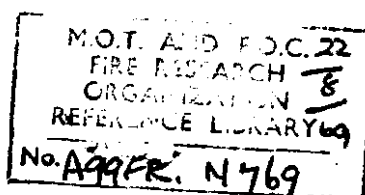


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Fire Research Note

No 769

A STUDY AND TOXIC EVALUATION OF THE PRODUCTS
FROM THE THERMAL DECOMPOSITION OF PVC IN AIR
AND NITROGEN

by

W. D. WOOLLEY

July, 1969.

FIRE
RESEARCH
STATION

**Fire Research Station,
Borehamwood,
Herts.
Tel. 01-953-6177**

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SUMMARY

The products from the thermal and thermal-oxidative decomposition of PVC from 300 to 500°C have been studied by gas chromatography and mass spectrometry. Approximately seventy-five products have been detected up to naphthalene by gas chromatography and shown to consist essentially of aromatic and aliphatic hydrocarbons. Weight loss experiments and time resolved chromatography indicate that these products are generated mainly during dehydrochlorination. The products are modified slightly by the presence of oxygen but no oxygenated organic materials have been detected. The products, apart from carbon monoxide, are shown to have little toxicity in relation to the hydrogen chloride. Difficulties encountered with the analysis of phosgene are recorded and some preliminary results from a series of specific phosgene experiments are given.

KEY WORDS: Combustion products, gas chromatography, hydrogen chloride, mass spectrometry, phosgene, plastics, pyrolysis, toxic gas, poly(vinyl chloride).

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JOINT FIRE RESEARCH ORGANIZATION

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A STUDY AND TOXIC EVALUATION OF THE PRODUCTS FROM THE THERMAL DECOMPOSITION OF PVC IN AIR AND NITROGEN

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1. INTRODUCTION

(a) General Introduction

Over 50 per cent of fatalities in fires can be directly attributed to the combined effects of smoke and toxic gases. Research is in progress to study the production of certain toxic materials from both traditional (cellulosic) and modern building materials, particularly plastics, in model and full-scale fires. To date, a detailed study has been made in this way of carbon monoxide² production from cellulosic fuels and carbon monoxide and hydrogen chloride production from PVC - cellulosic fuels^{3,4} under various fire conditions.

The release of toxic materials other than carbon monoxide and hydrogen chloride from fires involving PVC has been the subject of speculation for many years. Small amounts of phosgene, formaldehyde and other oxygenated species⁵ have been tentatively identified in the decomposition products of PVC, but the contribution of these materials to the overall toxicity of the fire gases is uncertain.

In fires, PVC may be subjected to temperatures in excess of 1000°C in atmospheres ranging from a nominal 20 per cent to as low as a few per cent of oxygen. Because of this, the overall generation of products in a fire is an extremely complex process and an attempt to break this process down into simple steps is shown in Figure 1.

Firstly, gaseous products are generated by the thermal and thermal-oxidative decomposition of the solid PVC. The pyrolysis products formed in this way contain only the atoms of carbon, hydrogen and chlorine. Under oxidative conditions, in addition to the well established carbon monoxide, carbon dioxide and water, organic and inorganic oxygenated species may be formed.

The decomposition products from the solid phase are released into a relatively mobile gaseous fire zone and are further decomposed in the gas phase in inert or oxidative-combustion environments. In general, in the inert gaseous zone pyrolytic degradations and cross reactions may take place, whereas in the oxidative or combustion zones combustible material is consumed with the generation of carbon monoxide, carbon dioxide, water, and possibly further oxygenated species.

Certain oxygenated materials such as phosgene or formaldehyde which may be formed during the decomposition of PVC can be highly toxic and it is extremely important to know of the presence of these materials in the fire gases. Recently,

in studies of the thermal and thermal oxidative decomposition of PVC (solid phase) Tsuchiya and Sumi⁶ have suggested that oxidation is not an important route in the formation of products other than carbon monoxide, carbon dioxide and water. This is rather surprising and clearly required elucidation.

The work outlined in this report was undertaken to study in detail the solid phase decomposition products of PVC in air and nitrogen (as in Fig.1A) by gas chromatography and mass spectrometry. It was anticipated that this study would clarify the role of oxygen in the solid phase decomposition, give information about possible toxic constituents and provide useful data for the study of the gas phase decompositions (as in Fig.1B) at a later date.

In this report, small samples of a commercial rigid sheet of PVC have been decomposed in a furnace at temperatures between 300 and 500°C in a stream of air or nitrogen. A flow system was used in this work in order to extract the decomposition products from the hot furnace zone and minimise gas phase interactions in the furnace section. Details are given of a special system for the on-line collection and direct injection of volatile decomposition products into a gas chromatograph for analysis.

Before undertaking chromatographic experiments a series of preliminary investigations based upon the weight loss of the PVC and the evolution of hydrogen chloride with time were undertaken. These experiments are recorded to show the almost quantitative release of hydrogen chloride, the correlation of general product formation with dehydrochlorination and at temperatures of 450°C and above in air the oxidation of the residue following dehydrochlorination.

Because of the rapid release of hydrogen chloride from PVC at temperatures above 300°C, two decomposition stages are defined for convenience in this report. The primary decomposition stage refers to the period between zero and complete dehydrochlorination and the primary products are those products generated during this period. The secondary decomposition stage refers to the decomposition period following complete dehydrochlorination. Products, both oxidative and pyrolytic eliminated from the dehydrochlorinated residue in the secondary stage are termed secondary products.

Experiments using a pure sample of PVC are outlined to compare the product formation between a pure and a commercial PVC sample.

From a quantitative survey of the main organic components of the decomposition products a toxic analysis of these components in relation to the toxicity of hydrogen chloride is presented. In this analysis, preliminary phosgene detection levels are quoted for the commercial PVC. Phosgene, a difficult material to detect quantitatively by chromatography due to the high reactivity and insensitivity to flame ionization detectors has been studied separately by thermal conductivity

experiments. This work will be recorded in detail in a future publication⁷.

Some relevant literature aspects of the dehydrochlorination reaction and existing knowledge about product formation from PVC in both laboratory and fire experiments are reviewed.

(b) The Dehydrochlorination Reaction

(i) Low Temperature Studies and Mechanism

The formation of hydrogen chloride from PVC has been established for many years and has probably been studied more extensively than any other single aspect of polymer degradation. In spite of this there is still a great deal of uncertainty about the mechanism.

It is beyond the scope of this report to examine the full aspects of the dehydrochlorination mechanism and the reader is referred to a series of excellent articles on the subject^{8,9,10}, and in particular to a recent report by Geddes¹¹. It is relevant to consider the fundamental aspects of the process.

It is well known that in nitrogen at temperatures between 150° and 200°C PVC loses a small percentage of hydrogen chloride and becomes highly coloured. Colour formation is attributed to the building up of a conjugated polyene structure. This type of structure is known to be highly coloured from work with certain natural products such as the carotenoids and related materials and between 7 and 17^{8,10} conjugated bonds are required for colour formation. It is clear that at these low levels of dehydrochlorination loss of hydrogen chloride is not a random process but occurs progressively along a chain from various initiation sites. This effect has led to the term 'zip' reaction.

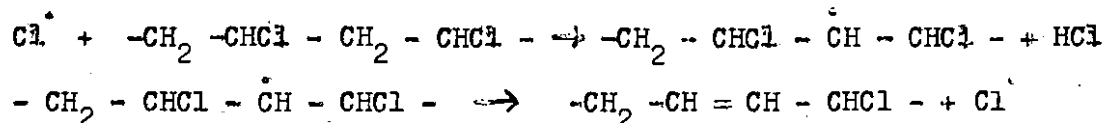
Oxygen plays an important part in the degradation^{8,11,12,13} and produces a distinct increase in the rate of dehydrochlorination. Also there is a decrease in the rate of colour formation and in fact the colour produced by the degradation of PVC in nitrogen may be bleached by the addition of oxygen during the heating cycle.

In early studies hydrogen chloride itself was thought to have a catalytic effect on the degradation. As a result hydrogen chloride absorbers (generally basic salts) were incorporated successfully into the polymer for commercial use. In 1953 Ruessow¹⁴ using an interrupted flow technique found that the evolution of hydrogen chloride did not depend upon the hydrogen chloride concentration near the polymer. This was confirmed in 1954 when Arlman¹⁵ in a study of the decomposition of PVC in air, nitrogen and oxygen showed that the injection of hydrogen chloride into the carrier gas prior to the furnace did not alter the degradation rate. These results appeared to resolve the catalytic question but more recent work by Talamini¹⁶ using a vacuum system showed a distinct catalytic effect.

At present there are two main theories for degradation.

Firstly, a unimolecular elimination theory and secondly and more probably the radical chain process.

In the radical chain process chlorine atoms are considered to be the most likely chain carrier^{8,10,17} namely:-



When an unsaturated unit is introduced into the polymer the hydrogen on the adjacent methylene group is abstracted more easily by the chlorine atom. The ease of abstraction increases with the length of the conjugated polyene and gives rise to the 'zip' removal of hydrogen chloride. The activating influence of the unsaturated bond is usually referred to as allylic activation. Chain termination occurs at abnormalities in the chain such as a cross link or by radical loss. There is some controversy over the chain initiation step and it is likely that the chain is not initiated by a C-Cl bond cleavage but by a radical produced from a structural defect¹¹. In the latter case oxygenated species either as impurities or from fragments of polymerisation catalysts incorporated into the chain may be responsible. Such sites could give radicals with a process requiring less activation energy than a C-Cl split.

Oxygen probably assists the dehydrochlorination rate by the formation of oxygenated materials (such as peroxides) which gives an increase in the number of initiation sites. Oxygen attack would also be expected at the unsaturated zones and this process could upset the conjugated polyene structure giving a bleaching effect.

The unimolecular elimination mechanism, as the name implies, considers the dehydrochlorination to be the loss of molecular hydrogen chloride. The unzipping of hydrogen chloride molecules progressively along a chain is again explained by a type of allylic activation.

Most of the information available appears to support a free radical process. However certain criteria, for example the stabilisation of PVC by inorganic materials which is not easy to explain by a radical process, need to be resolved before the full mechanism of dehydrochlorination can be elucidated.

(ii) High Temperature Studies

In dehydrochlorination studies experiments have generally been carried out at relatively low temperatures for reaction mechanism studies. Surprisingly little work has been performed on dehydrochlorination in excess of 200°C and it is in this region which is of particular interest in the production of hydrogen chloride in fires. In general it is accepted that at these temperatures dehydrochlorination is virtually quantitative^{7,18,19}.

The radical chain ('zip') elimination of hydrogen chloride where initiation depends upon structural abnormalities limits the general kinetic handling of experimental data for predicting the evolution of hydrogen chloride in fires. For example Telamini²⁰ reports that in a study at temperatures between 200 and 220°C the rate of dehydrochlorination is dependant upon the molecular weight of the polymer. Data of the kind produced by Stromberg²¹ looks more promising and in a study over the range 230 to 260°C showed that the rate of dehydrochlorination is a 3/2 order decomposition dependent upon the remaining chlorine in the polymer. This type of data could be used in estimating rates of production of hydrogen chloride in fires from temperature measurement but the correlation between different commercial samples would require investigation.

(c) Product Formation other than Hydrogen Chloride

Organic products from the thermal decomposition of PVC have not been widely studied but are known to be a complex mixture of aromatic and aliphatic hydrocarbons. The complex nature of the products and their identification in the presence of large quantities of hydrogen chloride has considerably inhibited analytical work. Madorsky⁹ and his co-workers at the National Bureau of Standards contributed much of the early data on the decomposition using a mass spectrometer to identify the products. Mechanisms for the production of these materials are very vague and aromatic production is briefly explained as a ring closure of the polyene chain formed by dehydrochlorination¹¹.

Recently, pyrolysis chromatography has been used for product studies and Noffz and his co-workers²² using a capillary column again demonstrated the complex nature of the products and identified many of the larger components as aromatic.

Few attempts have been made to study products during decompositions in air. Thinius²³ in 1964 by chromatography showed the presence of saturated and unsaturated hydrocarbons up to octadiene, benzene, toluene and other related aromatic hydrocarbons. In addition to this he noticed the formation of small amounts of chlorinated hydrocarbons and using paper chromatography detected formaldehyde, acetaldehyde and certain other oxygenated materials. No phosgene was detected.

More recently, Sumi⁶ again demonstrated the formation of aliphatic and aromatic hydrocarbons. He did not detect oxygenated species.

(d) Product Formation in Fires

The information relating to the generation of toxic gases other than carbon monoxide and hydrogen chloride from PVC in fires is rather vague. Mostly, and quite understandably, studies have been made on specific toxic gases rather than attempting to consider the general principles of product formation^{24,25}.

Existing data on the production of toxic gases from building materials up to 1963 are presented in a review by the American Underwriters Laboratories⁵. The data reported in this review for PVC are rather conflicting and although the general evidence supports the formation of the hydrocarbon materials there is still a controversy over the formation of oxygenated species.

2. EXPERIMENTAL

(a) The Decomposition System

The decomposition system is outlined diagrammatically in Figure 2. Essentially this consists of a silica tube (18 mm internal diameter) fitted into a tube furnace as shown. The furnace is controlled by a proportional temperature controller for operation up to 1000°C (Temperature stability $\pm 2^{\circ}\text{C}$ at 500°C). The sample (usually 15 mg of PVC) is placed into a small ceramic boat and introduced into the furnace by the influence of an external magnet on the steel plug P, attached to the boat with a length of chromel wire. A small locating mark on the glass tube, aligned with the steel plug ensures that the boat is always injected into the centre of the furnace. The gas flow over the sample during decomposition is introduced at the side arm A. A total injection flow rate of 100 ml/min at 20°C is used in all of the work outlined in this report. The flow rates of the gases are controlled by the needle valves V_1 and V_2 . High purity nitrogen (B.O.C. white spot grade) or compressed air (B.O.C. medical grade) are admitted via valves V_1 and V_2 respectively and monitored by flow meter F_1 . A silica gel - molecular sieve trap in each supply line between the cylinder and the needle valve ensures a supply of dry gas in each case.

The smoke and vapours produced by the decomposition of the PVC in the furnace are swept by the furnace carrier gas along a heated tube and into a stainless steel Perkin Elmer gas sampling valve. The valve is joined to the silica decomposition tube with a silica - pyrex graded seal and a pyrex - metal union. The sampling loop is a 35-mm length of stainless steel tubing (3.2 mm o.d) forming a double collecting loop as shown. The loop is connected to the valve with two short lengths of 3.2-mm stainless tubing coupled to the loop with brass unions as shown. The brass unions are internally enlarged to ensure a 'butt' joint of the stainless tubes in each union. The unions, silver soldered to a metal bracket serve two functions. Firstly, they provide a convenient point for detaching the loop for cleaning and secondly serve as a useful barrier between the hot and cold sections during collection.

The sampling valve is coupled into the helium carrier gas supply to the chromatograph between the flow regulator and the injection port with 3.2-mm stainless steel tubing. The valve, which contains a P.T.F.E. rotor, is maintained at 130°C by surrounding it with electrical heating tape controlled from the mains. In a similar way the line from the furnace to the valve, the injection tube connecting the valve to the chromatograph, the waste tube from the valve and the two short tubes from the valve to the brass unions are also maintained at 130°C . For convenience this heating tape is represented in Fig.2 by dotted lines.

For the collection of decomposition products in the loop the gas sampling valve is turned to the 'collect' position. In this position the products are

directed into the collecting loop where they are frozen out from the furnace carrier gas by surrounding the loop with a refrigerant. The furnace carrier gas continued to waste via the exit tube. An internal bypass in the valve maintains the supply of helium carrier gas to the chromatograph.

After collection of the products, the valve is turned to the 'inject' position and now the helium to the chromatograph flows through the loop while the furnace gas proceeds to waste via the internal bypass. As soon as the valve is turned to the 'inject' position the refrigerant is removed and replaced quickly with a hot fluid. In this way the trapped products are vaporised and carried by the helium carrier gas along the heated tube into the gas chromatograph for separation and identification. The valve and injection lines are maintained at 130°C to ensure that there is no condensation or absorption of material in the tubes and valve prior to entry into the chromatograph.

In a preliminary study of the products from the thermal decomposition of PVC in nitrogen the loop was immersed in liquid nitrogen (-196°C). For the vaporisation of the trapped products, the liquid nitrogen was removed and quickly replaced with a dewar vessel filled with water at 95°C . During collection, the level of the refrigerant was always maintained at a distance of not less than 20 mm from the brass unions to ensure that the unions did not cool to below 90°C . On injection, the hot water container was raised quickly until the hot water touched the brass unions. In this way, cold spots in the collecting loop were avoided.

It must be emphasised that liquid nitrogen cannot be used as a refrigerant in studies with air as the furnace carrier gas, due to the possibility of trapping liquid oxygen into the loop, possibly with disastrous consequences. In early experiments on the decomposition of PVC in air a constant temperature slurry of isopentane at -160°C was used²⁶ as a refrigerant. This was prepared in a dewar vessel and placed around the loop but in later experiments it was more convenient to prepare the slurry in situ, as shown in Fig.2. A small glass boiling tube containing isopentane was precooled in a fume cupboard and placed around the loop. The isopentane was then cooled down to -160°C by placing a dewar of liquid nitrogen around the boiling tube. A thermocouple, silver soldered to the base of the loop was used to monitor the loop temperature by displaying the thermocouple output onto a direct reading meter, calibrated at -160°C with a slurry. During a collection experiment the loop was maintained at -160°C simply by raising or lowering the liquid nitrogen; the phase change in the isopentane assisting the temperature control. In practice it was relatively easy to maintain $\pm 3^{\circ}\text{C}$ of this fixed point.

A hot water bath was not used generally to vaporise products in the loop for chromatography in experiments with the isopentane refrigerant, due to residual

isopentane causing spitting when in contact with the hot water. This problem was overcome by using a fluidised sand bath at 150°C. Experiments showed that the injection cycle from refrigerant to heating could be completed within eight seconds; this short time being necessary for good chromatographic resolution.

(b) Analysis of Hydrogen Chloride

A glass side arm was attached to the glass tube from the furnace to the gas sampling valve (as shown in Fig.2) for monitoring the hydrogen chloride. In these experiments the waste pipe from the gas sampling valve was closed to divert the furnace carrier gas to the analysis tube. The length of the analysis tube was adjusted to give the same flow time from the furnace to the hydrogen chloride trap as from the furnace to the product trap. Hydrogen chloride was monitored by bubbling the gas through 20 ml of distilled water* and titrating in situ with N/25 NaOH. In the experiments where the hydrogen chloride evolution was monitored with time, small aliquots of NaOH were added to the distilled water and the time recorded for the indicator to change colour. In experiments with nitrogen as the carrier gas phenolphthalein (pH 8 to 10) was used as indicator. In studies with air, dimethyl yellow (pH 3 to 4) was used to avoid possible problems from carbon dioxide. In the nitrogen experiments the two indicators gave identical results.

(c) Chromatographic Analysis

A Hewlett Packard 5750 research chromatograph was used for these experiments, fitted out as a dual column instrument with two 1 : 1 output splitters coupled to a flame ionisation and a thermal conductivity detector. The outputs of the two detectors could be monitored simultaneously with a dual pen whart recorder, although in most of this work the product concentrations were below the sensitivity limit of the thermal conductivity detector.

For analysis by mass spectrometry samples were collected from the exit of the non destructive thermal conductivity detector.

Two column types were used for the analytical separations. A silicone grease column gave an overall appraisal of the products and a Porapak Q column used for a more detailed separation of low molecular weight materials. The operating

* A collection system of two gas bottles connected in series, each fitted with a sintered glass disc to assist the collection of hydrogen chloride in the distilled water, was used in preliminary experiments. Time resolved titrations could not be performed in this way but final titration levels were identical to those using the simple single flask and this complex system was discarded.

conditions of these two columns are given below.

(1) Silicone grease on chromosorb P (Perkin Elmer column material No. 496 0769), 3 m x 3.2 mm in stainless steel. Temperature programmed from 30°C at 2°C/min to 250°C. Helium carrier gas, 30 ml/min.

(2) Porapak Q, 2 m x 3.2 mm in stainless steel. Temperature programmed from 30°C at 4°C/min to 250°C. Helium carrier gas, 30 ml/min.

(d) Mass Spectrometry

For the identification of materials separated by gas chromatography the components were collected from the effluent gases at the output of the thermal conductivity detector and analysed with an A.E.I. * MS10c2 mass spectrometer (resolution 1 in 350 at 10 per cent valley). Details for the collection, storage and mass spectrometric analysis of small amounts of material taken from the chromatograph have been outlined in a separate publication²⁷ and will not be considered here. This report also contains details of a modification to the inlet system of the mass spectrometer giving an increase in sensitivity of up to 30 times above the standard sensitivity. A calibration experiment showed that 3.5 µg of n-hexane collected from the chromatograph would give an acceptable mass spectrum. A lower limit in sensitivity of approximately 0.1 µg was estimated for the collection and identification process²⁷.

(e) Materials

Small cubes (approximately 3 to 4 mg each) of a rigid commercial sheet, of the type used at the Joint Fire Research Organization to study the behaviour of PVC in fires, were used in the majority of experiments outlined in this report. Essentially the material is a PVC emulsion polymer containing approximately 10 per cent of organic and inorganic additives with an overall chlorine content of 49.3 per cent.

Some comparative experiments are shown using a relatively pure PVC emulsion polymer in powder form. The weights of samples used in the experiments of this report are detailed below. As shown, sample weights during dehydrochlorination experiments were increased to 30 mg to assist the analysis of hydrogen chloride.

Commercial PVC (Solid pieces).

