DERIVATOGRAPHIC STUDY OF THERMAL DECOMPOSITION OF ELECTRICAL INSULATING MATERIALS AND INSULATORS

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Thermal stability of electrical insulators* is one of the basic problems in electrotechnics. There are methods for measuring and classification of thermal stability which first of all take into consideration the dependence of electrical and mechanical properties of the temperature [1, 2, 3, 4, 5].

Also study of chemical and physical changes occurring on the influence of raised temperature can give valuable data concerning production and technological application of insulators. A knowledge of the former can lead to the knowledge of the mechanism of ageing and thermal decomposition of insulators, and this gives a valuable support to the research, production and qualification of insulators.

It is especially important to observe thermal decomposition of insulators which are subject to higher temperature during usage. Such are e.g. the so called filament-bearers used in electrical heating equipments, and substances encasing the filament or separating it from metallic parts of the apparatus. Such materials are produced of ceramics, and in many cases from mica pressed into boards with an adhesive substance. The latter is called "heating micanite".

We began our thermal decomposition studies with heating micanites, which fact was justified by the need of speedy development, technological and ageing problems of these insulators and need of developing methods for their qualification.

A new instrument, the derivatograph involving in itself the various thermoanalytical methods seemed to be a very suitable instrument for the study of thermal decomposition of heating micanites and electrical insulators [6].

It was expected that from the derivatographic results a more exact concept could be obtained for the temperature range in which a heating micanite could be used and for possibly different interactions between the various micaceous base materials and a chosen adhesive. It was also anticipated to get data for optimal technology for the production of insulators of this type,

* Here and in the following insulating material stands also for insulator for the sake of shortness.

e.g. the advisable temperature limit in heat-treatment during production of a type of heating micanites, up to which temperature the product reaches its final state, i.e. it becomes stable under temperature conditions of employment.

In the first series of measurements we wanted to check the validity of these conceptions, and to establish applicability of the method to resolve special problems in this field.

The derivatograph registers simultaneously photographically and automatically

a) Thermal gravimetric (TG)

b) derivative thermal gravimetric (DTG)

c) differential thermoanalytical (DTA) curves and

d) temperature of the sample [6].

The thermal gravimetric curve presents the weight of the substance as the function of temperature. With the help of this the temperatures and the extent of weight change taking place at constant heating rate in the substance investigated can be established. The thermal decomposition of a substance takes place at a temperature characteristic — under given experimental conditions — for the substance; therefore from the temperature of thermal decomposition and the amount of the substance qualitative and quantitative conclusions can be drawn. Also physically bound water and solvent contents can be established by this method.

Since thermal decomposition processes mostly closely follow each other, the overlapping of the processes in many cases makes the evaluation of the TG curve more difficult.

In derivatography, however, also derivative thermogravimetric curve is obtained. It is produced by the instrument as follows: there is a coil hung onto one of balance arms and a current is induced in it when it moves in a homogeneous magnetic field. This current is registered on a photosensitive paper by means of a mirror galvanometer [7]. By means of DTG curve decomposition processes following (or possibly overlapping) each other can be separated and — by projecting minima of DTG curve onto TG curve — can be quantitatively evaluated.

The derivatograph simultaneously in the same sample also measures the differential thermoanalytical curve: enthalpy changes are detected by two counter-wise switched thermoelements which are immersed in the sample and in the inert substance, respectively. Thus — measuring enthalpy changes, which are not followed by weight changes — melting, recrystallisation, polymerisation, ageing, recombination of bonds etc. can be recorded.

Furthermore also the real temperature of the sample is measured in a special platinum crucible by means of a thermal element in the derivatogarph, in contrast with other thermobalances, where the temperature of the air space of the furnace is generally measured.

Our experiments were made with a PAULIK, PAULIK, ERDEY (*Orion Gyem* 676 Type) derivatograph, in air. The heating rate was 10°C/min and crucibles 18 mm in diameter and 22 mm high were used. The amount of the studied samples was about 500 mg.

