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THE THERMAL DECOMPOSITION BEHAVIOUR OF SOME COMMERCIALLY AVAILABLE FLEXIBLE POLYURETHANE FOAMS

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SUMMARY

Elemental ultramicroanalysis and a type of pyrolysis chromatography have been used as fingerprinting techniques to confirm that the decomposition behaviours of three commercially available polyether foams (including a flame retarded sample) are similar to that of a reference polyether foam recently studied in detail. The report gives the elemental compositions of each foam, shows the comparative data for the weight-and nitrogen - losses as a function of temperature for each foam and records the chromatograms of the decomposition products of each material at 600 and 900°C. In this way it has been shown that the decomposition proceeds in each case via the initial release of yellow smoke which decomposes at high temperatures to give the expected nitrogen-containing products of low molecular weight. This information is relevant for studies of large scale fire situations involving these commercially available foams.

KEY WORDS: Gas chromatography, polyurethane foam, pyrolysis, toxic gas.

DEPARTMENT OF THE ENVIRONMENT AND FIRE OFFICES' COMMITTEE

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1. INTRODUCTION

Earlier reports[1,2] on the thermal decomposition of flexible polyester and polyether polyurethane foams (T.D.I.) using elemental ultramicroanalysis and coupled gas chromatography - mass spectrometry show that the decomposition proceeds in stages. Firstly at low temperatures (200 to 300°C) there is a rapid and virtually quantitative release of the T.D.I. unit of each foam as a volatile yellow smoke leaving a polyester or polyether residue. Volatility tests show that the smoke is not free T.D.I. but may be a form of polymeric T.D.I. At intermediate decomposition temperatures (300 to 800°C) the yellow smoke, which is common to both foams, remains unchanged but the polyester and polyether residues decompose to give a complex pattern of hydrocarbons and oxygenated species. At temperatures above 800°C the yellow smoke decomposes to give a number of nitrogen containing materials particularly hydrogen cyanide, acetonitrile, acrylonitrile, pyridine and benzonitrile. The proportion of hydrogen cyanide in the products increases with temperature and at 1000°C (maximum temperature used) approximately 70 per cent of the theoretically available nitrogen has been recovered as hydrogen cyanide.

In these earlier studies two basic reference polyurethanes (polyester and polyether) were used. The work of this current report was undertaken primarily to study some commercially available foams (including a flame-retarded material) in order to ensure that the knowledge gained from the laboratory tests with the reference materials is directly applicable to the generally available materials which would be required for full scale fire experiments.

Essentially the examination will consist of two main approaches. Firstly a study of the weight - and nitrogen - losses at various temperatures will be undertaken to show that in each case the decomposition proceeds via the initial loss of a nitrogen containing material (ie yellow smoke) and secondly chromatographic analyses (quantitative only) of the decomposition products at 600 and 900°C will be used as finger-printing techniques for matching the foams.

These temperatures were chosen since it is known[2] that the intermediate temperature of 600°C is suitable for examination of the polyol whereas 900°C is a sufficiently high temperature to decompose yellow smoke.

2. EXPERIMENTAL

The main experimental details of the apparatus and techniques used for the work of this report have been outlined in detail[1-5] in earlier reports and will be considered only briefly here.

a) Elemental ultramicroanalysis studies

Elemental analyses (C, H and N) were undertaken using a commercial micro-analyser with samples weighing approximately 300 µg. For residue studies, samples of the various polyurethanes (50 mg) were decomposed in a small ceramic boat in a tube furnace (fitted with a borosilicate glass liner) in a stream of oxygen-free nitrogen at 100 ml/min for 15-minute periods. After the decomposition period, the residues were removed, allowed to cool naturally, weighed and then analysed for elemental composition. Oxygen, the only other element present in the residues of the non flame retarded foams can be obtained by difference from 100% of the C, H and N contents if required.

b) Chromatographic experiments

For the chromatographic analyses, 10-mg samples of each polyurethane were decomposed in turn at 600°C and 900°C in a furnace system in a stream of oxygen-free nitrogen at 100 ml/min for 15-minute periods. The products were collected in a refrigerated stainless steel trap (-196°C) coupled on-line to a research gas chromatograph. The products were separated using Porapak Q columns (2 m x 3.2 mm in stainless steel) temperature programmed from 30°C to 265°C at 4°C min with a helium flow rate of 40 ml/min and monitored using flame ionization detection.

c) Materials

The main details of the three foams used in this report are outlined below. All foams were reported to be polyether based.

Type D. A typical polyether foam used widely for furnishing applications. No flame retardant present. Density approximately 30 kg/m^3.

Type H. A special high resilience polyether foam for furniture application. No flame retardant present. Density between approximately 50 and 100 kg/m^3.

Type F. A typical polyether foam, comparable with type D, containing a flame retardant.

3. RESULTS

a) weight - and nitrogen - loss studies

The experimental elemental compositions (mean values) of the three foams and, for comparison purposes the polyether reference foam are given in Table 1.

Table 1. Elemental compositions (C, H and N) of the polyurethane foams

Polyurethane	Elemental composition		
	C%	H%	N%
Polyether reference	61.3	9.0	4.1
Type D	60.6	8.7	3.9
Type H	60.3	8.2	5.1
Type F	57.6	8.1	4.3

Samples of types D, H and F were then decomposed for 15-minute periods at temperatures between 200 and 400°C in a stream of oxygen-free nitrogen and the residues weighed and analysed for elemental composition as outlined in the experimental section and in earlier reports. The results showing the weight - and nitrogen - losses are plotted as percentages of the theoretical losses against the temperature in Fig. 1, 2 and 3. Recorded in Fig. 4 is the equivalent data for the polyether reference material for comparison purposes.

From Fig. 1 to 4 inclusive it is apparent that all the foams are similar in that the main material first released during the decomposition of each foam is rich in nitrogen*. Type D (Fig. 1) shows almost identical weight-and nitrogen- losses as found for the polyether reference material (Fig. 4). The flame retarded foam (Fig. 3) is again somewhat similar and conforms to the reference polyether behaviour. With the high resilience grade (Fig. 2) there is a considerable scattering of the nitrogen determinations and it appears that the total nitrogen-loss is attained less readily than in the other cases.