Dehydrochlorination Experiments - Sample weight 30.0 ± 1 mg

Data corrected to 30.0 mg

Weight Loss Experiments - Sample weight 15.0 ± 1 mg

Data corrected to 15.0 mg

Chromatography Experiments - Sample weight 15.0 ± 1 mg

No corrections

*Now G.E.C. - A.E.I. Ltd., Manchester

Pure PVC Polymer (Powder)

Chromatography Experiments

Sample weight 15.0 ± 0.5 mg

No corrections

3. RESULTS

(A) Dehydrochlorination Studies

Figures 3, 4 and 5 show the evolution of hydrogen chloride with time from 30 mg of the commercial PVC at temperatures of 300, 350 and 400°C respectively in nitrogen and air. Hydrogen chloride is plotted as percentage of the theoretical, calculated from the chlorine content. At 400°C the rate of evolution of gas was so rapid that no attempt was made to monitor the rate between 2.5 and 80 per cent of theoretical dehydrochlorination. The evolution was also followed at 500 and 600°C in the same way but is not shown in this report.

In the lower temperature experiments, namely at 300 and 350°C (Fig. 3 and 4), hydrogen chloride is given off at an increased rate in air and the final level is also greater in air than in nitrogen. At 400°C and above a reversal takes place and although it is difficult to compare rates in intermediate stages the final titration levels in nitrogen are somewhat greater than in air. For convenience the final hydrogen chloride levels at these various temperatures are shown in Fig. 6. The reversal in Fig. 6 is quite apparent, and a repeat experiment confirmed that this reversal was a real effect and not an experimental error. It should be noted that the final hydrogen chloride levels lie between 91 and 98 per cent of the theoretical.

The time scales in Figs. 3, 4 and 5 are given in minutes after injection of the boat and sample into the hot furnace. Clearly a time interval elapses before the hydrogen chloride produced is carried by the flow gas to the distilled water in the collecting flask. The injection flow rate of gas into the furnace was controlled at 100 ml/min at 20°C giving a calculated transit time of approximately 0.75 mins from the boat to the distilled water assuming the furnace and associated lines to be at 20°C.

From Figs. 3, 4 and 5 an extrapolation of the graphs to zero hydrogen chloride yield should give the collection interval. As expected the interval decreases with increasing furnace temperature but is much greater than anticipated. For example at 300°C the time for zero dehydrochlorination is approximately 2.0 minutes which is considerably greater than the calculated value for a furnace at ambient temperature. It is thought that this difference indicates an appreciable time for heating the sample to furnace temperature.

From the data in Figs. 3, 4 and 5 and equivalent data (not shown) for experiments at 500 and 600°C a time for 100 per cent of experimental dehydrochlorination (i.e. the time for complete dehydrochlorination as shown by the experimental curves) is estimated and tabulated in Table 1; also shown is an extrapolated time

for zero dehydrochlorination and a time for 50 per cent (of theoretical) dehydrochlorination. Table 1 also shows the times for 50 and 100 per cent dehydrochlorination based on real time of decomposition i.e. time from extrapolated dehydrochlorination.

Table 1
Experimental and Real times
for 0, 50 per cent and 100 per cent
Dehydrochlorination

	<u>Experimental Time</u> (mins)			<u>Real Time</u> (mins)	
	0	50 per cent	100 per cent	50 per cent	100 per cent
300°C Nitrogen	2.0	3.9	9.0	1.9	7.0
Air	2.0	3.85	9.0	1.85	7.0
350°C Nitrogen	1.3	2.0	5.0	0.7	3.7
Air	1.3	2.0	5.0	0.7	3.7
400°C Nitrogen	0.9	1.4	4.5	0.5	3.6
Air	0.9	1.4	4.5	0.5	3.6
500°C Nitrogen	0.5	0.75	3.5	0.25	3.0
Air	0.5	0.75	3.5	0.25	3.0
600°C Nitrogen	0.5	-	2.0	-	1.5
Air	0.5	-	2.0	-	1.5

These real times are recorded to assist other work at J.F.R.O. in a programme to investigate the production of hydrogen chloride from fires involving PVC. In this work a knowledge of the rates of evolution of hydrogen chloride based on the time and temperature history of a PVC sample in a fire would be very valuable. Some considerable effort was directed into an analysis of the evolution of hydrogen chloride at temperatures of 300° and 350°C (Fig. 3 and 4) to determine if a practical rate equation could be evolved to represent dehydrochlorination over the 0 to 80 per cent region. Unfortunately there is too rapid an evolution of hydrogen chloride to justify this evaluation at these temperatures and it is planned to extend this study to temperatures between 200 and 300°C. This work will be reported in a future publication²⁸.

(b) Weight Loss Experiments

Figures 7, 8, 9 and 10 show the weight of commercial PVC with time at 300, 400, 450 and 500°C in air and nitrogen from 15 mg samples, monitored simply by removing the boat and sample from the furnace after known time intervals and weighing. Also shown on these graphs is the experimental time for 100 per cent dehydrochlorination (from Table 1) and the theoretical weight loss due to hydrogen chloride removal.

Deviation of the experimental weight curve from the theoretical weight loss indicates product formation other than hydrogen chloride.

For convenience the deviation in weight from the theoretical (ΔM) is shown in Table 2 for various times and temperatures and from this table and the data of Figs. 7, 8, 9 and 10 certain interesting points are apparent.

Table 2
Deviations from the Theoretical Weight Loss (ΔM)
of PVC with Time at various Temperatures

	Time for 100 per cent HCl loss	ΔM (in mg) after		
		10 mins	20 mins	30 mins
300°C Nitrogen	0	0	0	0
Air	0	0	0	0
400°C Nitrogen	0.8	0.9	0.9	0.9
Air	0.9	0.9	0.9	0.9
450°C Nitrogen	1.7	2.5	2.6	2.6
Air	1.9	2.9	6.0	6.5
500°C Nitrogen	3.0	3.4	3.4	3.4
Air	3.0	6.4	6.5	6.5

- (1) At 300°C there is no appreciable deviation from the theoretical over a period of 30 minutes in air or nitrogen.
- (2) At 400°C a weight loss deviation of approximately 1 mg is apparent during the dehydrochlorination or primary* decomposition stage. The residue appears to be surprisingly stable in air and nitrogen.
- (3) At 450°C there is evidence of a secondary* weight loss in nitrogen although most of the loss occurs during dehydrochlorination. In air the primary process follows a similar path to the nitrogen case but a complete oxidation to non-combustible ash occurs in the secondary stage between about 10 and 30 minutes.
- (4) At 500°C the primary weight loss is quite considerable but similar in air and nitrogen atmospheres. The secondary weight loss in nitrogen compared to the 450°C case is rather small. After dehydrochlorination, secondary stage oxidation in air is very rapid.

The dehydrochlorination experiments indicate that the release of hydrogen chloride from PVC is virtually quantitative at temperatures above 300°C in air and

* In this report the primary processes refer to the decomposition period from zero to complete dehydrochlorination. Secondary processes refer to the period following complete dehydrochlorination.

nitrogen. Because of this, the deviation in weight loss from the theoretical is a direct measure of general product formation in addition to hydrogen chloride. The weight loss experiments clearly show that these general products are formed predominately during the primary decomposition or dehydrochlorination stage,

(c) Product Analysis

(i) General Studies

Because of the relatively slow but complete oxidation of PVC in air in the secondary decomposition zone at 450°C , this temperature was chosen for preliminary product analysis experiments. In order to separate the products from the two decomposition stages, product analysis experiments were performed over the two regions. This time resolved chromatography was undertaken for two reasons. Firstly to study the predominance of products in the primary decomposition stage and secondly to study possible toxic oxygenated species in the secondary oxidative stage without the interference of the many primary products.

Figures 11 and 12 show chromatographic traces on the silicone grease column using the flame ionisation detector of the products obtained in the primary (0 to 100 per cent dehydrochlorination) stage of 0 to 4 minutes in air and nitrogen from the commercial PVC. The flame ionisation detector is insensitive to inorganic materials and in general a substance must have a C - C or a C - H bond for analysis. As a result the relatively large amount of hydrogen chloride (approximately 7.5 mg) injected into the chromatograph with the minor products is not detected. In a similar manner water, carbon monoxide and carbon dioxide generated in oxidative stages are also not detected although carbon monoxide would not be retained in the collection trap.

The chromatographic traces in Figs, 11 and 12 show very good resolution and indicate an extremely complex series of components. Further, the two traces are very similar even in the detail and intensities of the fine structure.

The chromatographic traces were both recorded on an amplifier range 10 and attenuation 16. This relatively high sensitivity was chosen to show the fine structure and consequently many of the larger peaks are greater than the full scale recorder deflection. An arrow and attenuation near each of these peaks is given to show the peak height. For example, in Fig.11 toluene (peak 38) has a peak height shown by the point of the arrow at attenuation 32. The smaller numbers are given for peak identification. Approximately 75 peaks are distinguishable in the chromatographic trace although some of this fine detail may be lost during duplication. There are clearly some minor differences between the traces in air and nitrogen and in particular the enhancement of peak 75 in the air experiment.

A study was made of the large peaks in a repeat of the nitrogen experiment of Fig.11 by retention time experiments and mass spectrometry and the data are shown in Table 3. For retention data known materials were injected into the furnace carrier gas and trapped in the usual way in the collecting loop. In this way errors due to the transit time from the loop to the chromatograph and other injection errors were avoided.

Table 3
Identification of Decomposition Products on Silicone Grease

<u>Peak Number</u>	<u>Retention Data</u>	<u>Mass Spectrometry</u>
3) 4) D	C ₂ , C ₃ hydrocarbons	HCl Interference*
7) 8) D	C ₄ hydrocarbons	HCl Interference*
14) 15) D	C ₅ hydrocarbons	HCl Interference*
29	Benzene	Benzene
38	Toluene	Toluene
46	p-Xylene	Xylene
47	m-Xylene	Xylene
49	o-Xylene	Xylene
75	Naphthalene	Naphthalene (with difficulty)

D = Doublet
* = Mass spectrometry not possible due to
HCl Interference.

The relevant mass spectra of peaks 29, 38, 46, 47*, 49* and 75 are shown in the appendix. Mass spectrometry of doublet peaks 3:4, 7:8 and 14:15 proved inconclusive due to the elution of hydrogen chloride in this region. Thermal conductivity experiments showed that the huge hydrogen chloride peak was eluted near peak 4 and tailed very badly up to peak 15. Peak 75 was tentatively identified by the characteristic naphthalene odour prior to retention and mass spectrometric confirmation.

Figs. 13 and 14 show the chromatographic traces of the secondary decomposition stage, again of the commercial PVC (15 mg samples), at 450°C in nitrogen and air recorded as before on amplifier range 10 attenuation 16. In nitrogen the general decomposition pattern is similar in structure to the 0 to 4 min period (Fig. 11) but much lower in intensity and with certain exceptions. Firstly, although the aromatic structure is reduced considerably, toluene, the xylenes and naphthalene are quite distinct yet benzene is absent. Also peak positions do not agree exactly between the two stages. This deviation is small and associated with certain peaks up to benzene. Experiments showed that the injection of large quantities of hydrogen chloride slightly modified the retention time of a test material (n-hexane) and this inhibited the correlation of certain peaks between

*Mass spectra of peaks 46, 47 and 49 were identical and only the mass spectrum of peak 46 is shown in the appendix.

the two stages. Figures 13 and 14 are numbered as accurately as possible to show the peak correlation between the two stages.

In air in the 4 to 30 minute period there is a complete oxidation of approximately 4 mg of material but there is only a trace of products. Again the aromatic structure is distinct and rather surprisingly benzene is present. There is little evidence to support the formation of oxygenated materials during this oxidation.

(ii) Studies of Low Molecular Weight Materials

Because of the interference of hydrogen chloride in the mass spectrometric identification of materials eluted at low retention times, an attempt was made to assist the separation of these low boiling materials using a Porapak Q column. Details of the operation of this column are given in the experimental section. Essentially Porapak Q has a porous polymer bead structure and is reported to give good peak shape and resolution with polar and non-polar materials of small molecular size.

Initial experiments (again using 15 mg samples of PVC) showed very good separation of the low boiling hydrocarbons but there was little reproducibility in quantitative measurements between apparently identical experiments, particularly between the C_2 and C_3 materials. This was attributed to variations in the temperature of the collecting loop between experiments and in fact it is surprising that C_2 materials are collected at all at -160°C . In order to ensure the efficient collection of these hydrocarbons for mass spectrometric analysis some experiments were performed in a nitrogen atmosphere using liquid nitrogen for collection. Figure 15 shows a typical chromatographic trace of the hydrocarbons from a complete decomposition (i.e. 0 to 30 minutes) at 450°C . For identification purposes peaks are numbered alphabetically to avoid confusion with silicone grease nomenclature. The C_2 , C_3 , C_4 , C_5 , and C_6 patterns are quite distinct. Peak c is a disturbance in the detector from the elution of hydrogen chloride and does not interfere with any of the other materials. The trace was recorded on the flame detector at an amplifier range 10 attenuation 8, to show the fine structure. By retention time experiments and mass spectrometry the identifications as shown in Table 4 were made. The mass spectra of peaks a, b, d, e, j, k, q, and r are shown in the Appendix. The mass spectrum of peak w (benzene) has been recorded from silicone grease experiments and is not shown again. Samples of pentene and butene were not available for retention studies.

Table 4
Analysis of Hydrocarbons on Porapak Q

<u>Peak Identification</u>	<u>Retention Data</u>	<u>Mass spectrometry</u>
a	ethene	ethene
b	ethane	ethane
c	hydrogen chloride	-
d	propene	propene
e	propane	propane
j	-	butene
k	n-butane	n-butane
q	∅	pentene
r	n-pentane	pentane
u	∅	*
w	benzene	benzene

* Insufficient resolution from benzene for analysis
∅ not available for retention studies

For comparison Figure 16 shows the products from a 0 to 30 minute decomposition in air with product collection at -160°C . Because of the higher collection temperature the collection efficiency falls off rapidly towards C_2 but some peaks (peaks f,g,h,l,m,n,o and in particular peak f) are quite distinct. In fact these peaks are not new but do appear in the nitrogen experiment but are greatly enhanced in the presence of air. Several attempts were made to analyse peak f by mass spectrometry and although apparently present in sufficient quantity for identification gave no spectrum. Retention experiments showed that the peak had the exact retention time of vinyl chloride and experiments where a similar amount of vinyl chloride was introduced into the mass spectrometer also gave no spectrum. It is thought that in small amounts the material is lost either by polymerisation or by absorption on the walls inside the mass spectrometer. The data from the Porapak column supports the suspected retention data for doublets 3:4, 7:8, and 14:15 in the silicone grease experiments. For convenience table 5 shows the correlation of the peak numbering on Porapak Q with the alphabetical notation of the silicone grease column.

Table 5
Correlation between the Chromatographic Peaks
on Porapak Q and Silicone Grease

<u>Porapak Q</u>	<u>Peak Material</u>	<u>Silicone Grease</u>
a	ethene	} 3,4 ^D
b	ethane	
d	propene	
e	propane	
j	butene	} 7,8 ^D
k	butane	
q	pentene	} 14,15 ^D
r	pentane	
w	benzene	29
-	toluene	38
-	p-xylene	46
-	m-xylene	47
-	o-xylene	49
-	naphthalene	75

(iii) Temperature Dependence of General Products

In addition to the experiments outlined at 450°C, product studies on silicone grease were extended over the range 300 to 500°C using 15 mg samples of PVC. Again, time resolved chromatographic experiments were recorded to study the primary and secondary decomposition stages according to the times of Table 1. In general the results were the same as reported for 450°C.

In the primary stage the products were almost identical in air and nitrogen atmospheres. At 500°C the chromatographic traces showed the same structure of products as in the 450°C experiment but increased in magnitude, again identical in the air and nitrogen cases. Between 450 and 400°C the fine structure of the traces decreases rapidly and only the aromatics remained with benzene being predominant in all cases. At 300°C benzene was virtually the only product.

In the secondary stage, at temperatures up to 400°C, the amounts of secondary products were small compared with the primary yields. The chromatographic traces show similar general structure in both the air and nitrogen experiments, but with certain differences in the intensities of the aromatic structure. At 500°C in air there was only a very small amount of secondary products. There was no evidence to support the formation of oxygenated materials in these experiments.

It is not possible to show all the chromatographic traces which were recorded but for comparison purposes Figures 17, 18, 19 and 20 show the primary and secondary decomposition stages in nitrogen and air at 350°C. These were

again recorded on amplifier range 10 attenuation 16. These figures clearly show the simplification of the products in the lower temperature regions, the similarity between the primary products in air and nitrogen and the minor secondary stage differences in the aromatic structure.

Because of the interesting differences between the aromatic products, data for benzene, toluene, total xylenes and naphthalene are extracted from the chromatographic traces and shown graphically with temperature for the primary and secondary decomposition stages in figures 21 to 28. In each case, materials are given by weight in μg . Quantitative calibrations were performed on benzene and toluene and related to the other hydrocarbons by the relative sensitivity data of Dietz²⁹. A relative sensitivity factor was not available for naphthalene and a value of 1.0 based on the data of other aromatic hydrocarbons was used.

In the primary decomposition stage (figures 21 to 24) toluene, the xylenes and naphthalene show similar temperature dependence in both air and nitrogen. A marked increase in production occurs between 400 and 450°C. This is distinct in the xylenes and toluene but less pronounced in naphthalene. Also, yields in air are slightly greater than in nitrogen for toluene and naphthalene. The xylenes show equivalent temperature dependence in each atmosphere. With benzene (Fig. 21) yields in air are slight greater than in nitrogen but there is no evidence for a decrease near 400°C. It should be noted also that benzene is present in quantities considerably greater than the other aromatics.

In the secondary stage (Fig. 25 to 28) toluene, the xylenes and naphthalene again show similar temperature dependence but now the yields in air are less than in nitrogen; this difference being distinct in toluene and the xylenes and less distinct in naphthalene. Benzene formation (Fig. 25) shows a distinct increase in air. Benzene is absent in the inert decomposition case up to 450°C but is distinctly present at 500°C.

(iv) Temperature Dependence of Vinyl Chloride and C_4 Hydrocarbons

Earlier chromatographic studies using Porapak had indicated the formation of vinyl chloride and possibly other chlorides (Peaks g, l, m, n and t in figure 16). A series of experiments were undertaken using the Porapak column to study the formation of vinyl chloride in the primary decomposition stage⁶ at various temperatures in air and nitrogen. Figure 29 shows the production of vinyl chloride (in μg) during this primary stage in air and nitrogen from 300 to 500°C. The chromatograph was calibrated specifically for vinyl chloride since the area calibration factor²⁹ was not known. In the vinyl chloride production there is a marked increase in the formation rate at temperatures above 400°C in air. Vinyl chloride was detected in nitrogen above 400°C but only in very small amounts.

⁶ Vinyl chloride was not found in the secondary stage in air or nitrogen

Unfortunately it was not possible to monitor the C_2 and C_3 hydrocarbons during these experiments because of collection difficulties, but in order to show the general temperature dependence of hydrocarbons, the formation of total C_4 hydrocarbons (in μg) with temperature in air and nitrogen is shown in Fig.30. The total C_4 hydrocarbons show a very rapid increase with temperature at $400^\circ C$ in air and nitrogen comparable to the primary production of toluene and the xylenes. Below $400^\circ C$ these C_4 hydrocarbons are absent.

(d) Experiments with a pure PVC Polymer

The experiments outlined earlier in this report were all performed on a commercial rigid plastic containing certain additives (see experimental section). A series of experiments were undertaken on a relatively pure PVC polymer to see if any striking differences were apparent between the decomposition products of the pure and commercial materials.

Figures 31, 32, 33 and 34 show the chromatographic traces on silicone grease of the primary and secondary decomposition stages of the pure polymer (15 mg samples) in nitrogen and air at $450^\circ C$ recorded again on amplifier range 10 attenuation 16. The aromatic and fine structure agree in detail with the products from the commercial plastic except that the pure polymer gives much more product. For comparison with earlier studies peaks are numbered as before. Again the primary decomposition products are similar in nitrogen and air. Secondary products in nitrogen show the same correlation with the primary stage as in the commercial PVC case. As before, during the oxidative second stage there is no evidence to support the formation of oxygenated organic materials.

Product studies were extended to the primary and secondary stages at $400^\circ C$ and the primary stages at $500^\circ C$ in nitrogen and air.

Table 6 shows the weights of aromatic materials produced in these experiments. The aromatic yields in this table show generally equivalent data to that found for the commercial plastic. For example, in the primary stage the yield of benzene is considerably greater than the other aromatics and does not depend upon the temperature. Toluene, the xylenes and naphthalene show the characteristic increase in the 400° to $450^\circ C$ region as before. In general the amounts of secondary stage products are small compared with those for the primary stage.

Table 6
Aromatic Production from pure PVC
in Nitrogen and Air (400-500°C)

Material	Temp. (°C)	Primary stage		Secondary stage	
		Nitrogen (μg)	Air (μg)	Nitrogen (μg)	Air (μg)
Benzene	400	340	350	0	3
	450	340	320	0.1	1
	500	320	300	-	-
Toluene	400	7	8	8	1.5
	450	35	20	5	0.2
	500	40	15	-	-
Total Xylene	400	2	3	5	0.5
	450	16	25	4	0
	500	12	5	-	-
Naphthalene	400	3	16	1.5	2
	450	10	20	1	0.5
	500	25	25	-	-

Secondary products at 500°C were not recorded

(e) Phosgene Studies

Although there appeared to be little or no evidence to support the formation of oxygenated species in this work, because of the high toxicity and poor response of phosgene on the flame detector, a series of specific phosgene analyses using the thermal conductivity detector were undertaken. Many difficulties were encountered in the analysis of phosgene and a study of these difficulties and details of the analytical techniques will be recorded in a separate publication⁷, but preliminary results of phosgene measurements from the decomposition of the commercial PVC will be recorded here.

Because of analytical problems, particularly the partial loss of phosgene in the furnace and associated lines, a series of calibration experiments at various temperatures were performed by injecting fixed quantities of phosgene into the furnace during a decomposition experiment. By comparing the phosgene peak from the calibration experiment with the peak from a repeat experiment without added phosgene, an estimation of the phosgene yield could be made.

