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A PRELIMINARY STUDY OF THE THERMAL DECOMPOSITION OF POLYURETHANE FOAMS BY ELEMENTAL ULTRAMICROANALYSIS

by

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FIRE RESEARCH STATION

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SUMMARY

A study of the thermal decomposition of certain rigid and flexible polyurethane foams has been undertaken by monitoring the nitrogen contents of the residues from decomposition experiments using elemental ultramicroanalysis. With the rigid foams the nitrogen content is lost in each case by a general temperature dependent fragmentation process whereas the flexible foams each show a rapid complete loss of nitrogen at low temperatures.

KEY WORDS: plastics, polyurethane foam, pyrolysis, analysis.

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DEPARTMENT OF THE ENVIRONMENT AND FIRE OFFICES' COMMITTEE
JOINT FIRE RESEARCH ORGANIZATION

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1. INTRODUCTION

Polyurethane foams are now used widely within buildings. Most of these foams are present in flexible form in the furnishings but some rigid foams are now used within the building structures.

When involved in fires there is concern that the nitrogen contents of these foams may be released as toxic nitrogenous products such as hydrogen cyanide, organic cyanides and ammonia. Much of this concern is due to a lack of knowledge of the basic principles of the decomposition mechanisms of the various foams. To date, workers in this field have tended to study only selected products[1] (such as hydrogen cyanide) which are intuitively thought to be generated during thermal decomposition experiments. These selected nitrogenous products have accounted for only a small amount of the theoretically available nitrogen and no attempts have been made to determine the main decomposition routes involving the nitrogen contents of the foams.

The work outlined in this report forms part of a detailed study of the thermal decomposition and the decomposition products of flexible and rigid foams using gas chromatography - mass spectrometry for the quantitative and qualitative determinations of the products. This first report will examine some of the basic principles of the decomposition using elemental ultramicroanalysis (for the determination of the percentages of carbon, hydrogen and nitrogen in small samples) to determine the nitrogen contents of residues pyrolysed at different temperatures. The report will demonstrate that the losses of combined nitrogen from a number of flexible and rigid foams can, when compared with the overall weight losses, reveal a number of important features about the decomposition routes involving nitrogen.

2. EXPERIMENTAL

a) General experimental details

Weighed samples of foam (normally 50 mg) were decomposed in a ceramic boat in a tube furnace (temperature stability $\pm$ 1°C at 500°C) in a stream of nitrogen (B.O.C. white-spot grade) at 100 ml/min for periods of 15 minutes at temperatures between 200 and 500°C. After each experiment the residues were weighed and analysed for the percentages of carbon, hydrogen and nitrogen by elemental ultramicroanalysis[2].

b) Materials

Five different polyurethane foam samples were available for this study and are listed below:

(i) M.D.I. rigid polyether foam; based on diphenyl methane diisocyanate and a polyether polyol.

(ii) Isocyanurate foam (rigid); based on diphenyl methane diisocyanate which has been trimerised with an activator.

(iii) M.D.I. rigid polyester foam; based on diphenyl methane diisocyanate and a polyester polyol.

(iv) T.D.I. flexible polyester foam; based on tolylene diisocyanate and a polyester polyol.

(v) T.D.I. flexible polyether foam; based on tolylene diisocyanate and a polyether polyol.

c) Elemental ultramicroanalysis

All elemental analyses[2] were undertaken with a commercial ultramicroanalyser using samples weighing approximately 500 μg. The quoted accuracy of the instrument is %C $\pm$ 0.25%, %H $\pm$ 0.10% and %N $\pm$ 0.30%.

3. RESULTS

Before undertaking decomposition studies, the experimental elemental analyses of the 5 foams were determined, as recorded in Table 1 in order of decreasing nitrogen content. Each analysis represents a mean value of several determinations.

TABLE 1 - ELEMENTAL ANALYSES OF POLYURETHANE FOAMS

Foam	Elemental analysis*		
	%C	%H	%N
M.D.I. rigid polyether	67.5	6.2	8.9
Isocyanurate	64.2	4.9	7.4
M.D.I. rigid polyester	65.8	6.0	6.3
T.D.I. flexible polyester	59.2	6.9	4.3
T.D.I. flexible polyether	61.3	9.0	4.1

* Oxygen by difference from 100%.

