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# Fire Research Note No. 852

THE THERMAL DECOMPOSITION PRODUCTS OF  
PHENOL-FORMALDEHYDE LAMINATES

PART 2. THE PRODUCTION OF FORMALDEHYDE  
CARBON MONOXIDE AND CARBON DIOXIDE

by

W D Woolley and Ann I Wadley

December 1970

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SUMMARY

The production of formaldehyde has been studied by gas chromatography during the thermal and thermal-oxidative decomposition of two commercial phenol-formaldehyde laminates between 200 and 500°C. Formaldehyde has only been detected between 400 and 500°C. In nitrogen, the maximum formaldehyde yield is 0.85 mg/g which increases to 1.63 mg/g in air.

The release of carbon monoxide and carbon dioxide from one laminate only has been monitored between 250 and 550°C. In nitrogen, the maximum recorded yield of carbon monoxide is 76.0 mg/g at 550°C which increases to 240 mg/g at 450°C in air.

A toxic evaluation of the products is given to show that the toxic hazard of formaldehyde in the decomposition gases is small in comparison with carbon monoxide and phenolic products. The phenols, monitored in Part (1) of this report, appear to be the main toxic hazard of the thermal and thermal oxidative decomposition products.

KEY WORDS: Gas chromatography, pyrolysis, thermoplastic resin, toxic gas.

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1. INTRODUCTION

a) General Introduction

Part (1) of this report<sup>1</sup> outlines a study by gas chromatography and mass spectrometry of the products from the thermal and thermal-oxidative decomposition of phenol-formaldehyde laminates. In this work the production of phenol, o- and p- cresols, 2:4 - and 2:6 - xylenols were monitored at decomposition temperatures between 300 and 550°C. The maximum yields of the phenols were obtained at 460°C in nitrogen. The presence of air produced a distinct reduction in the yields of phenolic materials. A toxic evaluation of the products showed that under the worst decomposition conditions, hazardous quantities of the phenols could be generated.

Three trial fire experiments were undertaken and showed that the phenolic concentrations in the combustion gases were much less than anticipated and, for these tests, not hazardous in comparison with the carbon monoxide content.

When involved in fires, phenol-formaldehyde resins may release the toxic gas formaldehyde<sup>2</sup>. There are two sources of formation of this material. Firstly, formaldehyde may be produced from the direct thermal decomposition of the resin and, secondly, some formaldehyde may be generated during the solid phase oxidation of the resin in air.

In this report, decomposition experiments for formaldehyde studies have been performed on laminates A and B. It is known that these laminates contain cellulosic additives in the resin. Some formaldehyde will be released from the thermal and thermal-oxidative decomposition of the cellulosic content.

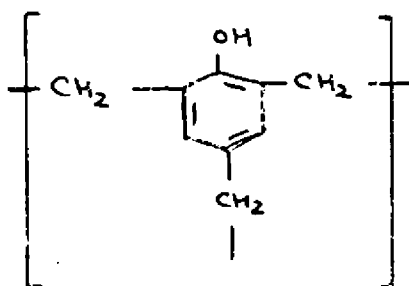
The toxic gas, carbon monoxide, is always present in fire gases. Carbon monoxide can be produced by the thermal and thermal-oxidative decomposition of both the phenol-formaldehyde resin and also the cellulosic content of the laminate. The results of an investigation of the release of carbon monoxide (and carbon dioxide) from the decomposition of laminate A in nitrogen and air are recorded.

Finally a toxic appraisal of the general decomposition products of the phenolic laminates is presented.

b) Chemistry of Phenolic Resins

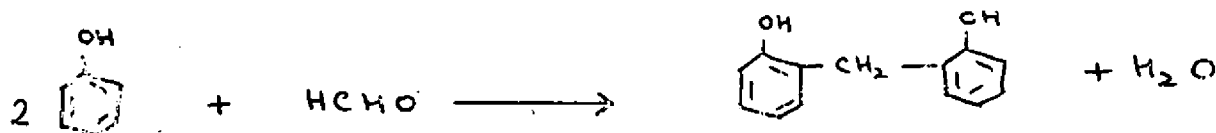
The chemistry of phenol-formaldehyde resins can be found in a series of excellent articles<sup>3,4,5</sup> and was summarized in Part (1) of this report<sup>1</sup>. Certain parts of the chemistry relevant here will be recorded again.

If phenol is condensed with formaldehyde in alkaline solution, the primary reaction product is termed a 'Resole', where the formaldehyde adds on to the benzene ring (ortho or para to the phenolic hydroxyl group) giving phenol alcohols (C<sub>6</sub>H<sub>4</sub>.OH.CH<sub>2</sub>OH). During the curing stages of the resoles (usually by heat) the methylol groups condense with vacant positions in the benzene ring (again ortho and para positions) giving a complex structure, cross linked with methylene bridges and of the general type



With phenol and formaldehyde in acid solution, phenol alcohols are again formed but immediately condense giving long chain compounds (Novolaks) joined with methylene bridges. Curing is effected by adding formaldehyde as para-formaldehyde or hexamethylene-tetramine, and cross linking the system with methylene bridges as in the formation and curing of the resoles.