A study was made in this way at temperature intervals of 50°C from 250°C to 500°C using the commercial PVC. No phosgene was detected during the decomposition of PVC. The seeding experiment ensured that the minimum amount of phosgene which could be detected at each temperature was known. This detection level varied between approximately 10 and 1 μg of phosgene from the 15 mg of commercial PVC. This work is now being extended to the pure polymer.

4. DISCUSSION AND TOXIC EVALUATION

(a) General Discussion of Products

Weight loss experiments and time resolved chromatography clearly demonstrate that at temperatures above 300°C product formation is essentially associated with dehydrochlorination. By separating the products between the primary and secondary stages, the chromatographic studies indicate that in the presence of oxygen, complete oxidation of material can take place in the second stage without the formation of oxygenated organic species. This is in good agreement with the experiments of Tsuchiya and Sumi⁶. Under the conditions studied in this report, product formation can be explained, depending on the environment, as:-

(i) primary dehydrochlorination and product elimination.

(ii) secondary pyrolysis or oxidation to CO, CO₂ and H₂O

The predominance of products in the primary stage suggests that the polyene structure formed by dehydrochlorination is inherently unstable or more likely that re-arrangements take place during the radical zip dehydrochlorination. Initiation of dehydrochlorination may take place at a chain end and a radical re-arrangement giving benzene could be a feasible mechanism during degradation. If this were the case then a study of dehydrochlorination and benzene formation during the initial stages of dehydrochlorination would be very valuable. Further a relationship between benzene formation and the molecular weight of various PVC polymers would be apparent and in fact this may explain the difference in the yields of benzene in this report between the pure and commercial materials. This type of mechanism could explain the temperature independence of benzene between 300 and 500°C but it is difficult to visualise why during the zip process that more cyclisation of the polyene chain does not take place. Possibly a cross linking reaction may explain this point.

In general the amounts of toluene, the xylenes and naphthalene are small compared with benzene and show different behaviour with temperature. At 400°C a marked increase in production of these materials takes place but without altering the benzene formation. Formation appears to correlate with dehydrochlorination and these products may again be produced during polyene formation. Although ring closure must take place for the formation of these aromatics, the presence of the side chains suggests that they could be eliminated from a cross linked structure.

The temperature of 400°C appears to be critical for hydrocarbon formation based on the total C₄ study. Gas chromatography and mass spectrometry of the C₂ to C₅ hydrocarbons revealed a predominance of saturated hydrocarbons (straight chain) with unsaturated hydrocarbons (again straight chain with one unsaturated group) in each case. These saturated and unsaturated hydrocarbons have been reported in other work^{5,6,9,23} and the production of these hydrocarbons from a

conjugated polyene chain certainly requires elucidation.

Oxygen plays a curious role during degradation. It assists dehydrochlorination and generally increases product formation. At 400°C, the temperature at which considerable disruption takes place in nitrogen atmospheres, oxygen assists this disruption and produces certain chlorides of which the monomer (vinyl chloride) appears to predominate. These chlorides are only found in the primary decomposition stage.

It is not possible to correlate organic halide production with final hydrogen chloride levels. Firstly, the small amount of halide detected would not appreciably alter the hydrogen chloride output and secondly, the final titration levels, although reproducible, may be misleading. At 300°C, weight loss curves show an exact correlation of the experimental weight loss with the theoretical loss in both air and nitrogen. Product analysis at this temperature shows benzene (60 µg) and traces of other aromatics which would not be detected in weight loss measurements. At this temperature final titration levels in air and nitrogen are different and although both are in the 95 per cent region there is a difference of about 4 per cent between the two, the level in air being somewhat higher than in nitrogen. The hydrogen chloride reversal in air and nitrogen at 400°C (Fig.6) could be associated with organic halide formation but this correlation is speculative. After 15 minutes at 300°C, sodium fusion tests on the residue showed virtually no remaining chlorine in air or nitrogen atmospheres.

This discrepancy between the final hydrogen chloride yields in air and nitrogen at 300°C is not understood. At 400°C the reversal of these yields may be associated with the production of organic halides but more likely to be associated with a loss of hydrogen chloride by absorption into the water generated during oxidative decomposition. Some of this water could condense into the cold part of the glass collection tube between the hot decomposition system and the distilled water trap and extract a proportion of the hydrogen chloride.

The formation of products during the secondary decomposition stage is also interesting. In general, although the amounts of these products are small compared with the primary products there are distinct differences between the aromatics in the two stages. For example, in nitrogen atmospheres, toluene, the xylenes and naphthalene are present but benzene is absent. In the secondary stage decomposition in air, benzene although small in amount is quite distinct.

The products from the decompositions of the relatively pure PVC emulsion polymer correlate extremely well in general nature with those from the commercial material. The additives in the commercial material do not produce striking differences in the chromatographic pattern. However, in the pure polymer the products are considerably greater in amount than in the commercial case.

This may be a reflection on the polymer itself, i.e. a molecular weight difference or an effect from the stabilisers added to the commercial material.

(b) Toxic Evaluation

Although oxygen alters the general products of decomposition the ability to correlate the overall products with a pyrolytic and oxidative (to CO, CO₂ and H₂O) decomposition clearly simplifies the toxic evaluation of the material.

Although there is some doubt about the final titration levels during dehydrochlorination studies, the values are in the 95 per cent region in all cases. Because of this, hydrogen chloride provides a useful yardstick for the comparison of other possible toxic products. It should be emphasised at this point that no attempts have been made to monitor carbon monoxide and carbon dioxide in this work. These are always present when organic material is involved in fire and the relationship between these gases and hydrogen chloride from fires involving PVC has been examined in detail at J.F.R.O.^{3,4}.

To date, it has been generally accepted that oxidative attack on PVC, both at low temperatures as in the increased dehydrochlorination in air and at high temperatures where oxidation produces inorganic materials could involve oxygenated organic intermediates. The elimination of these species which in general are highly toxic is in itself an important aspect of this work.

For a comparison of the toxicity of the products from PVC to that of hydrogen chloride, a toxicity factor T suggested by Tsuchiya and Sumi⁷ will be used given by

$$T = C_E / C_F$$

where C_E = concentration of experimental product in p.p.m produced from 1 g of PVC in a metre cube

C_F = concentration of material in p.p.m fatal in a short period.

In general the products from PVC increase in amount with temperature. At 500°C in air PVC is rapidly oxidised to inorganic materials. For aromatic materials the total yields in a 30-minute period at 500°C will be used for toxicity evaluation.

Aliphatic hydrocarbons (C₂ to C₅) will not be considered due to their inert toxic nature. Phosgene was not detected in any experiment between 250°C and 500°C and since the detection limit of this material varied with temperature a theoretical toxicity factor will be calculated for the least sensitive detection level of .01 mg: (see section 3(e)). The toxicity factor for vinyl chloride is estimated assuming the most serious conditions for production, in

this case at 500°C in air. Hydrogen chloride values are given based on 100 per cent of theoretical dehydrochlorination.

Table 7 shows the calculated toxicity factors for these materials from the commercial PVC. Values of C_E in p.p.m. are calculated from the yield of each product from one gramme of PVC in a metre cube. For each material a M.A.C. (maximum atmospheric concentration) and a concentration immediately hazardous

Table 7
Toxicity Factors of the Main Products from
a Commercial Sample of PVC

	Yield per 15 mg (mg)	Yield per gram (mg)	C_E (p.p.m.)	M.A.C. (p.p.m.)	C_F (p.p.m.)	T Toxicity Factor
Hydrogen chloride	7.6	505	338	5	1,500	2.25×10^{-1}
Benzene	0.060	4.0	1.25	25	20,000	5.0×10^{-5}
Toluene	0.012	0.80	0.213	200	10,000	2.1×10^{-5}
Xylene	0.011	0.73	0.195	200	(10,000)	1.9×10^{-5}
Naphthalene	0.0035	0.23	0.044	10	(200)	2.2×10^{-4}
Phosgene*	0.01	0.66	0.163	0.1	50	3.26×10^{-3}
Vinyl chloride	0.003	0.20	0.0782	500	120,000	6.5×10^{-7}

*Detection level

to life are extracted from the Toxicity Guides issued by the American Industrial Hygiene Association³⁰. For xylene and naphthalene C_F values were not readily available from the literature. For xylene, a value of 10,000 p.p.m. was used based on the similarity between toluene and xylene toxicology. The C_F value for naphthalene was based on a conservative estimate by Rasbash³¹ that C_F is approximately twenty times the M.A.C.

In each case the toxicity factor of the products is small compared with the hydrogen chloride factor. Making the reasonable assumption that at these levels synergistic effects, if any, are small then the main toxic material is hydrogen chloride. However, in experiments with pure PVC somewhat greater yields of aromatic materials were evolved. Toxicity data for these aromatic materials are shown in Table 8; Once again, toxicity factors are very small compared with hydrogen chloride. Hydrogen chloride is an irritating acid gas. At 1500 p.p.m, the C_F value used in Tables 7 and 8, it is directly hazardous to life within a short period. However, because of its acrid nature relatively low concentrations of the gas can be difficult to breathe and present an indirect hazard to personnel trapped in a fire. An atmosphere containing as low as 100 p.p.m. of hydrogen chloride can be intolerable to breathe. As a result a realistic toxicity factor of hydrogen chloride is probably much greater than the values shown in Tables 7 and 8, and hence the contribution of the other components to the overall toxicity much less than indicated.

Table 8
Toxicity Factors for Hydrogen Chloride
and Aromatics from Pure PVC

	Yield per 15 mg (mg)	Yield per gram (mg)	C _E (p.p.m.)	C _F (p.p.m.)	Toxicity Factor
Hydrogen Chloride	8.75	582	390	1,500	2.6×10^{-1}
Benzene	0.32	22	6.9	20,000	3.5×10^{-4}
Toluene	0.04	2.65	0.70	10,000	7.0×10^{-5}
Xylene	0.012	0.80	0.22	10,000	2.1×10^{-5}
Naphthalene	0.025	1.65	0.315	200	1.57×10^{-3}

5. CONCLUSIONS

1. At temperatures between 300 and 500°C the dehydrochlorination of PVC is a rapid and almost quantitative process in air and nitrogen.
2. In general, minor products (aromatic and aliphatic hydrocarbons) are generated mainly during the dehydrochlorination, or primary decomposition stage.
3. The formation of minor products excluding benzene is temperature dependent and a marked increase in production takes place at about 425°C.
4. Benzene shows little temperature dependence between 300 and 500°C.
5. At temperatures up to 450°C, the minor products are virtually identical during both the primary and secondary decomposition stages in air and nitrogen; the secondary stage referring to the decomposition period following complete dehydrochlorination.
6. At 450°C in air a rapid oxidation to CO, CO₂ and H₂O takes place in the secondary decomposition stage. Primary products in air and nitrogen at 450°C are very similar.
7. No oxygenated species other than CO, CO₂ and H₂O have been detected in this work.
8. Neglecting synergistic effects, the minor products make little or no contribution to the overall toxicity of the decomposition products based upon the toxicity from hydrogen chloride.
9. The main toxic hazards in the decomposition products are hydrogen chloride and carbon monoxide.

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7. REFERENCES

- (1) RASBASH, D.J., Smoke and Toxic Products Produced at Fires, Trans. J. Plastics Inst, 1967.
- (2) RASBASH, D.J., and STARK, G.W.V., The Generation of Carbon Monoxide by Fires in Compartments. F.R. Note No. 614.
- (3) STARK, G.W.V., EVANS, W, and FIELD, P., Toxic Gases from Rigid PVC in Fires. F.R. Note No. 752.
- (4) STARK, G.W.V., Toxic Gases from PVC in Household Fires. Rubber and Plastics Age, 1969, 50 (4), p.283.
- (5) Survey of Available Information on the Toxicity of the Combustion and Thermal Decomposition Products of Certain Building Materials under Fire Conditions. National Board of Fire Underwriters, Bulletin of Research 1963, 53. Offices at 207 East Ohio Str., Chicago 41, U.S.A.
- (6) TSUCHIYA, Y., and SUMI, K., Thermal Decomposition Products of PVC, J. App. Chem. 1967 17 (12), pp.364-366.
- (7) WOOLLEY, W.D. and WADLEY, A.I. Studies of Phosgene Production during the Thermal Decomposition of PVC in air. F.R. Note - In Preparation.
- (8) BENGOUGH, W.I., Weathering and Degradation of Plastics. Editor Pinner S.M., Columbine Press 1966, pp 66-80.
- (9) MADORSKY, S.L. Thermal Degradation of Organic Polymers, Interscience Publishers, 1964, p.160.
- (10) WINKLER, D.E. Mechanism of PVC Degradation and Stabilization, J. Polymer Sci, 1959, 35, pp 3-16.
- (11) GEDDES, W.C. Mechanism of PVC Degradation, Rubber Chemistry and Technology, 1967, 40 (1), pp 177-215.
- (12) TYRON, M., and WALL, L.A. Oxidation of High Polymers, Chapter 19 of Autoxidation and Antioxidants, New York Interscience Publishers Inc, 1962, 2, pp 919-984.
- (13) ARLMAN, E.J. Thermal and Oxidative Decomposition of PVC, J. Polymer Sci., 1954, 12, pp 547-558.
- (14) DRUESEDOW, D, and GIBBS, C.F., Nat. Bur, Std. Circular 525, 1953 p 69.
- (15) ARLMAN, J.E., Alleged Catalytic Effect of Hydrogen chloride on Decomposition of PVC at High Temperature, J. Polymer Sci, 1954, 12, pp 543-546.

- (16) TALAMINI, G., CINQUE, G., and PALMA, G. Nat.Plast.1964, 30, p 317.
- (17) GEDDES, W.C., The Thermal Decomposition of PVC - II, Eur.Polymer J., 1967, 3, pp 733-745.
- (18) GRASSIE, N., Chemistry of High Polymer Degradation Processes, Butterworths Scientific Publications, 1956.
- (19) SHEEHAN, D., Thermal Degradation of Various Polymers over the range 300-600°C, Royal Aircraft Establishment, Technical Note No. Chem.1280
- (20) TALAMINI, G., and PEZZIN, G., Makromol. Chem. 1960, 39, p 26.
- (21) STROMBERG, R.R., STRAUS, S., and ACHHAMMER, B.G. J.Polymer Sci., 1959, 35, p 355.
- (22) NOFFZ, D., BENZ, W., and PFAB, W. Untersuchung von Hochpolymeren mittels Pyrolyse - gas - chromatographic, Fresenius Zeit. Anal. Chemie, 1968, 235 (1), pp 121-37.
- (23) THINIUS, K., SCHRODER, E., and GUSTE, A. Contributions to the Analytical Chemistry of Plastics XX1; The Pyrolysis of Plastics in Air, Plaste and Kautschuk, 1964, 11 (2), pp 67-72.
- (24) COLEMAN, E.H., and THOMAS, C.H. The products of Combustion of Chlorinated Plastics, J.Appl. Chem. London, 1954, 4, pp 379-383.
- (25) SCHREISHEIM, A., Method for the Controlled Burning of Combustible materials and Analyses of the Combustion Gases, J.Res.Nat.Bur.Stand. 1956, 57 (4), pp 245-249.
- (26) MELVILLE, H., and GOWENLOCK, B.G. Experimental Methods in Gas Reactions, Macmillan and Co.Ltd., 1964.
- (27) WOOLLEY, W.D., An Improved Technique for Transferring Fractions from a Gas Chromatograph to a Mass Spectrometer, Analyst, 1969, 94, pp 121-125.
- (28) WOOLLEY, W.D. F.R.Note - In preparation.
- (29) DIETZ, W.A. Response Factors for Gas Chromatographic Analyses, J. of Gas chrom, 1967, 5 (2), pp 68-71.
- (30) Hygienic Guide Series, American Industrial Hygiene Association, 14125 Prevost, Detroit 27, Michigan, U.S.A.
- (31) CORNU, A., and MASSOT, R., Compilation of Mass Spectral Data, Heydon and Son, 1966.

8. APPENDIX

Mass spectra were recorded on an A.E.I.* MS 10c2 mass spectrometer modified with an improved leak unit for the analysis of small amounts of material²⁷. Spectra are shown recorded either on the fast or slow leak depending upon the amount of material for analysis. On the fast leak where some loss of material occurs during the scan the spectra are corrected as outlined recently²⁷. Spectra were interpreted by mass spectrometric data compiled by Cornu and Massot³¹. The spectra recorded in the subsequent pages show the main peaks of each spectrum. Some background, due to column bleed has been omitted to simplify the representation of the spectra. Spectra are numbered according to the peak number, column type, leak (fast or slow) and amplifier range (e.g. range 25). Peaks at 18^+ , 17^+ and 16^+ and at 44^+ are due to water and carbon dioxide respectively frozen from the atmosphere into the collecting tube when the tubes are fitted to the mass spectrometer. These peaks are of course more pronounced on the fast leak. Nitrogen (28^+) was very difficult to remove completely. Oxygen (32^+) does not appear due to absorption on the walls inside the mass spectrometer. Spectra are recorded with the base peak as 100 per cent. In ethene and ethane where the base peak is 28^+ and masked by the nitrogen peak the spectra are shown by correlating the second most intense peak with the value given by the reference spectrum (i.e. 27^+ at 63.4 per cent for ethene and 27^+ at 33.3 per cent for ethane).

Of the aromatic materials, benzene, toluene and naphthalene were identified readily. With xylene only one spectrum is shown since peaks 46, 47 and 49 on the silicone grease column gave virtually identical mass spectra. Ortho, meta and para nature were derived by chromatography.

Ethene, ethane, propene and propane gave easily recognisable patterns. The fine structure of the C_4 and C_5 materials were difficult to interpret from reference spectra alone. With butane the spectral data indicated n-butane rather than 2-methyl propane. With butene because of the similarity between the 39^+ and 56^+ intensities it was not possible to identify the fine structure. In a similar manner, the pentane spectrum indicated n-pentane but the fine structure of pentene was not clear.

In the following pages typical reference spectra are recorded (Tables 9, 10, and 11) followed by the experimental line spectra of materials collected from the chromatograph.

Mass spectra were recorded at 70 e.V. using a trap current of 50 μ a. The batch inlet system was operated at 95°C, and the ionisation tube at 50°C. For naphthalene the ionisation tube temperature was increased to 85°C.

* Now General Electric Company - Associated Electrical Industries Limited.

Table 9
Reference mass spectra for benzene
toluene, xylene and naphthalene

	m/e	%		m/e	%
<u>Benzene</u>	78	100	<u>Toluene</u>	91	100
	52	19.4		92	75.6
	51	18.6		39	18.7
	50	15.7		65	13.1
	77	14.4		51	9.6
	39	14.2		63	8.7
	79	6.4		90	8.0
	76	6.0		50	6.0
	38	5.8		45	5.3
	74	4.6		93	5.2
<u>O-Xylene</u>	91	100	<u>Naphthalene</u>	128	100
	106	59.8		51	12.5
	105	24.1		129	11.0
	39	16.2		64	10.6
	51	15.3		127	9.9
	77	13.2		63	7.5
	27	9.6		102	7.1
	65	7.9		50	6.4
	78	7.8		126	6.2
	92	7.5		75	5.0

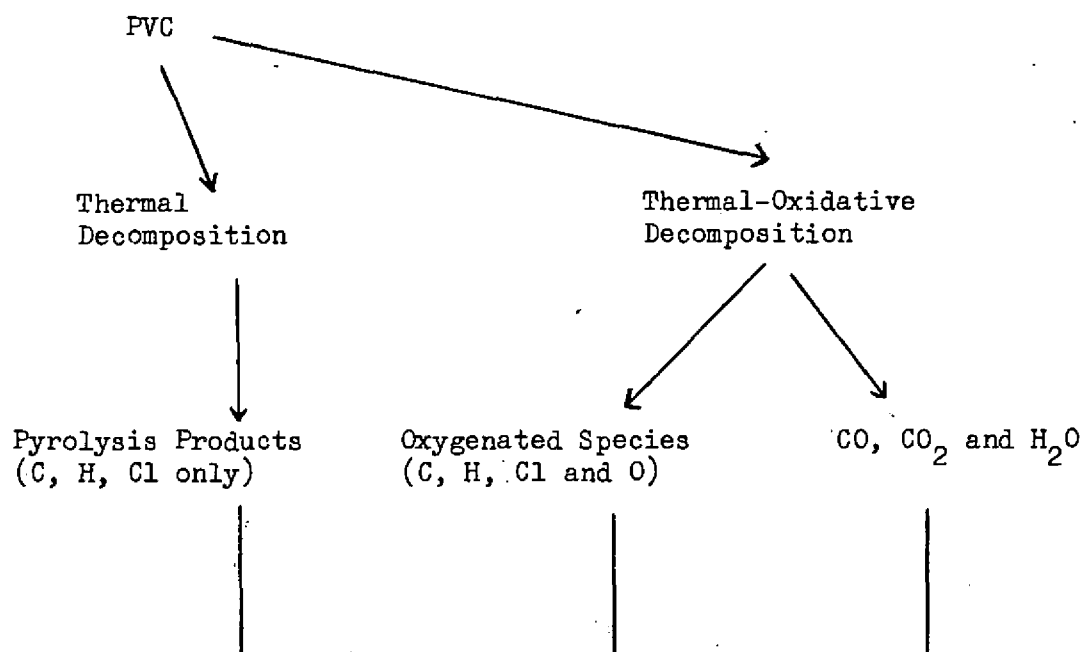
Table 10
Reference mass spectra for ethene,
ethane, propene and propane

	m/e	%		m/e	%
<u>Ethene</u>	28	100	<u>Ethane</u>	28	100
	27	63.4		27	33.3
	26	62.7		30	26.2
	25	12.2		26	23.0
	14	6.9		29	21.7
	13	3.7		15	4.6
	27	3.3		25	4.2
	12	2.1		14	3.4
	29	1.9		1	2.6
	15	0.6			
<u>Propene</u>	41	100	<u>Propane</u>	29	100
	42	69.2		28	61.5
	39	60.9		44	40.2
	27	24.7		43	33.6
	40	24.7		27	31.6
	38	14.4		39	16.5
	37	9.0		41	14.9
	26	5.8		42	6.1
	43	2.4		26	5.3
	19	1.4		38	4.3

