs

to the past of the studied sample, and this way conclusions can be drawn from the derivatogram for the characteristics of the ageing.

Fig. 3 shows derivatograms of four samples of a mica based insulating plate made with epoxy-type binding material, and aged to different extents.

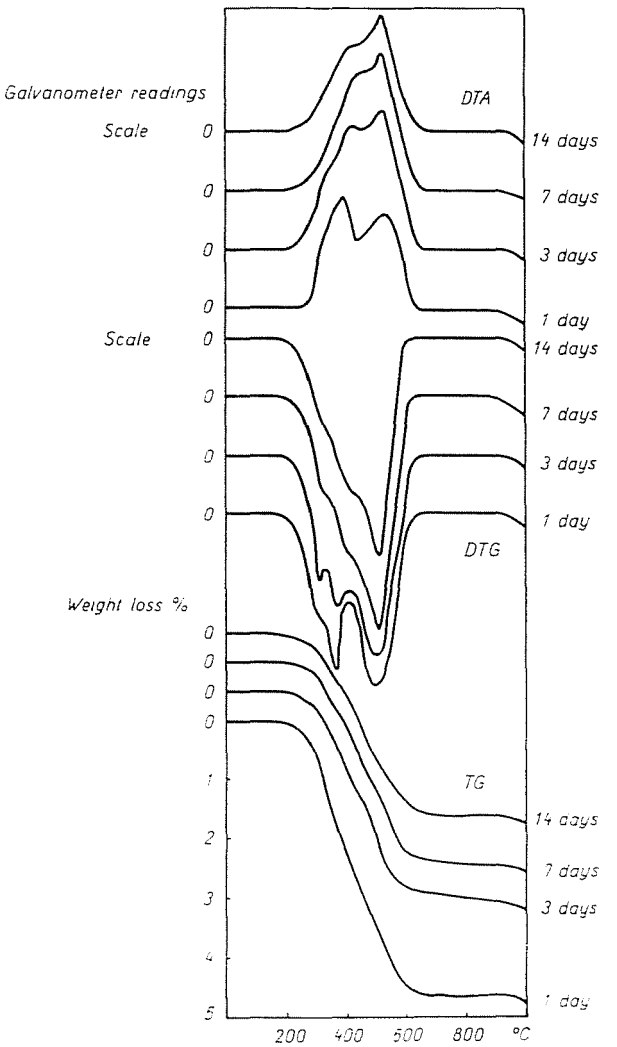

Fig. 3

The ageing was made at 200°C, for 1, 3, 7 and 14 days. As is to be seen all the four derivatograms show thermal decomposition of the sample in the derivatograph as three sectional processes.

These three processes can be distinguished by means of the DTG curve. This way the first process (I) could be marked off at about 330°C on the

basis of inflexion point of the DTG curve, the second one (II) on the basis of minimum of the DTG curve, the third one (III) was marked by the temperature range after the ending of the second process at about 420°: where the organic substances undergo a complete thermal decomposition and — according to the TG curve — completely leave.

Qualitative comparison of the four derivatograms shows first of all that the longer the time of ageing the simpler the derivatograms are. On the DTG curve of sample aged for 1 day is only slightly observable, that up to 330°C an independently existing sectional process controls the thermal decomposition. With sample aged for 3 days, rate of thermal decomposition becomes more stepwise, *i.e.* process I does not seem so insignificant beside processes II and III. On the effect of longer ageing (7, 14 days) differences between the rates of decompositions disappear and the decomposition processes can be separated only by the points of inflexion.

Comparing DTA curves similar statements can be made. It can also be established that process III becomes predominant at longer ageing from the point of view of the enthalpy change.

This can also be seen in comparing the TG curves, because organic substance *i.e.* binding material content of the samples decreases with increasing time of the ageing. This means that processes of drastic thermal decomposition in the derivatograph have begun — although very slowly — during the ageing at 200°C, and have appreciably gone forward during the passing time. It is obvious that decomposition processes belonging to lower temperatures have proceeded the most during the ageing, while ageing properties of components decomposing at higher temperatures are better, and their relative amount increases with increasing ageing time.

Even qualitative evaluation of the differential curves (DTA, DTG) shows that ageing of the insulating material presently studied is composed of more sectional processes (similarly to thermal decomposition), which develop to different extents with progress of ageing process at 200°C, *i.e.* various fractions of the substance show different ageing properties.

Also the quantitative evaluation of the derivatograms supports the validity of the above concept.

As it could already be seen, binding material content of the insulator appreciably decreases with progress of the ageing. The derivatograms, however, make it possible to arrive at more precise conclusions.

Limits of sectional processes projected from DTG curve onto the TG curve have marked out on the ordinate of the TG curve weight decreases (g) which belong to the processes. These weight decreases and ageing times are summarized in Table II, data of which are demonstrated by Fig. 4.

Weight decrease curves belonging to processes I, II and III have a shape similar to that of the so-called ageing curves, which show a change

Table II

Process	Time (days)	1	3	7	14
I.	Weight decrease %	1.1	0.7	0.5	0.4
II.	Weight decrease %	1.2	0.9	0.8	0.7
III.	Weight decrease %	2.3	1.9	2.0	1.9

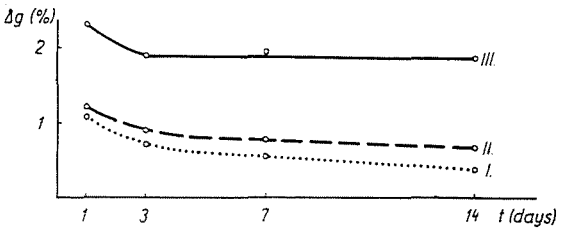

Fig. 4

for a chosen property — in the present case that of the weight decrease — with ageing. Since weight decrease is a property of the aged substance that stands in direct relationship with chemical transformations proceeding during the ageing, investigation of this can give a deeper insight into the kinetics of the ageing processes.

