

## **THERMAL BEHAVIOUR OF BINARY MIXTURES OF HIGH-MOLECULAR POLYOXYETHYLENE AND ALKALI METAL THIOCYANATES**

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The thermal behaviour of binary mixtures of sodium or potassium thiocyanate with two high-molecular polyoxyethylenes (POE) of different molecular weights was studied in a broad temperature range by means of a combined thermal analysis technique. Some thermal characteristics of the binary mixtures, which depend on the component content and the preparation method, were determined. It was established that the investigated alkali metal thiocyanates, which form molecular complexes with POE, exert a considerable thermostabilizing effect on the POE. The optimum content of sodium or potassium thiocyanate for the maximum thermostabilizing effect was found to be from 2 to 5 mass %.

Because of the widening fields of application of polyoxyethylene (POE) and its thermostable composition, study of their thermal behaviour is of considerable interest. A number of patents [1-9] and reports [10-16] on this problem have been published, but most of them deal with the oxidative decomposition of POE in the low-temperature range, about or slightly above the melting point, i.e. from 70° to 100° [1, 4, 5, 7, 9, 11] and rarely in the temperature range of 100° to 150° [2, 3, 6, 10]. The change in the molecular mass of the polymer as a consequence of heating up to different temperatures has most often been used to characterize the influence of different types of stabilizers. Investigations on the mass and heat release during the thermal decomposition of POE at higher temperatures, especially in the presence of thermostabilizers [10, 13, 15, 17], are scarce and incomplete. Such investigations can throw light upon the total mechanisms and kinetics of thermal decomposition reactions influenced by stabilizers.

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The thermostability of POE is known to increase in the presence of different organic and inorganic substances, including phenols, amides of carboxylic acids, aliphatic and aromatic amines, sulphur- and phosphorus-containing organic compounds, organometallic compounds, and compounds containing alternate double bonds [17]. Some patents report the use of thiocarbamide, dithiocarbamide, and potassium and sodium thiocyanates [1]. The molecular complexes of POE with sodium and potassium thiocyanates [18], the ways they can be obtained and some of their properties have been studied, but investigations on their thermostability and data on their thermal behaviour have not been reported.

The aim of the present work was to study the influence of alkali metal (sodium and potassium) thiocyanates, which form molecular complexes with POE, on the thermal behaviour of high-molecular POE in a broad temperature range in a dynamic regime of heating.

## Experimental

Binary mixtures of sodium/potassium thiocyanates (p.a.) with three types of high-molecular POE having different mean viscosity molecular masses ( $M_v$ ), denoted POE-1 ( $M_v=5.5 \cdot 10^6$ ), POE-2 ( $M_v=2.7 \cdot 10^6$ ) and POE-3 ( $M_v=1.8 \cdot 10^6$ ), were analysed. The binary mixtures were prepared in three ways:

1. By mixing the components (POE-1 or POE-3 and sodium/potassium thiocyanate) in the solid state and homogenizing the mixture by grinding at room temperature for one hour.

2. By mixing POE and the molecular complex (MC) of POE with sodium thiocyanate in the solid state and homogenizing the mixture in the same way as above. The MC of POE with sodium thiocyanate (38 mass% thiocyanate) was prepared by mixing a 1% chloroform solution of POE with a saturated solution of sodium thiocyanate in acetone and then separating the solvent.

3. By mixing a 1% solution of POE-2 in methanol with a saturated solution of sodium thiocyanate in methanol at room temperature and then separating the solvent.

The content of sodium thiocyanate in the mixtures was varied from 0.1 to 58.8 mass%, and that of potassium thiocyanate from 0.1 to 35.5 mass%.

For the study of the thermal behaviour of the initial compounds and binary mixtures, a combined dynamic thermal analysis apparatus, an OD-102 derivatograph (MOM, Budapest), was used under the following conditions: temperature range – 20-500°; heating rate – 5 deg/min; sample weight –

100±0.5 mg; medium – air (static) and a continuous flow of nitrogen flowing over the sample at a rate of 17 l/h; holder – a ceramic metal crucible; no inert substance; thermocouples – Pt/PtRh.

