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STUDIES OF THE THERMAL DECOMPOSITION OF FLEXIBLE POLYURETHANE FOAMS IN AIR

by

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SUMMAR Y

The thermal decomposition of various polyester and polyether flexible polyurethane foams has been carried out in air atmospheres between 300 and 1000°C. It is shown that the main decomposition processes are similar to those observed in inert atmospheres, namely that the decomposition proceeds via the initial release (200 to 300°C) of a nitrogen-rich material which subsequently decomposes at temperatures above about 500°C (800°C in inert atmospheres) to give nitrogencontaining materials of low molecular weight, particularly hydrogen cyanide, acetonitrile, acrylonitrile and benzonitrile. The intermediate nitrogen-rich material has not been directly isolated from oxidative environments but the experiments of this report indicate that it is probably identical to the 'yellow smoke' observed under inert conditions. The main nitrogen-containing material observed in this work produced from the thermal-oxidative decomposition of the intermediate is hydrogen cyanide of which the yield increases with temperature from 500 up to 700°C, decreases at 800°C then increases again at 900 and 1000°C. At 700°C approximately 10 to 20 per cent of the theoretically available nitrogen is released as hydrogen cyanide and at 1000°C this figure rises to 35 to 40 per cent of the theoretical.

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

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1. INTRODUCTION

Earlier work in this laboratory 1,2,3,4 has shown that the thermal decomposition (inert atmosphere) of flexible polyurethane foams (T.D.I.) proceeds via a low temperature depolymerisation process. At temperatures between about 200 and 300°C the TDI unit of the foam is released as a volatile yellow smoke (probably a form of polymeric TDI) leaving a polyol residue. It is the high temperature decomposition (over 800° C) of the yellow smoke which generates the nitrogen-containing materials of low molecular weight, particularly hydrogen cyanide, acetonitrile, acrylonitrile, pyridine, and benzonitrile.

The above experiments were carried out in an atmosphere of oxygen-free nitrogen. The work outlined in this current report extends this study to oxidative atmospheres and will essentially be carried out in two parts. This first report will examine basic decomposition processes in air atmospheres particularly those leading to the formation of nitrogen-containing materials. A further report will outline current studies of the formation of oxides of carbon and nitrogen during the oxidative (and inert) decomposition of the foams and polyols⁵.

In this present report, samples of various polyester and polyether foams are decomposed in a furnace system in a flow of air and the residues weighed and analysed for elemental composition (C,H and N). In this way the weight and nitrogen-loss characteristics have been obtained as a function of temperature (200 to 400° C) and when compared with the equivalent inert data show important features of the oxidative decomposition.

Chromatographic analyses of the decomposition products of a typical polyester and polyether foam and the respective parent polyols at temperatures between 300 and 1000°C in air atmospheres are recorded. This study, which involves both quantitative and qualitative interpretations of the chromato-graphic traces, has been undertaken to study the release of nitrogen-containing products particularly hydrogen cyanide in oxidative environments.

The results of the chromatographic analyses of yellow smokes decomposed in air at temperatures between 600 and 1000° C are also recorded. These smokes were prepared under inert conditions ie at 300° C in a stream of nitrogen^{2,4} then decomposed at higher temperatures in air. Attempts to prepare similar smokes under oxidative conditions have not been successful due to contamination from the volatilization of the polyol constituents. This report will show the presence of a nitrogen-rich material during the decomposition of the foams in air using elemental ultramicroanalysis and weight loss studies and verify by decomposition experiments that this nitrogen-rich material is probably identical to the yellow smoke observed under inert conditions.

It should be emphasised that the work outlined in this report is essentially an extension of the earlier 'inert' work on the thermal decomposition of flexible polyurethane foams to oxidative atmospheres. In order to avoid unnecessary duplication it will be assumed that the reader is familiar with the main details of Fire Research Note 881 or its published equivalent⁴.

2. EXPERIMENTAL

a) Weight-and nitrogen-loss experiments

Weighed samples of each foam (50 mg) were decomposed in a small ceramic boat in a tube furnace (fitted with a 20 mm I.D. borosilicate glass liner), in a stream of air (B.O.C. Medical grade) at 100 ml/min for 15 minute intervals at isothermal temperatures between 200 and 400° C. After each experiment the residues were removed, allowed to cool naturally, weighed, and then analysed directly for the percentages of carbon, nitrogen and hydrogen by elemental ultramicroanalysis¹. For presentation in this report the weight- and nitrogen-losses are recorded as percentages of the maximum theoretical losses.

b) The main decomposition system

The decomposition system coupled to a research chromatograph is almost identical to that used in the studies of the nitrogen-containing products from the thermal decomposition of flexible polyurethane foams^{2,3} and in other previous work involving PVC^6 and the phenolics⁷.