Table 11
Reference mass spectra for 1-butene,
n-butane, 1-pentene and n-pentane

<u>1-Butene</u>	m/e	%	<u>n-butane</u>	m/e	%
	41	100		43	100
	56	46.6		29	33.7
	39	29.8		41	26.3
	28	22.6		28	24.6
	55	21.6		27	22.5
	27	19.5		58	16.7
	29	10.7		42	13.0
	53	5.9		39	9.1
	40	5.7		44	3.5
	26	5.4		26	2.6
<u>1-pentene</u>	42	100	<u>n-pentane</u>	43	100
	55	60.1		42	57.9
	41	44.3		41	40.2
	39	34.6		27	34.6
	27	32.1		29	24.4
	70	30.9		39	14.2
	29	27.1		57	12.6
	40	8.6		72	8.8
	15	5.8		28	6.0
	26	5.6		15	4.7

A. Solid Phase Decomposition



B. Gas Phase Decompositions and Reactions

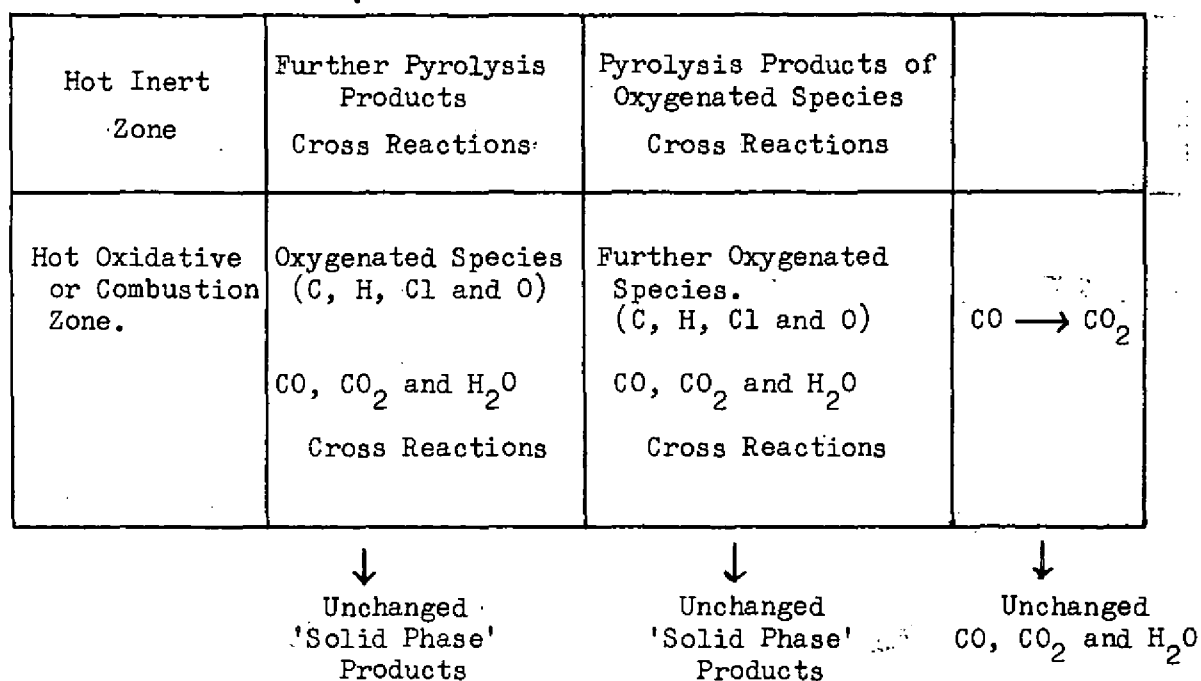


FIG 1. PRODUCT FORMATION ROUTES FOR PVC IN FIRES

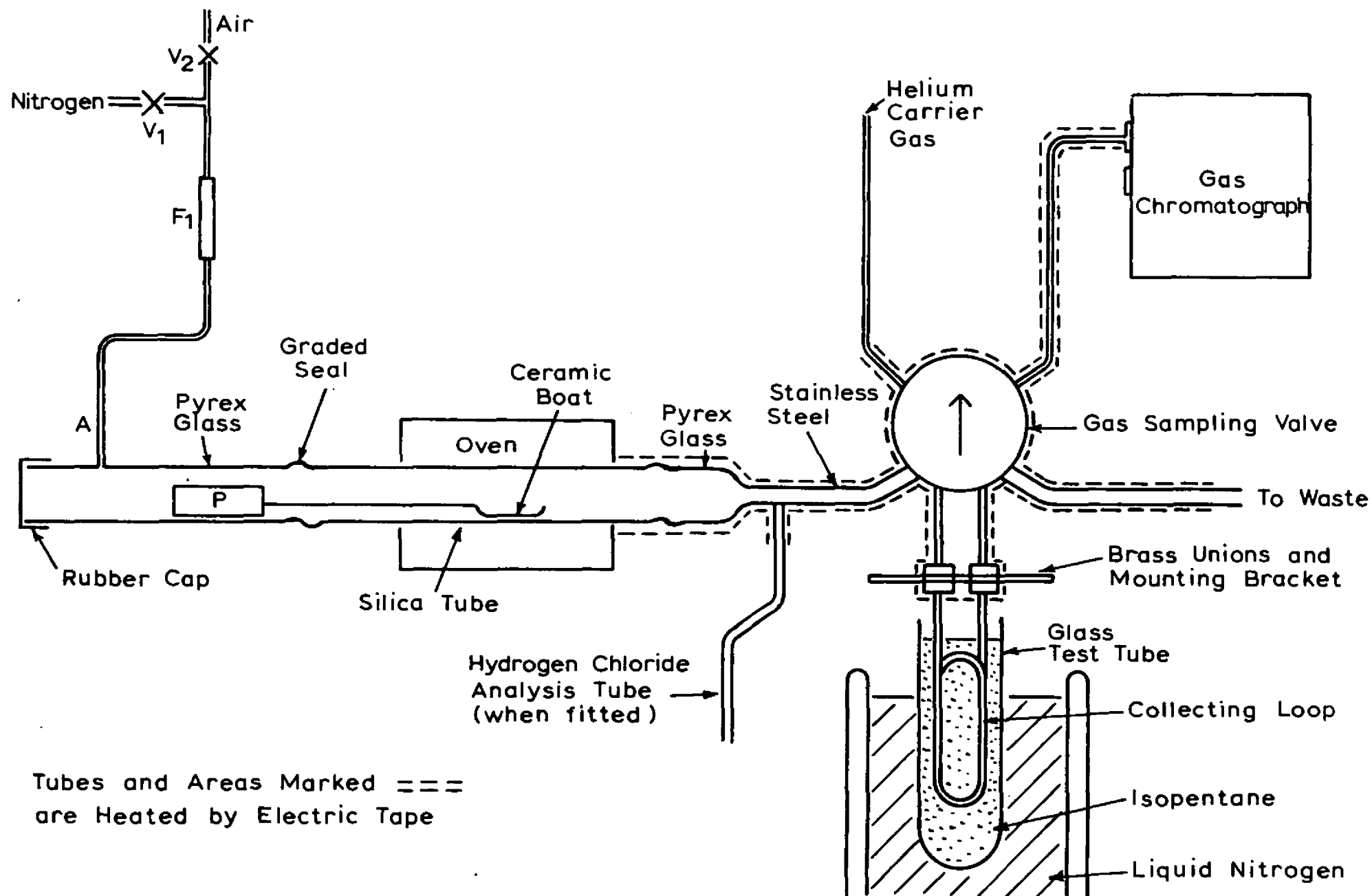


FIG. 2. THE DECOMPOSITION SYSTEM

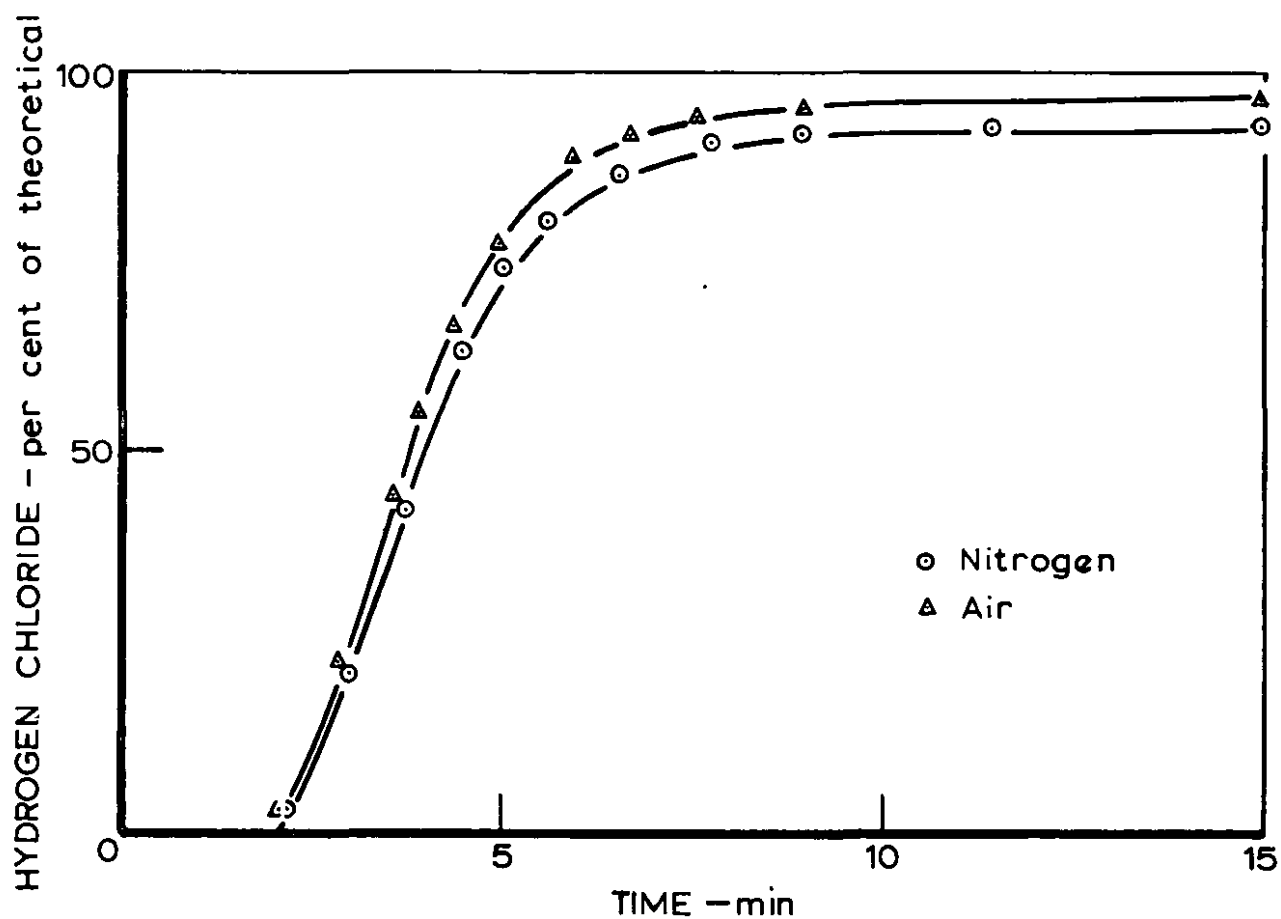


FIG. 3. FORMATION OF HYDROGEN CHLORIDE AT 300°C

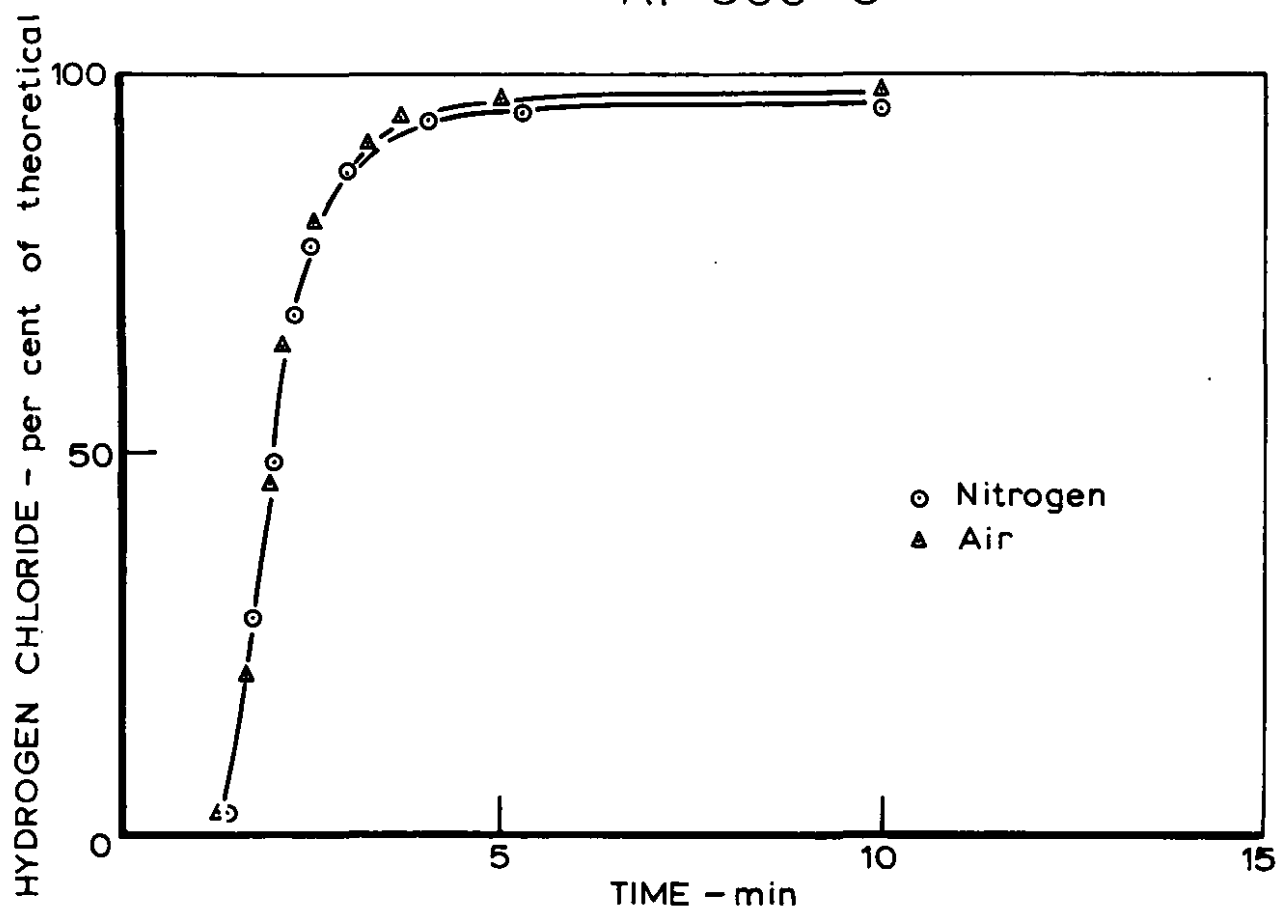


FIG. 4. FORMATION OF HYDROGEN CHLORIDE AT 350°C

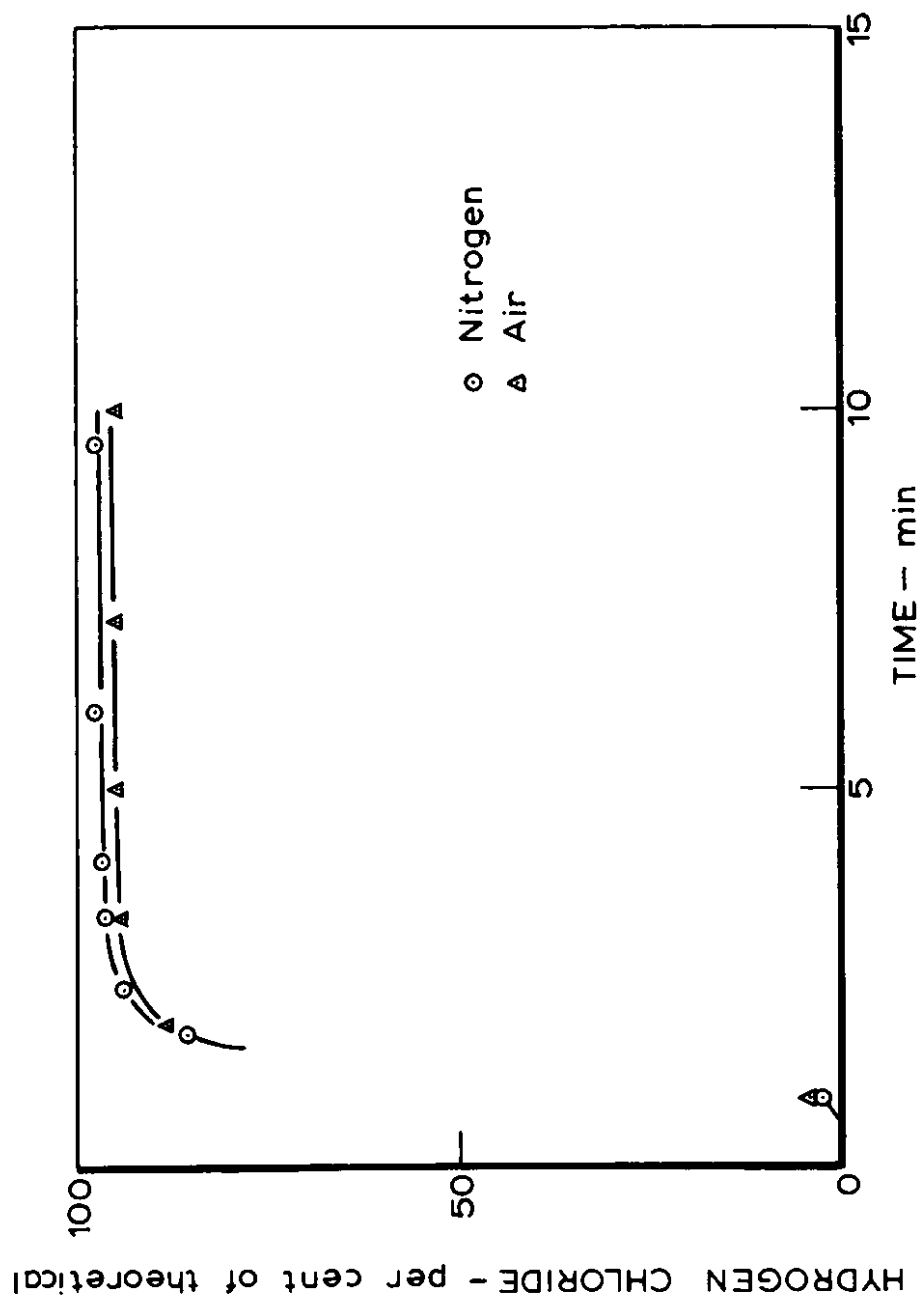


FIG. 5. FORMATION OF HYDROGEN CHLORIDE
AT 400°C

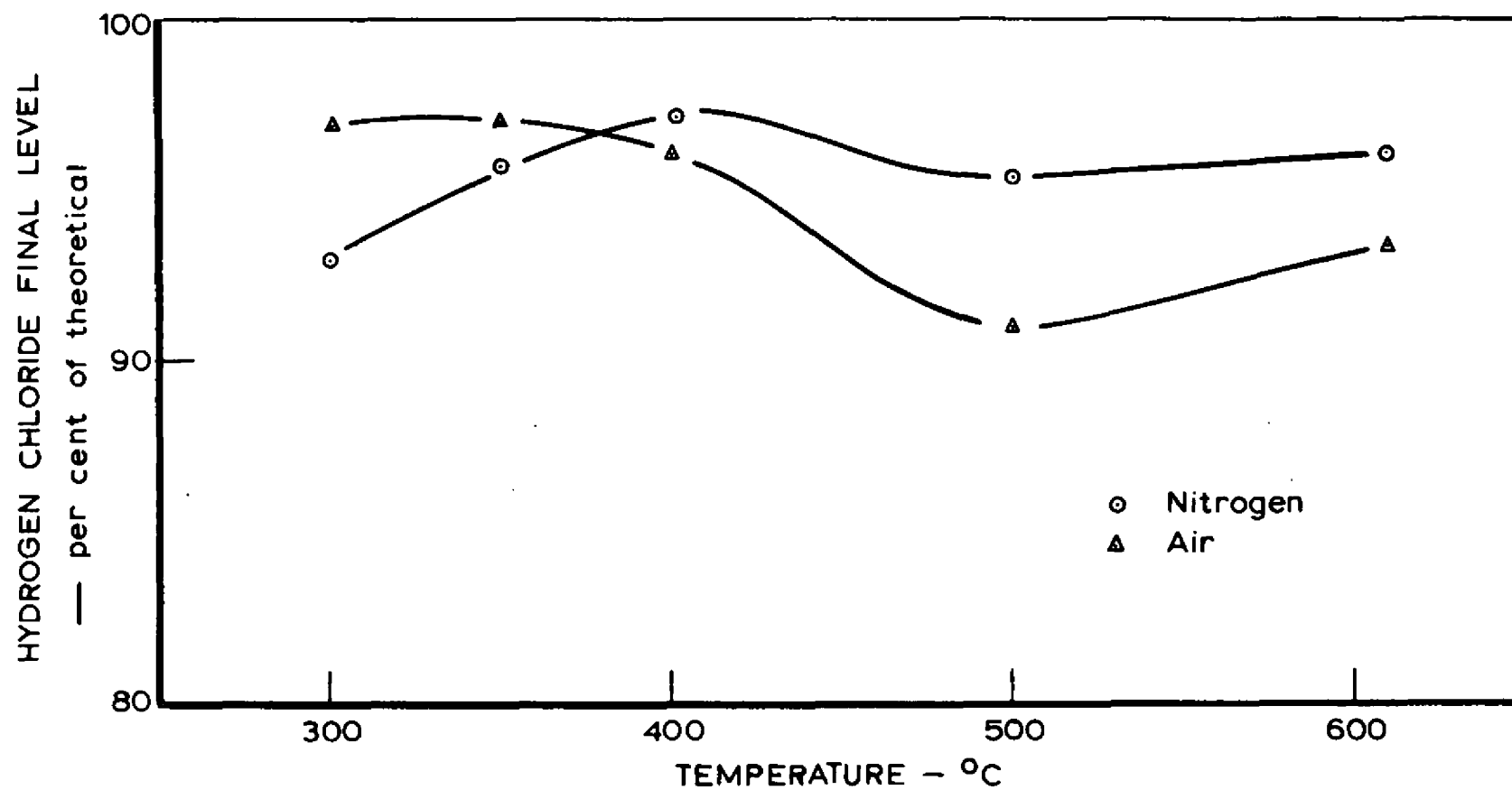
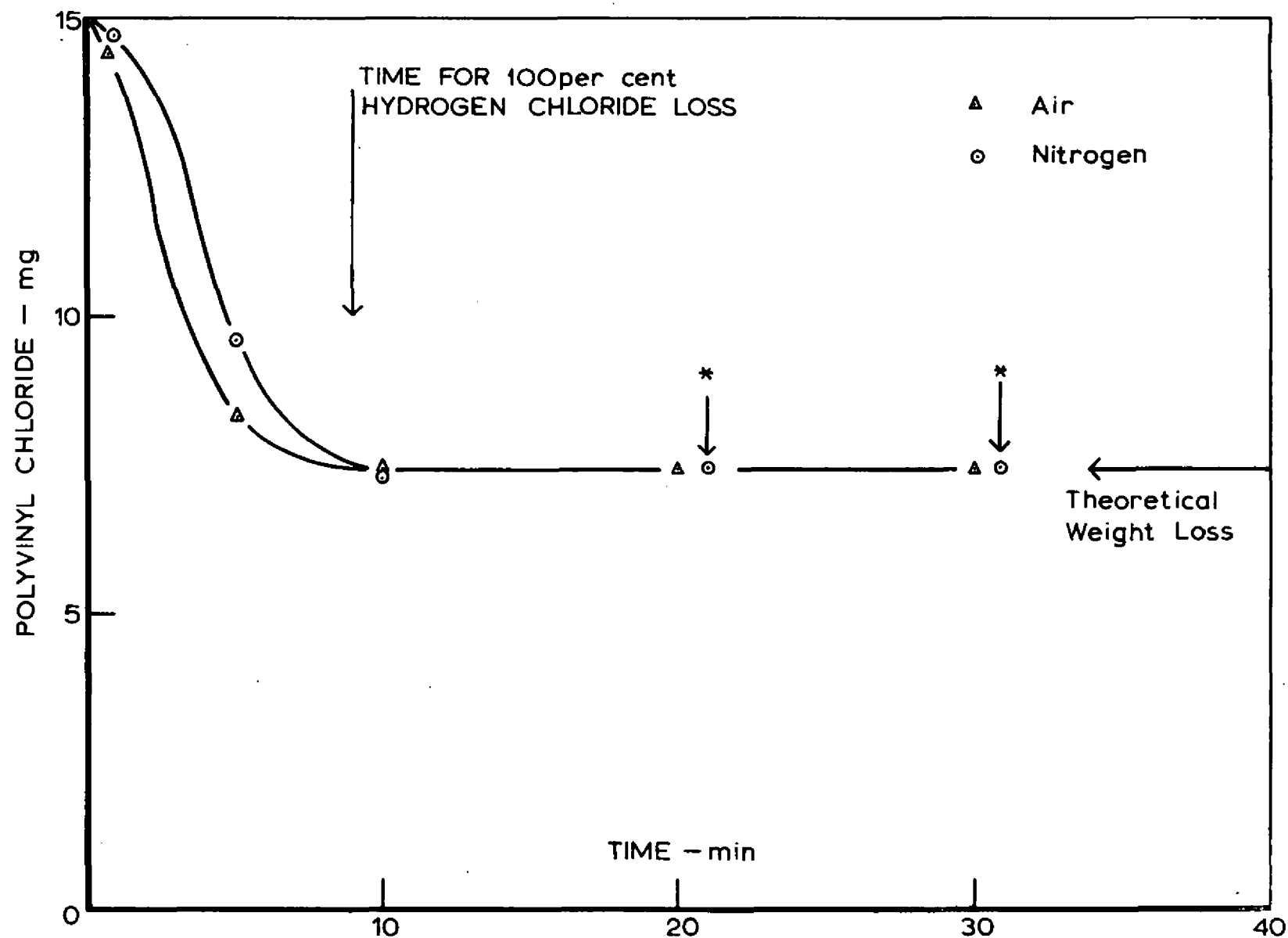


FIG. 6. REVERSAL OF TOTAL HYDROGEN CHLORIDE YIELD WITH TEMPERATURE



* These points have been moved 1 minute → to assist representation

FIG. 7. VARIATION OF POLYVINYL CHLORIDE WEIGHT WITH
TIME AT 300°C