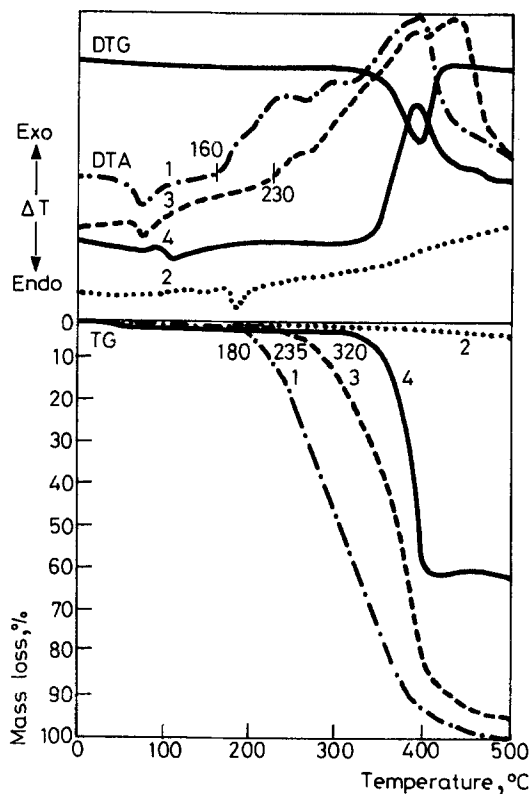
Through measurement of the mass loss in the characteristic temperature interval, the effective activation energy ( $E_a$ ) of the thermal decomposition was calculated by Reich's method [19, 20].

The areas of the melting peaks and the total exothermal effects of the oxidative decomposition ( $S_{ox}$ ), registered by the DTA curves under the same experimental conditions, were measured by graphical integration.

## Results and discussion

### 1. Initial components

The DTA, TG and DTG curves (1 and 2 in Fig. 1) of POE-1 illustrate its thermal and thermooxidative transformations: the influence of oxygen on the progress of the decomposition reaction under the condition of the derivatographic analysis. The decomposition processes in air medium (curve 1) were accompanied by an intensive release of heat throughout the whole temperature range of decomposition (185-500°), the maximum rates of both the mass and heat release being at 395°. In nitrogen medium (curve 2), the low-temperature exothermal effects disappeared completely and the remaining exothermal effects were greatly reduced, which proved that they were oxidative in character. As a result of the lack of oxidation reactions, the initial mass release ( $T_o$ ) shifted towards higher temperatures by about 120 deg. Thus, the thermal decomposition of POE-1 in an inert medium took place in a narrower temperature interval, and no appreciable change in the temperature of its maximum rate ( $T_{max.rate}$ ) was observed. The residual mass measured from the TG curve at 500° ( $M_{500}$ ) (Fig. 1) was retained, which shows that the influence of atmospheric oxygen is of crucial importance, mainly in the initial stages of the thermal decomposition of POE. The increase in the thermostability in nitrogen medium was connected with an increase in the effective  $E_a$  of the total decomposition reactions (ranging from 48.0 kJ/mol in air medium to 96.5 kJ/mol in inert medium), as well as with a decrease in the total heat release in the thermooxidative decompositions ( $S_{exo}$ ) (Fig. 1). The increase in the maximum amplitude of the DTG curve ( $A_{max}$ ) in nitrogen medium was connected with a narrowing of the temperature interval of decomposition, which brought about an increase in its rate.



**Fig. 1** Thermal curves of POE-1 (curves 1 and 2); NaSCN (curve 3) and their mixtures prepared by the first method (curves 4 and 5). NaSCN content in mass %: 1 and 2 - 0%; 3 - 100%; 4 - 0.1%; 5 and 6 - 5.0%. Curves 1, 3, 4 and 5 - in air medium, curve 2 - in nitrogen medium

The thermal behaviour of POE-2 (Table 1) and POE-3 (Fig. 9, curve 1), studied under the same conditions, was similar to that of POE-1, the only differences being that their respective temperatures of decomposition ( $T_o$ ) were lower by about 20 deg and there was a certain retardation of the decomposition rate, which could be expected because of the lower molecular masses of POE-2 and POE-3.