First we took derivatograms of three micaceous based materials: that of muscovite, phlogopite and mikape* (Diagram 1, 2 and 3).

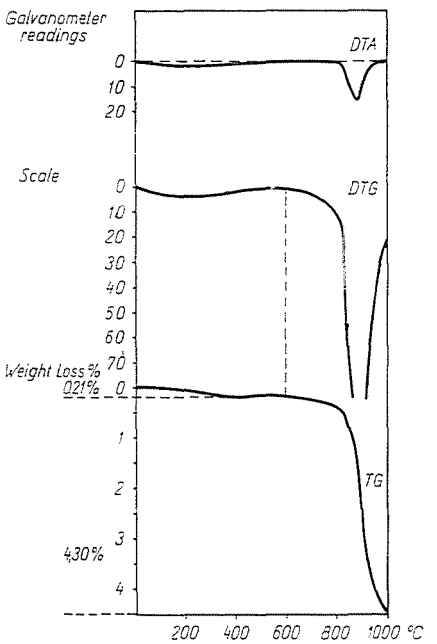

Fig. 1

Fig. 2

The derivatograms later served as comparison bases, but it was worth while comparing derivatograms of number 1 and 3. It is to be seen from these — as is already known — that "mikape" made of muscovite contains less structural water than the original native muscovite mica. But from this the new fact can also be seen that micaceous layers of mikape bind water in weaker, probably in a less ordinately bound form. It can be seen from the shape of the curve that weight decrease of mikape is strong above 700°C, while muscovite begins to decompose only above 800°C. The steeper shape of TG and DTG curves of muscovite moreover means, that a substance of

* Mikape is the Hungarian manufacture-name of the so called mica paper which is made of muscovite mica attached to elementary layers by using a thermal-chemical method. The mica paper name is reasonable because the elementary micaceous layers, since they form very fine flakes, can be gathered together similarly to the cellulose fibres on a papermaking machine into a paper-like product.

greater order decomposes at 800°C, this decomposition process is, however, quicker than that of mikape. This is also indicated by the sharp minimum of DTA curve occurring here too. The corresponding curves for mikape have a smaller slope, and the DTA curve indicates a slow, endothermic process, from which one can conclude that the water leaving has been in a less ordinate state in the mikape. In the following we wanted to study whether thermal de-

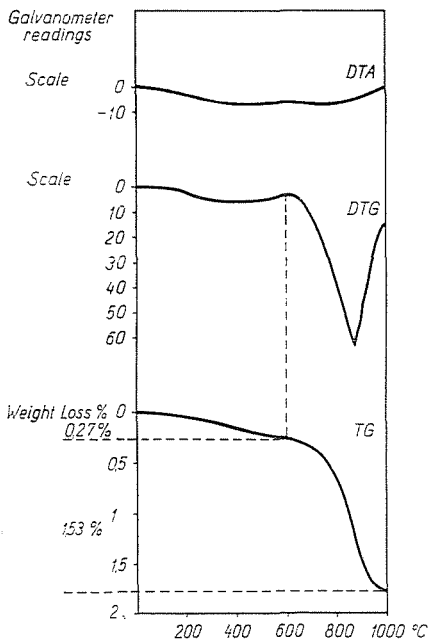

Fig. 3

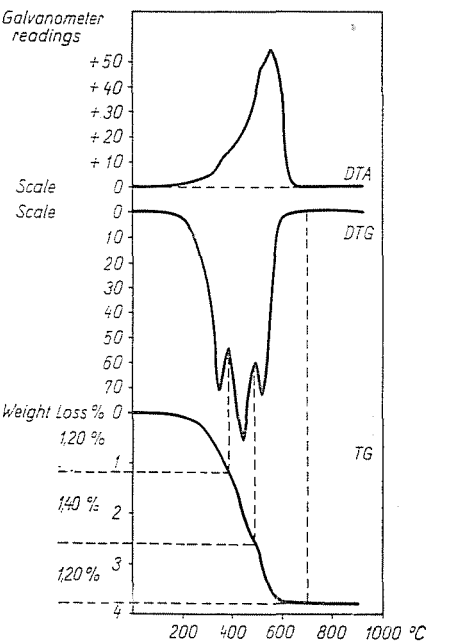

Fig. 4

composition of adhesive being present in lower amounts (4—10%) as compared to mica base materials — can be followed by the method.