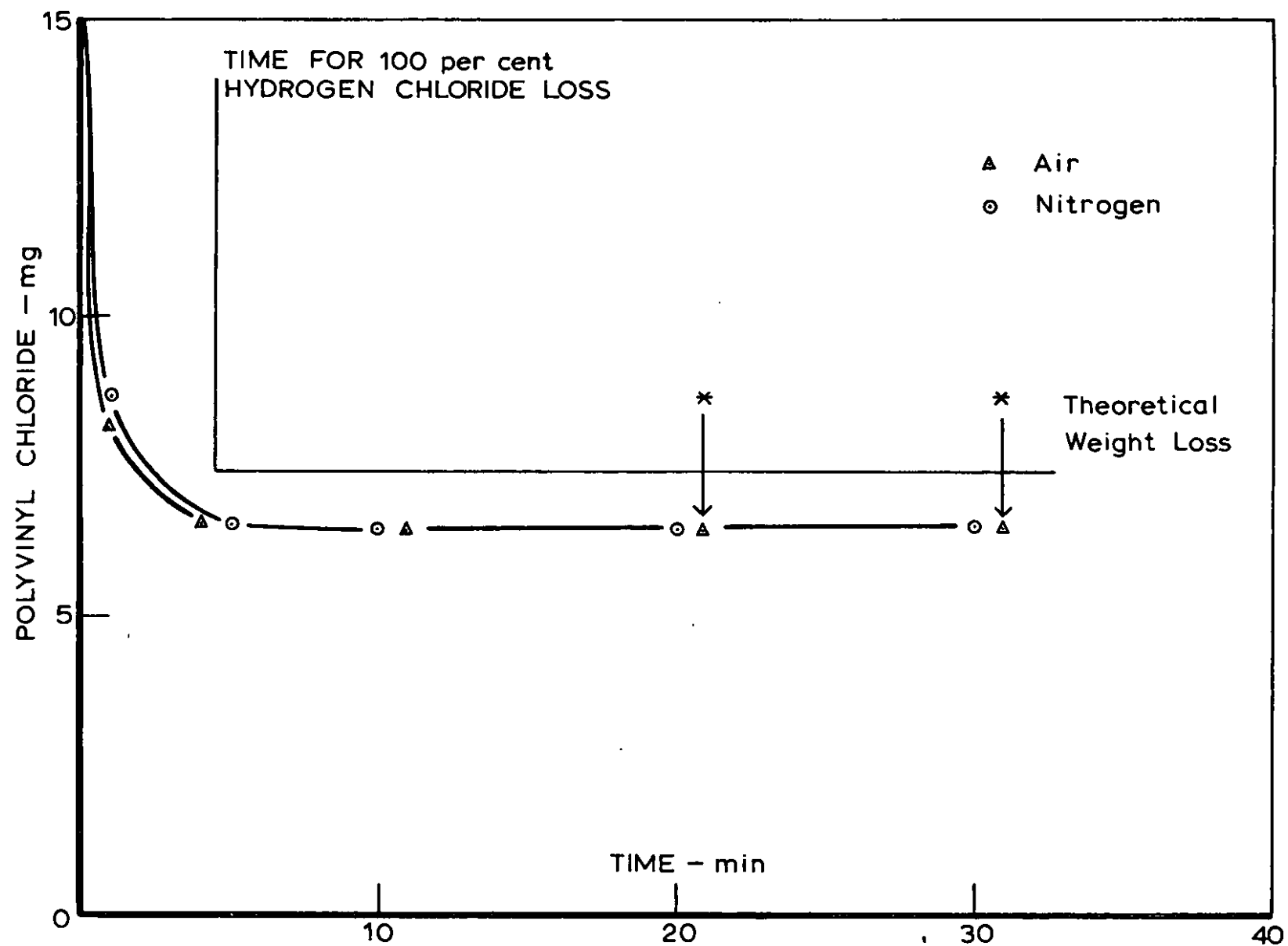


FIG. 8. VARIATION OF POLYVINYL CHLORIDE WEIGHT WITH
TIME AT 400°C

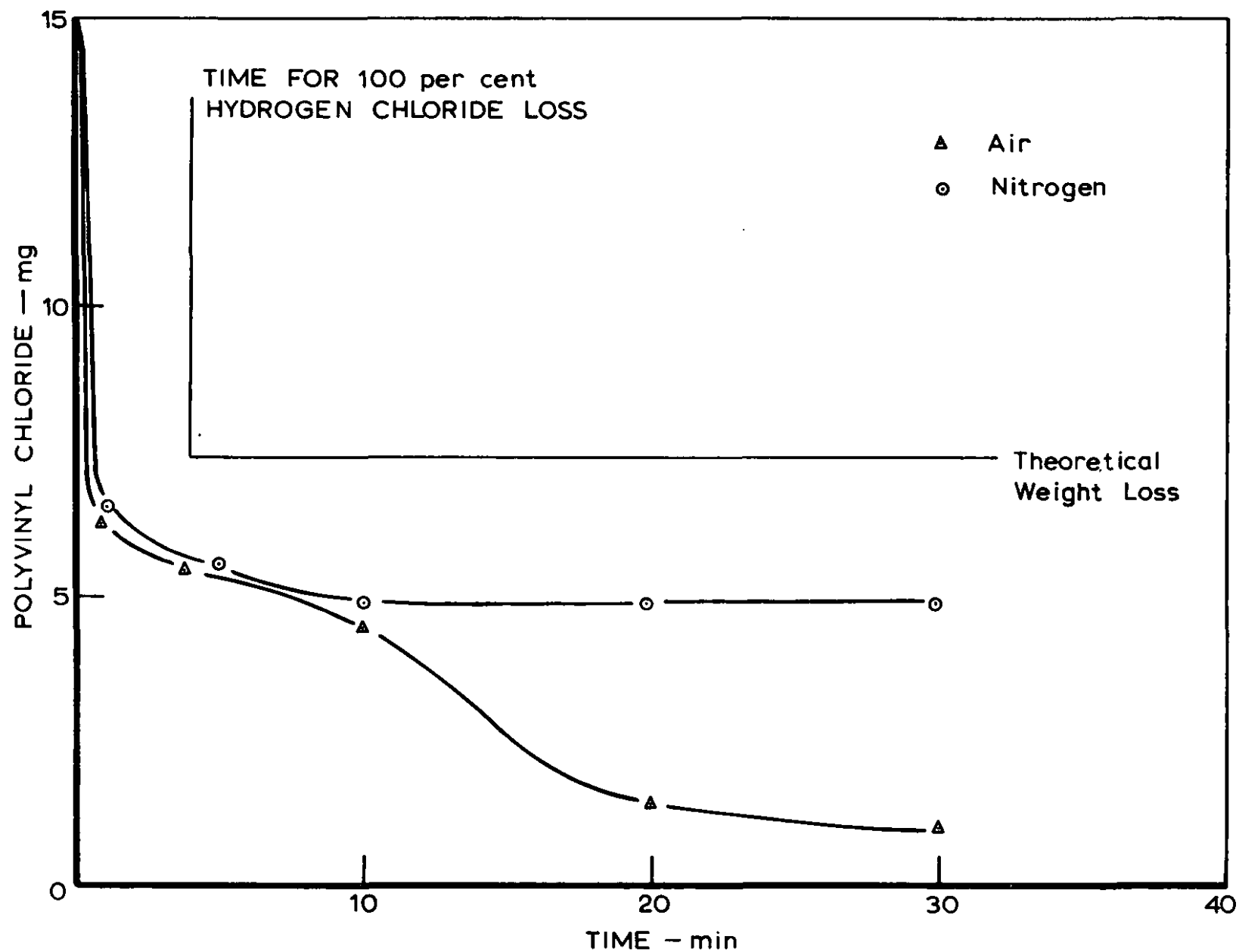


FIG. 9. VARIATION OF POLYVINYL CHLORIDE WEIGHT WITH TIME AT 450°C

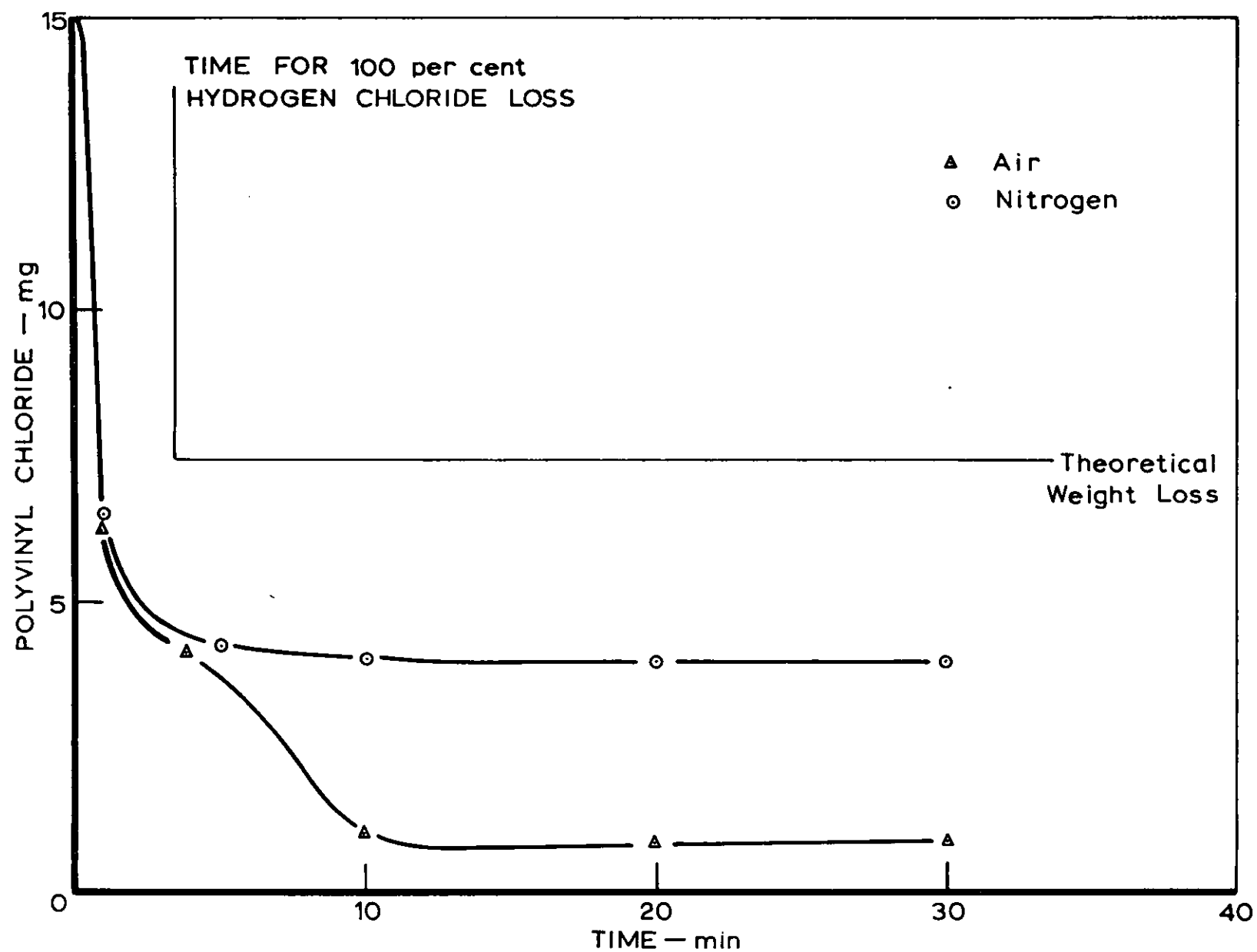


FIG. 10. VARIATION OF POLYVINYL CHLORIDE WEIGHT WITH TIME AT 500°C

Chromatogram showing the separation of aromatic compounds over 70 minutes. The x-axis is labeled "MINUTES" from 70 to 0. The y-axis is labeled "Attenuation x 16".

Key peaks and labels:

- Naphthalene**: Peak at approximately 65 minutes, labeled with m/z 75.
- Xylenes**: Peaks at approximately 38 minutes, labeled with m/z 49, 47, and 46. A label "o mp" is present near the 38-minute mark.
- Toluene**: Peaks at approximately 25 minutes, labeled with m/z 32 and 38.
- Benzene**: Peaks at approximately 15 minutes, labeled with m/z 32, 256, 25, and 24.
- Other labeled peaks include m/z 62, 41, 33, 29, 15, 14, 7,8, and 3,4.

Attenuation x 16

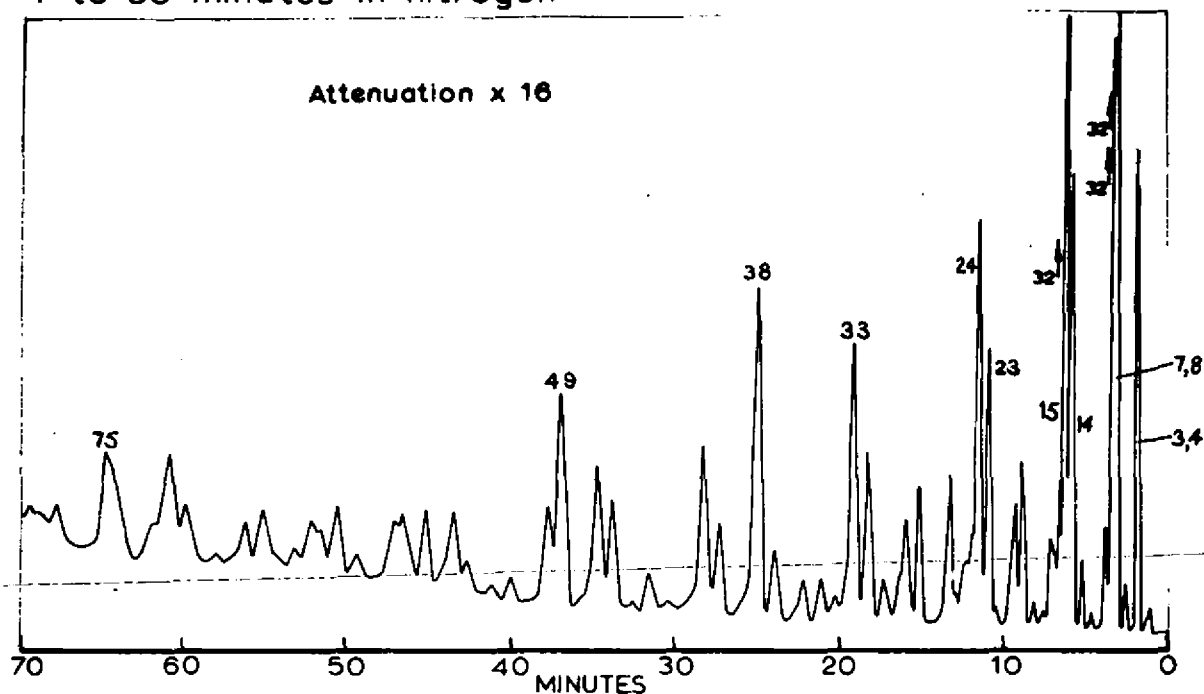
MINUTES

70 60 50 40 30 20 10 0

32 75 62 49 47 46 41 38 64 33 29 256 25 24 15 32 64 64 128 14 7,8 3,4

PRIMARY DECOMPOSITION PRODUCTS
OF P.V.C. IN NITROGEN AND AIR AT 450 °C

4 to 30 minutes in nitrogen



4 to 30 minutes in air

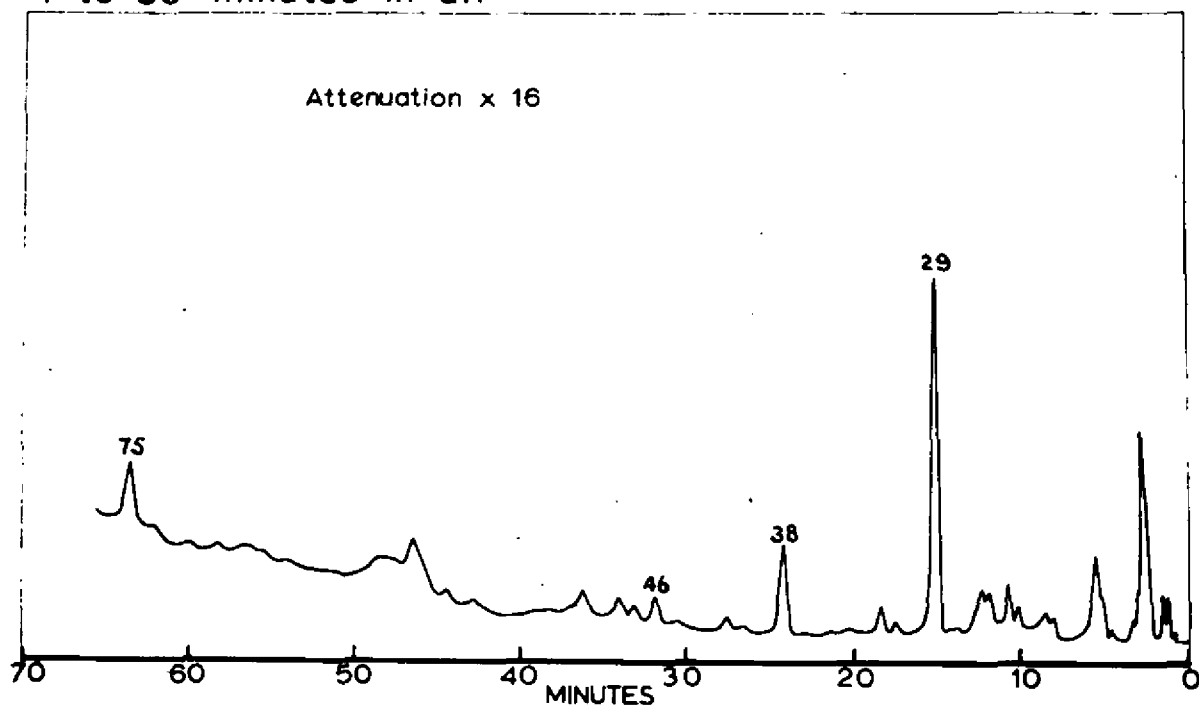
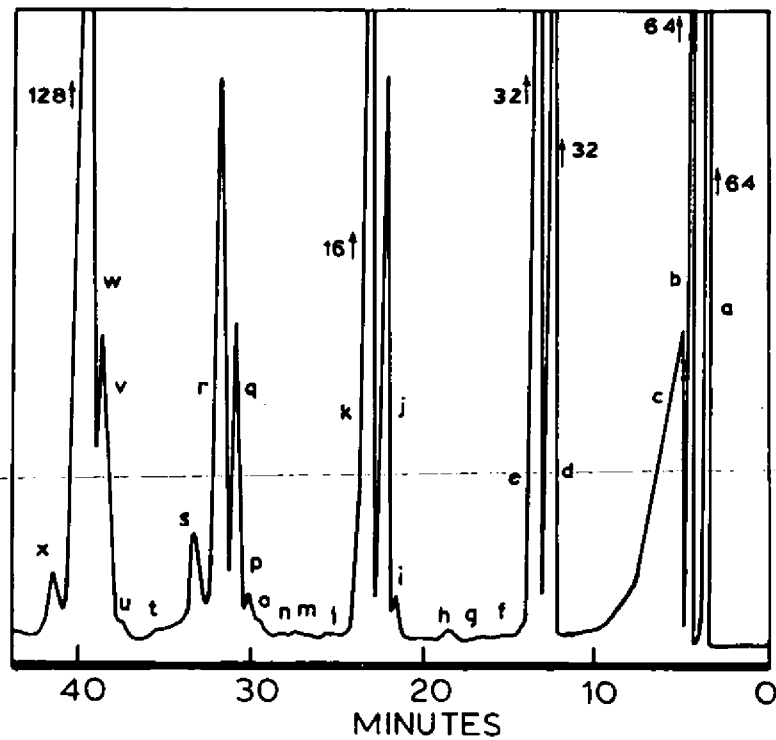


FIG. 13. and 14.