The experimental thermal curves of the initial sodium and potassium thiocyanates, registered under the same conditions and compared in Fig. 1 (curve 3) and Fig. 9 (curve 2), show that up to the end of the analyzed temperature interval (500°) the basic decomposition reaction has not yet begun; up to that temperature sodium thiocyanate loses about 10% of its mass and potassium thiocyanate only 2%. The thermal effects of the melting

of the salts were registered in the DTA curves at 310° for sodium thiocyanate and at 140° and 180° for potassium thiocyanate.

**Table 1** Thermal characteristics of binary mixtures of POE-2 and NaSCN, prepared by dissolving of components

NaSCN content, mass %	$T_{\text{melt.}}$ POE-2, °C	$T_{\text{melt.}}$ MC, °C	$T_{\text{melt.}}$ NaSCN, °C	$T_0$ , °C	$T_{10}$ , °C	$T_{50}$ , °C	$T_{\text{max. rate}}$ , °C	$A_{\text{max}}$ , mm
0	75	-	-	170	235	325	385	17
1.0	75	-	-	220	295	380	395	42
2.0	75	-	-	270	340	395	400	45
5.0	70	-	-	270	340	390	395	47
15.5	65	-	-	300	350	380	385	90
17.0	60	-	-	310	350	385	385	93
38.0	-	190	-	330	365	390	380	67
58.5	-	190	305	330	365	-	380	34
100.0	-	-	305	425	-	-	-	-

## 2. Binary mixtures of POE and sodium thiocyanate

The thermal analysis data on mixtures of POE-1 with sodium thiocyanate prepared in the first way (Figs 1-7) show considerable changes in their thermal characteristics, connected with the mass and heat release in the thermal decomposition reactions, in comparison with those of the initial POE-1. With increase of the sodium thiocyanate content, a slight tendency towards a lowering of the melting temperature and heat of the crystal phase is observed, which is confirmed by the differential scanning calorimetry data.

The analysis of the initial oxidation temperatures determined from the DTA curves (Fig. 2, curve 1) reveals their sharp increase, even at quite low contents of sodium thiocyanate, in comparison with that for the initial POE-1. It can be seen from Fig. 1, curves 1 and 5, that, besides the considerable shift towards higher temperatures, there is also a certain reduction in the initial exothermal effects of POE oxidation. The other exothermal effects connected with the basic thermooxidative decomposition of the sample also change, though to a lesser extent (Fig. 2, curves 3, 5, 7 and 11). When the content of sodium thiocyanate is more than 1 %, the first exothermal effect vanishes almost completely, and there are sharp reductions in the others, while the general heat release and the areas of the exothermal effects are

reduced by more than 50 % in comparison with those for the initial POE-1 when the content of sodium thiocyanate is more than 4% (Fig. 3).

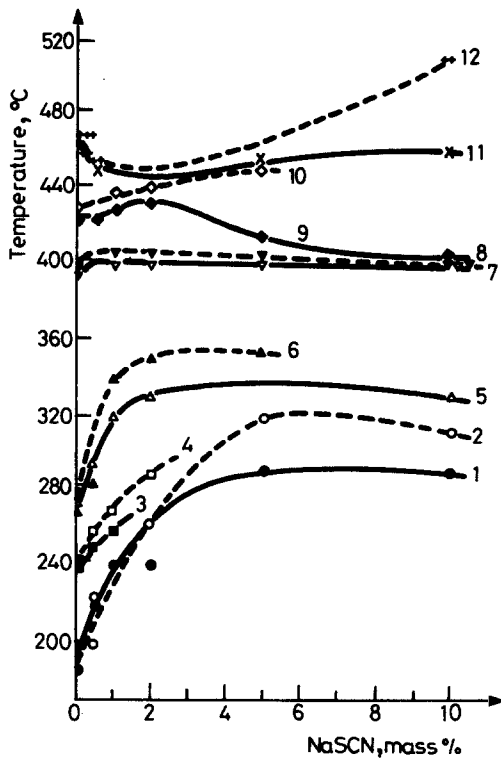


Fig. 2 Dependence of the temperatures of the beginning of oxidation ( $T_{\text{ox}}$  - curves 1 and 2) and of the temperatures at the maximum of the exothermal effects of I, II, III, IV, V and VI exothermal effects ( $T_{\text{II}}$  - curves 3 and 4;  $T_{\text{III}}$  - curves 5 and 6;  $T_{\text{IV}}$  - curves 7 and 8;  $T_{\text{V}}$  - curves 9 and 10;  $T_{\text{VI}}$  - curves 11 and 12), registered on DTA curves, for mixtures of POE-1 and NaSCN prepared by the first method (curves 1, 3, 5, 7, 9, 11) and by the second method (curves 4, 6, 8, 10, 12) on the NaSCN content.