Weighed samples of the foams (10 mg) or yellow smokes (2.5 or 2.4 mg) were decomposed in a ceramic boat which was introduced into a quartz decomposition tube (18 mm 0.D.) surrounded by a tube furnace (maximum temperature 1000° C) with a temperature stability of $\pm 1^{\circ}$ C at 500° C. The decomposition products were carried from the furnace zone by a stream of air (BOC Medical grade) at 100 ml/min at 20° C along a heated outlet tube into a heated stainless-steel gas sampling valve coupled in the normal manner

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to a research gas chromatograph. During the 15-minute collection periods, the volatile products were trapped from the air stream by surrounding the loop (stainless steel tubing, 3.2 mm O.D.) of the valve with a refrigerant consisting of isopentane cooled with liquid nitrogen to form a constant temperature slurry of -160° C.

After collection, the products were transferred to the chromatograph by turning the valve to the inject position, removing the refrigerant and heating the loop quickly to 200° C by direct ohmic heating. The collection valve and all flow lines coupling the valve to the furnace tube and chromatograph respectively are heated to 150° C with electrical heating tape in order to avoid condensation problems prior to chromatography. The collection valve is constructed of stainless steel with a PTFE (polytetrafluoroethylene) rotor.

c) Chromatography

Chromatographic analyses were performed using a Hewlett-Packard 5750 Research Chromatograph, fitted as a dual column instrument with output flow splitters for the simultaneous operation of thermal conductivity (T.C.) and flame ionization (F.I.) detectors. The products were separated using Porapak Q columns (2 m x 3.2 mm in stainless steel) temperature programmed from 30 to $265^{\circ}C$ at $4^{\circ}C/min$ with a helium flow rate of 40 ml/min.

For quantitative interpretations, peak areas were determined using a Hewlett Packard 3370 automatic electronic integrator equipped with printing facilities.

d) Materials

The reference samples² of polyester and polyether foams^{*} of known compositions were obtained commercially. Both foams were prepared from T.D.I. (tolylene diisocyanate). The polyester foam is based on a lightly branched polyester of adipic acid and diethylene glycol and the polyether foam prepared from a polyether (mean molecular weight of 3500) produced from glycerol, propylene oxide and ethylene oxide. A very small addition of green pigment is present with the polyether foam. Samples of each parent polyol were available.

Mean elemental composition (oxygen by difference from 100 per cent) Polyester foam - 59.2 per cent C 6.9 per cent H 4.3 per cent N Polyether foam - 61.3 per cent C 9.0 per cent H 4.1 per cent N

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Some weight- and nitrogen-loss experiments are recorded using typical commercially available foams 3 used for furnishing applications and identified as:-

TYPE D

A typical polyether foam without flame retardants.

Density approximately 30 kg/m³. Mean elemental compositions -60.6 per cent C, 8.7 per cent H, 3.9 per cent N

A special high resilience foam without flame retardant.

TYPE H

Density between approximately 50 and 100 kg/m².

Mean elemental composition - 60.3 per cent C, 8.2 per cent H.

5.1 per cent N

TYPE F A typical polyether foam, comparable with type D

> containing a flame retardant. Mean elemental composition 57.6 per cent C, 8.1 per cent H, 4.3 per cent N.

Unless otherwise stated in this report, experiments involving simply a polyether or polyester foam will refer to the standard reference samples.

The yellow smoke used in decomposition experiments was prepared from the thermal decomposition (inert) of the polyester or polyether foams.

RESULTS 3.

a) Weight- and nitrogen-loss results

Comparative weight- and nitrogen-loss data (recorded as percentages of the theoretical loss in each case) at temperatures between 200 and 400°C for the polyester foam, the polyether foam and foams type D, H and F are shown in Fig 1 to 5 respectively. These data were obtained simply by decomposing samples of each foam at different temperatures for 15-minute periods, weighing the residues and then analysing for elemental composition as outlined earlier. The nitrogen-loss is determined from the initial weight and composition of each sample and the weight and composition of the residues.