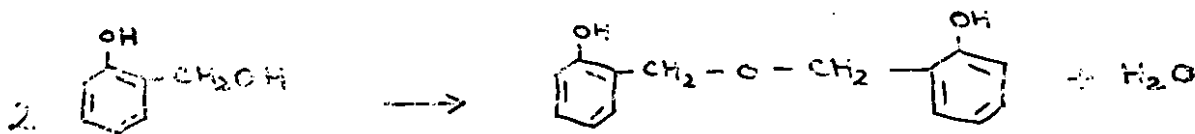
It is important to note that, in both cases, i.e. resoles and novolaks, the overall condensation reaction namely



is irreversible. In the case of addition polymers, such as PVC, polyethylene and polystyrene, depolymerisation can take place but depends upon the bond strengths of the polymer. With condensation polymers, depolymerisation cannot take place since part of the unit, in this case water, is eliminated.

Formaldehyde cannot be regenerated by the depolymerisation of the fully cured resin.

In the curing stages of the resoles, some methylol groups may condense with one another giving ether links namely



This ether link is a possible source of formaldehyde since at high temperatures elimination of formaldehyde can take place forming the conventional methylene bridge. This elimination may occur during the hot curing process.

In the manufacture of laminated building boards the curing is effected at relatively high temperatures and pressures. It is unlikely, therefore, that the commercial laminates used in this report contain many ether links or free formaldehyde. Further, since depolymerisation is not a possible source of formaldehyde, one would not expect any appreciable quantities of formaldehyde to be released during the thermal decomposition (in inert atmosphere) of these resins.

There are, unfortunately, very few references in the literature to studies of formaldehyde production from the decomposition of phenol-formaldehyde resins. Recently, in 1966, Shulman<sup>2</sup> and his co-workers studied the decomposition of a resin 'in vacuo' using a mass spectrometer and detected some formaldehyde only between 250 and 400°C, with a maximum rate of formation at about 325°C. Unfortunately, the curing history of the resin is unknown.

## 2. EXPERIMENTAL

### a) The decomposition apparatus

For the studies of the release of formaldehyde, a separate furnace and associated flow system was constructed capable of handling 1 gram loads of phenolic resin. The essential features of the apparatus are shown diagrammatically in Fig. 1.

Samples of the phenolic resin (1 gram) are introduced into the furnace in a ceramic boat by the influence of an external magnet on the steel plug P. A flow of dry air or nitrogen (at 100 ml/min at 20°C) carries the decomposition products down a short lagged exit pipe into 1 ml of distilled water, chilled with ice. The formaldehyde content of the distilled water is then estimated by injecting 1  $\mu$ l samples into a research gas chromatograph with a syringe.

## b) Chromatography

The chromatographic separation and analysis of formaldehyde was undertaken using a Hewlett Packard 5750 research chromatograph fitted with two Porapak N columns (stainless steel 3.2 mm o.d. x 1 m long) operated isothermally at 130°C, with a helium flow rate of 25 ml/min. The formaldehyde was detected using thermal conductivity detectors coupled both to a recorder and also to a Hewlett Packard 3370A electronic integrator for automatic area print out.

## c) Materials

Two commercial laminates of types A and B were used in the formaldehyde experiments of this report. In each case the thin decorative surface of melamine and urea formaldehyde was physically removed and discarded. The remaining phenolic resin together with the paper and other fillers was then broken up into fragments of about 10 mg each for study. A total sample weight of 1 gram was used in all formaldehyde determinations.

## d) Permanent gas analyses

The production of carbon monoxide and carbon dioxide from the thermal decomposition of laminate A in air and nitrogen at temperatures between 250 and 550°C was undertaken using the decomposition furnace and flow system as outlined in Part (1) of this report. In this study 150-mg samples of the resin were decomposed in a flow of air or nitrogen at 100 ml/min at 20°C and the decomposition gases collected in a heavy duty polyethylene bag for a period of 30 minutes for each experiment. After the collection period, the gas in the bag was thoroughly mixed and samples taken for gas chromatography with a syringe in the normal manner. The details of a modification to fit molecular sieve and silica gel columns to the inlet of the gas chromatograph for the analysis of the permanent gases has been recorded in detail in a separate publication<sup>6</sup>. Gas compositions (in volume percentages) obtained in this way were corrected to direct weights of carbon monoxide and carbon dioxide for this report.

## 3. RESULTS

### a) Preliminary investigations of the chromatography of formaldehyde

The separation of formaldehyde from water by gas chromatography for quantitative analysis has proved to be a difficult analytical problem. However several column systems<sup>7,8,9</sup> are reported in the literature for this separation mainly for the analysis of free formaldehyde (i.e. unreacted) in phenol-formaldehyde resins. More recently Porapak N has been reported<sup>10</sup> to give a good separation of water and formaldehyde with excellent peak shape. Since formaldehyde is eluted before water, this column appears to be ideally suited to the analysis of dilute formaldehyde solutions.

Preliminary experiments were undertaken with the research chromatograph fitted with Porapak N columns as outlined in the experimental section and operated at 130°C. Because of the low sensitivity of flame ionization detectors<sup>11</sup> to formaldehyde all experiments were undertaken using thermal conductivity detection.

A trace of the separation of a test formaldehyde solution is shown in Fig. 2 obtained by injecting 1  $\mu$ l of 40 per cent W/V of an aqueous solution of formaldehyde (with methanol impurity) into the chromatograph in the normal manner. Although the column gave the predicted separation of formaldehyde from water, certain limiting conditions were soon apparent namely:

(i) The separation was dependent upon the total amount of solution injected into the column. Injection levels below 1  $\mu$ l improved the separation whereas levels in excess of 1  $\mu$ l rapidly deteriorated the separation. The 1  $\mu$ l injection level (an unusually low level for this size of column) proved to be largest quantity of liquid which could be satisfactorily handled by the column.