Samples of each foam were then decomposed for 15-minute periods in a flow of nitrogen as outlined in the experimental section at temperatures between 200 and 500°C. The results showing the elemental analysis of the residue, the nitrogen loss (as a percentage of the theoretical nitrogen loss) and the weight loss (again as a percentage of the theoretical weight loss) for each experiment are recorded in Table 2. The nitrogen content of the original foams in each case is calculated from the weight of foam and the elemental analyses of Table 1. Decomposition experiments involving the flexible foams were limited to a maximum temperature of 300°C because of the virtually complete loss of nitrogen at this temperature.

For convenience the nitrogen and weight losses from Table 2 are recorded graphically in Figs 1-5 inclusive for each foam.

4. DISCUSSION

For the rigid polyether and polyester foams (Figs 1 and 3 respectively) there is a distinct correlation between the weight losses and the nitrogen losses. The losses of nitrogen from these foams must therefore be associated with the main weight loss processes ie general fragmentations take place during the decomposition with the extent of the fragmentations dependent upon the temperature.

TABLE 2. ELEMENTAL ANALYSES OF RESIDUES DURING THE THERMAL DECOMPOSITION (15-MINUTE PERIODS) OF POLYURETHANE FOAMS

Temperature	Foam		Residue					Nitrogen loss	Weight loss
(°C)	weight (mg)	nitrogen content (mg)	weight (mg)	C (%)	H (%)	N (%)	nitrogen content (mg)	(percent)	(percent)
M.D.I. rigid polyether									
200	50	4.45	46.0	66.9	6.4	9.6	4.41	0.1	8.0
250	50	4.45	40.1	71.2	6.4	10.1	4.05	9.0	20
300	50	4.45	24.7	75.1	6.7	10.9	2.70	39	51
400	50	4.45	9.6	80.3	5.1	10.3	0.99	78	81
500	50	4.45	4.5	80.0	3.4	6.8	0.31	93	91
Isocyanurate									
250	50	3.70	42.9	67.5	5.3	8.7	3.73	0	14
300	50	3.70	37.4	70.0	5.4	9.8	3.70	0	25
400	100	7.40	36.6	79.4	5.0	9.5	3.48	53	63
500	50	3.70	4.6	82.0	2.9	5.0	0.23	94	91
M.D.I. rigid polyester									
300	50	3.15	27.5	71.5	6.3	7.3	2.01	36	45
400	50	3.15	12.0	83.0	5.4	7.7	0.92	71	76
500	50	3.15	8.2	85.0	3.5	5.0	0.41	87	84
T.D.I. flexible polyester									
210	50	2.16	47.1	56.9	6.9	4.2	1.98	8.3	5.8
250	50	2.16	38.4	55.5	7.0	1.1	0.42	80	23
300	50	2.16	30.3	55.4	7.5	0.4	0.12	94	39
T.D.I. flexible polyether									
200	50	2.05	49.3	61.2	9.0	4.1	2.02	1.5	1.4
250	50	2.05	39.7	63.5	9.9	1.4	0.56	72	21
300	50	2.05	32.9	64.5	10.9	0.16	0.05	98	34

The isocyanurate foam (Fig 2) shows the same general correlation of the nitrogen losses with the weight losses as for the rigid polyether and polyester foams but there is some evidence that the initial loss of material at low temperatures may be nitrogen free.

With the flexible foams (Fig 4 and 5) there are distinct similarities between the decomposition behaviours of the two foams and in each case there is a rapid loss of nitrogen in comparison with the weight loss. For example at 300°C there is an almost complete loss of nitrogen in each case with weight losses only of approximately 35 per cent. The decompositions of these flexible foams must therefore proceed via specific decomposition routes which favour the production of nitrogen-containing materials.

In conclusion, there appears to be distinct differences between the decomposition behaviours of rigid and flexible foams. The rigid M.D.I. foams show a typical fragmentation-type decomposition whereas the T.D.I. flexible foams show specific routes favouring the loss of nitrogen.