*It should be noted that in the flame retarded case (Fig. 3) there is a detectable weight-loss at 200°C without any significant nitrogen-loss; this effect may be associated with volatilization of the flame retardant.

It should be noted that the high resilience grade is not only exceptional in the weight-and nitrogen-loss behaviour but also contains a higher proportion of nitrogen (5.1%) than the other foams (3.9 - 4.3%). Studies of certain rigid foams (M.D.I) in an earlier report[1] showed that in general these foams contained relatively high contents of nitrogen (6.3 - 8.9%) and showed almost identical weight-and nitrogen-loss behaviours (ie no preferential loss of nitrogen rich material). This may indicate that this high resilience material is a flexible foam but containing some of the structure normally associated with rigid foams.

b) Chromatographic experiments

For the identification of the polyols used in the preparation of the foams, samples of the foams were decomposed for 15-minute periods at 600°C and the products analysed by chromatography as outlined in the experimental section and in an earlier report.

The chromatograms (flame ionization detection - F.I.D.) recorded at a chromatographic range of 10^2 x 8 for the foams type D, H and F and, for comparison purposes, the reference polyether foam are recorded in Fig. 5(a), 6(a), 7(a) and 8(a) respectively.

Samples of each foam were then decomposed at 900°C in order to examine the high temperature decomposition products of the foams, since this temperature is sufficient to decompose any yellow smoke which may be present.

The chromatograms of the decomposition products at this temperature for foams type D, H and F and the reference polyether foam are given in Fig. 5(b), 6(b), 7(b) and 8(b) respectively. All chromatograms are shown with flame ionization detection at attenuation of 10^2 x 8.

From Fig. 5 to 8 inclusive, a number of points are apparent. Firstly, from the decomposition data at 600°C, the three foams (Types D, H and F) are clearly all polyether based and quite different to the polyester chromatograms recorded in an earlier report[2]; in fact the 'finger-printing' technique suggests that the polyethers used in each case are similar and also similar to the polyether used in the preparation of the reference foam. However there is some evidence in the chromatogram of the flame retarded foam (type F) that this particular polyether may be somewhat different to the others or alternatively it may be the same polyether but the decomposition products have been modified by the presence of the flame retardant. This point will be discussed further in a later section. Secondly, the chromatograms recorded at 900°C for the three foams are similar and again almost identical to that of the reference polyether. The chromatogram of the reference material (900°C) is known from

earlier work to be the summation of the chromatograms of the polyol and yellow smoke. For identification purposes the main nitrogen containing peaks in this chromatogram associated with the decomposition of the yellow smoke are recorded. These are g : hydrogen cyanide, j : acetonitrile, k : acrylonitrile, r : pyridine and x : benzonitrile.

4. DISCUSSION

The report demonstrates that the decomposition processes of the three foams are similar and comparable with that of the reference polyether foam. In each case the decomposition proceeds via the initial loss of a nitrogen-containing material (termed yellow smoke) which decomposes at the test temperature of 900°C to give the expected nitrogen containing products analysable by chromatography. The behaviour of foam type D appears to be almost identical to that of the reference material throughout the study. There are some slight differences in the nitrogen-loss characteristics of the high resilience foam in comparison with the reference material which, as outlined in an earlier section, was attributed to the relatively high nitrogen content of this foam.

The weight-and nitrogen-loss behaviours of the foams of type D and F are interesting. It is known that type F is similar to type D but with a flame retardant added. From Fig. 1 and 3 it appears that the flame retardant does not significantly alter the formation of yellow smoke (as a function of the temperature) but distinctly increases the loss in weight of the foam for any particular temperature. There is some evidence from the chromatograms of the decomposition products at 600 (Fig. 8) that the retardant may alter the nature of the products from the polyol but this is not conclusive. It should be noted however that recent experiments[5] by chromatography of the decomposition products of cellulose and flame retarded cellulose (ammonium phosphate) showed a similar effect; namely at low temperatures (approximately 250°C) the retardant increased the rate of product formation but at higher temperatures the reverse became true. In addition, the ammonium phosphate altered the course of the decomposition and selectively produced only four main components. The flame retardant in the polyurethane foam (probably a phosphorus additive) may also have a similar mode of action to the ammonium phosphate in a selective manner; quantitative interpretations of product formation with and without the flame retardant are not possible from these experiments alone.

In conclusion all three foams undergo the expected behaviour of T.D.I. polyether flexible foams. These foams will therefore release nitrogen-containing products of low molecular weight (mainly hydrogen cyanide, acetonitrile, acrylonitrile, pyridine and benzonitrile) at temperatures above about 800°C. The proportion of hydrogen cyanide in the products will increase with temperature and above 1000°C virtually all of the available nitrogen may be released as hydrogen cyanide.