We therefore studied thermal decomposition of heating mikanites made from muscovite, phlogopite and mikape base materials and different adhesives.

The derivatogram numbered 4. was obtained for heating mikanite produced in Ganz Villamossági Gyár (Ganz Electric Works) from phlogopite mica, with about 4% shellac adhesiveness. On the figure the shape of the DTG curve between 200 and 600°C characteristic for shellac used as an adhesive can be well seen. This triplet subdivision as it can be seen on derivatograms 5 and 6 — is so very characteristic for shellac used as binding material that it can be used for the detection of it. In the same temperature range DTA curve shows a strongly exothermic character, which can be explained by oxidation. The triplet subdivision can be distinguished within the exothermic peak which agrees well with three processes of weight decrease.

It can also be seen from the TG curve that removal of volatile substances is practically finished at 600°C.

Figures 5 and 6 show a derivatogram of mikape based heating micanite also stuck with shellac. The two measurements were made with two samples taken from two points of the same heating micanite board. The board was taken from a railway-Elekthermax heating oven used for quite a long time and afterwards disassembled. The heating micanite is a product of *Mechanikai Művek* (Mechanic Works).

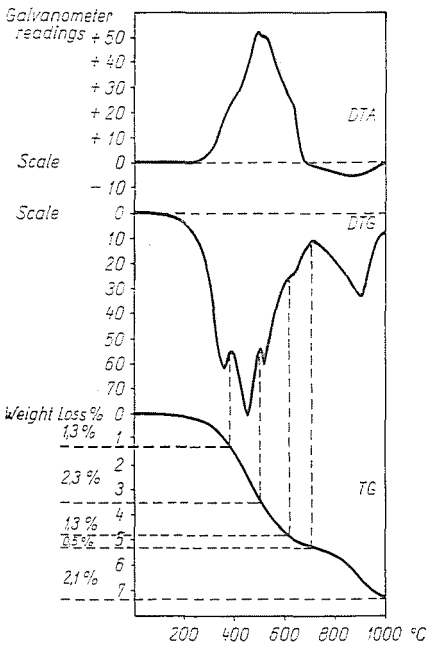

Fig. 5

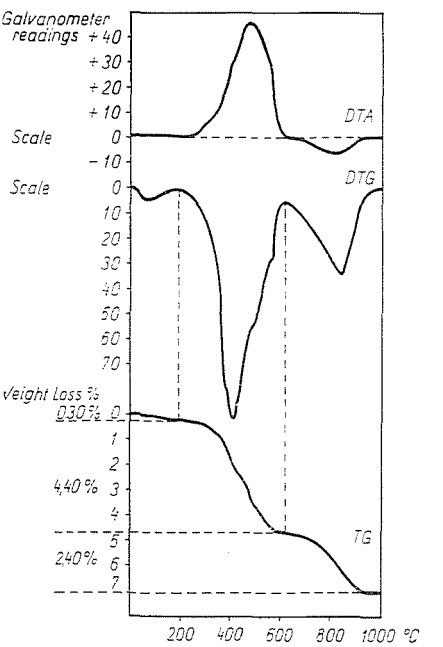

Fig. 6

On comparing the derivatograms it can well be seen, that the DTG peaks of triplet subdivision characteristic for shellac and mentioned in connection with Figure 4 are definite only in Figure 5, while in Figure 6 this subdivision occurs only in the form of slight inflections, however the character remaining.