In reality by logarithmic representation quantitative content of the derivatograms discernibly becomes connected with other relations obtained by other methods or known from the literature.

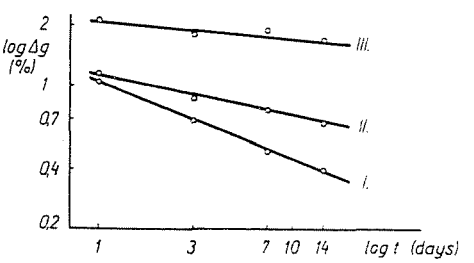

Fig. 5

In Fig. 5 percentage weight decreases of the above-mentioned processes give linear curves — if logarithmic scale is chosen. The lines represent amounts of the fractions of epoxy binder decreasing during the ageing. Therefore their slopes are connected with the kinetics of the processes. Even solely qualitative evaluation of the derivatograms has shown that ageing rates of various fractions having various temperatures of decomposition and found at thermal decomposition of the epoxy resin are different at a chosen temperature.

This obvious, but generally, less considered fact is well proved by Fig. 5. As it is to be seen on the slope of process I having the lowest decomposition temperature is the greatest, while, as the decomposition temperatures increase with processes II and III the slopes of the processes decrease. Ageing rates of fractions of an epoxy resin aged at 200° C, that is, duration of life is different and the higher the temperature of decomposition of the fraction, the smaller the rate of ageing is. On the basis of the drawing, the lines can be written as:

$$\log \Delta g = b - a \log t \tag{1}$$

where Δg is the percentage amount of fractions of the substance, that has not departed nor has been transformed, t is time of the ageing in days, a and b are constants characteristic of the sectional process. Writing relation (1) in the next form:

$$\log t = \frac{b}{a} - \frac{1}{a} \log \Delta g \tag{2}$$

it can be seen that it shows a very striking and remarkable formal and substantial correlation with the known [9, 10]

$$\ln t_T = \frac{B}{T} - \ln D \tag{3}$$

expression.

Here t_T is the duration of life, T is the absolute temperature, $D = \frac{1}{A} \ln \frac{C_0}{C_v}$, an expression containing initial and final concentration of the component taking part in the transformation, or ageing, A and B are constants characteristic of the transformation.

Equation (3) is usually used for expression and representation of the duration of life as function of temperature, when it gives a straight line in a coordinate system with axes $x = \frac{1}{T}$ and $y = \ln t_T$, but formal similarity of equations (2) and (3) becomes a substantial one after considering the correspondences of Δg and D meaning concentration, and of t and t_T meaning time.

Hence thermal ageing of the substance studied is the resultant of the three processes. At a given temperature and ageing rate, duration of life is determined by the rate of sectional process belonging to the concerned temperature range.

Such an investigation method of "higher resolution" for studying thermal ageing of insulating materials and insulators may be suitable for

checking the criteria and for correlation of the criteria with transformations in the substance, on the basis of which criteria conclusions are usually drawn for duration of life of insulators.

*

We express our thanks to Dr. J. Urbanek, Head of the Research Institute for Electrical Industry, for giving us help in raising and resolution of the problem. We owe thanks to the Ganz Electric Works for out-of-turn production of the samples.

Summary

The authors studied by derivatographic method changes proceeding in the various insulating materials on the effect of thermal treatment. In the case of the studied pressing powder of phenoplast type the various states of heat-treating could be detected, and also the empirically determined optimal conditions of heat-treating could be checked by the derivatographic method.

They also studied ageing with the derivatography and interpreted the results and correlated them with the so-called duration of life curves.

References

1. PAULIK, F.—PAULIK, J.—ERDEY, L.: Z. anal. Chem. **160,** 241 (1958).
2. LIPTAY, G.—DÁVID, P.—ERDEY, L.: Periodica Polytechnica El. **8,** 243 (1964).
3. LIPTAY, G.—DÁVID, P.—ERDEY, L.: Elektrotechnika **57,** 392 (1964).
4. MURPHY, C. B.: Modern Plastics **37,** 125 (1960).
5. PAULIK, F.—MACSKÁSSY, H.—PAULIK, J.—ERDEY, L.: Plaste und Kautsuk **8,** 588 (1961).
6. LIPTAY, G.—MRS. BIRÓ—SZŐLLŐSI, I.: Műanyag **1,** 105 (1964).
7. PAULIK, F.—PAULIK, J.: Thermal Analysis. Budapest, 1964. (In Hungarian).
8. DÁVID, P.: Elektrotechnika **57,** 11 (1964).
9. BÜSSING, W.: Archiv Elt. **36,** 333 (1942).
10. DAKIN, TH. W.: Trans. AIEE **67,** 113 (1948).

Prof. Dr. László ERDEY
Dr. György LIPTAY
Budapest XI. Gellért tér 4. Hungary

Péter DÁVID, Budapest II. Lövőház utca 39