5. REFERENCES

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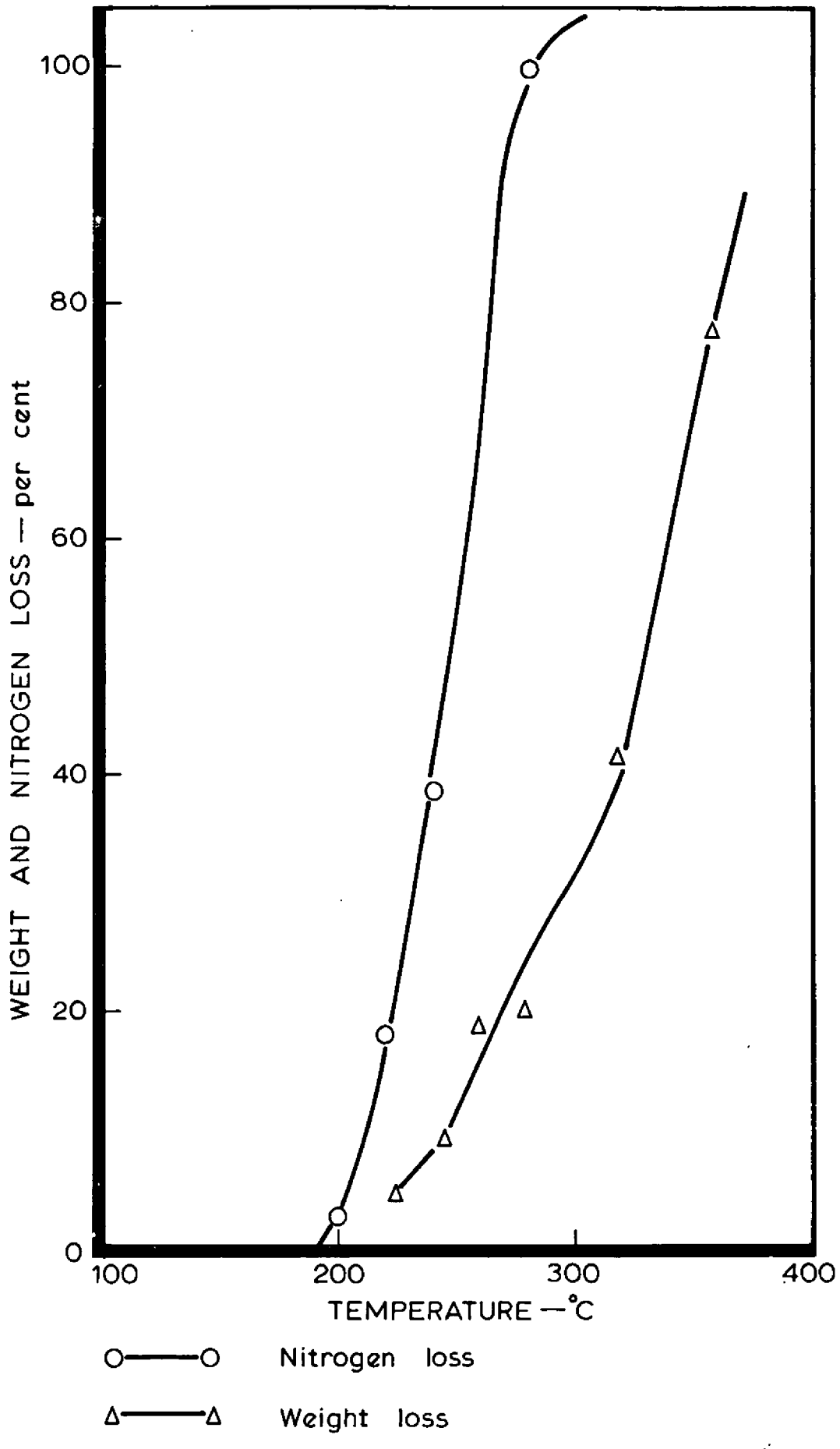