(ii) For studies of very dilute formaldehyde solutions the column gave a history effect, namely that an analysis of distilled water following a formaldehyde determination gave a small but positive formaldehyde peak. One, or sometimes two, washings of the column with 1  $\mu$ l samples of distilled water were necessary to clean the column. With a clean column, formaldehyde analyses were consistent and reproducible.

(b) Calibration of the chromatograph for formaldehyde

In the studies of the release of formaldehyde from the laminates A and B outlined later in this report, the formaldehyde is extracted from the decomposition gases by bubbling through 1 ml of chilled water. For calibration purposes small amounts (up to 10  $\mu$ l) of 40 per cent W/V formaldehyde solution were added to 1 ml samples of distilled water and analysed by chromatography (using 1  $\mu$ l samples) as outlined previously. Fig. 3 shows the calibration graph recording the integrator counts (i.e. peak area) versus the weight of formaldehyde (directly in mg) in the 1 ml of distilled water. In all cases the column was washed between experiments. The lower limit of detection was about 0.15 mg of formaldehyde.



(c) Formaldehyde collection tests from furnace

Before undertaking direct formaldehyde estimations from the phenolic resins, a collection test was undertaken to confirm that formaldehyde could be collected efficiently from the gas stream simply by bubbling through the distilled water. For this test, 5  $\mu$ l of 40 per cent W/V of formaldehyde solution (i.e. 2 mg of formaldehyde) were placed into the boat with a syringe and introduced into the furnace which was operated at the highest temperature used in this report (500°C) with nitrogen as the furnace carrier gas. Samples of the distilled water were taken at 0, 5, 15 and 30 minutes of experimental time and analysed by chromatography. The recovered formaldehyde and the collection efficiency is recorded in Table 1.

TABLE 1

Recovery of 2 mg of formaldehyde  
from the furnace at 500°C in Nitrogen

Time (mins)	Formaldehyde (mg)	Recovery efficiency (%)
0	*	-
5	1.75	87
15	1.80	90
30	1.74	87

\* Not integrated

(d) Formaldehyde production from laminates A and B

The release of formaldehyde from the two laminates was monitored at furnace temperatures between 200 and 500°C in air and nitrogen. At temperatures up to and including 450°C, samples of the distilled water were taken at 10, 20, 30 and 40 minutes of experimental time. At 500°C sampling times were modified to 5, 15, 25 and 40 minutes. The column was washed as necessary after each positive formaldehyde analysis. The tabulated results for the experiments are recorded in Table 2. Formaldehyde levels below about 0.15 mg were insufficient to trigger the electronic integrating mechanism; these small peaks were only just visible on the recorder on the most sensitive attenuation and other methods of area assessment were not possible.

In all cases experiments were limited to a maximum furnace temperature of 500°C for practical reasons. At 550°C, and above, tarry products tended to condense in the collection tube and block the gas stream causing a pressure build up in the furnace tube and a subsequent blow out of the rubber safety cap. Some modifications were made to the shape and operating temperature of the collecting tube but this did not satisfactorily eliminate the problem.

In Table 2, laminates A and B release approximately equivalent amounts of formaldehyde in nitrogen. In air the yields are generally larger than in nitrogen with laminate A apparently producing more formaldehyde than laminate B.

For convenience the maximum yields of formaldehyde at each temperature over the 40 minutes of experimental time have been extracted from Table 2 and are shown graphically in Fig. 4.

TABLE 2

The production of formaldehyde from samples (1g) of laminates A and B in air and nitrogen between 200 and 500°C

Temp (°C)	Time (mins)	Yield of Formaldehyde (mg)			
		Nitrogen		Air	
		A	B	A	B
200	10	*	-	-	-
	20	-	-	-	-
	30	-	-	-	-
	40	-	-	-	-
300	10	-	-	-	-
	20	-	-	-	-
	30	-	-	-	-
	40	-	-	0.17	-
400	10	0.44	-	0.51	0.54
	20	0.60	0.65	0.56	0.68
	30	0.68	0.64	0.72	0.74
	40	0.68	0.65	0.76	0.85
450	10	0.63	0.43	1.26	0.67
	20	0.71	0.57	ND	0.84
	30	0.64	0.70	1.54	0.96
	40	0.72	ND	1.42	0.95
500	5	0.48	0.71	1.34	1.08
	15	0.84	0.75	1.62	1.41
	25	0.85	0.76	1.63	1.20
	40	0.83	0.82	1.60	1.30

\* Not integrated i.e.  $< 0.15$  mg

N.D. Not determined due to an analysis fault.

- e) The production of carbon monoxide and carbon dioxide from laminate A

A series of decomposition experiments of laminate A were undertaken in order to examine the release of carbon monoxide and carbon dioxide from the resin under both oxidative and inert conditions.

These tests were undertaken by decomposing 150-mg samples of the laminate in a flow of air or nitrogen at 100 ml/min at 20°C and the decomposition gases collected in a polyethylene bag during the 30-minute experiments and analysed by gas chromatography as outlined recently in a separate publication<sup>12</sup>. An analysis of a gas mixture in a closed polyethylene bag every hour confirmed that diffusion losses through the bag were negligible.

The yields of carbon monoxide and carbon dioxide (directly in mg) collected in the polyethylene bag in air and nitrogen between 250 and 550°C are shown graphically in Fig. 5, with the relevant data given in the Appendix.

In nitrogen, the yields of carbon monoxide and carbon dioxide are similar. At low temperatures (i.e. less than 400°C) the amount of carbon dioxide is somewhat larger than the carbon monoxide. At temperatures above 400°C the two gases are formed in equivalent amounts.

In air, increased yields of carbon monoxide and carbon dioxide are apparent at temperatures as low as 300°C. At temperatures of 400°C, and above, considerable quantities of carbon dioxide are evolved.

