Studies of Temperature and Atmosphere Composition Influence on Thermal Degradation Products of Polyurethane Foam

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Synopsis

The paper presents studies on the influence of temperature and atmosphere composition on the thermal degradation products evolved from flexible polyurethane foam. The experiments have been carried on within the temperature range 200–700°C in air atmosphere and oxygen–nitrogen–helium mixtures. The main volatile toxic products and weight losses during thermal degradation of the polyurethane foam have been determined. The test results have been presented graphically.

INTRODUCTION

Thermal degradation process of plastics involves the emission of many volatile and nonvolatile substances which may create serious life hazard especially under fire conditions. The qualitative and quantitative composition of the substances evolved depends on the type of material, the thermal degradation temperature, and oxygen concentration. According to several authors,[1-8] significant hazard can take place as early as in the initial phase of fire when the material begins to smolder. It is essential to determine the thermal degradation products under different temperatures corresponding to various fire phases. Although certain materials do not flame, they nevertheless can create serious hazard as a result of toxic products emission during a nonflaming combustion.[1-3,9-11]
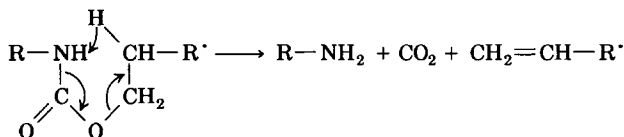
At temperatures up to 400°C plastics decompose forming complex products. Within the temperature range 400–700°C the composition of products becomes the most miscellaneous, and often the highest concentrations of emitted substances are observed. In that temperature range, polymers can form oxygenated particles through binding the atmospheric oxygen. At higher temperatures over 700°C, the complex organic compounds decompose. The main degradation products are aliphatic and aromatic hydrocarbons and low molecular weight substances[1-3,6-8,11] like water, carbon monoxide, and dioxide.

One of the widely used and hazard creating plastics are polyurethane foams.[2,6,8] During the thermal degradation of polyurethane foams, many toxic substances are emitted. The studies[3,8,12,13] have shown that within the temperature range 200–300°C a polyurethane bond cleavage takes place with the evolution of isocyanate and alcohol. Grassie and Zulfiqar[13] and Foti et al.[14] suggest that the main degradation products of urethane plastics can be
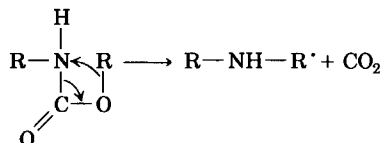
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evaluated on the basis of the following reactions:

1.

$$R-N \overset{\overset{H \rightarrow O-R'}{|\;|}}{\underset{\underset{O}{\|}}{C}} \longrightarrow R-N{=}C{=}O + R'-OH$$
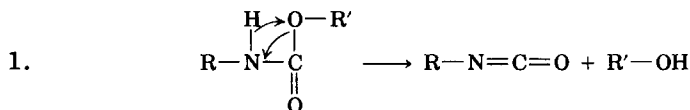
2. Dissociation to amine, carbon dioxide, and olefin through the intermediate state of six-membered ring:

$$R-NH \overset{H}{\underset{\underset{O}{\overset{|}{C}} \overset{}{\underset{O}{}}}{\diagdown}} CH-R^{\cdot} \longrightarrow R-NH_2 + CO_2 + CH_2{=}CH-R^{\cdot}$$

3. Dissociation to secondary amine and carbon dioxide through the intermediate four-membered ring:

$$R-N \overset{H}{\underset{\underset{O}{\overset{|}{C}}{\leftarrow}O}{\leftarrow}R} \longrightarrow R-NH-R^{\cdot} + CO_2$$

According to Jellinek and Dunkle[15] the thermal degradation process of polyurethane under oxidative conditions proceeds according to the following radical mechanism:

$$HRNH + O_2 \overset{\nearrow\; ^{\cdot}RNH + HO_2^{\cdot}}{\searrow\; HRN^{\cdot} + HO_2^{\cdot}}$$

$$^{\cdot}RNH + O_2 \rightarrow {}^{\cdot}OORNH$$

$$HRN^{\cdot} + O_2 \rightarrow HRNOO^{\cdot}$$

$$^{\cdot}OORNH + HRNH \rightarrow HOORNH + HRN^{\cdot}$$

$$^{\cdot}OORNH + HRNH \rightarrow HOORNH + {}^{\cdot}RNH$$

$$HRNOO^{\cdot} + HRNH \rightarrow HROOH + HRN^{\cdot}$$

$$HRNOO^{\cdot} + HRNH \rightarrow HRNOOH + {}^{\cdot}RNH$$

$$HRNOOH \overset{\nearrow\; HCN + HRNO^{\cdot} + {}^{\cdot}OH}{\searrow\; \text{inert products}}$$