FIG. 1. DECOMPOSITION DATA FOR FOAM TYPE D

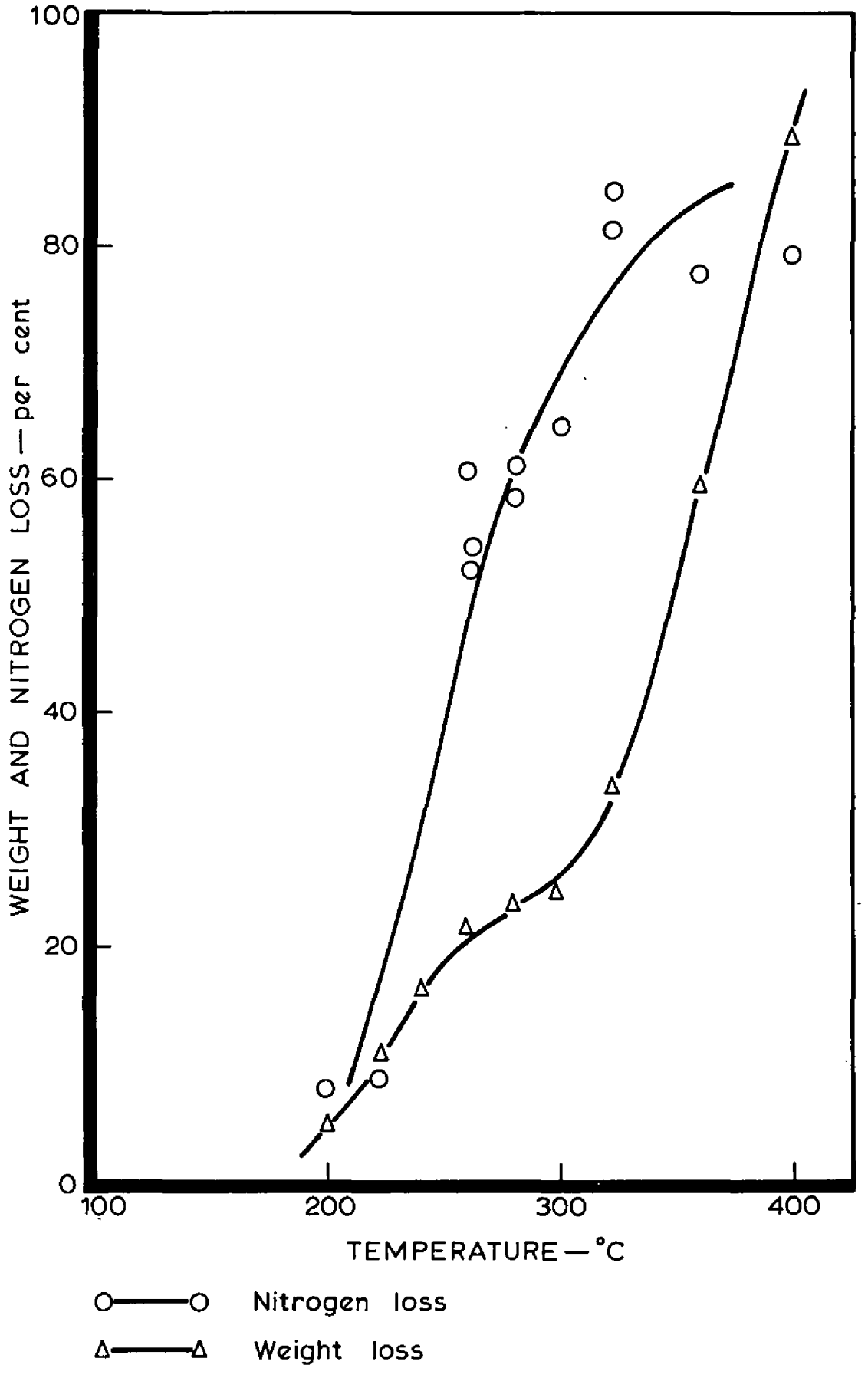

FIG. 2. DECOMPOSITION DATA FOR HIGH RESILIENCE GRADE (TYPE H)

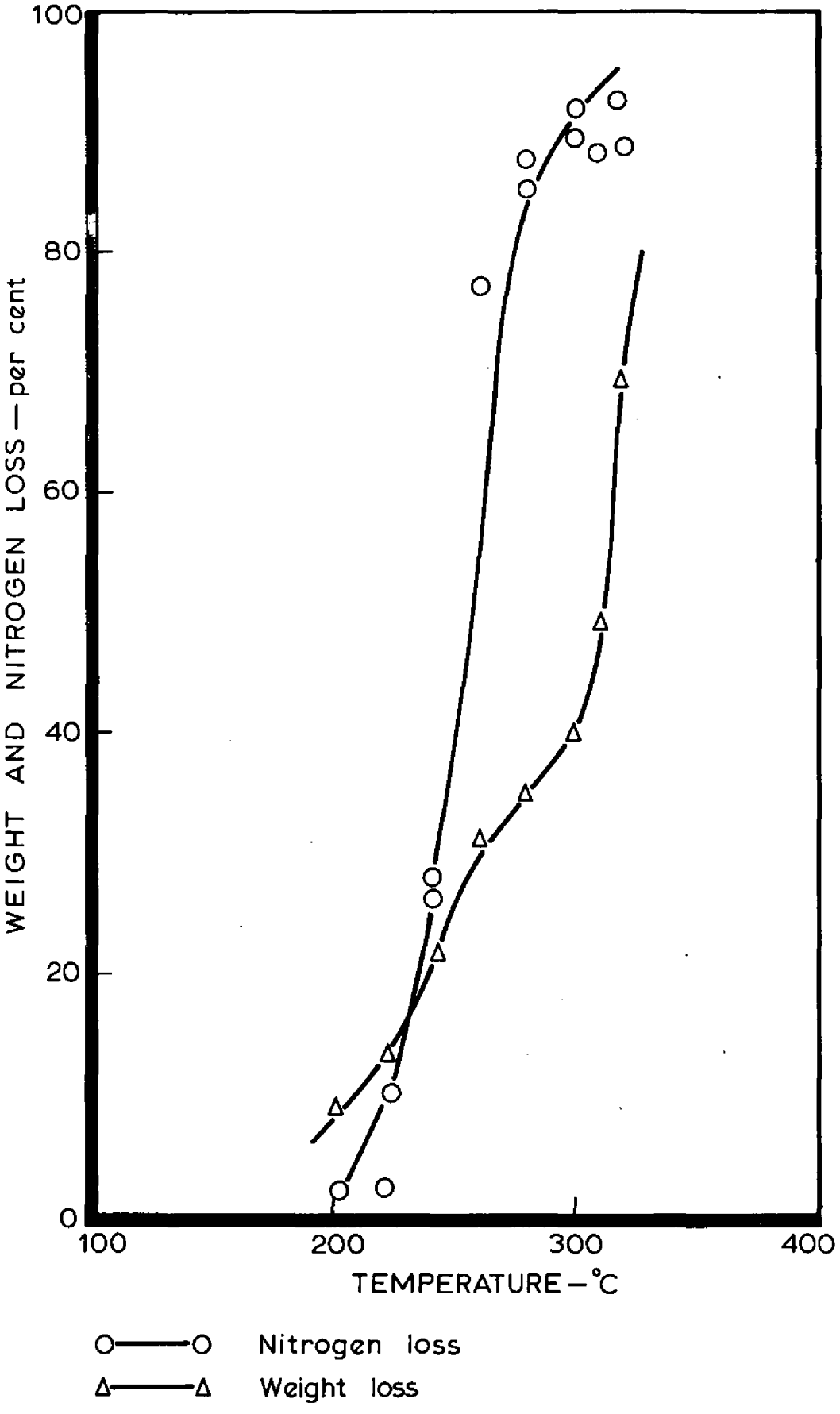

FIG. 3. DECOMPOSITION DATA FOR FLAME RETARDED GRADE (TYPE F)