the first exothermal effect is clearly displayed only for the initial POE

Figure 4 (curves 1, 3, 5, 7 and 9) shows that the change in the thermostability, measured via the mass loss displayed in the TG curves, is quite substantial and the initial temperatures of mass release ( $T_0$ ) are very close to those of the beginning of oxidation ( $T_{\text{ox}}$ ), established from the DTA curves (Fig. 2, curve 1). With increase of the sodium thiocyanate content, the initial temperature of decomposition ( $T_0$ ) and the temperature of 10% decomposition ( $T_{10}$ ) increase considerably, whereas the temperature of 50% decom-

position ( $T_{50}$ ) increases less so and the temperature of the maximum rate of decomposition ( $T_{\max.\text{rate}}$ ) increases least. A certain increase is observed in the temperature of the end of the step in the TG curve ( $T_{\text{end.step}}$ ), which corresponds to the basic decomposition of POE-1, and at a sodium thiocyanate content of about 5 mass% a separate stage appears in the decomposition of the by-product formed after the basic decomposition of the sample (Fig. 1, curve 5). The same curve also reveals a distinct splitting of the high-temperature exothermal effect of the burning of the by-product. At a sodium thiocyanate content of 10 mass%, the two constituent effects are already entirely separated and the respective steps in the TG curve in this temperature interval are differentiated from each other. With increase of the sodium thiocyanate content, the residues obtained at  $T_{\max.\text{rate}}$ ,  $T_{\text{end.step}}$  and  $T_{50}$  constantly increase (Fig. 5, curves 1, 3 and 5).

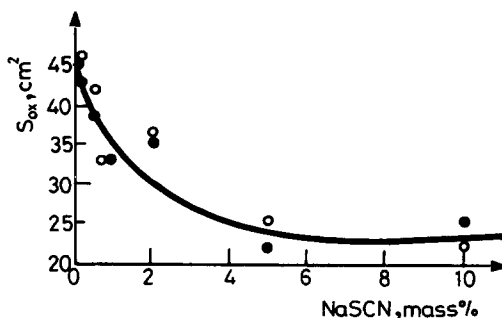


Fig. 3 Dependence of the total exothermal effects registered for thermooxidative decomposition ( $S_{\text{ox}}$ ) of mixtures of POE-I and NaSCN prepared by the first method (●) and by the second method (○) on the NaSCN content.  $S_{\text{ox}}$  is reduced to 100 mass % content of POE-I

The established data show that in the presence of sodium thiocyanate there is a considerable stabilizing influence over the whole process of thermooxidative decomposition of POE and especially in the stage of initial thermooxidative decomposition. The increase in the initial thermostability of POE-1 in the presence of sodium thiocyanate is similar in character and extent to that of the initial POE-1 subjected to heating in an inert medium and is achieved because of the narrowing of the decomposition reaction interval and the increase in its rate, indicated by the maximum amplitude of the DTG curve ( $A_{\max}$ ) (Fig. 6). With increase of the sodium thiocyanate content, the thermostability of POE-1 increases together with the values of

the effective  $E_a$  of thermooxidative decomposition (from 48 kJ/mol for the initial POE up to 142 kJ/mol for a sodium thiocyanate content of 10 mass.%) determined in the temperature intervals of the basic decomposition of the samples (Fig. 7).