$$HOORNH \overset{\nearrow\; HCN + {}^{\cdot}ORNH + {}^{\cdot}OH}{\searrow\; \text{inert products}}$$

$$HRNO^{\cdot} + HRNOOH \rightarrow HRNOO^{\cdot} + HRNOH$$

$$^{\cdot}ORNH + HOORNH \rightarrow {}^{\cdot}OORNH + HORNH$$

$$^{\cdot}OH + HRNOOH \rightarrow HRNO_2^{\cdot} + H_2O$$

$$^{\cdot}OH + HOORNH \rightarrow {}^{\cdot}O_2RNH + H_2O$$
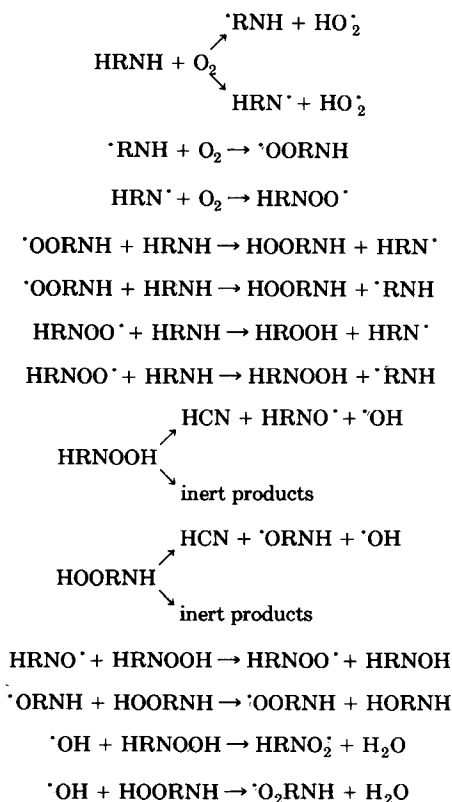
Woolley[8] and Grassie and Zulfiqar[13] state that during the thermal degradation of polyurethane foams isocyanates may form carbodiimide in a reaction:

$$2\,R\!-\!N\!=\!C\!=\!O \rightarrow R\!-\!N\!=\!C\!=\!N\!-\!R + CO_2$$
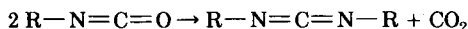
or can react with the amine to form volatile polyureas. Thus isocyanate can be evolved at relatively low temperature and may be collected as so called "yellow smoke." Following the "yellow smoke" degradation in air the low molecular weight products like hydrogen cyanide, carbon monoxide, and dioxide are formed.[3,8,15] Furthermore, other toxic substances such as acetonitrile, acrylonitrile, benzonitrile, benzene, toluene, and pyridine may be emitted.[3,7,8] However, in the literature there are only scarce data concerning concentrations of toxic substances emitted during the thermal degradation of polyurethane foams. The aim of this paper is to study temperature and atmosphere composition influence on the emission of volatile toxic substances during thermal degradation of flexible polyurethane foam.

EXPERIMENTAL

The commercial flexible polyurethane foam P30/34 MV Dunlopillo has been tested. The experiments have been carried on using the test apparatus shown schematically in Figure 1. The 100 mg samples have been placed in the ceramic tube heated to a required temperature. The flow rate of air and gas mixtures through the tubular furnace was kept at 0.03 m^3/h. Tests have been conducted under isothermal conditions in the temperature range 200–700°C at intervals of 100°C for 20 min. At the outlet of the reactor tube a fiber glass filter has been placed to trap nonvolatile thermal degradation products. The volatile products have been collected in a glass container of 0.0125 m^3 volume and then analyzed. To determine the composition and concentrations of thermal degradation products and of atmosphere after the experiment, the gas chromatographic and colorimetric methods have been employed. The Carlo Erba Fractovap 2450 and Chromatron GCHF 18.3 with FID and TCD
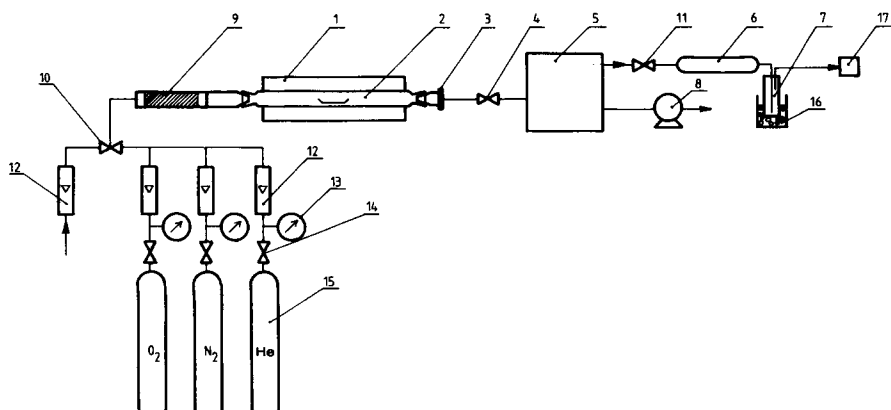