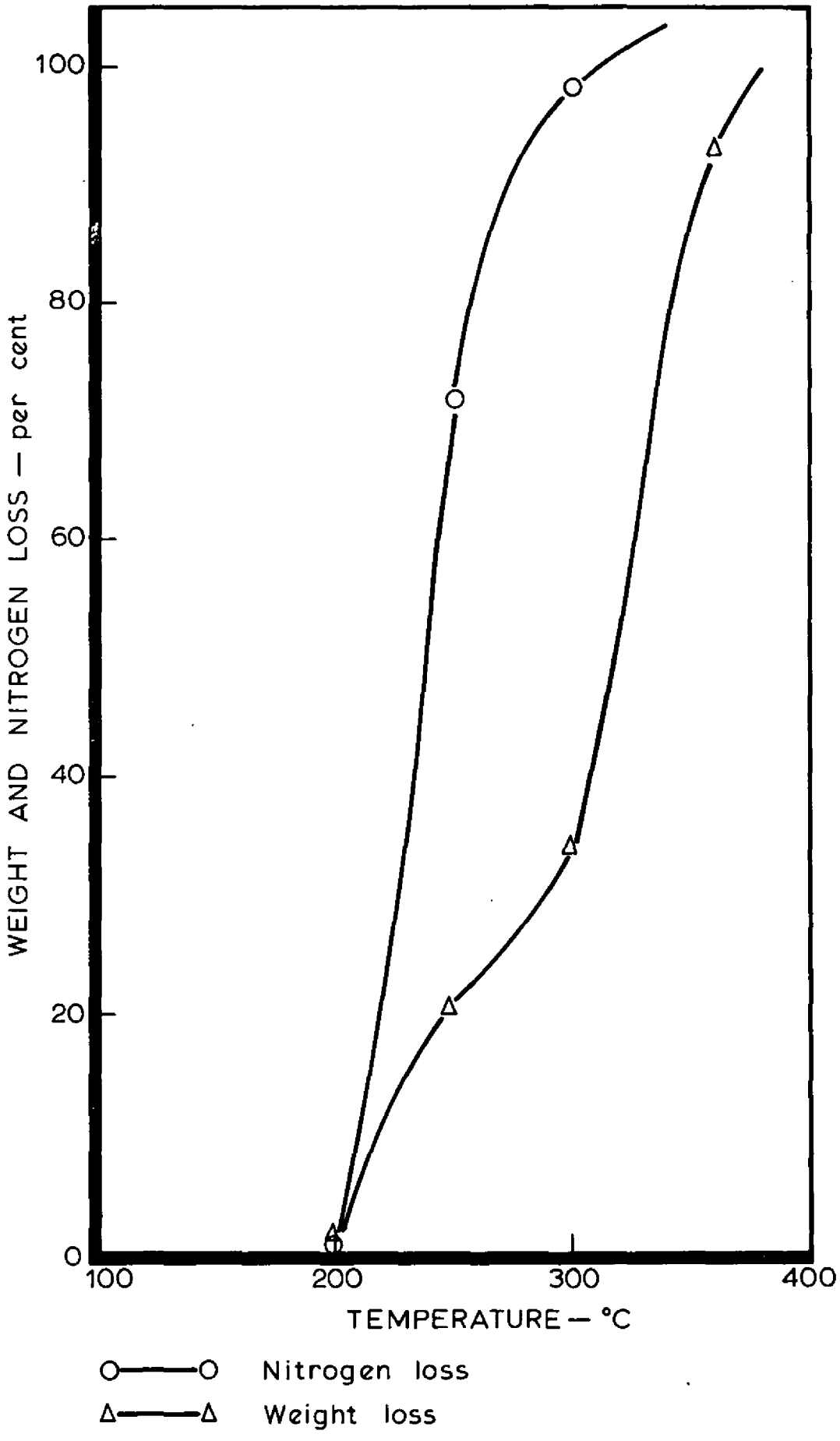

FIG. 4. DECOMPOSITION DATA FOR THE POLYETHER REFERENCE MATERIAL

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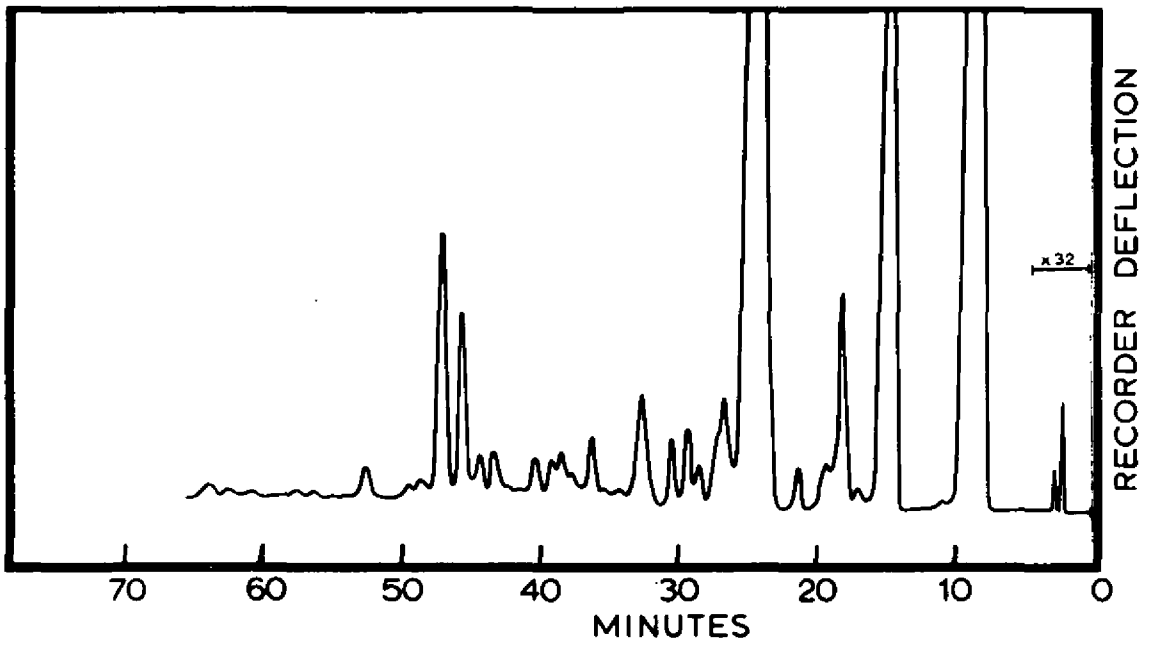
(a)



(b)