SECONDARY DECOMPOSITION PRODUCTS
OF P.V.C. IN NITROGEN AND AIR AT 450°C

0 to 30 minutes in nitrogen
Products collected at -196°C



0 to 30 minutes in air
Products collected at -160°C

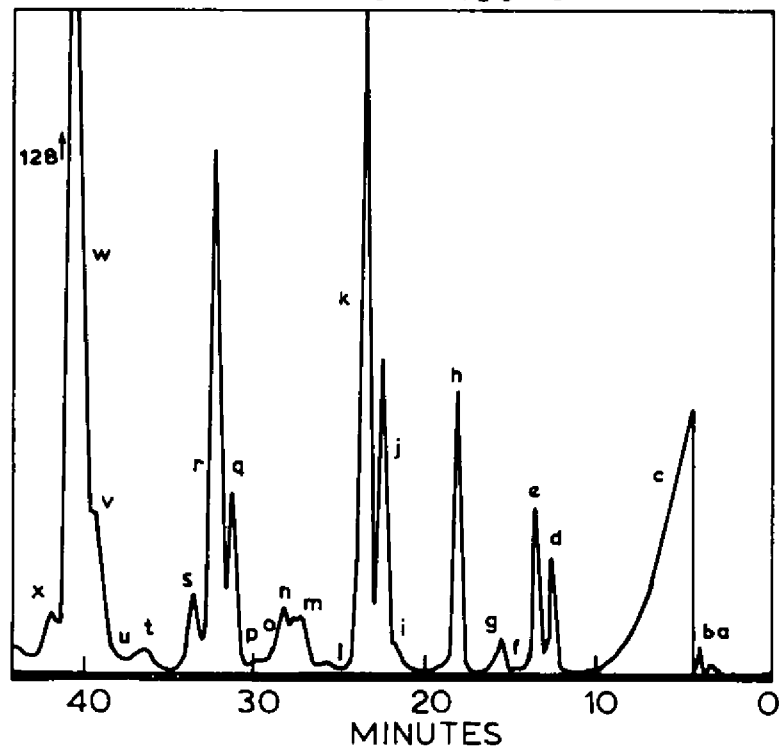
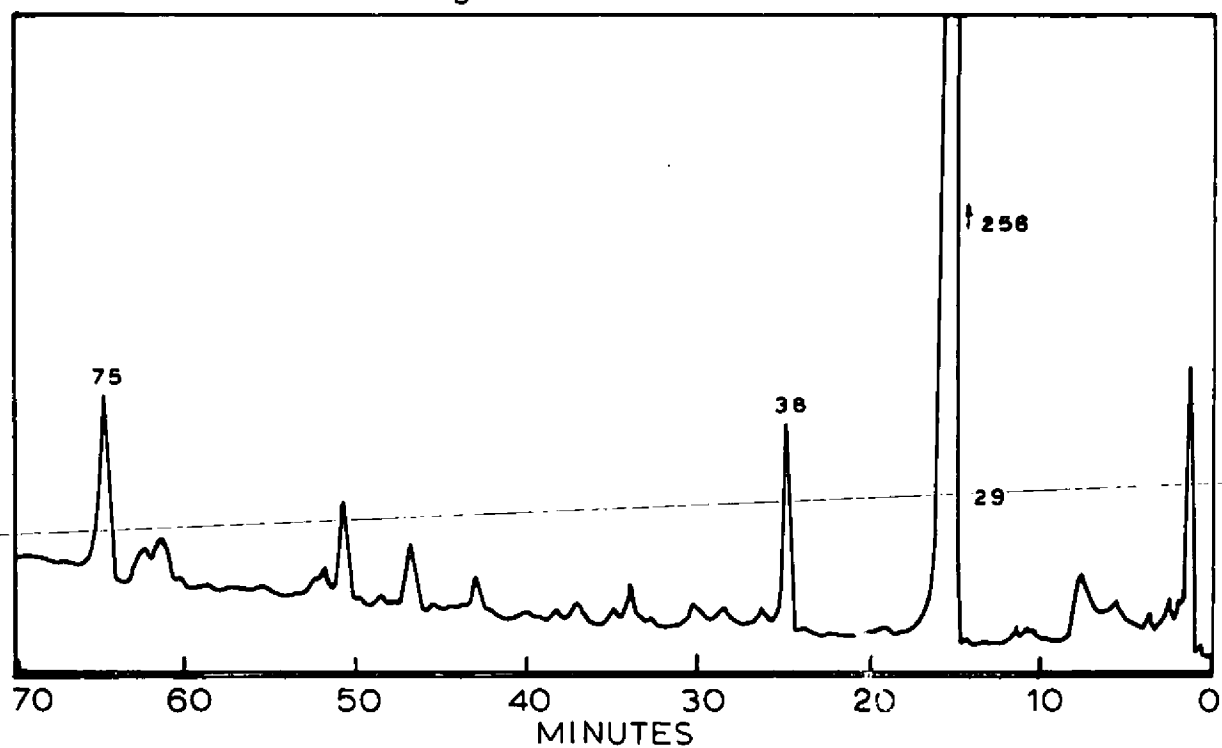


FIG. 15. and 16.
DECOMPOSITION PRODUCTS OF P.V.C.
IN NITROGEN AND AIR AT 450°C
SEPARATED BY PORAPAK Q.

0 to 5 minutes in nitrogen



0 to 5 minutes in air

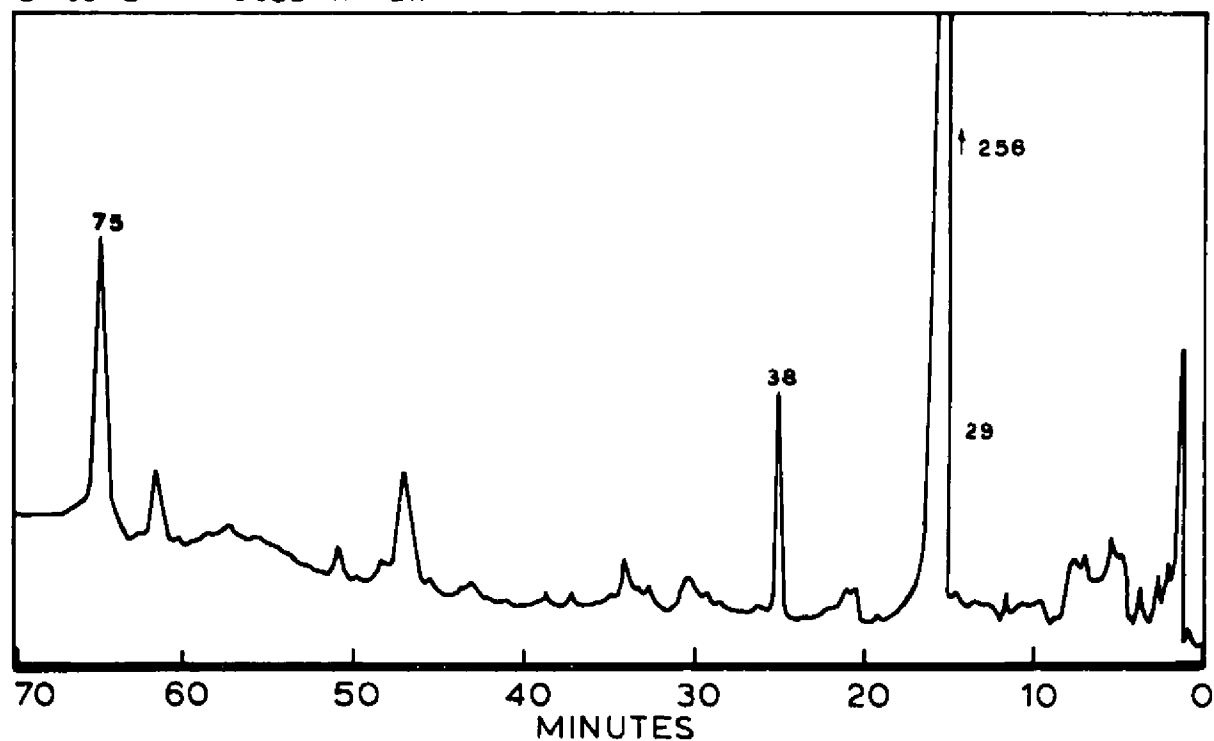
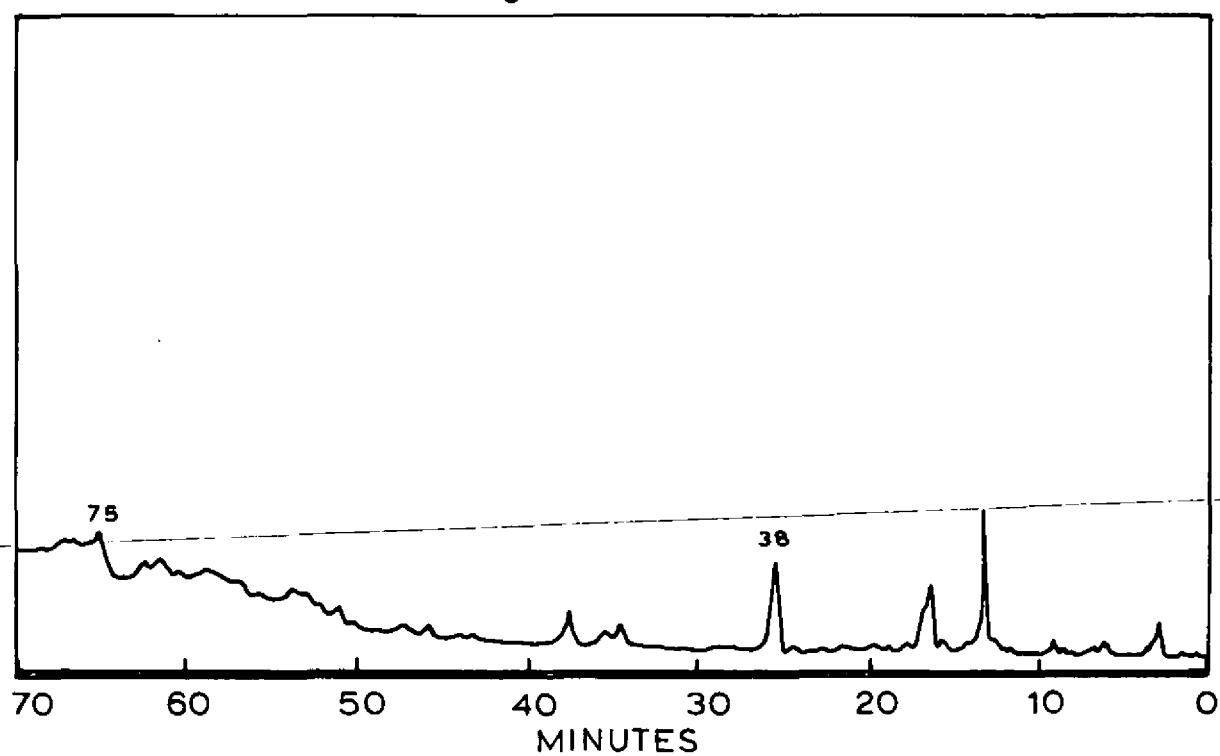


FIG. 17. and 18.

PRIMARY DECOMPOSITION PRODUCTS
OF P.V.C. IN NITROGEN AND AIR AT 350°C

5 to 30 minutes in nitrogen



5 to 30 minutes in air

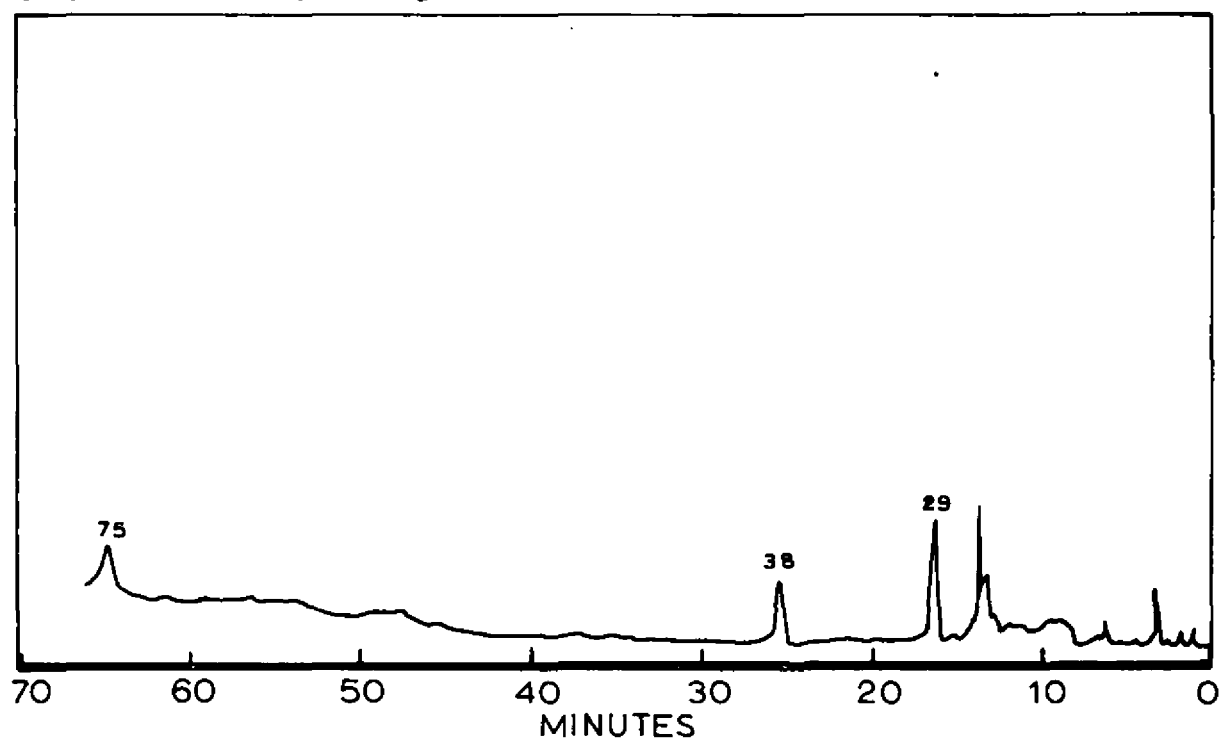


FIG. 19. and 20.