This subdivision is a picture of thermal decomposition of shellac used as adhesive, and therefore its shape obviously depends on the "past of the sample". The shellac as thermosetting adhesive is also used in electrotechnics, and it is a practice to set it simultaneously during manufacturing of micaceous products between 160 and 180°C. With heating micanite studied by us the „past" of the sample is determined not only by this — i.e. heat treatment during productionbut also by thermal employment during use. This latter may be the cause of less striking DTG singularities of Figure 6 which show thermal decomposition of samples taken from the two ends of the heater,

these having suffered a smaller thermal employment. Strict subdivision of Figure 5 originates from a sample obtained from the middle of the heater which had suffered greater heat treatment, the temperature being higher there. It could be established that designs of thermal decomposition of shellac adhesives having had different heat treatments are also different.

It can also be concluded from comparing Figures 5 and 6 that the derivatogram of the sample taken from the middle of the heater Figure 5 shows

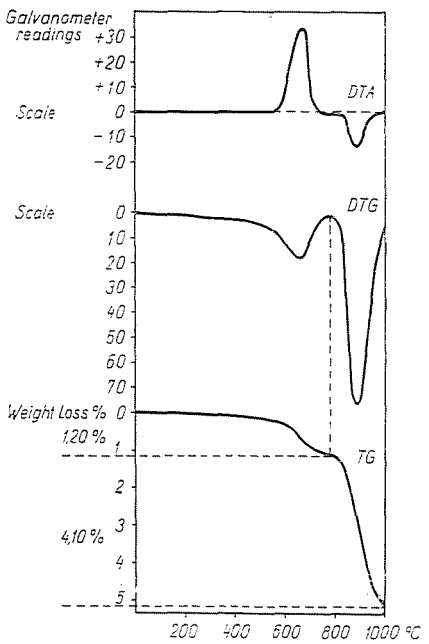

Fig. 7

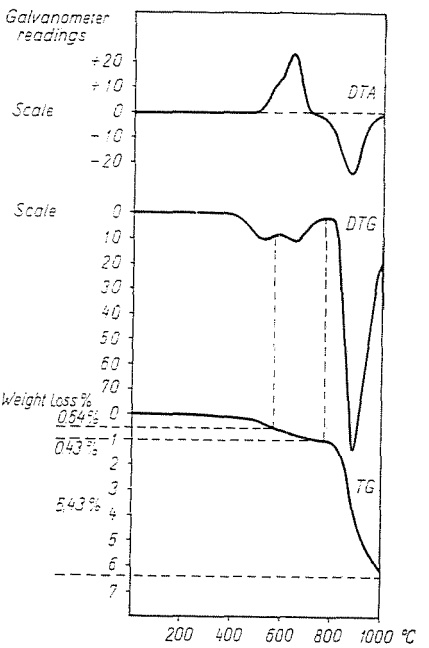

Fig. 8

temperature of total decomposition of the adhesive above 700°C and gives amount of adhesive as high as 5,5%, while the adhesive content of sample taken from the end of the heater (Figure 6) already decomposes above 600°C and the adhesive content is about 4,7%. These phenomena can be explained by mass transfer occurring in the heater and by different thermal employments during its use. Investigations concerning these are still in progress.

For the sake of comparison and for spreading the field of derivatographic measurements, heating micanites made with silicon based adhesives have also been examined.

Figure 7 and 8 show thermal decomposition of heating micanites made of muscovite mica with adhesive by *Nitrokémia V.* (Nitrochemical Works) offered for this purpose with the designation "Silonit 4610". We produced the samples — from the mentioned base materials — in *Villamosipari Kutató Intézet* (Research Institute for the Electrical Industry), under the same technological

conditions. These samples differ from each other only by that in the case of a sample corresponding to Figure 8 also accelerator was added to the adhesive lacquer. It can be seen in the two derivatograms that — though application of the accelerator means important technological advantages — it is not advisable to use an adhesive "catalysed" in this way for the purpose of heating micanites, because thermal stability of such products — as is clear from the comparison of Figures 7 and 8 — is much smaller than that made without accelerator.