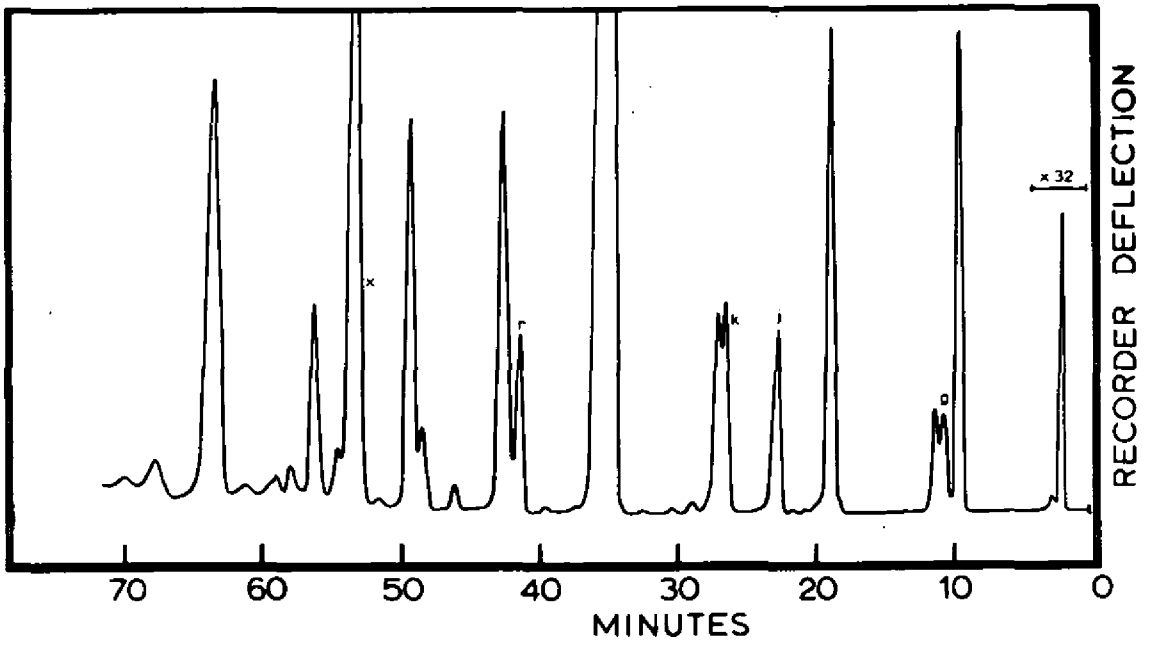
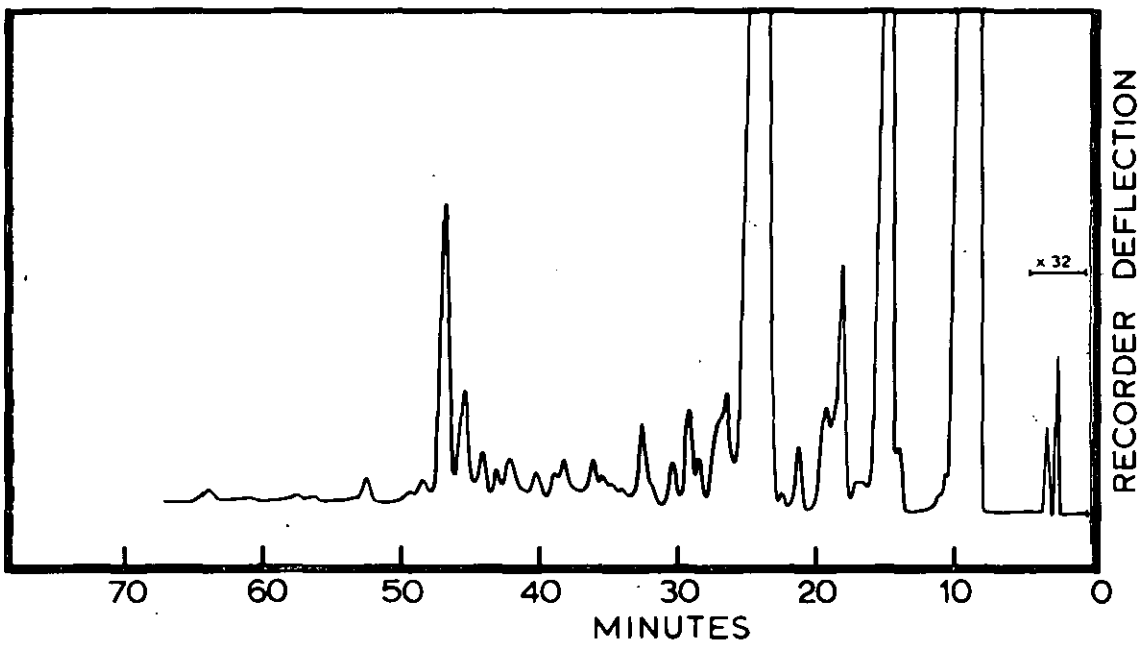


FIG. 5. CHROMATOGRAMS (FID) OF THE DECOMPOSITION PRODUCTS OF FOAM TYPE D AT (a) 600 °C AND (b) 900 °C

(a)



(b)