SECONDARY DECOMPOSITION PRODUCTS
OF P.V.C. IN NITROGEN AND AIR AT 350°C

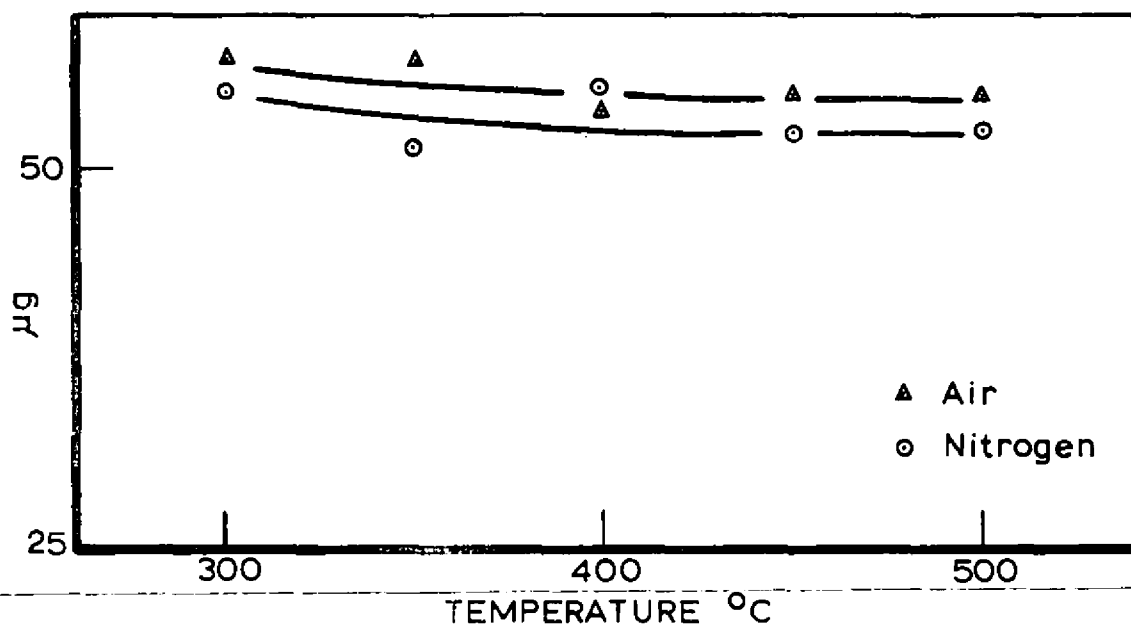


FIG. 21. PRIMARY STAGE PRODUCTION OF BENZENE IN NITROGEN AND AIR

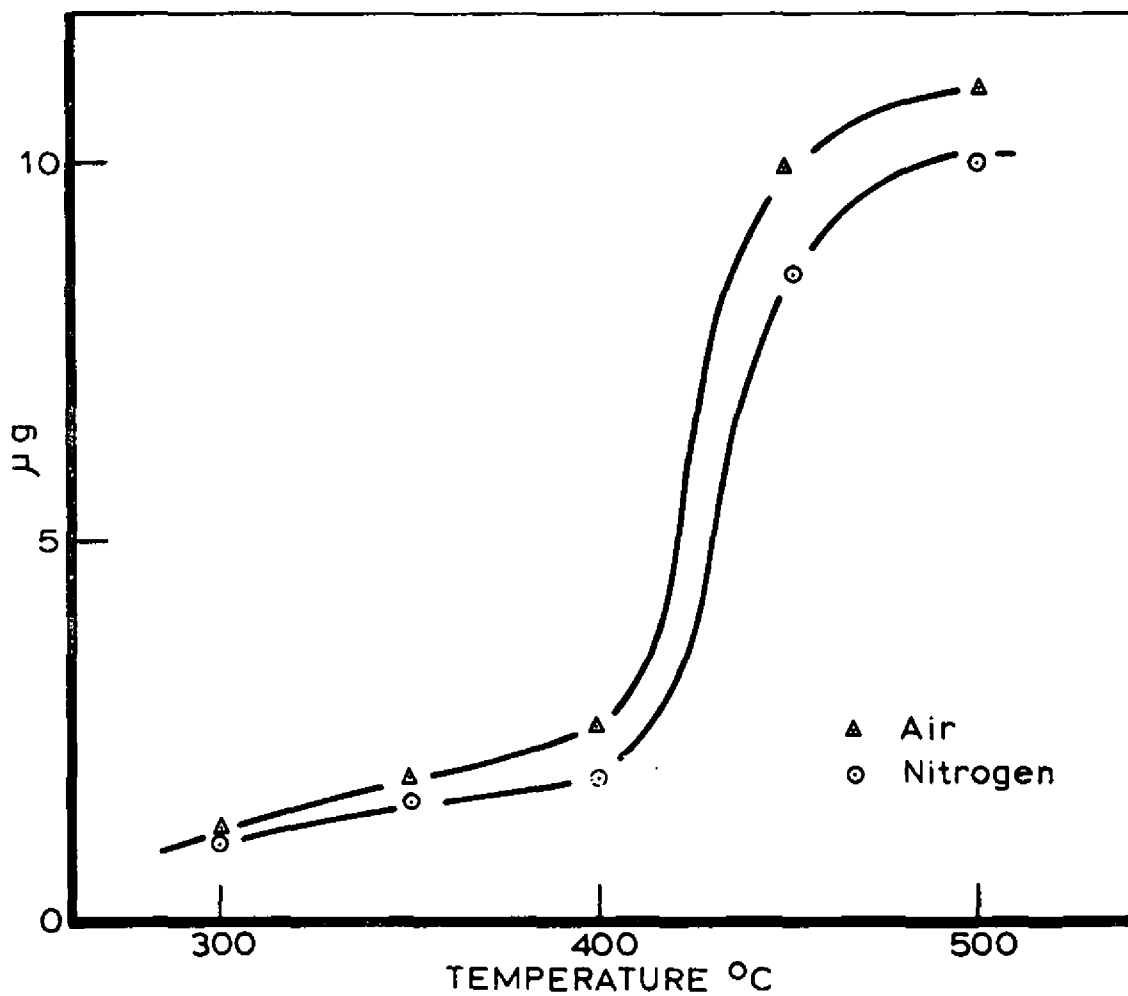


FIG. 22. PRIMARY STAGE PRODUCTION OF TOLUENE IN NITROGEN AND AIR

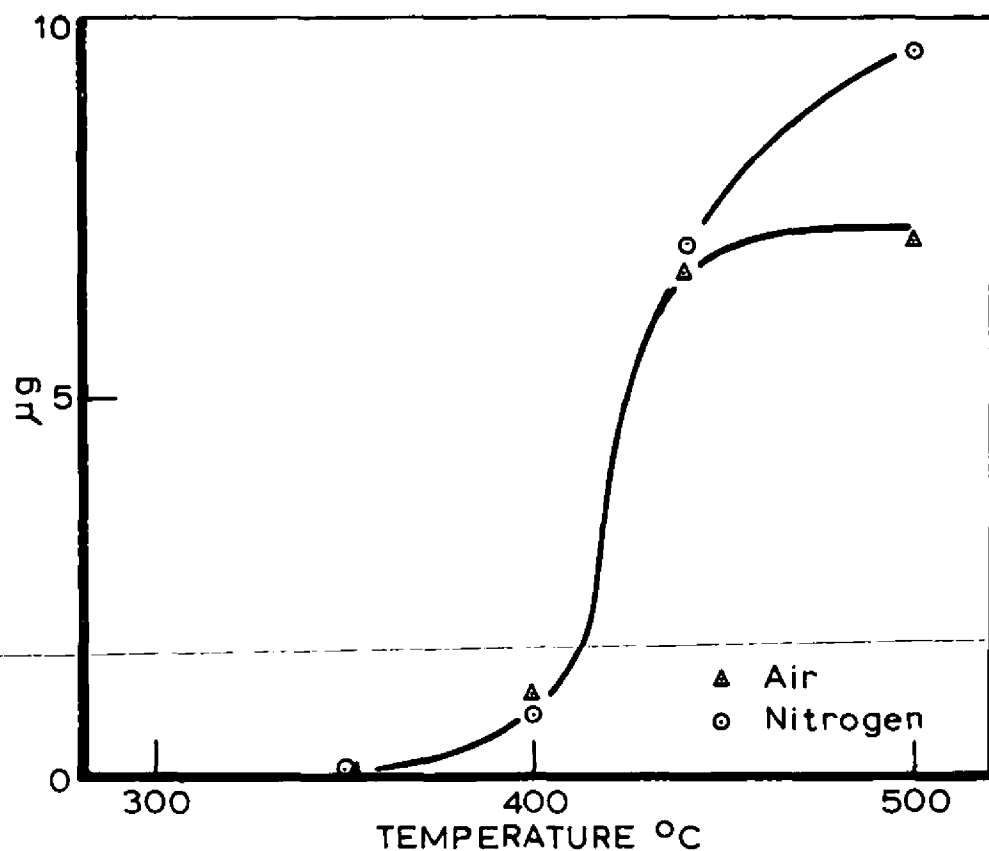


FIG. 23. PRIMARY STAGE PRODUCTION OF TOTAL XYLENE IN NITROGEN AND AIR

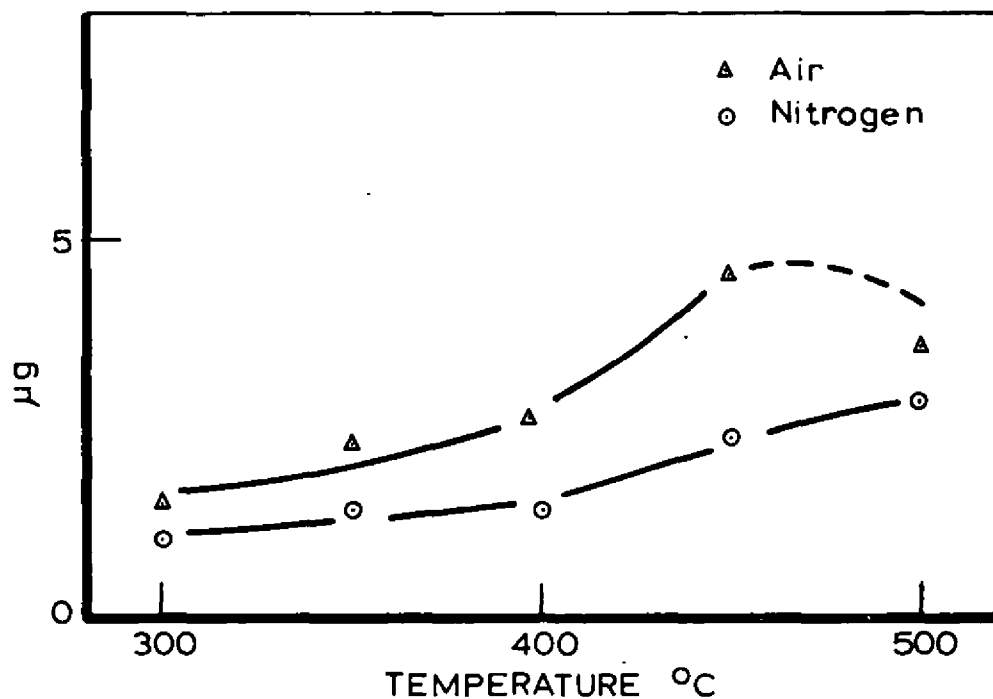


FIG. 24. PRIMARY STAGE PRODUCTION OF NAPHTHALENE IN NITROGEN AND AIR

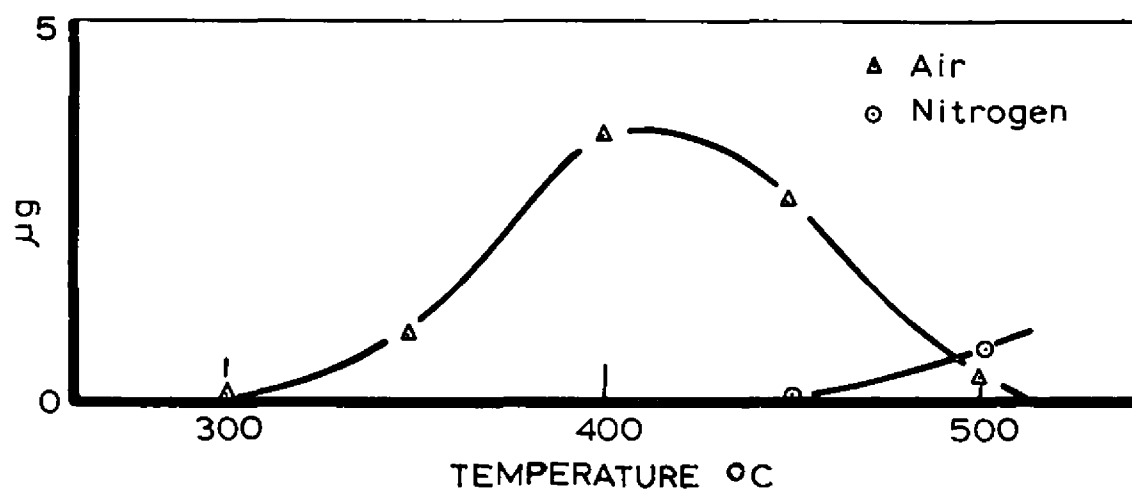


FIG. 25. SECONDARY STAGE PRODUCTION OF BENZENE IN NITROGEN AND AIR

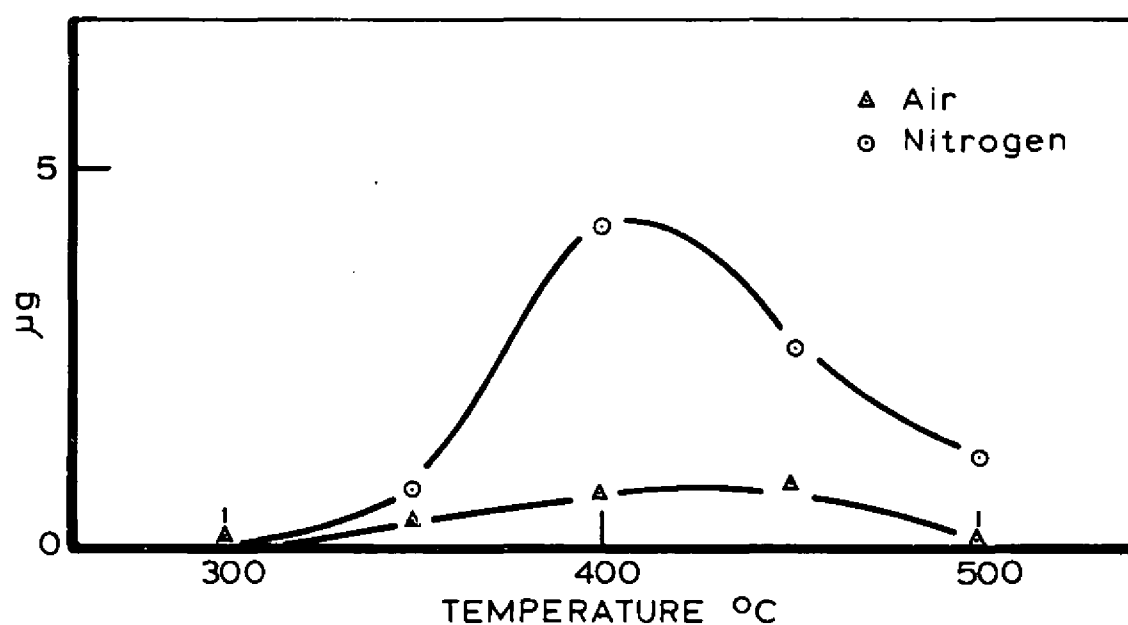


FIG. 26. SECONDARY STAGE PRODUCTION OF TOLUENE IN NITROGEN AND AIR

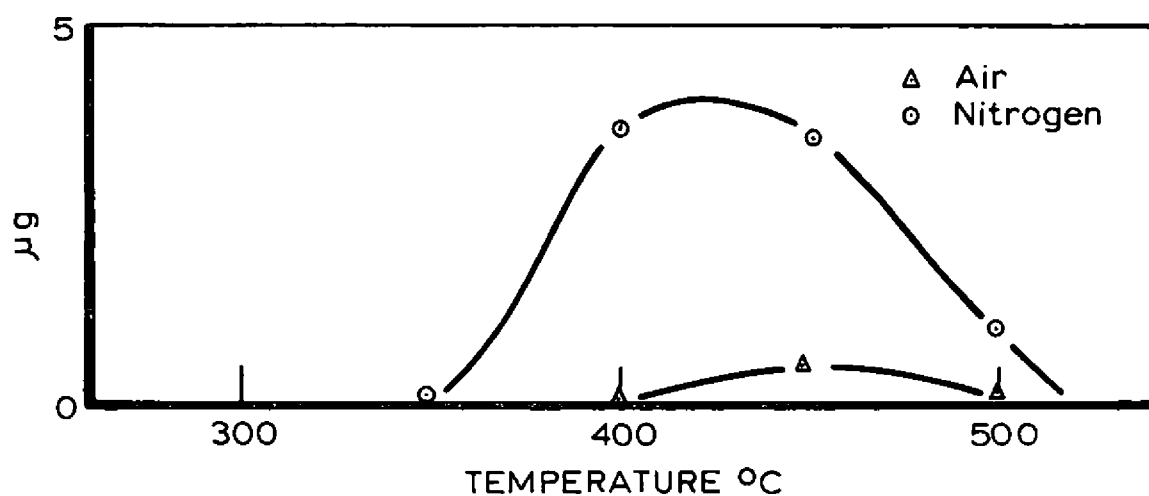


FIG. 27. SECONDARY STAGE PRODUCTION OF TOTAL XYLENE IN NITROGEN AND AIR

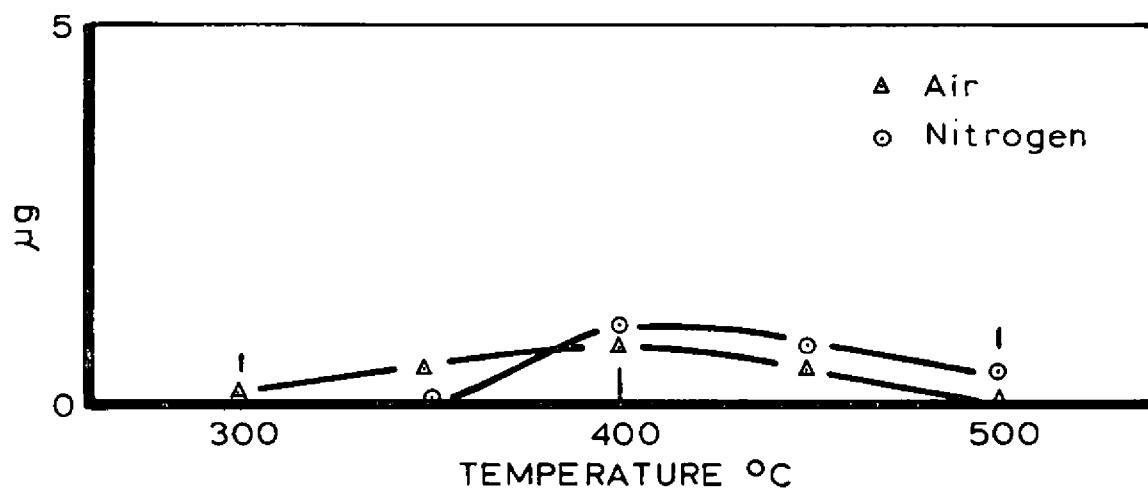


FIG. 28. SECONDARY STAGE PRODUCTION OF NAPHTHALENE IN NITROGEN AND AIR

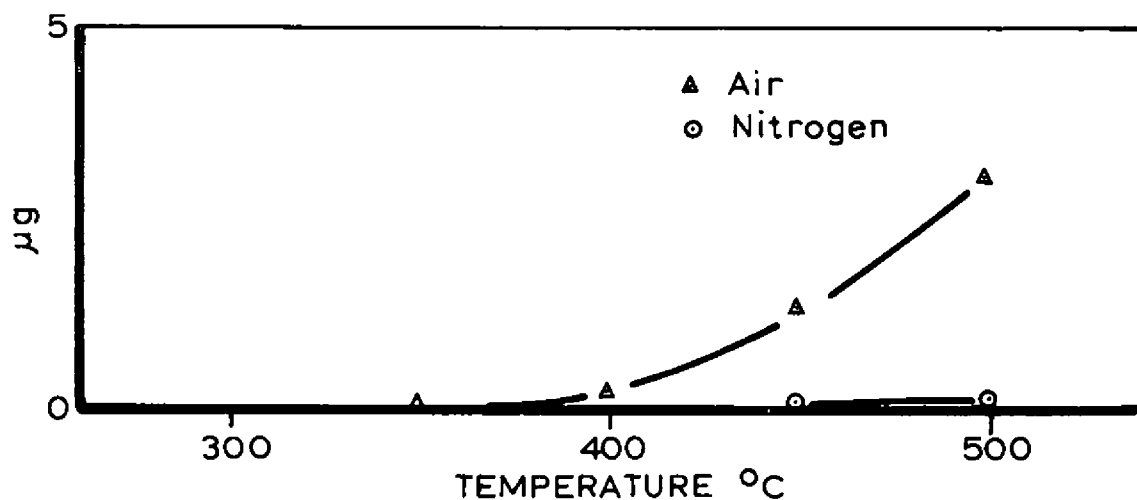


FIG. 29. PRIMARY STAGE PRODUCTION OF VINYL CHLORIDE IN NITROGEN AND AIR

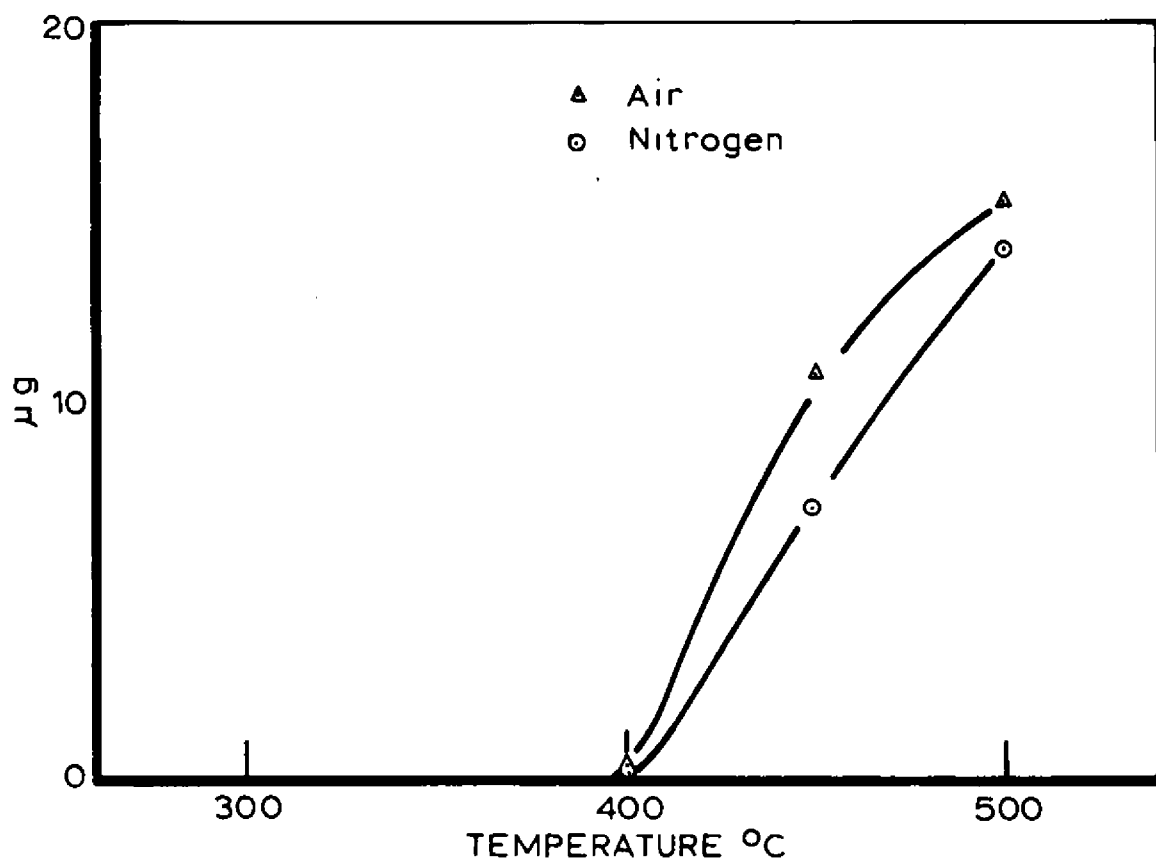
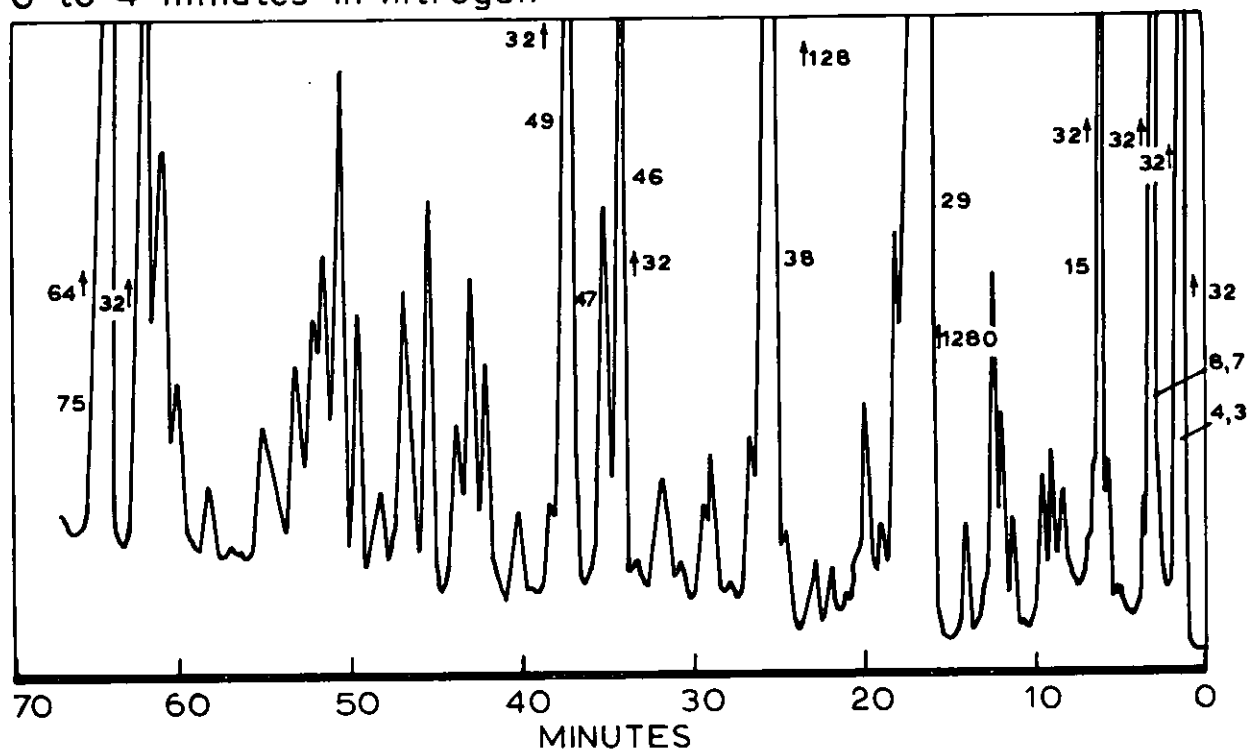