Fig. 1. Scheme of apparatus used for the thermal degradation studies of materials: (1) flow tubular furnace; (2) ceramic tube with boat for the sample; (3) glass fiber filter; (4) needle valve; (5) vacuum container; (6) gaseous pipette; (7) absorption bubbling washer; (8) vacuum pump; (9) gas cleaning filter; (10, 11) glass cocks; (12) flowmeter; (13) monometer; (14) pressure reducing valve; (15) compressed gases containers; (16) cooling bath; (17) aspirator.

detectors and following packed columns have been used: SE 30 (10%) on Celite 80–120 mesh; Reoplex 400 (10%) on Celite 80–120 mesh; Carbowax 20M (10%) on Chromosorb P 80–100 mesh; activated alumina 60–80 mesh; molecular sieve 5 Å 60–80 mesh; silicagel 50–100 mesh. With the TCD detectors helium and hydrogen carrier gases of 30 cm^3/min flow rates have been used and with FID detectors nitrogen of 40 cm^3/min. The operation temperature of columns were 20, 80, 100, 120, and 140°C.

Hydrogen cyanide, isocyanates, ammonia have been analyzed colorimetrically.[5]

TEST RESULTS

After completing the thermal degradation tests in air atmosphere, the sample weight losses have been evaluated. The weight losses of polyurethane foam as a function of the thermal degradation temperature have been shown in Figure 2. The greatest changes of sample weights occurred within the range 200–300°C. At higher temperatures (above 300°C) the foam decomposed almost completely.

The analysis of volatile degradation products has shown that the main substances emitted were carbon monoxide, carbon dioxide, C_1–C_4 aliphatic hydrocarbons, acrylonitrile, acetonitrile, and methyl alcohol. The concentrations of substances determined in thermal degradation products of the tested polyurethane foam in air atmosphere are given in Table I. The dependence of major substances on the degradation temperature are presented in Figures 3 and 4. The maximum yield of carbon monoxide has been observed at 600°C, and the concentrations of carbon dioxide, aliphatic hydrocarbons, and hydrogen cyanide increased with the temperature rise. As for methyl alcohol,
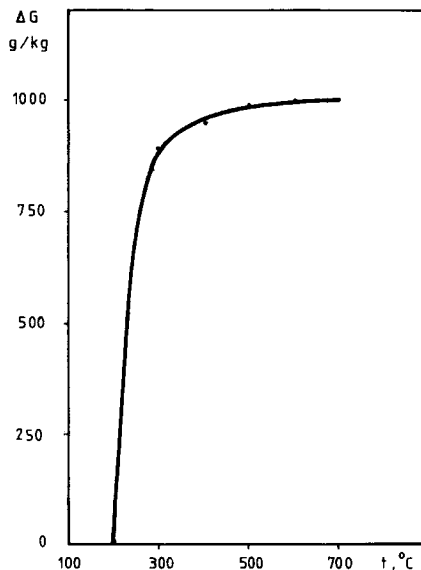

Fig. 2. Weight losses changes as a function of thermal degradation temperature of flexible polyurethane foam P30/34 MV.