Because of the extensive use of flexible foams within buildings and the rapid and quantitative loss of the nitrogen contents at 300°C, these foams could present a serious toxic hazard in fires. It is therefore most important that the main nitrogen containing products from the decomposition of these foams should be determined. This work is currently being undertaken using coupled gas chromatography-mass spectrometry and will be recorded in a future publication[3].

5. REFERENCES

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3. Woolley, W.D., Wadley, A.I., and Field, P. The formation of nitrogen-containing products from the thermal decomposition of flexible polyurethane foams. Joint Fire Research Organization, Fire Research Note No 881.

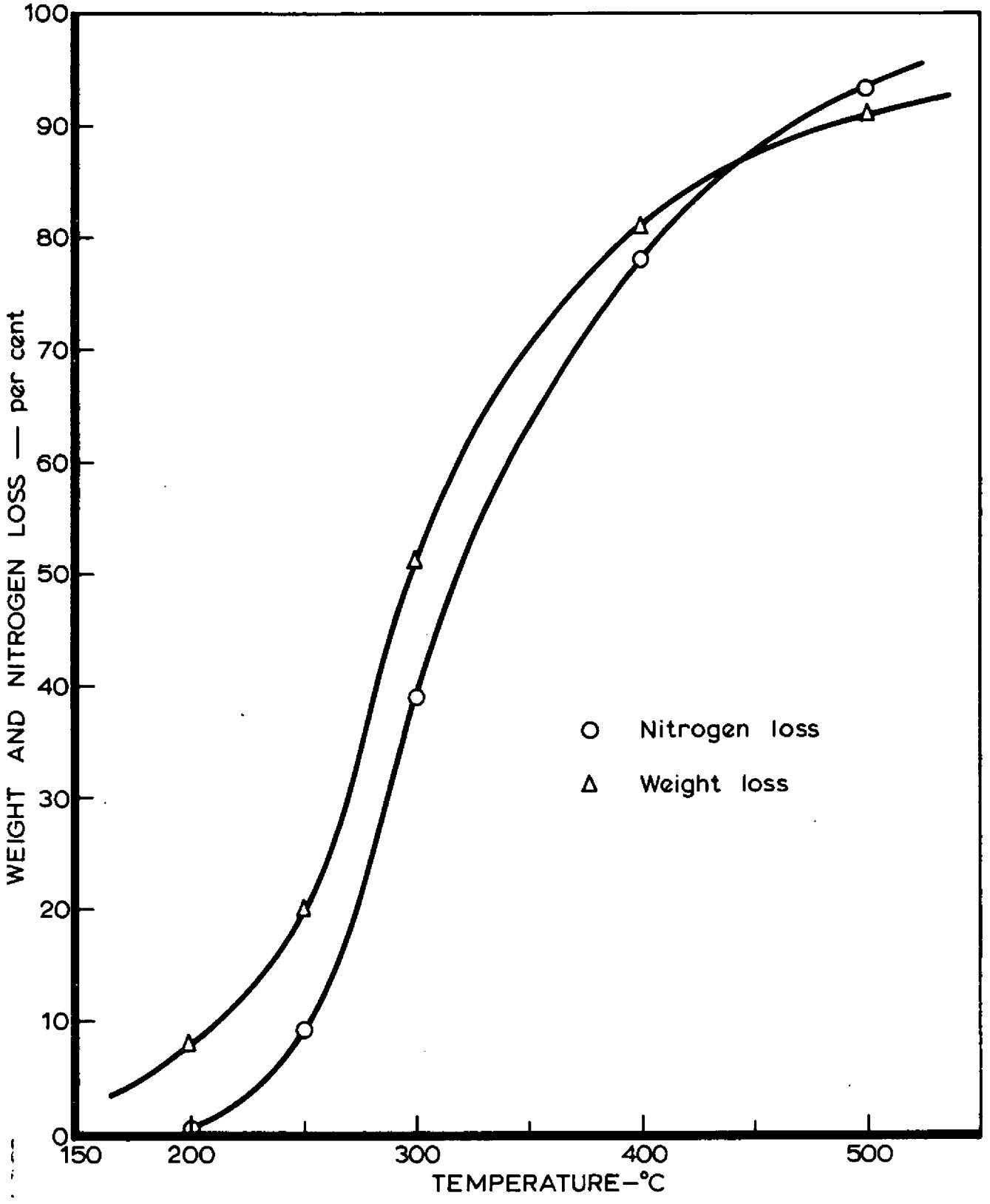

FIG. 1. DECOMPOSITION DATA FOR M.D.I. RIGID POLYETHER FOAM

10490 F.R. Mem 42 + F.R. 880