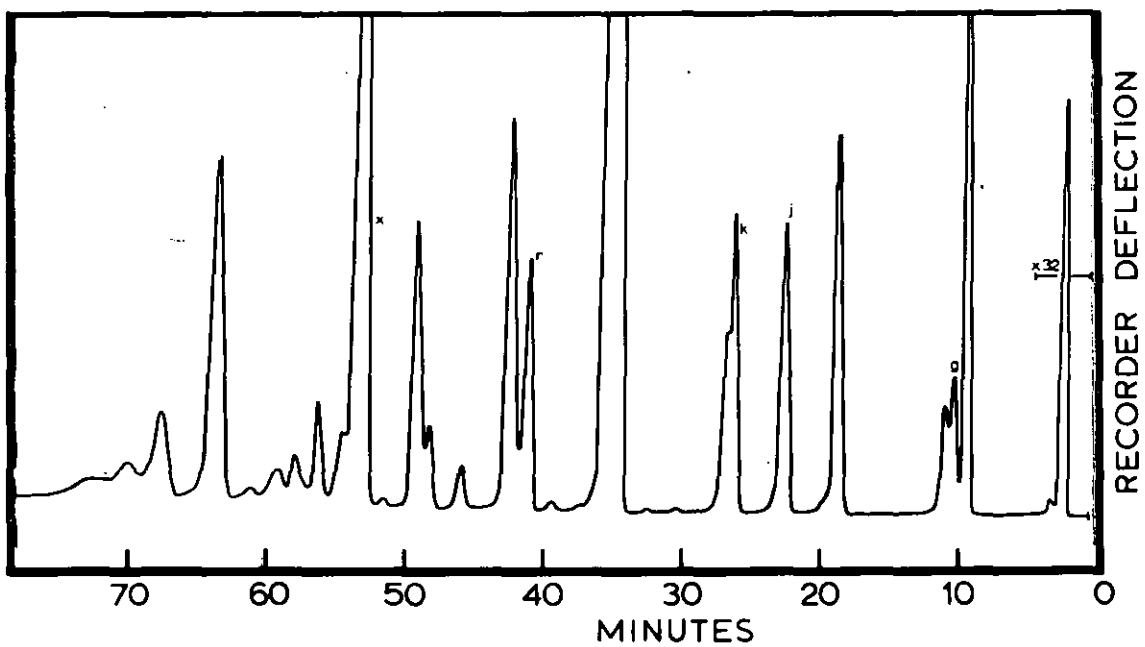
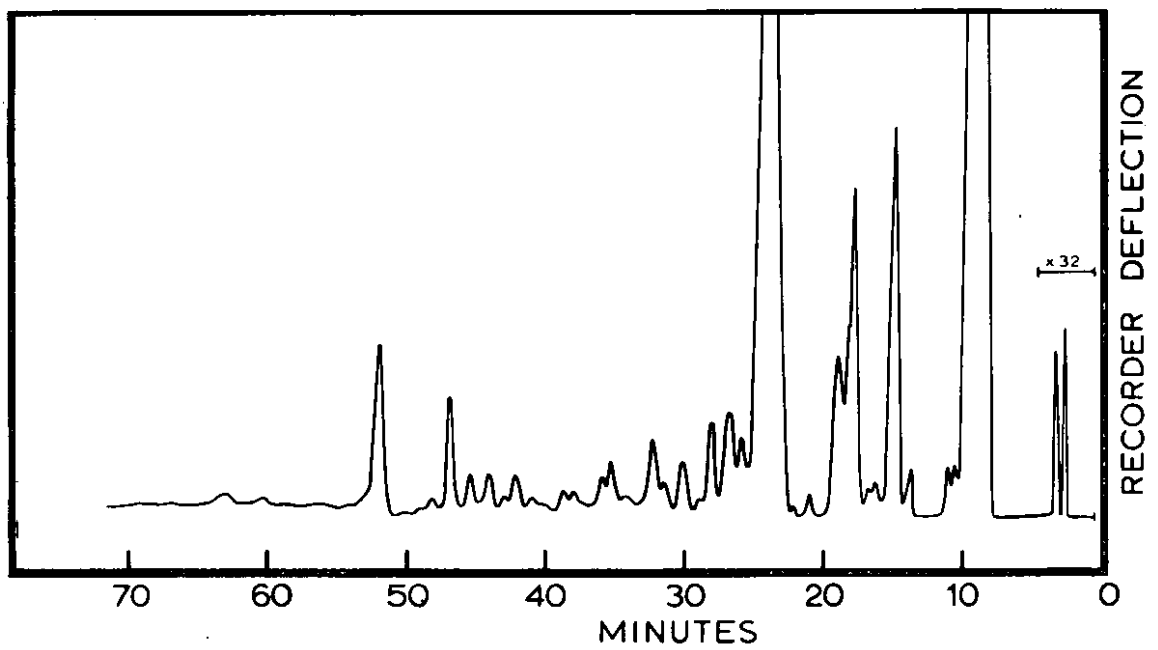


FIG. 6. CHROMATOGRAMS (FID) OF THE DECOMPOSITION PRODUCTS OF FOAM TYPE H AT (a) 600 °C AND (b) 900 °C

(a)



(b)