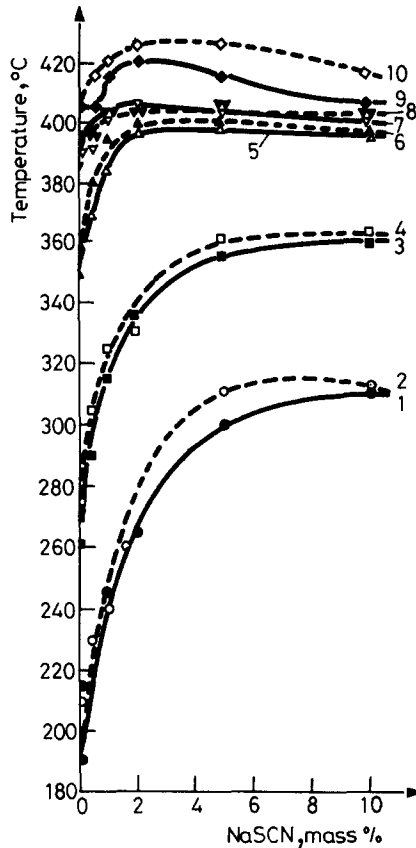
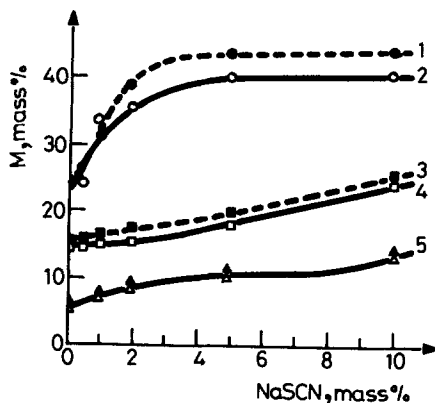


Fig. 4 Dependence of the characteristic temperatures of decomposition of mixtures of POE-1 and NaSCN prepared by the first (curves 1, 3, 5, 7, 9) and by the second method (curves 2, 4, 6, 8, 10) on the NaSCN content: initial temperature of decomposition ( $T_0$ ); temperature of 10 mass% decomposition ( $T_{10}$ ); temperature of the maximal rate of decomposition ( $T_{\max \text{ rate}}$ ); temperature of 50 mass% decomposition ( $T_{50}$ ); temperature of the end of the basic step of the TG curve ( $T_{\text{end step}}$ )

It should also be noted that the mass of the residue after the decomposition reaction, measured from the TG curves at different stages of heating, is proportional to the content of sodium thiocyanate in the initial mixture



(Fig. 5, curves 1, 3 and 5). The presented data show that to a first approximation the total residue of a mixture after heating, measured at  $T_{\text{end,step}}$ , and that measured at  $500^{\circ}$  do not differ much from the sum of the residues of the initial POE and sodium thiocyanate at the same temperatures.



**Fig. 5** Dependence of the residual mass in some characteristic points of the TG curve for mixtures of POE-1 and NaSCN prepared by the first method (curves 1, 3, 5) and by the second method (curves 2, 4, 5) on the NaSCN content; curves 1 and 2 - at  $T_{\text{max}}$  rate; 3 and 4 - at  $T_{\text{end,step}}$ ; 5 - at  $T=500^{\circ}\text{C}$  (resultant curve of the temperatures of the mixtures prepared by the first and the second method)

It is interesting to note that the results obtained for the thermal stability of mixtures having a content of sodium thiocyanate of from 2 to 5 mass% in air are not considerably different (especially in mass loss) from those in nitrogen, or from that for the initial POE in nitrogen medium (Fig. 1, curves 2, 5 and 6). Therefore, it can be assumed that the influence of sodium thiocyanate is limited to eliminating the oxidative effect of atmospheric oxygen on POE during heating. In this case, there should be a concentration boundary for the stabilizer and probably a limit of increase in the thermostability, which should be close to that for POE heated in an inert medium. Our investigations prove that beyond a certain concentration of sodium thiocyanate (2-5 mass%) the thermal characteristics of the mixtures remain almost constant. Other investigators define the optimum content for different POE stabilizers to be 0.5 to 5 mass% [1-3].

Curves 1 and 2 in Fig. 8 show the thermal transformations of a mixture of POE-1 and sodium thiocyanate in air and inert media. The mixture was prepared from their solutions by evaporating off the solvent. The mixture

has considerable thermostability, in accordance with the stoichiometric content of the molecular complex of POE-1 and sodium thiocyanate (3 mol POE-1 and 1 mol thiocyanate), in comparison with that of the initial POE-1 (Fig. 1, curve 1). Similar thermal behaviour has been established for the molecular complex of sodium thiocyanate and POE-2 (Table 1), which has a lower molecular mass in comparison with POE-1.