From Fig 1 to 5 inclusive and with reference to the equivalent data in nitrogen atmospheres of earlier reports^{2,3,4}, the following points are apparent:

(i) The weight-and nitrogen-loss characteristics of the polyester foam (Fig 1) are virtually identical to those observed in nitrogen atmospheres. The presence of oxygen does not appear to alter the activation energy for the release of the nitrogen rich component or seriously affect the stability of the polyester polyol.

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(ii) The characteristics of the polyether foam (Fig.2) and the foam type D (Fig 3) are, as expected, very similar. In each case the nitrogen-loss characteristics are similar to those observed in nitrogen, but the presence of oxygen gives a marked decrease in the temperature stability of the polyol.

(iii) With the high resilience foam (Fig.4) the general weight- and nitrogenloss characteristics are not unlike those observed in nitrogen although the polyol appears to be less stable under an oxidative environment. The distinct discontinuity in the characteristics at 285° C was attributed to a change in the physical nature of the foam. At temperatures below 285° C the foam retained its cellular structure throughout the decomposition period whereas at higher temperatures the foam 'melted' to a liquid phase. Such a transition would affect decomposition parameters particularly heat transfer and surface area for oxidation. This discontinuity was not observed in the graphical data of the other foams where foam collapse tended to occur at lower temperatures. The structural differences between this high resilience foam and the other foams, observed in the nitrogen atmospheres, is not distinct under the oxidative conditions.

(iv) The weight- and nitrogen-loss characteristics of the flame retarded foam (Fig 5) are similar to those observed in the nitrogen atmosphere. As in the inert decomposition case a weight-loss (probably volatilisation of the flame retardant) is observed at 200° C.

In conclusion, the nitrogen-loss characteristics of these foams are, in general, similar to those observed in nitrogen atmospheres, and comparable with the concept of the release of a nitrogen rich material. The release of this material as a function of temperature is not affected by the presence of oxygen and it is likely that this nitrogen-rich material is the same yellow smoke observed in the inert atmospheres. The main effect of oxygen at these temperatures is that it seriously reduces the stability of the polyether polyol.

b) Qualitative studies by gas chromatograph

(i) Decomposition of polyester foam, polyol and yellow smoke.

Comparative chromatograms of the decomposition products of the polyester foam and polyol at 300 and 400° C are shown in Fig 6 and Fig 7 respectively. These were obtained by decomposing 10-mg samples of the foam (or the equivalent weight of polyol - 7.3 mg) for 15-minute periods in air, collecting the products

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at -160 °C and injecting them into the chromatograph as outlined in the experimental section. The chromatograms were recorded using simultaneous flame ionization detection (F.I.D.) and thermal conductivity detection (T.C.D.) but only the F.I.D. traces are recorded here, which in common with all chromatograms of this report are recorded on range $10^2 \ge 8$. This is the same sensitivity as used in all polyurethane work to date^{2,3,4}.

From a study of Fig 6 and 7 and by comparison with the equivalent chromatograms in a nitrogen atmosphere^{2,4}, it is clear that the presence of oxygen alters the nature of the products i.e. the 'fingerprint' pattern of decomposition products is different in the two atmospheres. Further, in air, there is a distinct relationship (particularly apparent at 400° C) between the decomposition products of the foam and polyol, although the amounts of products (ie peak areas) are larger when the polyol is alone rather than bonded in the polyurethane polymer. No peaks are present which can be attributed to the decomposition of the T.D.I. part of the polyurethane.

At 600°C (as shown in Fig 8) the amounts of material generated from the foam and polyol as detected by flame ionization detection are small in comparison with the large quantities released at 600° C under inert conditions. This is indicative of rapid oxidation to inorganic species (water, carbon monoxide, carbon dioxide and possibly oxides of nitrogen) which will be studied and recorded in future reports. Also, at 600° C, although the chromatogram of the foam is basically similar to that of the polyol there are some additional peaks, identified by direct seeding techniques as hydrogen cyanide (g), acetonitrile (j) and acrylonitrile (k) in the chromatogram of the foam. These peaks are marked on the foam chromatogram (F.I.D) of Fig 8 but because of the low sensitivity of flame detectors to nitrogenous products of low molecular weight, the peaks are not as distinct as obtained by the simultaneously operating thermal conductivity detector.

