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## EXAMINATION OF ION-EXCHANGE RESINS BY DERIVATOGRAPHY

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### SUMMARY

The possibility of observing the thermal behaviour of polymeric ion-exchange resins by means of a derivatographic method is considered. The thermal processes that take place during thermal decomposition are discussed and their nature is elucidated.

Information has been obtained on the process of thermal decomposition of the most frequently used Hungarian ion-exchange resins, and relationships are established between the thermal characteristics, the ionic form of the resin and its divinylbenzene content.

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### INTRODUCTION

In water treatment in thermal and nuclear power stations, the investigation of the thermal and radioactive stability of ion exchangers based on synthetic polymeric resins has great importance. We have obtained derivatographic results in order to be able to examine the correlation between the thermal characteristics of the resin samples by observation of the thermal behaviour of the ion-exchange resins submitted to radioactive irradiation at various dosages and, on this basis, to draw conclusions on the thermal and radioactive radiation stability of the resin structure<sup>1</sup>.

In addition to the influence of the radioactive irradiation, we have also observed the influence of the ionic form and the divinylbenzene content of the resins and the influence of the quality of the gaseous medium applied when obtaining derivatographic results<sup>2</sup>.

Mainly Hungarian ion-exchange resins were examined, but for comparison derivatographic results for some Lewatit products of the same type were also obtained. These results support the conclusions drawn in the course of testing the Hungarian resins<sup>3,4</sup>.

### EXPERIMENTAL

Anion exchangers of type Varion AT-400, AT-660, Varion AD, Varion ADM, Varion AD-P and cation exchangers of type Varion KS, Varion KSM and Varion KS-P were used. The resin samples were examined in various ionic forms ( $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{BO}_3^{3-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Fe}^{3+}$ ,  $\text{H}^+$  and  $\text{NH}_4^+$ ) and at different dosages of radioactive irradiation.

tion (0, 50, 100 and 150 Mrad). The derivatographic pictures of the samples were taken in air and nitrogen flows with a Paulik-Erdey derivatograph under identical experimental conditions in the temperature range 20–900° with the following parameters:

Calibration	from a 40-mg sample dried for 1 h at 40° and powdered.
Temperature curve (T)	instrument setting, 1000°.
Thermogravimetric curve (TG)	measuring range, 0–500 mg.
Differential thermogravimetric curve (DTG)	galvanometer sensitivity, 1/5.
Differential thermoanalytical curve (DTA)	galvanometer sensitivity, 1/15.
Heating velocity	10°/min.
Starting voltage	96 V.
Row of pins	3.
rpm of photographic drum	1/100 min.
220-V heating voltage	after 100 min.
Air or nitrogen flow-rate	30 l/h.

In addition to these pictures of the ion-exchange resins, samples of type Lewatit SP-120, MP-62, MP-500, MP-500-A and MP-600 and Varion ADA and ADAM were also examined. Of these samples, Lewatit SP-120 was a sulpho-acidic cation exchanger in the Na<sup>+</sup> form and the others anion exchangers in the OH<sup>-</sup> form.

Firstly, under our experimental conditions, on the basis of duplicate measurements, the limit of reproducibility of the individual pictures was determined and found to be 10°. This value of 10° can be considered as the threshold value for the identification of the DTG peaks obtained under the same conditions. That is, if the difference between the DTG peaks of two different samples examined under identical conditions does not exceed 10°, then the two peaks have occurred as a result of the same thermal process. If the difference between the two DTG peaks is greater than 10°, then different thermal processes have taken place or some effect of factors that cause dissimilarity in the samples has occurred.

## RESULTS

The DTG peaks for the anion-exchange resins are distributed in four temperature ranges, as follows:

In temperature range I (68–157°):

peak at 68°

peak at 117°

peak at 133°

peak at 157°

In temperature range II (196–220°):

peak at 196°

peak at 220°

In temperature range III (260–277°):

peak at 260°

peak at 277°

In temperature range IV (396–430°):

peak at 396°

peak at 415°

peak at 430°

The individual temperature ranges are separated from one another by a minimum of 35°, in which region none of the samples examined gave a DTG peak. Thus the thermal process that takes place in the samples and results in variations of weight proceeds with maximum velocity in one of these four temperature ranges.

From a comparison of the pictures, it can be stated that the first temperature range is the band of water peaks. In this temperature range, the adsorbed moisture and the water of constitution are expelled from the samples. The temperature of the latter depends on the ionic form of the resin and the gas medium employed to a much greater extent than on the resin structure and on the intensity of the radioactive irradiation. The ionic  $\text{OH}^-$  form and nitrogen as the gas medium retard the expulsion of water.