TABLE I
Test Results of Volatile Thermal Degradation Products of Flexible Polyurethane Foam P30/34 MV in Air Atmosphere

| Substance determined | Product concentration (mg/m³) | | | | | |
| | Temperature (°C) | | | | | |
	200	300	400	500	600	700
Carbon monoxide	11.0	398.7	765.6	1071.9	1378.1	764.6
Carbon dioxide	230	1382	2016	2651	6741	9343
Hydrogen cyanide	0.2	4.2	15.6	44.5	58.8	105.8
3,4-Toluene diisocyanate	12.2	1.4	< 0.5	< 0.5	< 0.5	< 0.5
Ammonia	< 0.2	0.3	0.4	0.2	0.4	4.1
Methyl alcohol	< 0.5	152.8	204.7	239.3	175.2	47.6
Methylethyl ketone	< 2	16.2	19.8	9.9	< 2	< 2
Acrylonitrile	< 5	300.8	810.1	991.3	570.4	188.0
Acetonitrile	< 5	163.6	694.8	937.6	639.3	150.4
Benzene	< 0.5	< 0.5	4.0	7.2	7.8	9.4
Toluene	< 1	< 1	< 1	< 1	< 1	< 1
C₁–C₄ aliphatic hydrocarbons	16.6	85.2	230.2	431.7	1253.7	1549.2
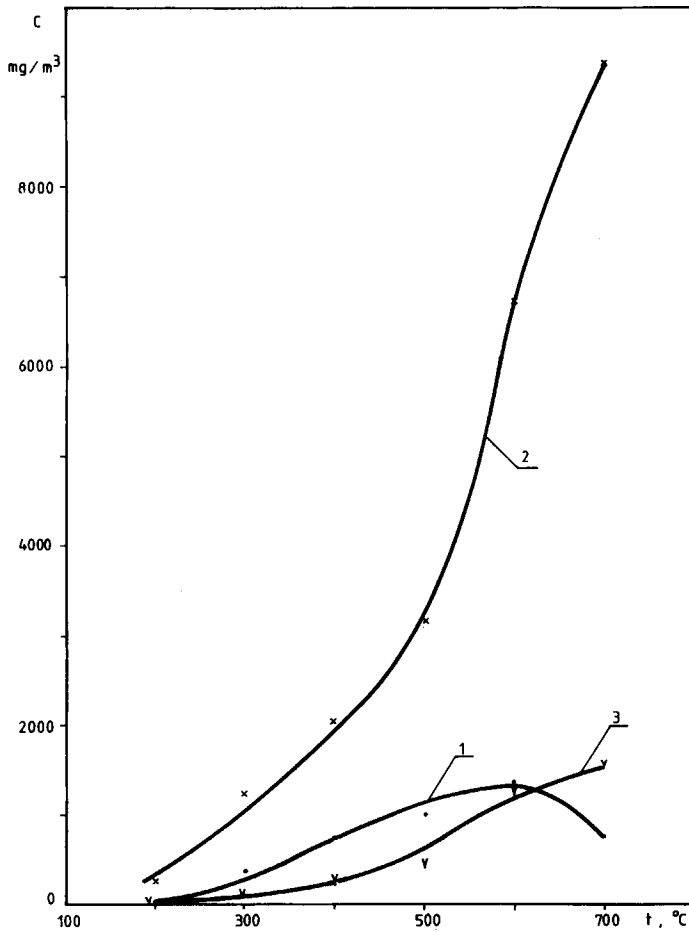
Fig. 3. Concentration changes of volatile degradation products of flexible polyurethane foam P30/34 MV as a function of temperature: (1) carbon monoxide; (2) carbon dioxide; (3) C_1-C_4 aliphatic hydrocarbons.

acetonitrile, and acrylonitrile, the maximum concentrations have occurred at 500°C.

The subsequent step is comprised of studies of atmosphere composition influence on thermal degradation process of flexible polyurethane foam P30/34 MV Dunlopillo. The experiments have been conducted with the oxygen–nitrogen–helium mixtures at 400°C, corresponding to practically complete degradation of foam. The test method was the same as described above. The gas mixture compositions have been selected as to meet the physiological requirements of breathing mixtures used under hyperbaric conditions. The gas mixture compositions are listed in Table II.