Also shown in Fig 8 is the chromatogram of the decomposition products of 2.5 mg of polyester yellow smoke (prepared under inert conditions^{2,4}) at 600° C in air, which shows peaks g, j and k as observed from the foam. At this temperature no benzene, pyridine, toluene or benzonitrile is detected from the yellow smoke. In inert atmospheres no decomposition of the smoke can be detected below 800° C.

The equivalent data for the decomposition of the foam, polyol and yellow smoke at 700° C are shown in Fig.9. At this temperature hydrogen cyanide (g), acetonitrile (j) and acrylonitrile (k) are distinct and some

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benzene (n) and benzonitrile (x) are detected from the yellow smoke. Again, there is an agreement between the chromatogram of the yellow smoke and the 'additional' peaks in the chromatograms of the foam. This is in agreement with the concept of a release and oxidative-decomposition of a yellow smoke. It should be noted that the yellow smoke used in this report was prepared under inert conditions^{2,4}, and hence the above conclusion implies that the yellow smoke generated under oxidative conditions is probably identical to that obtained in an inert atmosphere. At 800°C, there is a marked reduction in the yield of hydrogen cyanide which increases again with temperature at 900 and 1000° C (maximum temperature used). At these temperatures (800 to 1000°C), in addition to the compounds detected at 700°C from the yellow smoke small quantities of toluene are present; no pyridine can be detected. For comparison purposes the chromatograms of the foam, polyol and yellow smoke at 1000°C in air, are recorded in Fig. 10. In Fig 10 it is clear that the chromatogram of the foam can be constructed by superimposing the chromatograms of the polyol and yellow smoke, confirming the importance of the yellow smoke intermediate. It is also apparent that the polyol chromatogram (and the peaks in the foam chromatogram of polyol origin) shows relatively large quantities of products with benzene (n) predominating. Further there is a general resemblence of these products to those encountered in inert conditions^{2,4} which indicates that there may be two distinct decomposition regions in air under these conditions. Firstly an oxidative-decomposition region at temperatures between 500 and 800° C but at higher temperatures the reaction may be 'explosive' and the rapid release of products vitiate the atmosphere around the material in the furnace. High temperature decomposition in air may in fact be significantly pyrolytic in nature. This will be discussed further in a later section.

(ii) Decomposition of polyether foam, polyol and yellow smoke.

The chromatograms of the polyether foam (10 mg) and polyol (7.5 mg) at 300 and 400° C are shown in Fig 11 and 12 respectively. At each temperature there is a marked similarity between the chromatogram of the foam and polyol although, as observed in the polyester case, the polyol tends to give larger quantities of products when alone than when bonded in the polyurethane. Again, as observed in the polyester case the general pattern of products is different in the oxidative atmosphere to that of inert environments. Further, the overall quantities of materials generated at these temperatures in air are greater than those observed in nitrogen. This general instability of the polyether foam to oxidative environments was noted during the weight loss work of an earlier section.

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At 600° C (Fig 13), as observed for the polyester materials and attributed to oxidation to inorganic species, there is a marked reduction in the quantities of materials as analysed by flame ionization detection, in relation to the products observed at lower temperatures. At 600° C the similarities between the chromatograms of the foam and polyol are distinct and certain peaks, particularly the hydrogen cyanide (g) acetonitrile (j) and trace of acrylonitrile (k) observed from the yellow smoke are masked in the chromatoģram of the foam.

At 700° C (Fig 14) the chromatograms of the foam and polyol are similar to those observed at 600° C except that the contribution of peaks from the yellow smoke is somewhat greater. At this temperature as in the polyester case, the yellow smoke releases, in addition to hydrogen cyanide (g), acetonitrile (j) and acrylonitrile (k), small quantities of benzene (n) and benzonitrile(x). No toluene is detected from the smoke.

At 800° C a marked reduction in the yield of hydrogen cyanide was observed which, in common with the polyester case, increased again between 900 and 1000° C. At these higher temperatures and particularly at 1000° C the decomposition products of the polyol were again typically pyrolytic in nature. Toluene, as in the polyester case, was detected from the yellow smoke only at temperatures at and above 800° C. The chromatograms of the decomposition products of the foam polyol and yellow smoke are recorded in Fig 15.

c) Quantitative studies by gas chromatography

For quantitative analysis of the nitrogen-containing products, the decomposition experiments between 600 and 1000[°]C were repeated at 100 degC intervals with full electronic integration of relevant peak areas for the polyester and polyether foams and yellow smokes. The weight of yellow smoke (ie 2.5 and 2.4 mg for the polyester and polyether yellow smokes respectively) represents the weight present in 10 mg of each foam as described in an earlier report. The yellow smokes used in this report in studies of oxidative degradation are the yellow smokes prepared at 300[°]C under inert conditions.