In temperature ranges II and III, splitting off of the active groups takes place. This process involves the rupture of chemical bonds and the expulsion of low-molecular-weight gaseous products. Parallel with this endothermic process, exothermic recombination of the broken bonds of the resin structure also occurs.

It also can be seen in the pictures that the temperature of splitting off the active groups depends primarily on the ionic form of the ion-exchange resin. For example, the thermal stability resins in the  $\text{Cl}^-$  and  $\text{BO}_3^{3-}$  forms is greater by 40° than that of resins in the  $\text{OH}^-$  form.

Temperature range IV is the band of the decomposition of the skeletal structure. During this decomposition, some of the chemical bonds rupture in an endothermic process and gaseous products split off from the resin skeleton, and probably undergo combustion in the presence of air. Recombination of the broken bonds occurs which involves endothermic alteration of the structure corresponding to the stable form at higher temperatures. Thus the double peaks on the DTG curves resulted from endothermic bond rupture, exothermic recombination and endothermic alteration processes.

The interpretation of the DTG peaks of cation-exchange resins is not as unambiguous. The spectrum of the DTG peaks does not show a band arrangement (with the exception of the band of water peaks) similar to that for anion exchangers. This difference can be explained by the fact that with anion exchangers, after expulsion of the water of constitution in temperature ranges II and III, fission of the active groups occurs to give mainly gaseous products which leave the region under consideration, while with cation exchangers, after the departure of the water of constitution, mainly solid reaction products are formed, which do not leave the reaction area. Various compounds that contain sulphur, sodium, potassium, iron and oxygen suffer the greatest changes. The occurrence of DTG and DTA peaks showing these changes inhibits the band arrangement of the spectrum of DTG peaks.

## EVALUATION OF THE RESULTS

On the basis of the derivatographic examinations, it can first be stated that the derivatographic methods can be used successfully for investigating the thermal

characteristics of ion-exchange resins and for performing comparative evaluations of the thermal stability of various products.

The results show that in the course of the thermal decomposition of the ion-exchange resins examined, first the adsorbed moisture and the water of constitution depart, then the active groups binding the ions split off from the skeletal structure of the resin and finally the skeletal structure decomposes. This three-stage decomposition process, especially in the case of anion exchangers, can be clearly followed on the DTG curves, where for each decomposition stage there is a corresponding DTG peak with a definite shape expressing the decrease in weight (Fig. 1). The DTG curves for cation exchangers show a more complicated picture (Fig. 2). Similarly, the enthalpy variations accompanying the thermal decomposition can also be followed on the DTA curves. These variations give information even about the modifications that often follow the individual decomposition cycles but are not accompanied by changes in weight.

Further, it has been shown that the positions of the DTG peak temperatures expressing the points of maximal velocities of the different decomposition processes in the temperature ranges are determined not by the radiation dosage, but by the ionic form of the resin sample, the divinylbenzene content of the resin structure and

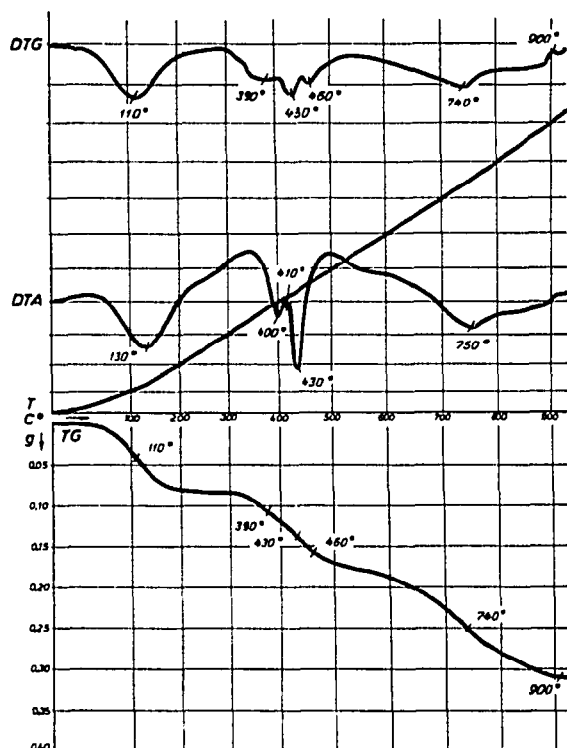
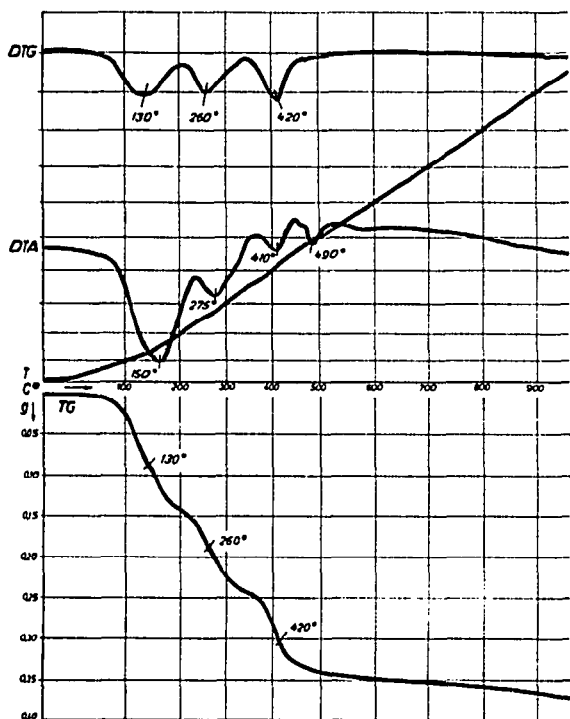