## DISCUSSION

- a) General discussion

Formaldehyde has been detected from both the thermal and thermal-oxidative decomposition of laminates A and B at temperatures between 300 and 500°C. Formaldehyde has not been detected between (detection limit 0.15 mg of formaldehyde from 1 g of resin) 250 and 300°C. Experiments at temperatures above 500°C were not possible.

As expected, the yields of formaldehyde, although relatively small, are greater in air than in nitrogen. In nitrogen the yields are very similar for both laminates and at the highest temperature of study (500°C) the maximum recorded yield of formaldehyde is about 0.85 mg per gram of laminate.

In air, laminate A produced more formaldehyde than laminate B. The maximum recorded yields (again at 500°C) are 1.63 and 1.41 mg of formaldehyde from 1 gram of laminates A and B respectively.

It is possible that the maximum yields of formaldehyde are generated not at the highest temperature used in this report (500°C) but at somewhat higher temperatures. However, it is evident from Fig. 4 that the yields of formaldehyde in both air and nitrogen atmospheres are tending to level off at temperatures above about 450°C. In this report, the formaldehyde yields at 500°C will be taken as representing the maximum yields.

The efficiency of collecting and analysing formaldehyde from the furnace was estimated in section 3(c) as being of the order of 90 per cent. This is a relatively high value and is probably due to the stability of dilute formaldehyde solutions<sup>13</sup>. Because of this high collection efficiency, no attempts will be made to correct the actual formaldehyde yields to true yields.

In general, very little information can be deduced from these experiments alone about the origin of the formaldehyde. The formaldehyde yield in nitrogen is less than 1 mg per gram of laminate. Some of this yield is certainly derived from the cellulosic content of the laminate and consequently the yield from the resin itself is less than this value.

Carbon monoxide is released from the thermal (i.e. inert) decomposition of laminate A at temperatures of 250°C and above. A maximum recorded yield of 11.4 mg per 150-mg of laminate (76.0 mg/g) occurs at 550°C. In air the carbon monoxide has a maximum value of 36.0 mg/150 mg (240 mg/g) at 450°C.

In nitrogen, carbon dioxide is released in quantities very similar by weight, to those of the carbon monoxide. In air large quantities of carbon dioxide are generated with a maximum recorded value of 223 mg/150 mg or 1490 mg/g.

In general, the yields of carbon monoxide and carbon dioxide from the inert decomposition are rather large and incompatible with a resin, structurally built up of phenol units joined in the ortho and para positions with methylene bridges. It seems logical that these two gases are produced mainly by the thermal decomposition of the paper content of the laminate. In air the two gases will be generated by the oxidation of both the phenol-formaldehyde resin and the paper laminations.

b) Toxic evaluation

In previous work and in Part (1) of this report, the toxic potentials of the decomposition products of plastics have been evaluated by calculating toxicity factors (T) first introduced by Tsuchiya and Sumi<sup>14</sup> and defined as

$$T = \frac{C_E}{C_F}$$

where  $C_E$  = Experimental concentration in p.p.m (at 25°C)  
produced from 1 gram of material in a metre cube

$C_F$  = Concentration in p.p.m fatal in a short exposure.

Formaldehyde is known to be a highly toxic gas. The maximum atmospheric concentration (M.A.C.) has been recommended as 5 p.p.m<sup>15,16</sup>. Atmospheres containing between 10 and 20 p.p.m produce immediate eye irritation and burning sensations in the nose and throat, but recovery is prompt. The concentration immediately hazardous to life is not known but 30-minute exposures to rats at 815 p.p.m. produced a 50 per cent mortality<sup>16</sup>. It is reported that an exposure of 5 to 10 minutes at 50 to 100 p.p.m. could cause serious respiratory injury to man<sup>16</sup>. On the basis of these figures a concentration of 750 p.p.m of formaldehyde will be used in this report as being directly hazardous to life for a short exposure.

The toxicity of carbon monoxide is now well established and documented<sup>16</sup>. A concentration of 5000 p.p.m is known to produce rapid collapse, unconsciousness and death within a few minutes<sup>16</sup>. This concentration will be used as the  $C_F$  value for toxicity measurements.

The toxicity factors for formaldehyde and carbon monoxide from the decomposition of laminate A in nitrogen and air are shown in Table 3. In all cases, the toxicity factors are based upon the maximum recorded yields of products and are essentially maximum toxic factors. Also shown for comparative purposes is the maximum toxicity factor of the total phenolic compounds obtained in Part (1) of this report.

TABLE 3

Maximum toxicity factors of formaldehyde,  
Carbon monoxide and total phenols from Laminate A

Product	Atmosphere	Yield per gram (mg)	$C_E^*$ (p.p.m)	$C_F$ (p.p.m)	Toxicity factor (T)
Formaldehyde	Nitrogen	0.85	0.69	750	$9.24 \times 10^{-4}$
	Air	1.63	1.33	750	$1.77 \times 10^{-3}$
Carbon Monoxide	Nitrogen	76.0	62.0	5000	$1.24 \times 10^{-2}$
	Air	240	209	5000	$4.18 \times 10^{-2}$
Total Phenols	Nitrogen only	See Part (1) of Report			$1.35 \times 10^{-1}$ to $1.35 \times 10^{-2}$

\* At 760 mm. Hg<sup>16</sup> and 25°C

Formaldehyde  $1 \text{ mg/m}^3 = 0.815 \text{ p.p.m}$

Carbon monoxide  $1 \text{ mg/m}^3 = 0.873 \text{ p.p.m.}$

The maximum toxicity factors given in Table 3 indicate the general orders of magnitudes of the toxic products from Laminate A. For a comparison with other plastics, it is known that the toxicity factor of hydrogen chloride<sup>17</sup> from a commercial UPVC is  $2.26 \times 10^{-1}$ . Phosgene from UPVC<sup>18</sup> has a toxicity factor less than  $3.26 \times 10^{-3}$ .