The integrator counts (in arbitrary units) for hydrogen cyanide, acetonitrile, acrylonitrile, benzene,toluene and benzonitrile for the polyester foam and yellow smoke and the polyether foam and yellow smoke are given in Appendix I and II respectively. These counts have been adjusted for the change in sensitivity of the chromatograph since the earlier studies in inert atmospheres, using benzene as a reference. The integrater counts and

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sensitivities used in this report may therefore be directly compared with those used in the earlier work. As in the inert decomposition experiments^{2,4}, hydrogen cyanide was monitored using thermal conductivity detection (T.C.D) and the remainder of the products using flame ionization detection (F.I.D.). It was not possible to obtain accurate integrator counts for acrylonitrile, benzene and toluene during decomposition experiments involving the foam due to interference from the polyol content.

Tables 1 and 2 record the yields of hydrogen cyanide, acetonitrile, acrylonitrile, benzene, toluene and benzonitrile from the decomposition of polyester foam and yellow smoke and the polyether foam and yellow smoke respectively as computed from the data of Appendix I and II respectively. From Tables 1 and 2 it is evident that the general yields and temperature dependence of the products from the yellow smokes are with some exceptions in broad agreement with those of the foams (where measured). In air atmospheres, as in the inert decomposition situations, it appears that in studies of nitrogencontaining materials of low molecular weight, the decomposition of each foam can be adequately represented by the decomposition of an equivalent weight (on a nitrogen basis) of yellow smoke.

With both the polyester and polyether foams and yellow smokes, the hydrogen cyanide 'peak' at 700° C, as noted during qualitative tests is distinct. This is also evident with acrylonitrile. Acetonitrile, benzene, toluene and benzonitrile tend to rise gradually with temperature with a maximum rate of production at 900° C.

For comparison purposes with earlier work in inert atmospheres, the nitrogen recoveries (in percentages of the theoretical), of the nitrogencontaining materials of Tables 1 and 2 are given in Tables 3 and 4 respectively.

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	Peak		Yellow	smoke	$(/^{p_{\mathcal{B}}})$			Fo	am (/uf	 3)	
Material	letter	600°C	700 ⁰ C	800°C	900°Ç	1000°C	600°C	700°C	800 ⁰ C	900°C	1000°C
Hydrogen cyanide	Ę	47.6	208	95•4	146	343	2.3	153	67.7	208	380
Acetonitrile	j	0.3	6.9	7.8	8.6	5.6	*	6.8	7.9	13.7	11.2
Acrylonitrile	k	0,2	10.5	4.7	4.1	0.6	-	_	-	~	_
Benzene	n	0	0.2	0.9	11.2	29.6	-	' –	-	-	-
Toluene	S	0	0	0.5	1.4	0.1	-	-			
Benzonitrile	x	0	1.0	1.8	33.3	16.1	0	3.5	16.6	31.8	20.4

TABLE 1. The decomposition products of the polyester yellow smoke (2.5 mg) and certain equivalent products from the polyester foam (10 mg) in air between 600 and 1000°C/

 \neq 2.5 mg of polyester yellow smoke has the same nitrogen content as 10 mg of polyester foam *Not determined due to interference from polyol

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	Peak		Yellow	smoke	(/ug)			Fo	am (/ug)	
Material	letter	600°C	700 ⁰ C	800°C	900°C	1000°C	600 ⁰ C	700 ⁰ C	800°C	900°C	1000 ⁰ C
Hydrogen cyanide	£	34.3	147	65.6	134	244	27.5	66.1	36.7	151	281
Acetonitrile	j	0.8	5.0	5•7	9•7	4.1	_*	9.0	10.2	12.5	9•5
Acrylonitrile	k	1.5	7.1	4.1	5.5	0.5	-	-	-	-	-
Benzene	n	0	0.2	0,8	7•5	18.1	-	-	H	1	-
Toluene	ß	0	0	0.2	1.4	0.1	-	-	_	-	-
Benzonitrile	x	0	1.5	12.5	15.7	16.3	-	3.5	17.1	18.2	8.0