The test results of major thermal degradation products of the polyurethane foam in oxygen–nitrogen and oxygen–nitrogen–helium mixtures have been shown graphically vs. oxygen fraction. From Figures 5–8 it can be seen that carbon monoxide, carbon dioxide, hydrogen cyanide, and acrylonitrile con-
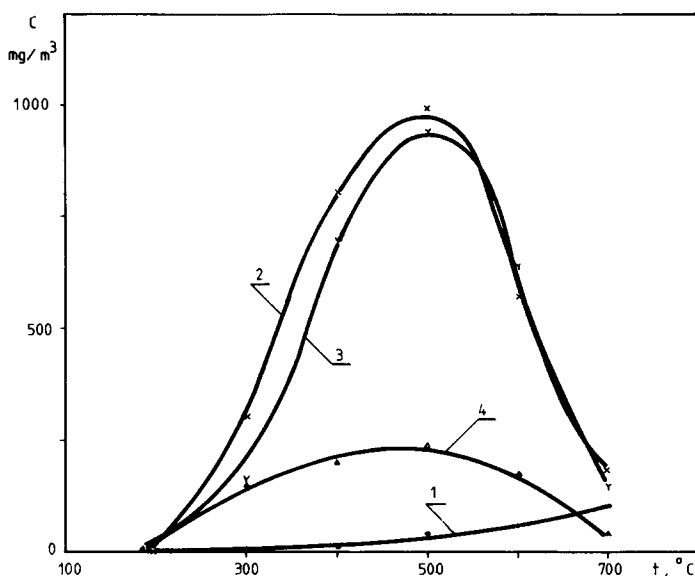
Fig. 4. Concentration changes of volatile degradation products of flexible polyurethane foam P30/34 MV as a function of temperature: (1) hydrogen cyanide; (2) acrylonitrile; (3) acetonitrile; (4) methyl alcohol.

TABLE II
Composition of Gas Mixtures Used in the Thermal Degradation Tests of
Flexible Polyurethane Foam

Mixture no.	Mixture composition (vol %)		
	Oxygen	Nitrogen	Helium
I	6.5	23.5	70.0
II	10.6	38.8	50.6
III	16.0	62.8	21.2
IV	6.5	93.5	—
V	10.6	89.4	—
VI	16.0	84.0	—

centrations increase with oxygen fraction rise in the mixture. The higher concentrations of products have been determined as a result of thermal degradation of polyurethane in the mixtures containing helium. The dependences presented show that the process of toxic products evolution during the polyurethane foam thermal degradation is influenced not only by oxygen fraction but also by the inert gases in the atmosphere. Thus in the O_2-N_2-He mixtures the higher concentrations of the main thermal degradation products have been observed comparing with the test results in O_2-N_2 mixtures at the same temperature. The reason of such differences lies probably in the helium features (higher thermal conductivity, higher specific heat, lower specific gravity compared to oxygen and nitrogen), which affect the heat and mass transfer at the reaction zone.
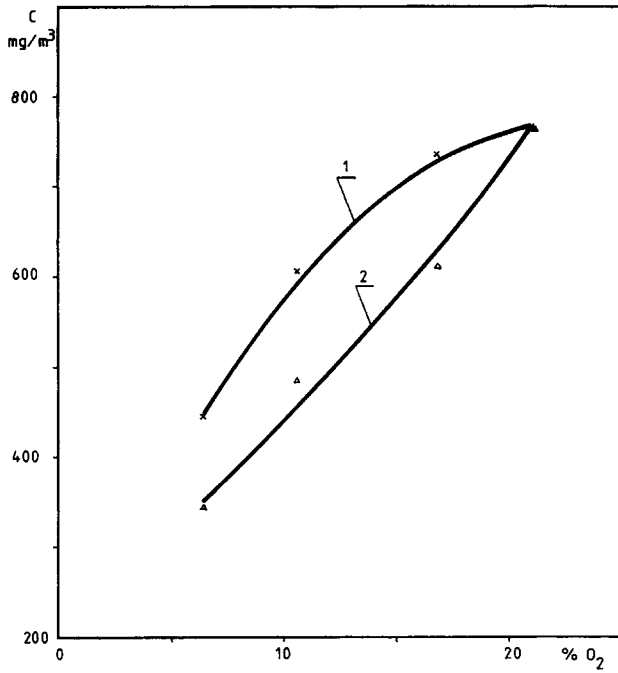
Fig. 5. Dependence of carbon monoxide concentrations in thermal degradation products of flexible polyurethane foam P30/34 MV on atmosphere oxygen fraction: (1) O_2-N_2-He: (2) O_2-N_2.
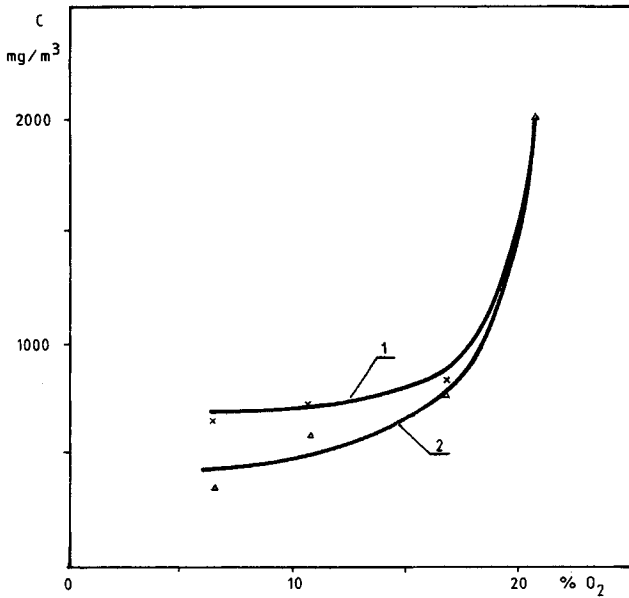