In Table 3, formaldehyde in air and nitrogen atmospheres has a low toxicity factor and neglecting synergistic effects does not appear to be a significant hazard in the decomposition gases. The toxicity factor of the total phenols, as discussed in Part (1) of this report is relatively high and is a possible hazard. Carbon monoxide production is significant but apparently not the major hazard in the thermal and thermal-oxidation decomposition gases.

It should be emphasised that the toxic evaluation given in this report refers only to the products from the thermal decomposition of the laminate in air or nitrogen. In fires, any combustible gases generated by the decomposition can be destroyed either partially, or fully, by the flame. Destruction, in this way, tends to decrease the hazard of the toxic product and generate in its place some carbon monoxide.

At present, very little information is known about the destruction of decomposition products by the flame under various fire load and ventilation conditions. This report must therefore be regarded only as indicating the types of products which should be monitored in model and full scale fires. In this context, it is recommended that further work is carried out to study the production of phenol and related compounds in actual fire experiments involving laminated boards to determine if these materials present a hazard in relation to the carbon monoxide.

## 5. CONCLUSIONS

- (1) Formaldehyde has been detected at temperatures between 400 and 500°C during the decomposition of two commercial laminates in nitrogen and air. The maximum recorded yields of formaldehyde are 0.85 mg/g in nitrogen and 1.63 mg/g in air.
- (2) Carbon monoxide and carbon dioxide have been monitored between 250 and 550°C from laminate A only. The maximum recorded yields of carbon monoxide are 76.0 mg/g at 400°C in nitrogen and 240 mg/g at 450°C in air.
- (3) It is shown that the toxic hazard of formaldehyde is small in comparison with that of carbon monoxide and the phenolic products.
- (4) The major toxic hazard in the decomposition gases is the phenol and related compounds studied in Part (1) of this report.

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7. APPENDIX

Yields of carbon monoxide and carbon dioxide  
 from the decomposition of Laminate A  
 (150 mg) in nitrogen and air

Decomposition Temperature (°C)	Carbon Monoxide (mg)		Carbon Dioxide (mg)	
	Nitrogen	Air	Nitrogen	Air
250	0.8	0.9	0	1.8
300	1.6	4.9	5.5	15.4
350	8.2	13.1	14.6	35.9
400	9.0	34.4	9.2	135.8
450	9.8	36.0	11.0	176.8
500	9.8	26.2	9.7	169.1
550	11.4	27.8	11.5	222.9