It was found that the binary mixtures of POE-2 and sodium thiocyanate prepared by the first method acquired considerable thermostability, of the order of the above-mentioned data for POE-1. As can be seen from the contents and the thermal characteristics of the binary mixtures of POE-2 and sodium thiocyanate prepared by the third method, there was a similar thermostabilizing influence of sodium thiocyanate over POE-2 in this case, too.

In order to obtain comparable data for the binary mixtures of POE-1 and sodium thiocyanate prepared by the first and the second methods, mixtures of the two types having equal thiocyanate contents (in the second type it was introduced as a molecular complex in POE-1) were investigated. The respective thermal characteristics of the mixtures were measured under identical conditions (Figs 2-7). It was established that, with increase of the sodium thiocyanate content, the changes in the thermal characteristics towards an increase in the thermal stability were of the same order; the change was modified almost only by the sodium thiocyanate content and did not depend on the way the mixture has been prepared. The graphical dependences (Figs 2-7) show that some of the thermal characteristics of the mixtures prepared by the second method are slightly better, as far as their thermostability is concerned, in comparison with those of the mixtures prepared by the first method. In other, unpublished studies of ours, the partial formation of a molecular complex of POE and sodium thiocyanate after mixing in the solid state at room temperature is proved by X-ray radiographic and calorimetric analyses, while their complete transformation takes place at temperatures higher than the melting temperature of POE. The content (3:1 molar ratio) and the structure of the molecular complex obtained are the same as for the molecular complex of POE and sodium thiocyanate obtained from their solutions after separation of the solvent. Therefore, it can be assumed that the mixtures of POE with a molecular complex of POE and sodium thiocyanate are similar but more homogeneous in their composition in comparison with the mixtures prepared from POE and the initial sodium thiocyanate. This fact accounts for the better thermostability exhibited in some cases by the mixtures prepared by the second method.

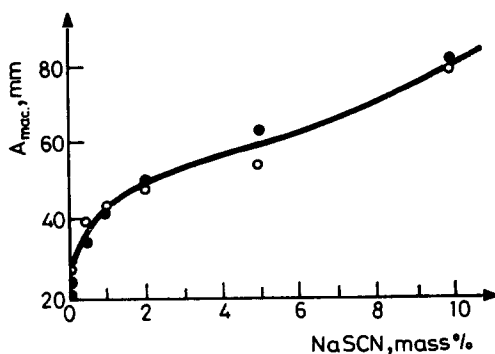


Fig. 6 Dependence of the amplitude of the DTG curve at maximal rate of decomposition ( $A_{max}$ ) for mixtures of POE-1 and NaSCN prepared by the first (●) and by the second method (○) on the NaSCN contents

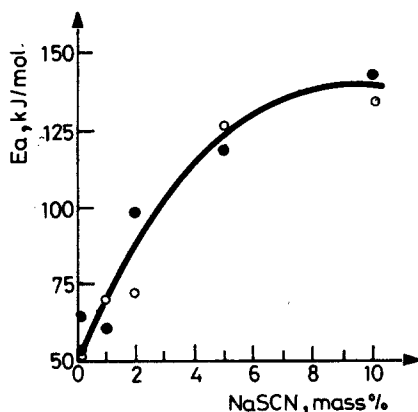


Fig. 7 Dependence of the effective activating energy ( $E_a$ ) of the thermal decomposition of mixtures of POE-1 and NaSCN prepared by the first (●) and by the second method (○) on the NaSCN contents

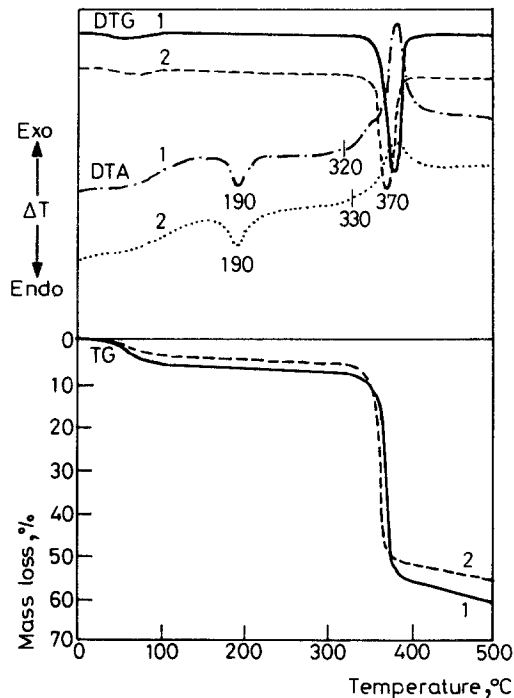
### 3. Mixtures of POE and potassium thiocyanate