Fig. 6. Dependence of carbon dioxide concentrations in thermal degradation products of flexible polyurethane foam P30/34 MV on atmosphere oxygen fraction: (1) O_2-N_2-He; (2) O_2-N_2.
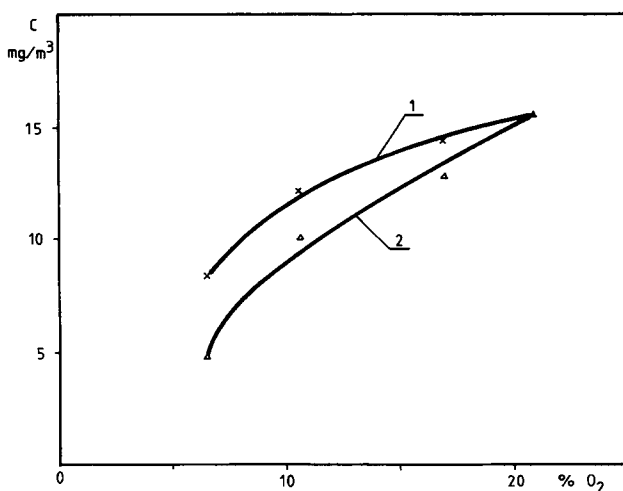
Fig. 7. Dependence of hydrogen cyanide concentrations in thermal degradation products of flexible polyurethane foam P30/34 MV on atmosphere oxygen fraction: (1) O_2–N_2–He; (2) O_2–N_2.
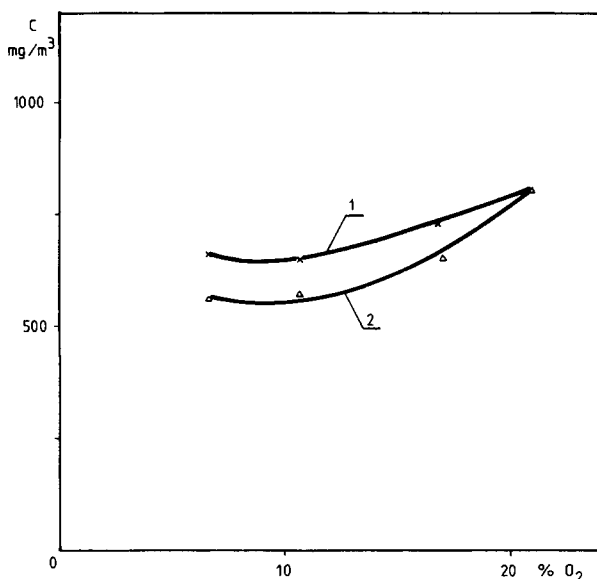

Fig. 8. Dependence of acrylonitrile concentrations in thermal degradation products of flexible polyurethane foam P30/34 MV on atmosphere oxygen fraction: (1) O_2–N_2–He; (2) O_2–N_2.

CONCLUSIONS

On the basis of the thermal degradation studies of flexible polyurethane foam P30/34 MV Dunlopillo, it has been found that the main volatile thermal degradation products were carbon monoxide, carbon dioxide, hydrogen cyanide, acrylonitrile, acetonitrile, methyl alcohol, and C_1–C_4 aliphatic hydrocarbons. With the temperature rise the increase of hydrogen cyanide, carbon dioxide, and aliphatic hydrocarbon concentrations has been observed while carbon

monoxide, acrylonitrile, acetonitrile, and methyl alcohol have reached maximum at about 500°C.

Higher concentrations of products emitted during the thermal degradation of polyurethane foam in helium containing atmospheres have been determined.

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