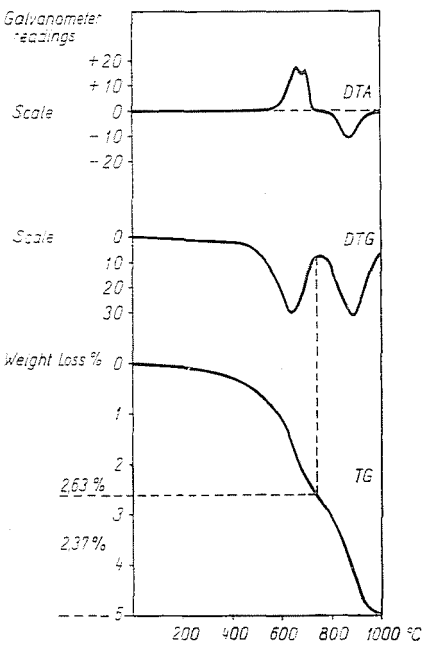

Fig. 9

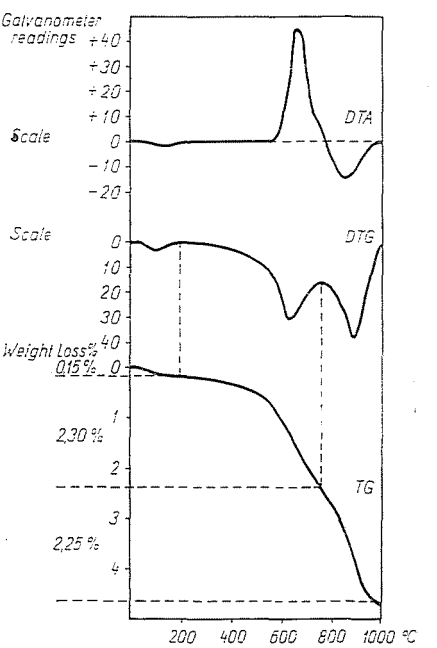

Fig. 10

Derivatograms of mica paper based heating micanites fixed by various silicon adhesives can be seen in Figures 9, 10 and 11.

Figures 9 and 10 show the thermal decomposition of heating micanites made with silicon adhesive lacquer designated "Silonit 4610" and "Silonit 4660", respectively. Considering that both samples were produced from mikape base material and under the same technological conditions, comparison of the two derivatograms means comparison of the two adhesive lacquers which — as can be seen — does not show essential difference as to thermal decomposition of the two products i.e. adhesives.

Figure 11 shows derivatogram of a heating micanite which is also mica paper based and made with silicon adhesive and was produced in Czechoslovakia. It is clear from the Figure that the silicon based adhesive used in this suffers much greater thermal decomposition than those of samples 9 and 10.

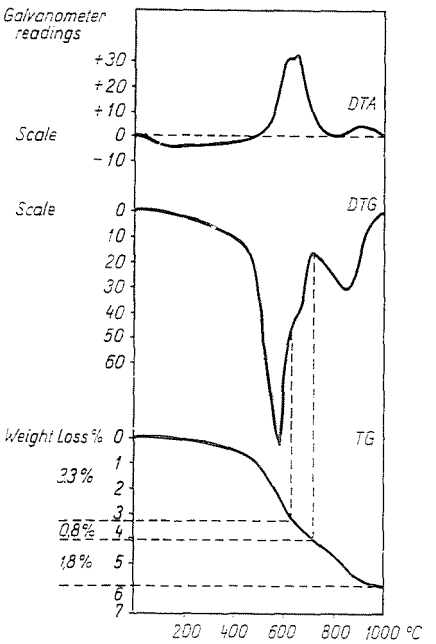

Fig. 11

Summary

Derivatograph appears to be applicable for the investigation of thermal decomposition of insulating materials and insulators, and to study the changes during their production and industrial use.

Our measurements were taken on insulators intended for high temperatures, on heating micanites, observing thermal properties of the occurring components: muscovite, phlogopite, mica paper, shellac adhesive and silicon adhesives.

We have established that thermal decomposition of muscovite mica starts later than that of mica paper made from same, and this can be attributed to structural factors. Thermal decomposition of heating micanites stuck with shellac is different, depending on their past. Also thermal stability of silicon based adhesives can be compared with the method.

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