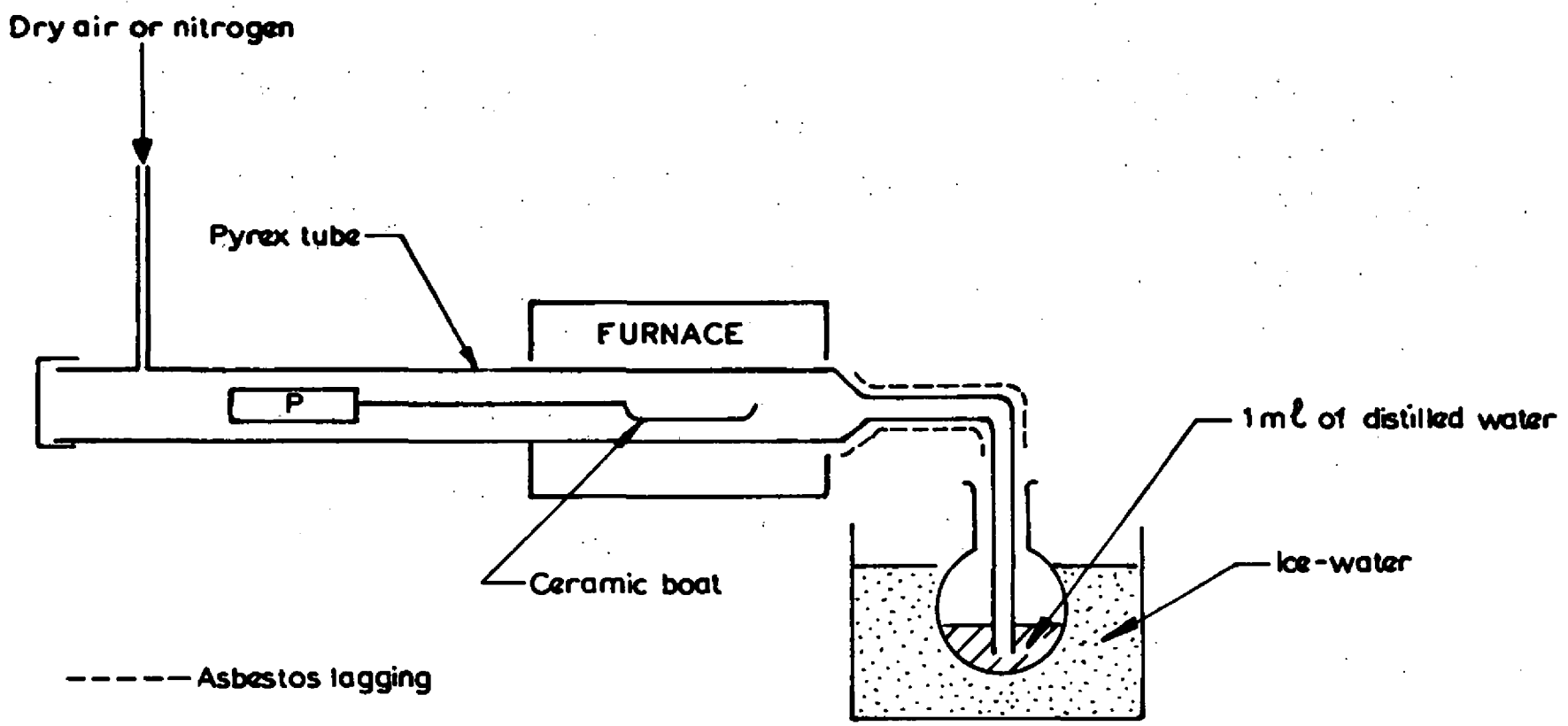


FIG.1 THE DECOMPOSITION SYSTEM FOR FORMALDEHYDE STUDIES

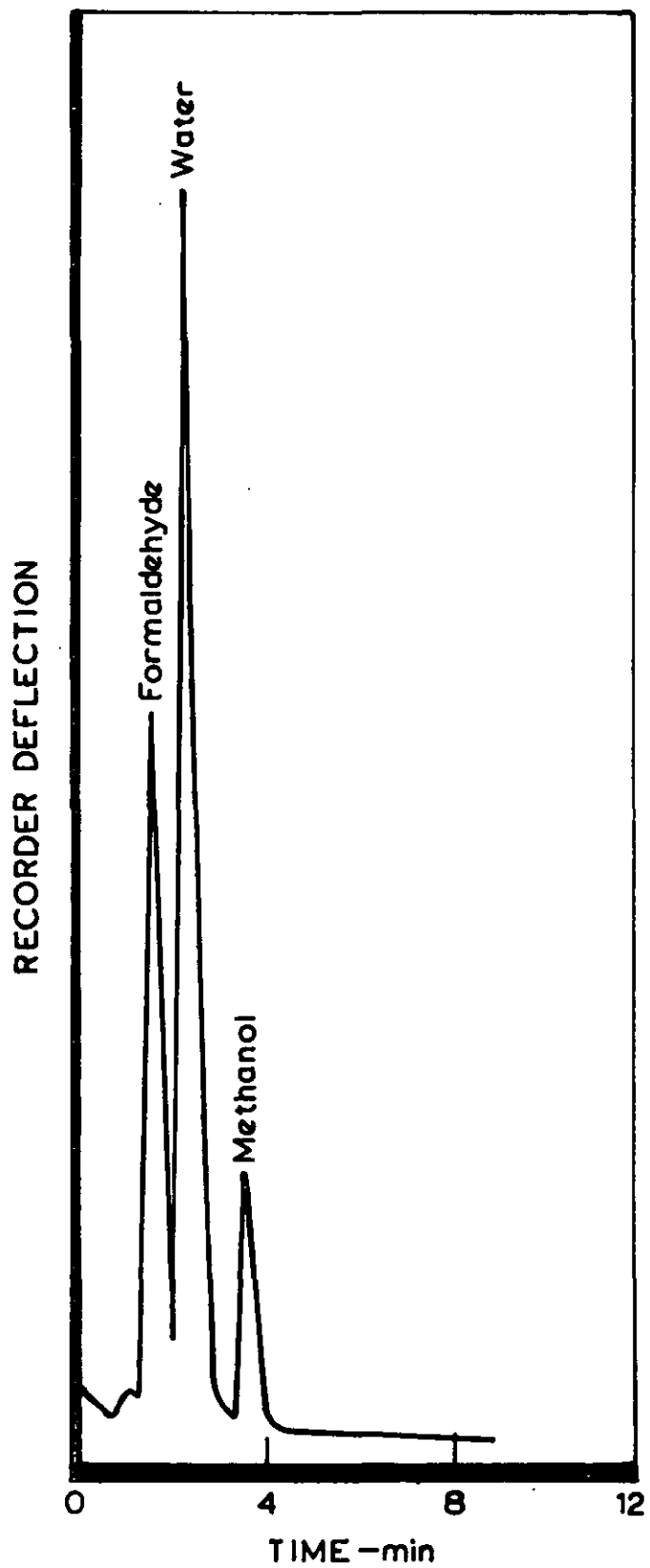


FIG.2 GAS CHROMATOGRAPHIC SEPARATION OF FORMALDEHYDE FROM WATER WITH PORAPAK N