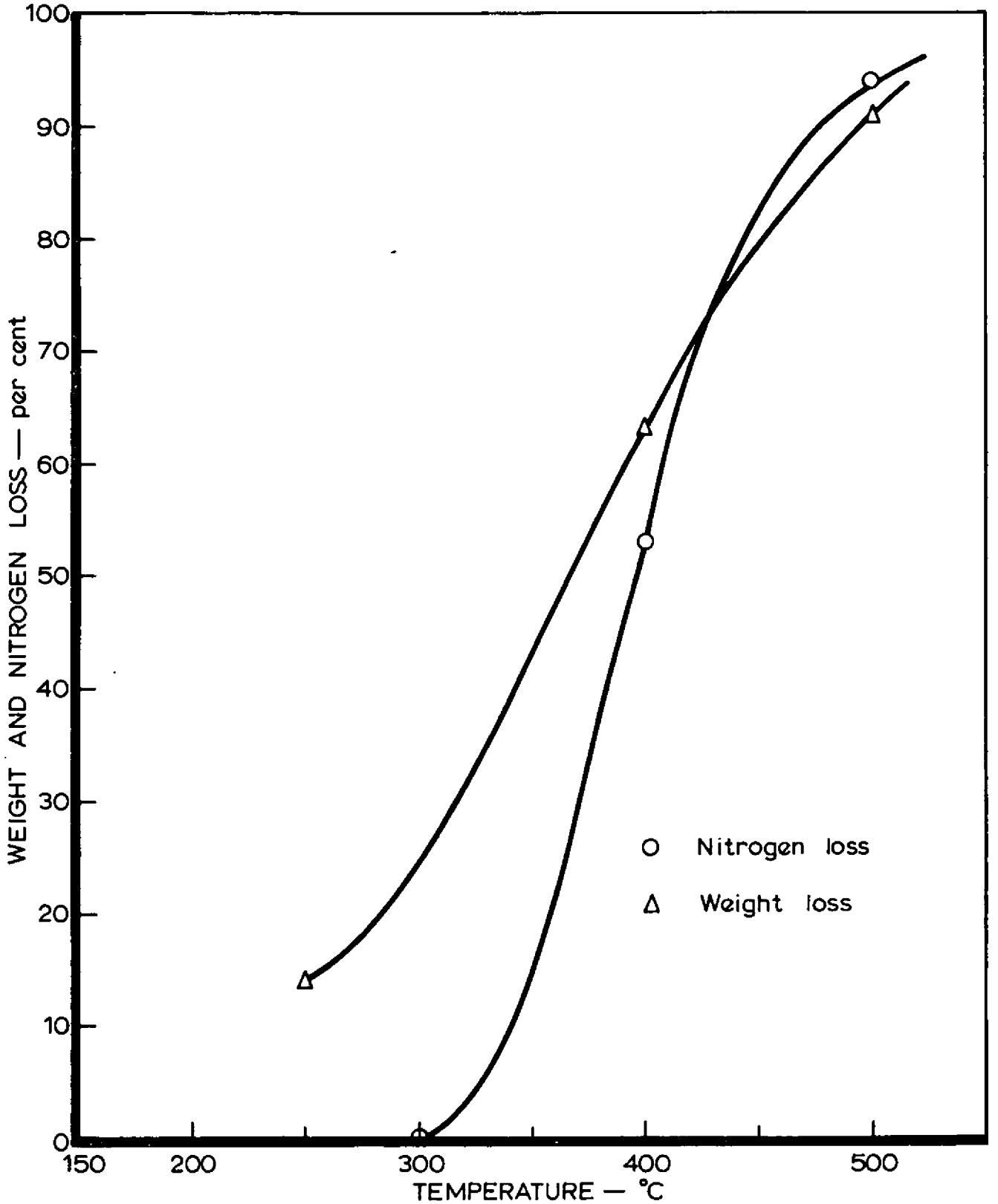

FIG. 2. DECOMPOSITION DATA FOR ISOCYANURATE FOAM

10491 F.R. Memo 42 + F.R. 880

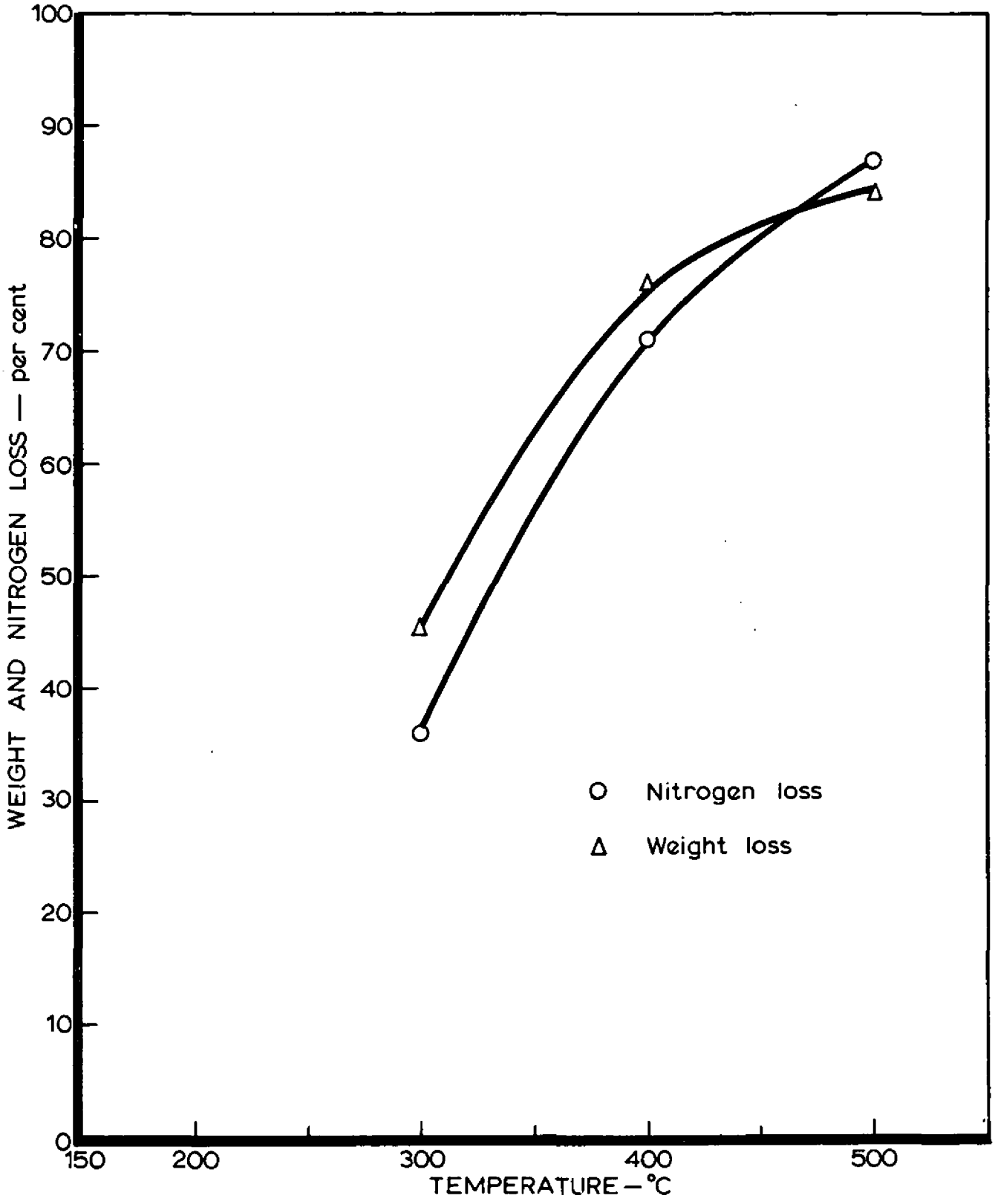

FIG. 3. DECOMPOSITION DATA FOR M.D.I. RIGID POLYESTER FOAM

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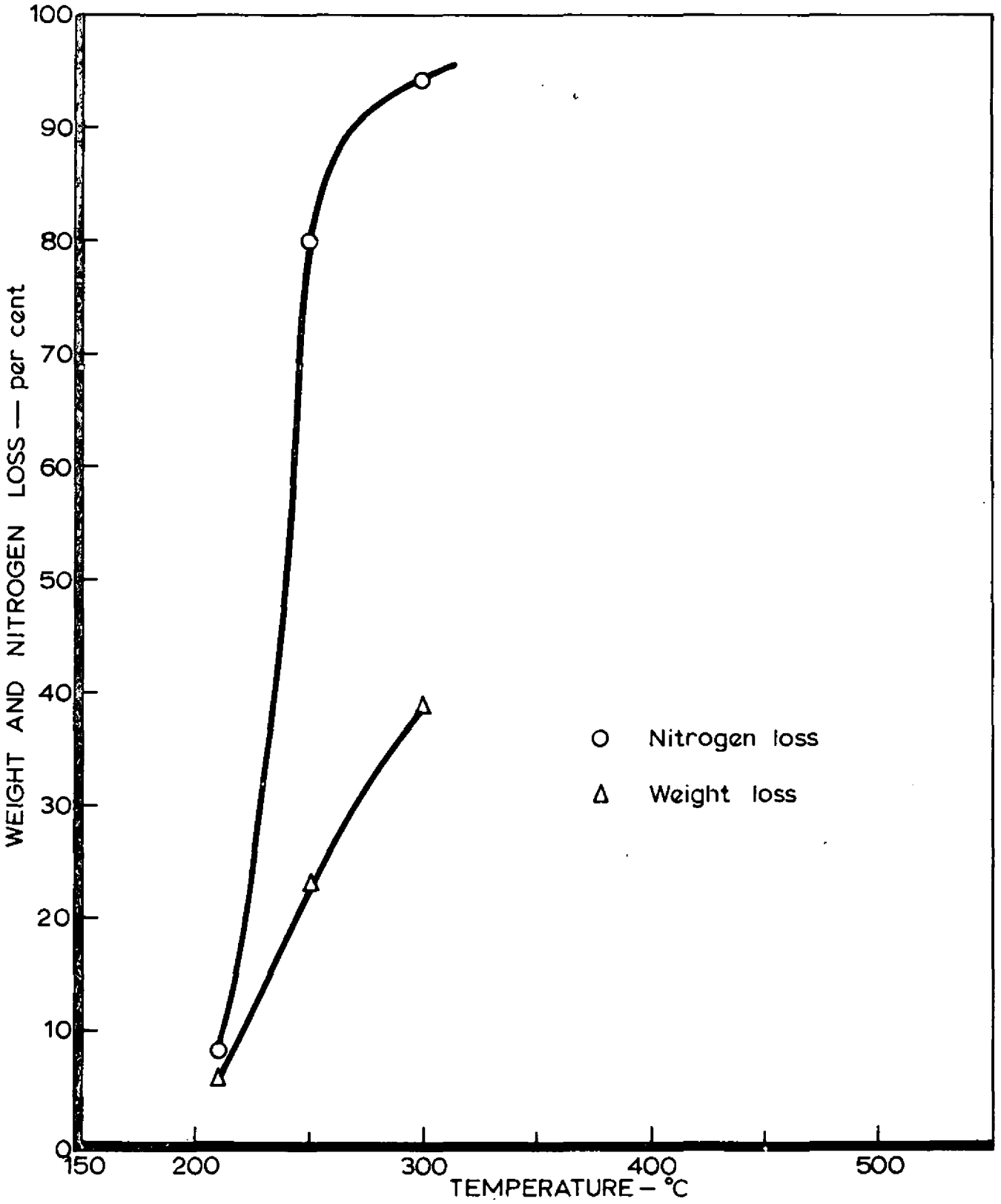