TABLE 2. The decomposition products of the polyether yellow smoke (2.4 mg) and certain equivalent products from the polyether foam (10 mg) in air between 600 and 1000°C/

¹2.4 mg of polyester yellow smoke has the same nitrogen content as 10 mg of polyether foam *Not determined due to interference from polyol

Material	Per cent	N	itrogen Yel	recove low smo	ry (%) ke		Nitrogen recovery (%) Foam					
	nitrogen ^p	600°C	700°C	800°C	900°C	1000°C	600°C	700°€	800°C	900°C	1000°C	
Hydrogen cyanide	51.8	5.7	25.1	11.5	17.6	41.3	0.3	18.4	8.2	25.1	45.8	
Acetonitrile	34.2	0.02	0.5	0.6	0.7	0.4	_	0.5	0.6	1.1	0.9	
Acrylonitrile	26.4	0.01	0.6	0.3	0.3	0.04	_	-	_	-	-	
Benzonitrile	13.6	0	0.03	0.06	1.1	0.5	0	0.1	0.5	1.0	0.6	
TOTAL		5•7	26.2	12.5	19.7	42.2	0.3*	19.0*	9.3*	27.2*	47•3*	

TABLE 3. Nitrogen recoveries from the thermal decomposition of polyester yellow smoke (2.5 mg) and foam (10 mg) in air between 600 and $1000^{\circ}C$

Note: Nitrogen content of 2.5 mg of polyester yellow smoke or 10 mg of polyester foam is 430 /ug $\wp_{\rm Of\ product}$

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*Sub-totals for hydrogen cyanide, acetonitrile and benzonitrile only.

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Material	Per cent nitrogen	N	itrogen Yell	recove ow smok	ry (%) e	<u> </u>	'n	itrogen	recove Foam	ry (%)	· <u> </u>
	%	600°C	700°C	800°C	900°C	1000°C	600°C	700°C	800°C	900°C	1000 ⁰ C
Hydrogen cyanide	51.8	4.3	18.6	8.3	16.9	30.8	3.5	8.4	4.6	19.1	35.5
Acetonitrile	34.2	0.07	0.4	0.5	0.8	0.3	-	0.8	0.9	1.0	0.8
Acrylonitrile	26.4	0.1	0.5	0.3	0.4	0.03	-	1	-	_	-
Benzonitrile	13.6	0	0.05	0.4	0.5	0.5	_	0.1	0.6	0.6	0.3
TOTAL		4.5	19.6	9•5	18.6	31.6	3.5*	9.3*	6.1*	20.7*	36.6*

TABLE 4. Nitrogen recoveries from the thermal decomposition of polyether yellow smoke (2.4 mg) and foam (10 mg) in air between 600 and 1000° C

Note: Nitrogen content of 2.4 mg of polyether yellow smoke or 10 mg of polyether foam is 410 /ug $\phi_{\rm Of\ product}$

*Sub-totals for hydrogen cyanide, acetonitrile and benzonitrile

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4. DISCUSSION

The weight- and nitrogen-loss experiments undertaken in the air atmospheres of this report indicate that the basic decomposition processes are similar to those observed in inert atmospheres, namely that there is an initial split of the polymer to give a volatile nitrogen rich material leaving a polyol residue. The nitrogen-loss characteristics of the foams as a function of temperature are virtually identical to those observed in inert atmospheres indicating that the nitrogen-rich material is probably the same yellow smoke observed under inert conditions. This has been substantiated during chromatographic decomposition experiments since, for the production of nitrogen containing materials, the oxidative decomposition of the foams can be adequately represented by the decomposition of an equivalent weight of 'inert' yellow smoke. Under oxidative conditions the residual polyester polyol is relatively stable whereas the polyether polyol is prone to rapid decomposition.

This latter effect is particularly noticeable during the chromatographic experiments between 300 and 400° C. The overall quantities of products from the polyether foam (as assessed from the approximate total peak area of the relevant F.I.D.trace) are much greater in air than in nitrogen. With the polyester foam, the relevant chromatograms reflect the stability of the material to oxidative environments. However, with both foams the presence of oxygen alters the nature of the decomposition products.