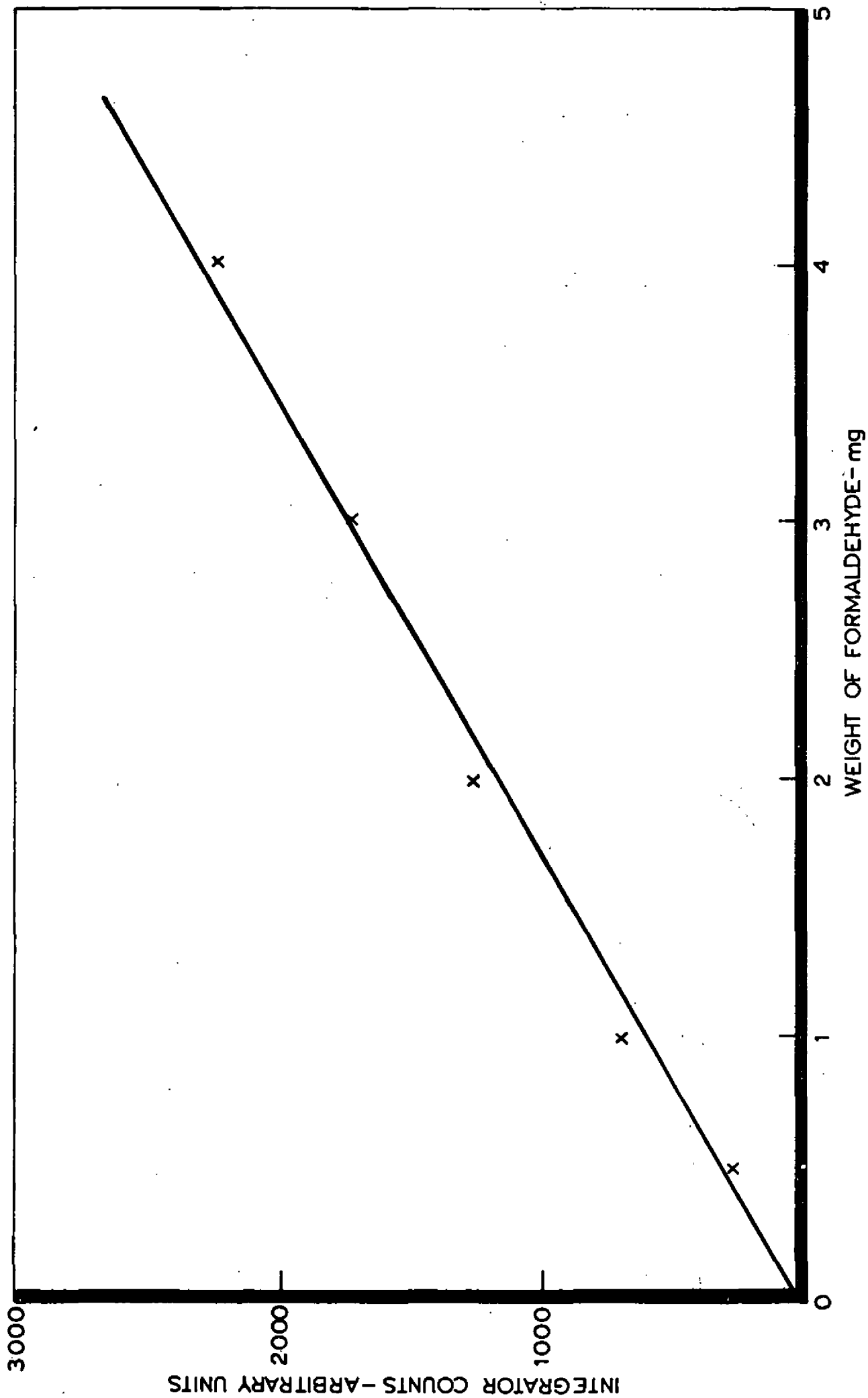


FIG.3 CALIBRATION GRAPH OF FORMALDEHYDE

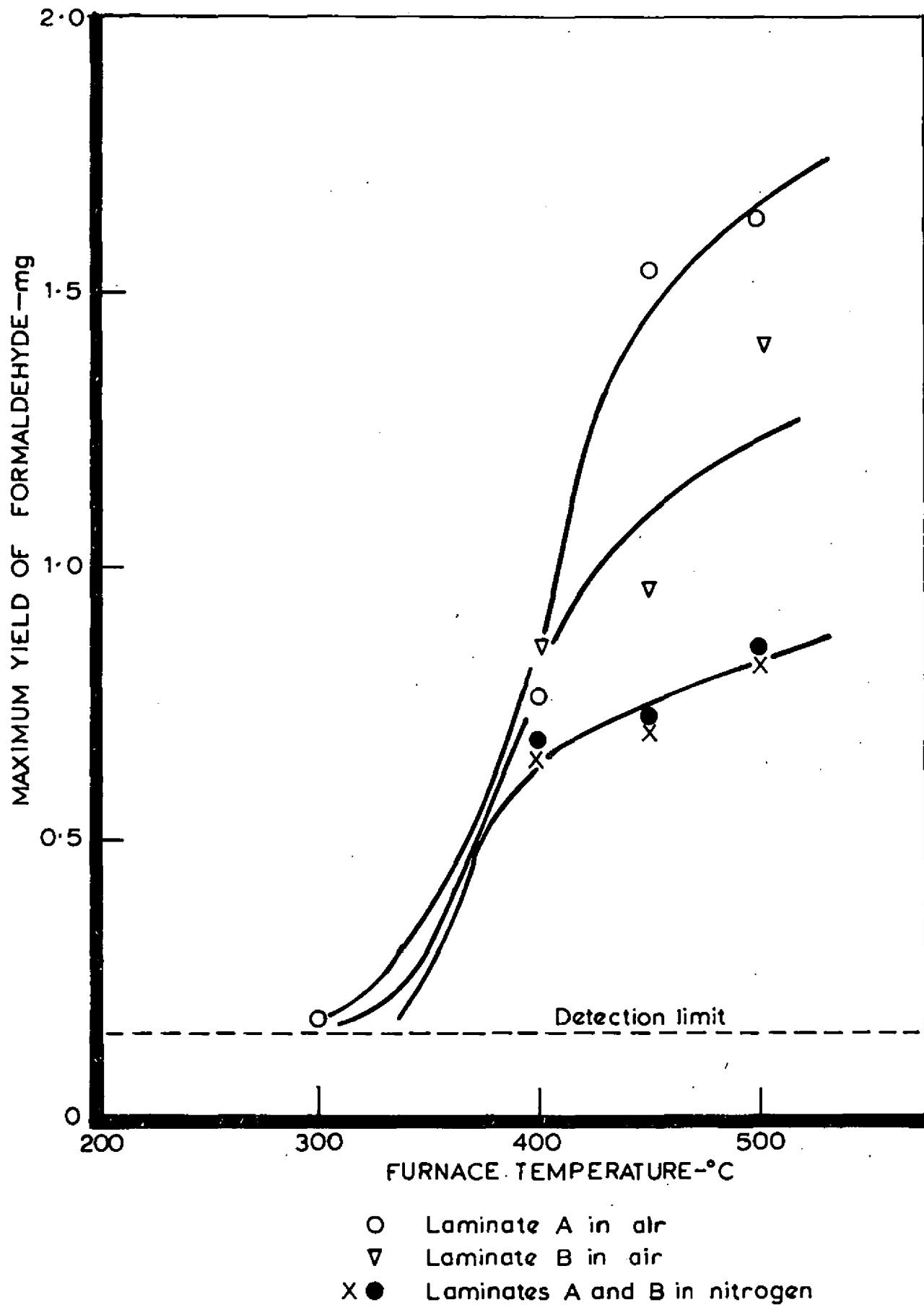
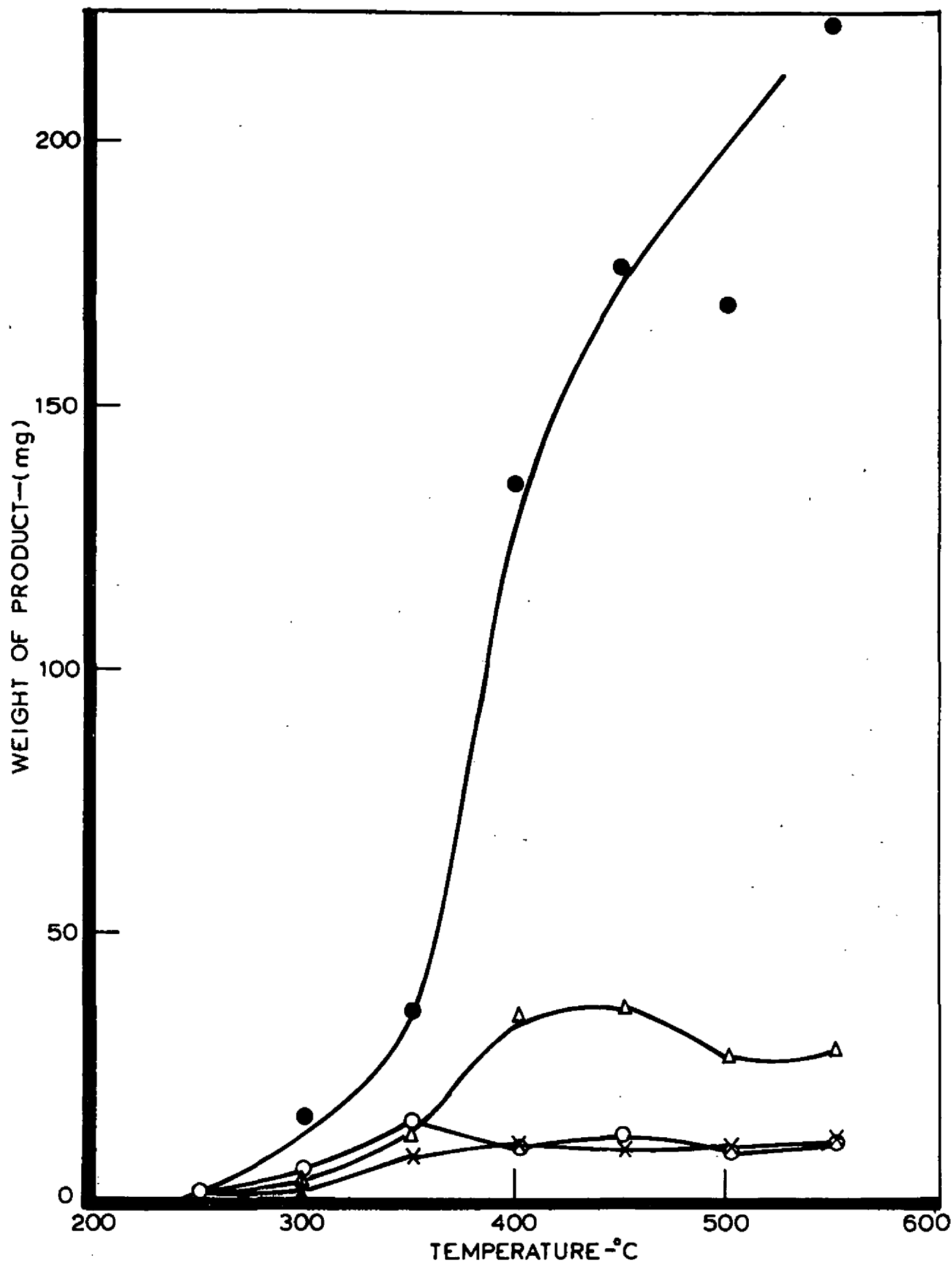


FIG.4 THE PRODUCTION OF FORMALDEHYDE FROM LAMINATES A AND B (1g samples) BETWEEN 200 AND 500°C



- X CO in nitrogen
- O CO<sub>2</sub> in nitrogen
- Δ CO in air
- CO<sub>2</sub> in air

FIG.5 YIELDS OF CO AND CO<sub>2</sub> FROM LAMINATE A (150mg)