FIG. 4. DECOMPOSITION DATA FOR T.D.I. FLEXIBLE POLYESTER FOAM

10493 F.R. Memo 42 + F.R. 880

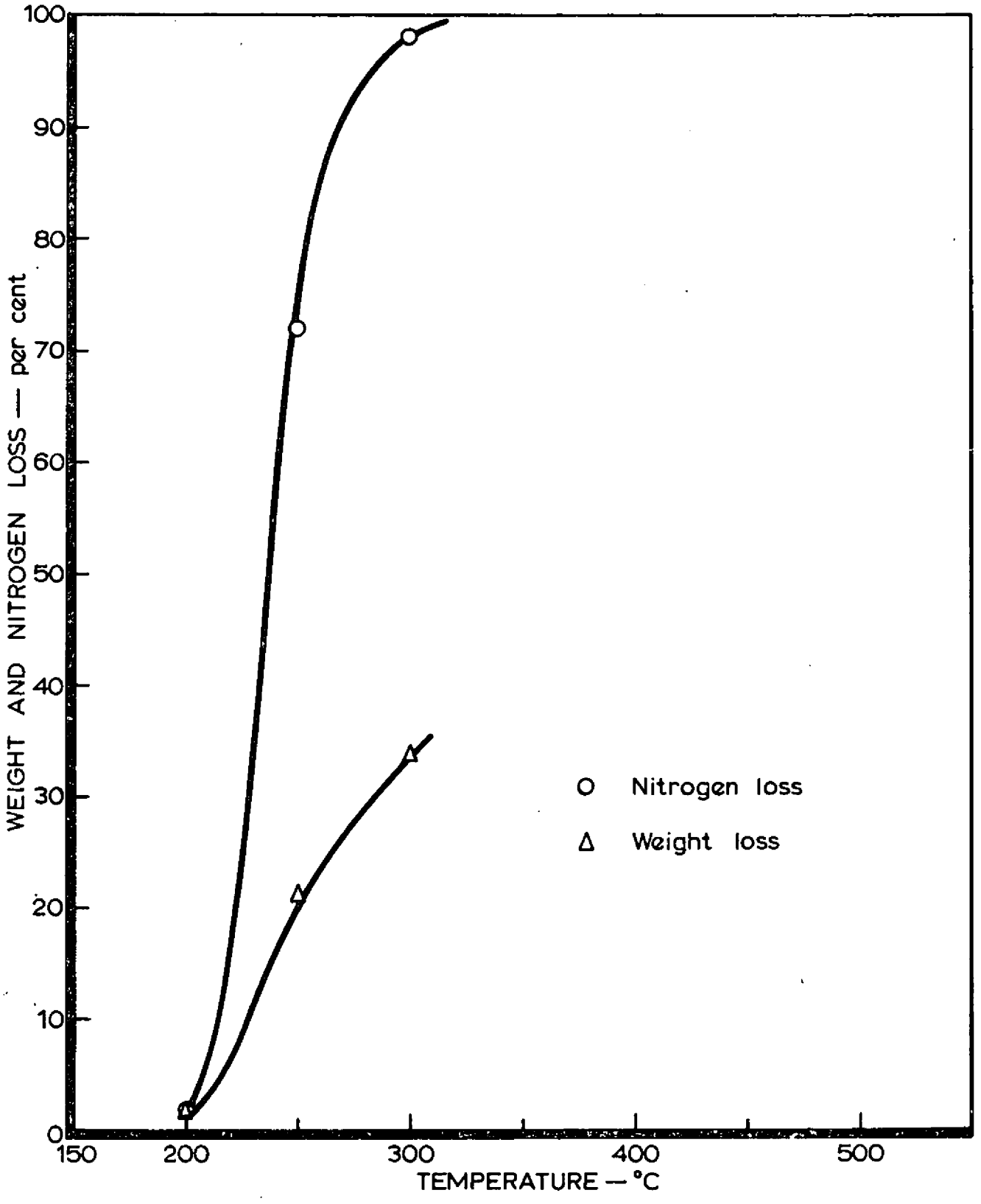

FIG. 5. DECOMPOSITION DATA FOR T.D.I. FLEXIBLE POLYETHER FOAM