Figure 9 shows the thermal curves of some of the mixtures of POE-3 and potassium thiocyanate, which reveal the effect of potassium thiocyanate as a thermostabilizer of POE. Since a wide range of concentrations of potassium thiocyanate were investigated (from 0.1 to 35.5 mass%), it can be stated that the principal regularities observed in part 2 as concerns the increases in the

initial thermostability and the other thermal characteristics of POE hold true for potassium thiocyanate, too. The optimum concentrations of potassium thiocyanate are of the order of 4 to 5 mass%.

## Conclusion

1. Sodium and potassium thiocyanates have considerable thermostabilizing effects on POE, regardless of the way they are introduced into the POE - by preliminary mixing in the solid state, or by dissolving them with subsequent evaporation off of the solvents, or in the form of a molecular complex with POE. According to the thermal analysis data, the resulting thermostability effects are of the same order and mechanism.



**Fig. 8** Thermal curves of the molecular complex of POE-1 and NaSCN (38 mass % NaSCN) prepared by the third method. Curves: 1 - in air medium, 2 - in nitrogen medium

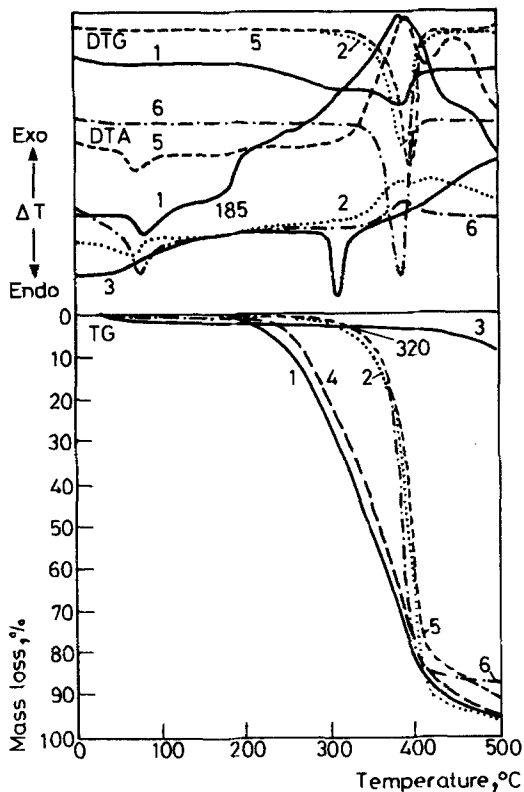


Fig. 9 Thermal curves of POE-3 (curve 1), KSCN (curve 2) and their binary mixtures (curves 3 and 4) prepared by the first (curve 3) and by the third (curve 4) method, registered in air medium. KSCN content, mass%: 1 - 0; 2 - 100; 3 - 1; 4 - 35.5

2. For all three methods of mixing, the optimum thermostability effect is observed at contents of thiocyanate (sodium or potassium) of 2 to 5 mass. %.

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**Zusammenfassung** — Mittels kombinierter Thermoanalysetechniken wurde in einem breiten Temperaturbereich das thermische Verhalten binärer Gemische aus Natrium- oder Kaliumthiocyanat und zwei hochmolekularen Polyoxyethylenen (POE) verschiedenen Molekulargewichtes untersucht. An diesen binären Gemischen wurden einige thermische Eigenschaften bestimmt, die von Komponentenzusammensetzung und Darstellungsverfahren abhängen. Es wurde festgestellt, daß die untersuchten Alkalimetallthiocyanate, die mit POE Molekülkomplexe bilden, die Thermostabilität von POE beträchtlich erhöhen. Der größte gefundene thermostabilisierende Effekt zeigt sich bei einem optimalen Natrium- oder Kaliumthiocyanatgehalt von 2-5 m%.