Fig. 1. Picture of a sample of Varion AT-660 ( $\text{Cl}^-$ ) irradiated with 0 Mrad radiation dosage in a nitrogen flow.

Fig. 2. Picture of a sample of Varion KS ( $\text{K}^+$ ) irradiated with 50 Mrad radiation dosage in an air flow.

the gaseous medium employed when taking the pictures. Of these determining factors, the ionic form is of primary importance.

For example, in the first stage of the decomposition process, during the expulsion of water, the positions of the DTG peaks of the individual samples within the band of water peaks were determined by the ionic form of the resin and by the gaseous medium used. This can be illustrated by the following events connected with the band of water peaks (68–157°):

68°	Expulsion of adsorbed moisture from some badly prepared samples.
110°	Removal of the water of constitution of cation exchangers in the $K^+$ form in the case of air flow.
117°	Removal of the water of constitution of anion exchangers in the $Cl^-$ and $BO_3^-$ forms in the case of air flow.
128°	Removal of the water of constitution of cation exchangers in the $Na^+$ , $Fe^{3+}$ , $NH_4^+$ and $H^+$ forms in the case of air and nitrogen flows.
133° and 157°	Removal of the water of constitution of anion exchangers in the $Cl^-$ form in the case of nitrogen flow and in the $OH^-$ form in the case of air and nitrogen flows.

The role of the divinylbenzene content of the resin composition is shown by the results for cation exchangers. The cation-exchange resins examined contain more divinylbenzene (Varion KS, 8%; Varion KSM, 20%) than do the anion exchangers (Varion AT-400, 4%; Varion AT-660, 6.6%; Varion AD, 6.6%). The results showed that a larger divinylbenzene content results in fission of the active groups at lower temperatures, but the fission temperature is determined by the ionic form, as can be seen from the comparison in Table I.

In the fission of the active groups of anion exchangers, the decomposition temperature found in the case of ionic forms of the resin with lower molecular weight was lower by 40° than in the case of ionic forms with higher molecular weight. Thus the decomposition of resins in the  $OH^-$  form occurs at 196° and 220°, while that of resins in the  $Cl^-$  and  $BO_3^-$  forms occurs at 280° and 277°.

TABLE I  
FISSION TEMPERATURES OF CATION EXCHANGERS IN DIFFERENT IONIC FORMS

Ionic form	Fission temperature (°C)	
	Varion KSM (20% divinylbenzene)	Varion KS (8% divinylbenzene)
$Na^+$	350	430
$K^+$	320	390
$Fe^{3+}$	240	315
$NH_4^+$	355	395

## CONCLUSION

From the results obtained, it can be stated that the thermal decomposition of ion exchangers based on styrene-divinylbenzene is influenced primarily by their

ionic form and secondly by their divinylbenzene content. The radioactive radiation used has no influence on the process.

As regards the practical application of the results obtained during this work, new possibilities have become apparent in the employment of derivatographic methods in the production and use of ion-exchange materials. Results and relationships can be obtained that may contribute to a great extent in solving the problems that arise in the application of ion-exchange materials in high-temperature condensate treatment (Powdex) and in other theoretical and practical aspects of ion exchangers.

#### REFERENCES

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