In the chromatograms of the foams recorded at 600° C there is evidence of the decomposition products of yellow smoke namely from the distinct generation of hydrogen cyanide, acetonitrile and acrylonitrile. At 700° C the yields of these materials are greater than observed at 600° C and benzonitrile is detected. At 800° C there is a marked drop in the yields of hydrogen cyanide from both foams which increase again towards 1000° C. Decomposition experiments between 600 and 1000° C show that the yellow smoke products (known to arise from yellow smoke from comparisons of the chromatograms of the foams and respective polyols) can be adequately simulated by separate decompositions of yellow smoke prepared under inert conditions. It is therefore concluded that the oxidative and inert yellow smokes are probably identical materials.

The 'maximum' or 'peak' value of hydrogen cyanide production observed at about 700°C for both the foams and yellow smokes is interesting. Clearly the yellow smokes, whether injected directly into the furnace or formed indirectly

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from the decomposition of the foams 'in situ' in the furnace, decompose in air at temperatures above about 600°C. At this temperature the total nitrogen recoveries for the yellow smokes (direct injection) are of the order of 5 per cent of the theoretical (see Tables 3 and 4). At 700°C the total nitrogen recoveries are of the order of 20 to 25 per cent but fall to approximately one half this value at 800°C and then increase rapidly with temperature between 800 and 1000°C (maximum temperature used). The reason for this behaviour is not understood but, as mentioned in an earlier section, may be associated with the rapid release of volatiles at higher temperatures which vitiates the atmosphere near the sample in the furnace. The mode of decomposition at high temperatures (ie 800°C and above) may follow the same course as in inert conditions whereas maximum oxidative decomposition takes place at lower temperatures of around 700°C. There is some evidence to support this view in that the decomposition products at 1000°C, as fingerprinted by chromatography show distinct pyrolysis-type patterns. However, this concept would suggest that at high temperatures the hydrogen cyanide production should be of the same order as that observed during inert decompositions. In fact at 1000°C (see Tables 3 and 4) the yields in air are somewhat lower than those of the inert atmospheres but there is a rapid increase in the yields between 900 and 1000° C. At temperatures above 1000°C the above hypotheses may be true.

Atmosphere vitiation during high temperature decomposition in air should be reflected in the production of inorganic combustion products. Work is currently in progress to study the production of oxides of carbon and nitrogen during the thermal and thermal oxidative decompositions of the polyester and polyether foams and parent polyols between 200 and 1000°C. The results of this work and additional comments about the effects of the decomposition atmospheres will be recorded in a future report⁵.

5. CONCLUSIONS

(1) In air, the basic decomposition processes of the foams are similar to those observed in nitrogen; namely that the decomposition proceeds in each case via the initial release of a nitrogen-rich material leaving a polyol residue.

(2) The experiments of this report suggest that the nitrogen-rich material is the same yellow smoke as observed in inert atmospheres.

(3) The presence of oxygen markedly reduces the stability of the polyether polyol residue but has little effect on the polyester polyol. The decomposition products (300 to 600° C) of the polyols are different to those of inert atmospheres.

(4) The yellow smoke decomposes at temperatures above about 600° C to give hydrogen cyanide and small quantities of acetonitrile, acrylonitrile and benzonitrile.

(5) There appears to be two distinct decomposition regions above 600° C. Firstly 600 to 800° C which is predominantly oxidative in nature, and secondly 800 to 1000° C (maximum used) which may have some pyrolytic character due to atmosphere vitiation.

(6) The yields of hydrogen cyanide tend to be lower than observed in nitrogen. The yields from the foams during the oxidative region $(700^{\circ}C)$ are of the order of 10 to 20 per cent of the theoretical and at 1000° are of the order of 35 to 50 per cent.

(7) Between 900 and 1000° C there is a steep rise in the production of hydrogen cyanide. At temperatures above 1000° C the yields may be substantially higher than recorded in (6) above.

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7. APPENDIX

. a) Appendix 1. Integrator counts (arbitrary units) for the products from the thermal decomposition of polyester yellow smoke (2.5 mg) and foam (10 mg) in air.