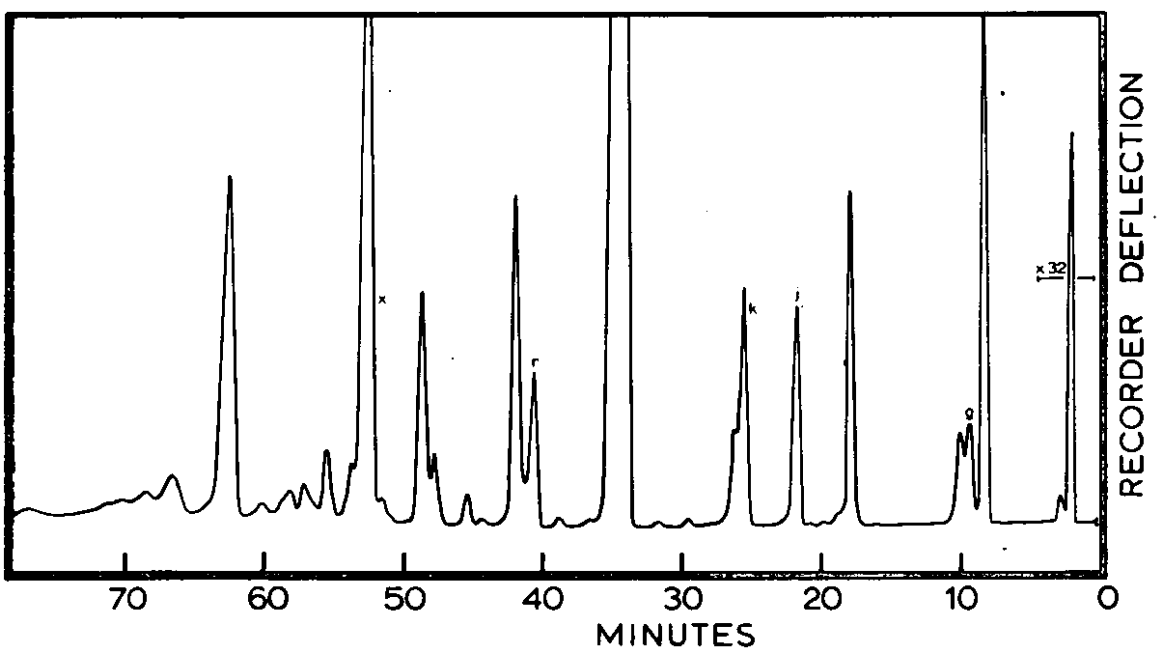
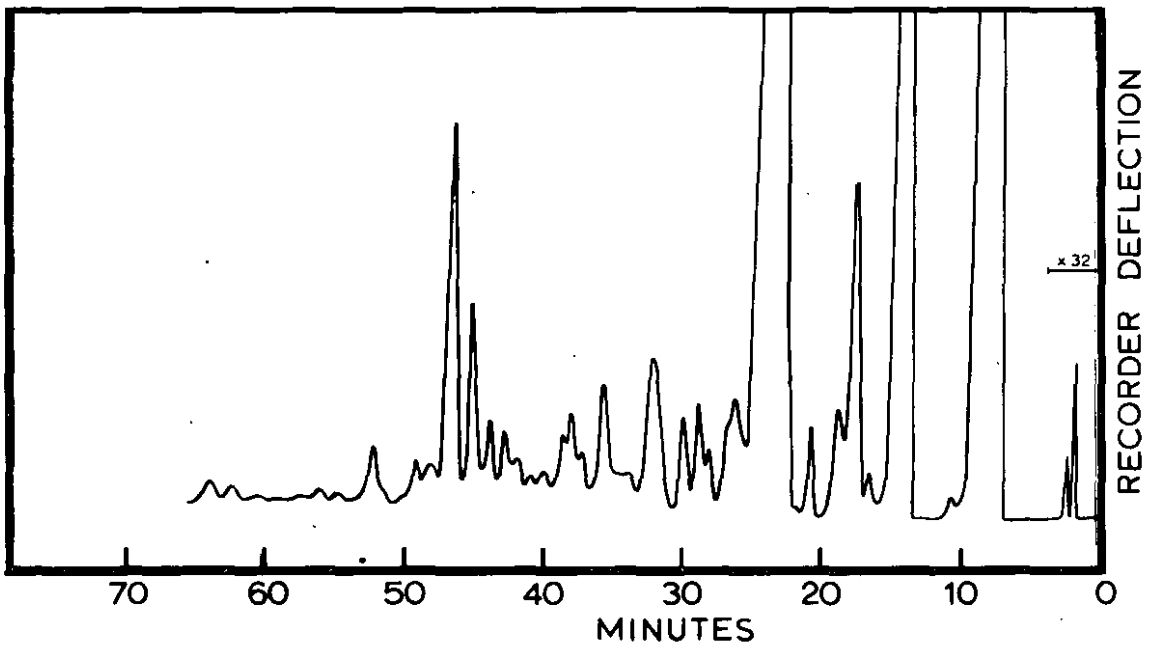


FIG. 7. CHROMATOGRAMS (FID) OF THE DECOMPOSITION PRODUCTS OF THE FOAM TYPE F AT (a) 600°C AND (b) 900°C

(a)



(b)

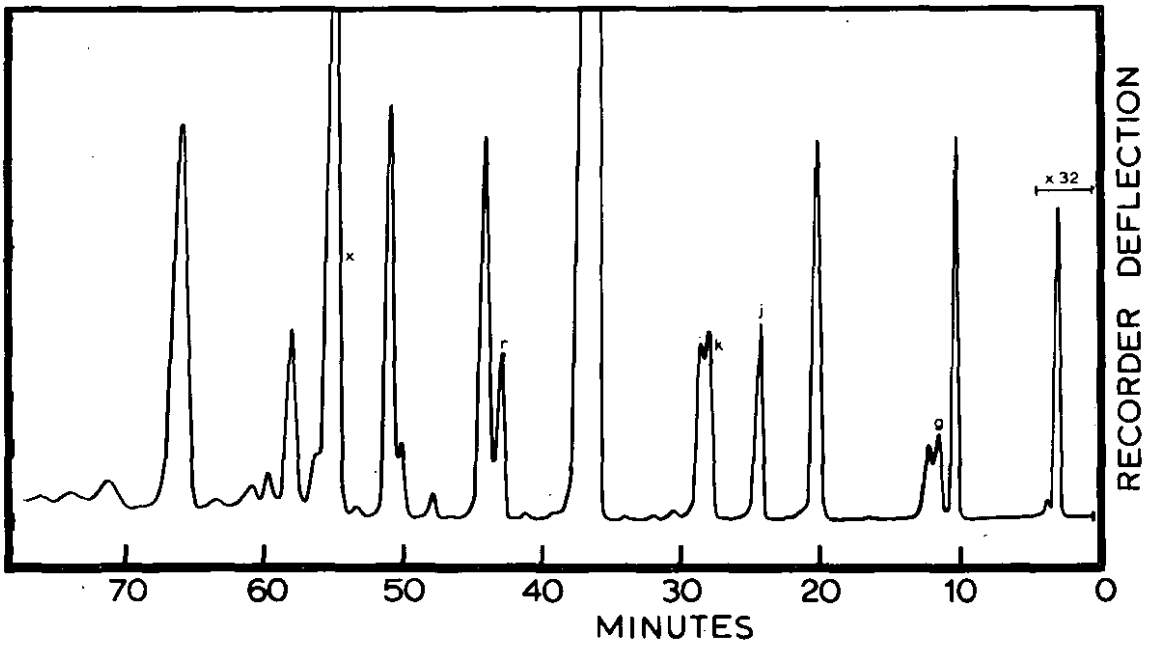


FIG. 8. CHROMATOGRAMS (FID) OF THE DECOMPOSITION PRODUCTS OF THE REFERENCE FOAM AT (a) 600°C AND (b) 900°C