Material	Peak			Yell	ow smoke					Foam		
	letter	Detector	600°C	700°C	800°C	900°C	1000°C	600°C	700°C	800°C	900°C	1000°C
Hydrogen cyanide	g	T.C.D.	2497(1)*	1089(2)	5000(1)	7655(1)	1800(2)	1200	8000(1)	3549(1)	1092(2)	1990(2)
Acetonitrile	j	F.I.D.	2000	4415(1)	5009(1)	5531(1)	3586(1)	_ø	4327(1)	5062(1)	8761(1)	7175(1)
Acrylonitrile	k	F.I.D.	2000	1000(2)	4534(1)	3874(1)	5335	-	_	_	-	-
Benzene	n	F.I.D.	0	5000	2000(1)	2497(2)	6600(2)	-	-	_	- -	-
Toluene	s	F.I.D.	0	0	1000(1)	3000(1)	2000	_	-	_	-	_ ·
Benzonitrile	x	F.I.D.	0	1460(1)	2589(1)	4712(2)	2275(2)	0	5021(1)	2343(2)	4501(2)	2893(2)

*Number in brackets denotes the powers of ten; for example 2497(1) = 24970 arbitrary units

 $\phi_{\rm Not\ measured\ due\ to\ polyol\ interference}$

b) Appendix 2. Integrator counts (arbitrary units) for the products from the thermal decomposition of polyether yellow smoke (2.4 mg) and foam (10 mg) in air

Material	Peak	Detector		Yell	ow smoke]	Foam		
	letter		600°C	700°C	800°C	900°C	1000°C	600°C	700°C	~800°c	900°C	1000 ⁰ C
Hydrogen cyanide	đ	T.C.D.	1797(1)*	7680(1)	3441(1)	7014(1)	1281(2)	1440(1)	3466(1)	1924(1)	7905(1)	1473(2)
Acetonitrile	j	F.I.D.	4811	3213(1)	3659(1)	6216(1)	2618(1)	_ø	5769(1)	6508(1)	7992(1)	6050(1)
Acrylonitrile	k	F.I.D.	1389(1)	6818(1)	3896(1)	5223(1)	5000	-		-	<u> </u>	·
Benzene	n	F.I.D.	0	5000	1814(1)	1669(2)	4034(2)	-		-	-	_
Toluene	ន	F.I.D.	0	0	5000	2894(1)	2000	-	-	-	_	_
Benzonitrile	x	F.I.D.	0	2061(1)	1773(2)	2225(2)	2305(2)	-	5000(1)	2424(2)	2577(2)	1134(2)

*Number in brackets denotes the powers of ten; for example 1797(1) = 17970 arbitrary units.

 $\phi_{\rm Not\ measured\ due\ to\ polyol\ interference}$

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FIG 1 WEIGHT AND NITROGEN LOSSES DURING THE THERMAL DECOMPOSITION OF POLYESTER FOAM IN AIR

C C Z Z Z

|| 8 52



X Weight loss

FIG2 WEIGHT AND NITROGEN LOSSES DURING THE THERMAL DECOMPOSITION OF POLYETHER FOAM IN AIR

11833 SI951



THE THERMAL DECOMPOSITION OF FOAM TYPE D



X Weight loss

0

FIG 4 WEIGHT AND NITROGEN LOSSES DURING THE THERMAL DECOMPOSITION OF FOAM TYPE H IN AIR



X Weight loss

FIG 5 WEIGHT AND NITROGEN LOSSES DURING THE THERMAL DECOMPOSITION OF FOAM TYPE F IN AIR

1 955





50

70

60

IG. 6 CHROMA TOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYESTER FOAM AND POLYOL AT 300°C IN AIR

40

20

30 MINUTES

1.5

10

0





FIG. 7 CHROMA TOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYESTER FOAM AND POLYOL AT 400°C IN AIR

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FIG. 8 CHROMATOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYESTER FOAM, POLYOL AND YELLOW SMOKE AT 600°C IN AIR

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FIG. 9 CHROMATOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYESTER FOAM, POLYOL AND YELLOW SMOKE AT 700°C IN AIR



CHROMATOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYESTER FOAM, POLYOL AND FIG. 10 YELLOW SMOKE AT 1000°C IN AIR





FIG. 11 CHROMATOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYETHER FOAM AND POLYOL AT 300°C IN AIR





FIG. 12 CHROMATOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYETHER FOAM AND POLYOL AT 400°C IN AIR



FIG.13 CHROMATOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYETHER FOAM, POLYOL AND YELLOW SMOKE AT 600°C IN AIR

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CHROMATOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYETHER FOAM, POLYOL AND YELLOW SMOKE AT 700°C IN AIR FIG. 14



FIG. 15 CHROMATOGRAMS (F.I.D.) OF THE DECOMPOSITION PRODUCTS OF POLYETHER FOAM, POLYOL AND YELLOW SMOKE AT 1000°C IN AIR

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