FIG. 30. PRIMARY STAGE PRODUCTION OF TOTAL C₄ HYDROCARBONS IN NITROGEN AND AIR

0 to 4 minutes in nitrogen



0 to 4 minutes in air

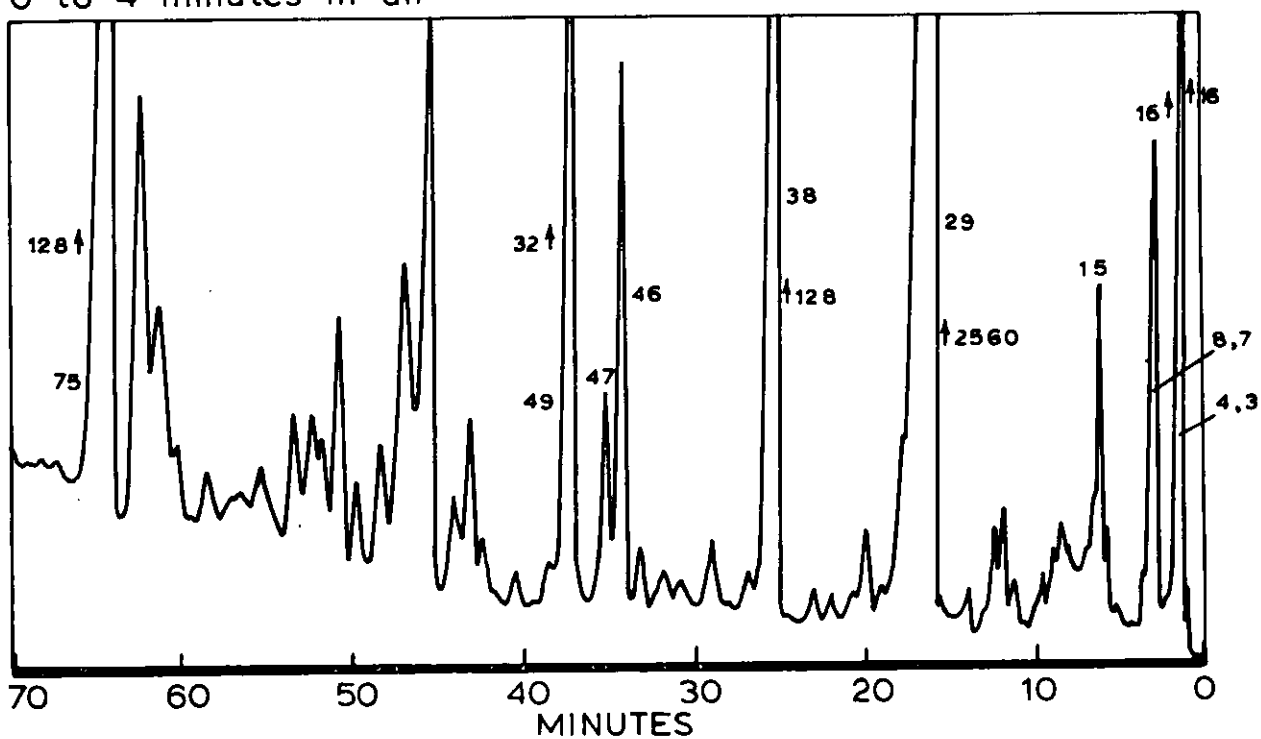
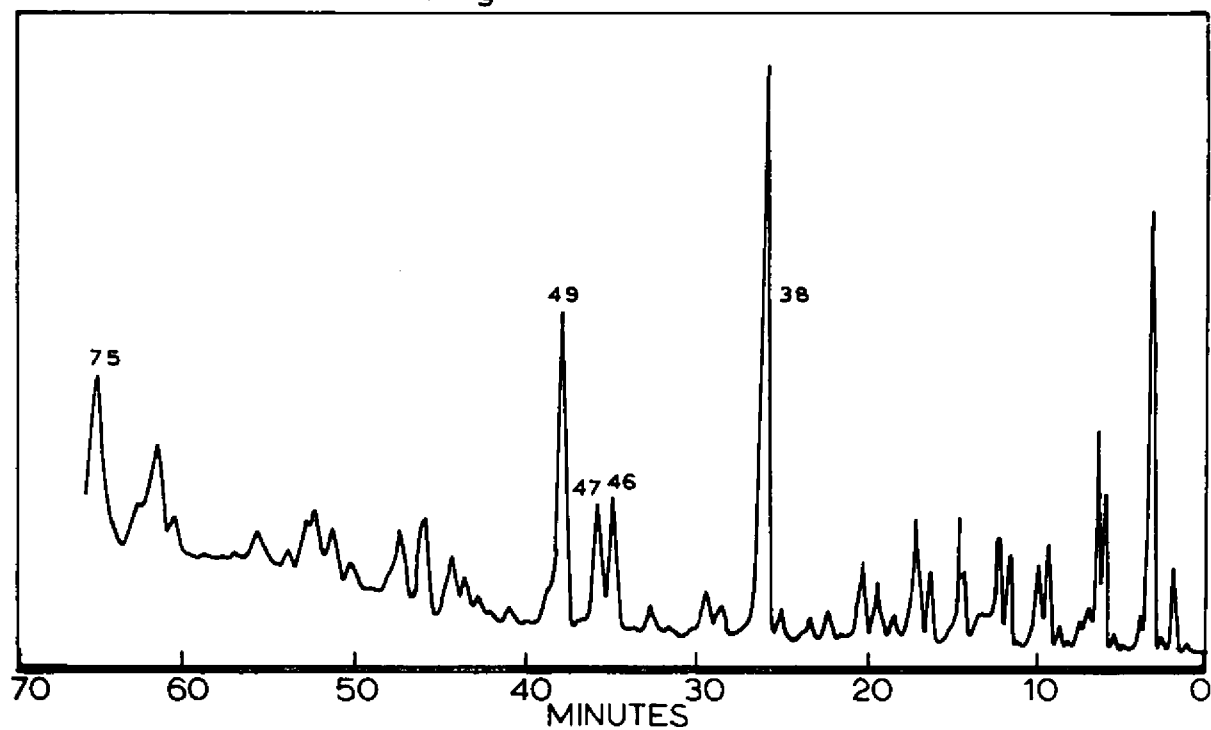


FIG. 31, and 32.

PRIMARY DECOMPOSITION PRODUCTS
OF A PURE P.V.C. POLYMER AT 450°C
IN NITROGEN AND AIR

4 to 30 minutes in nitrogen



4 to 30 minutes in air

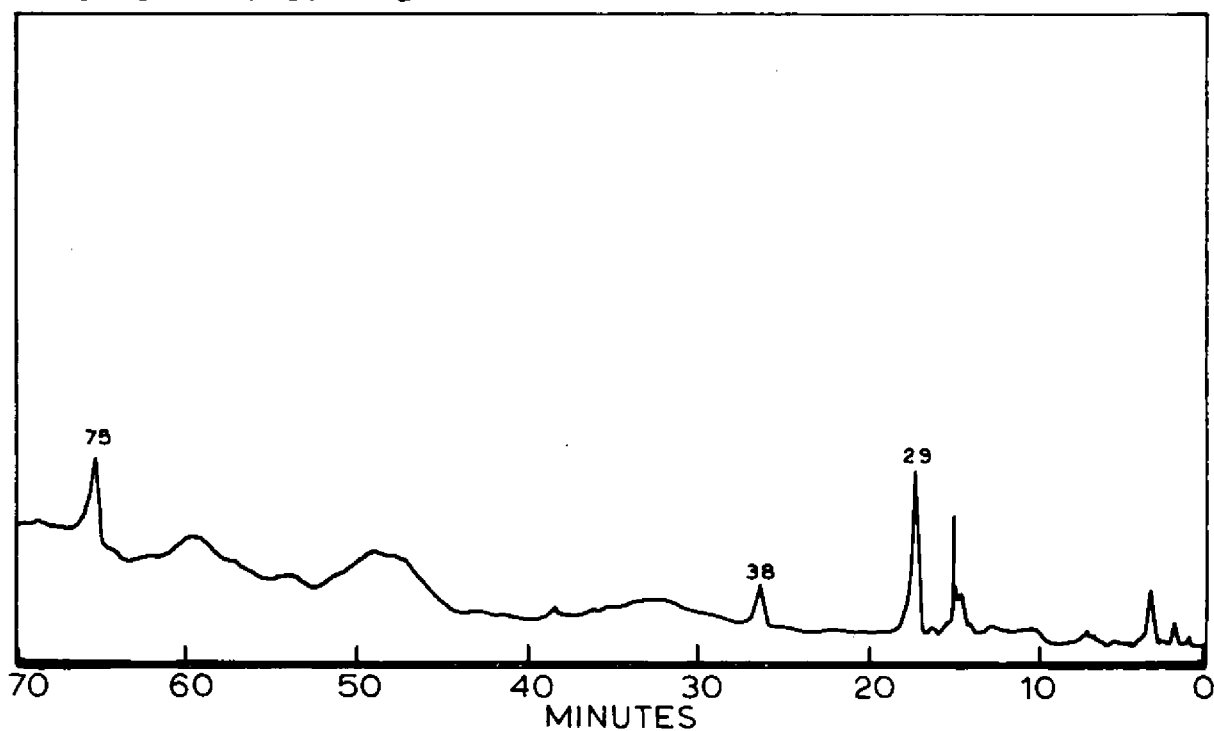


FIG. 33. and 34.
SECONDARY DECOMPOSITION PRODUCTS
OF A PURE P.V.C. POLYMER AT 450°C
IN NITROGEN AND AIR

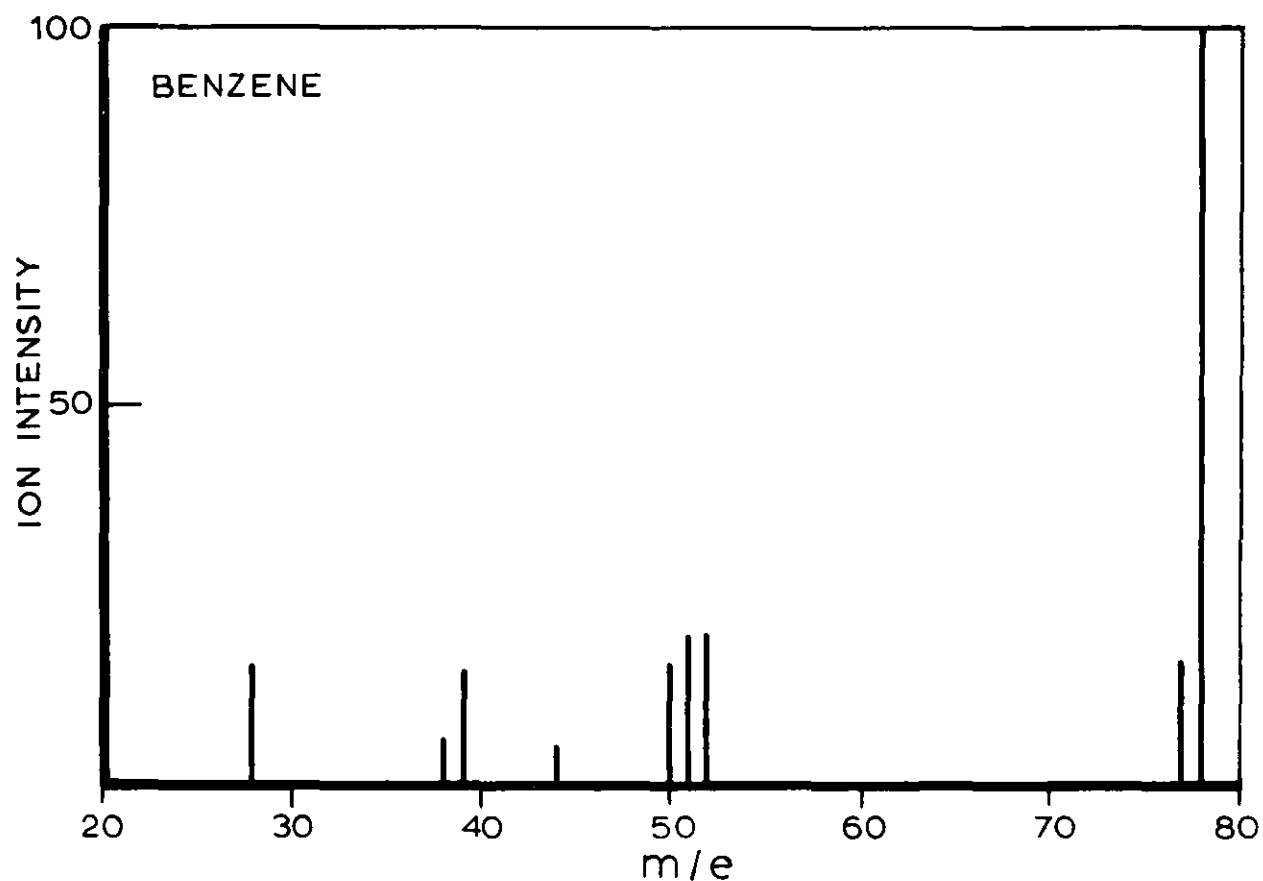


FIG. 35. MASS SPECTRUM OF PEAK 29 FROM SILICONE GREASE. RANGE 10. SLOW LEAK.

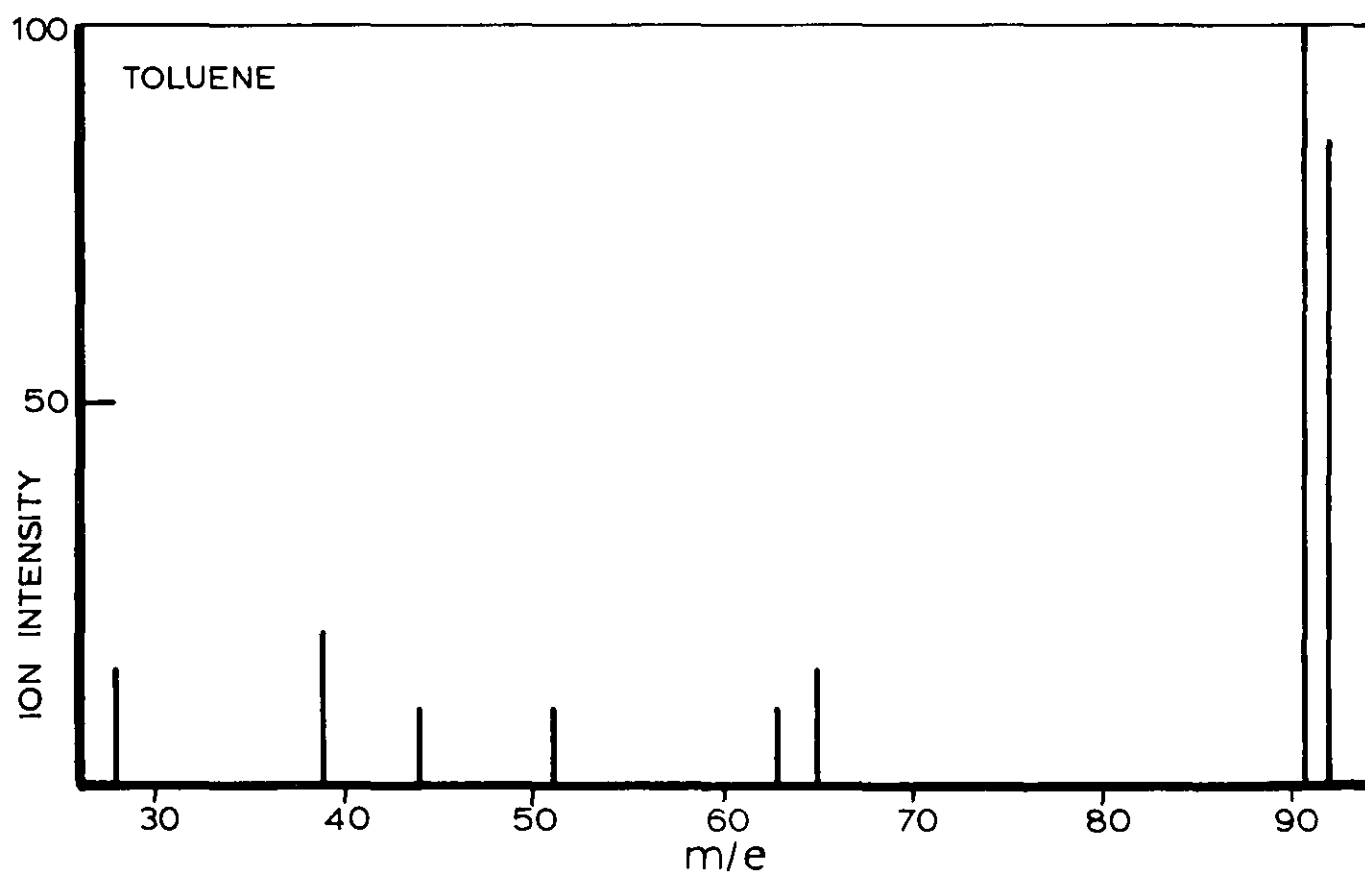


FIG. 36. MASS SPECTRUM OF PEAK 38 FROM SILICONE GREASE. RANGE 2.5. SLOW LEAK.

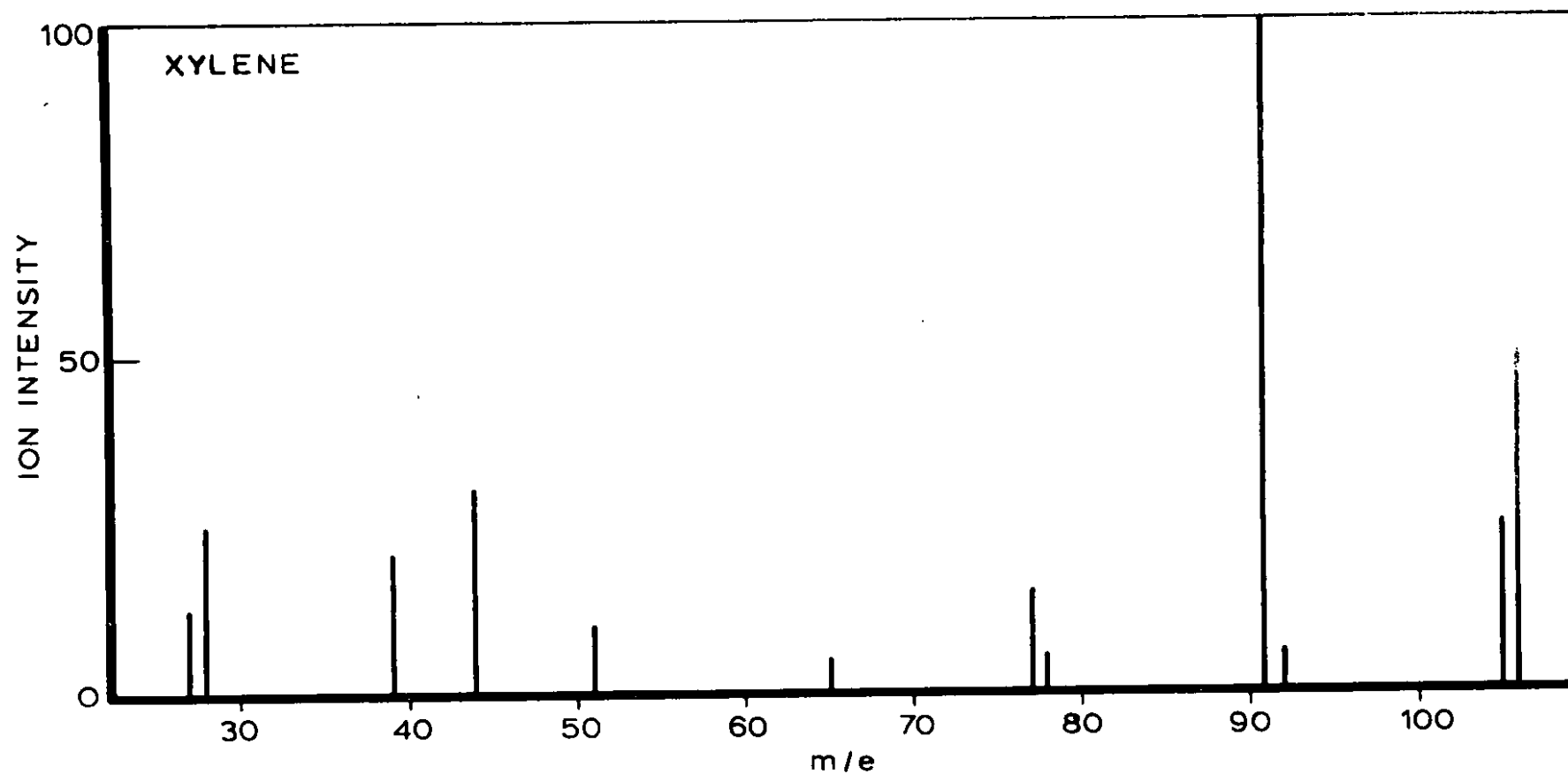


FIG. 37. MASS SPECTRUM OF PEAK 46 FROM SILICONE GREASE
RANGE 100. FAST LEAK.

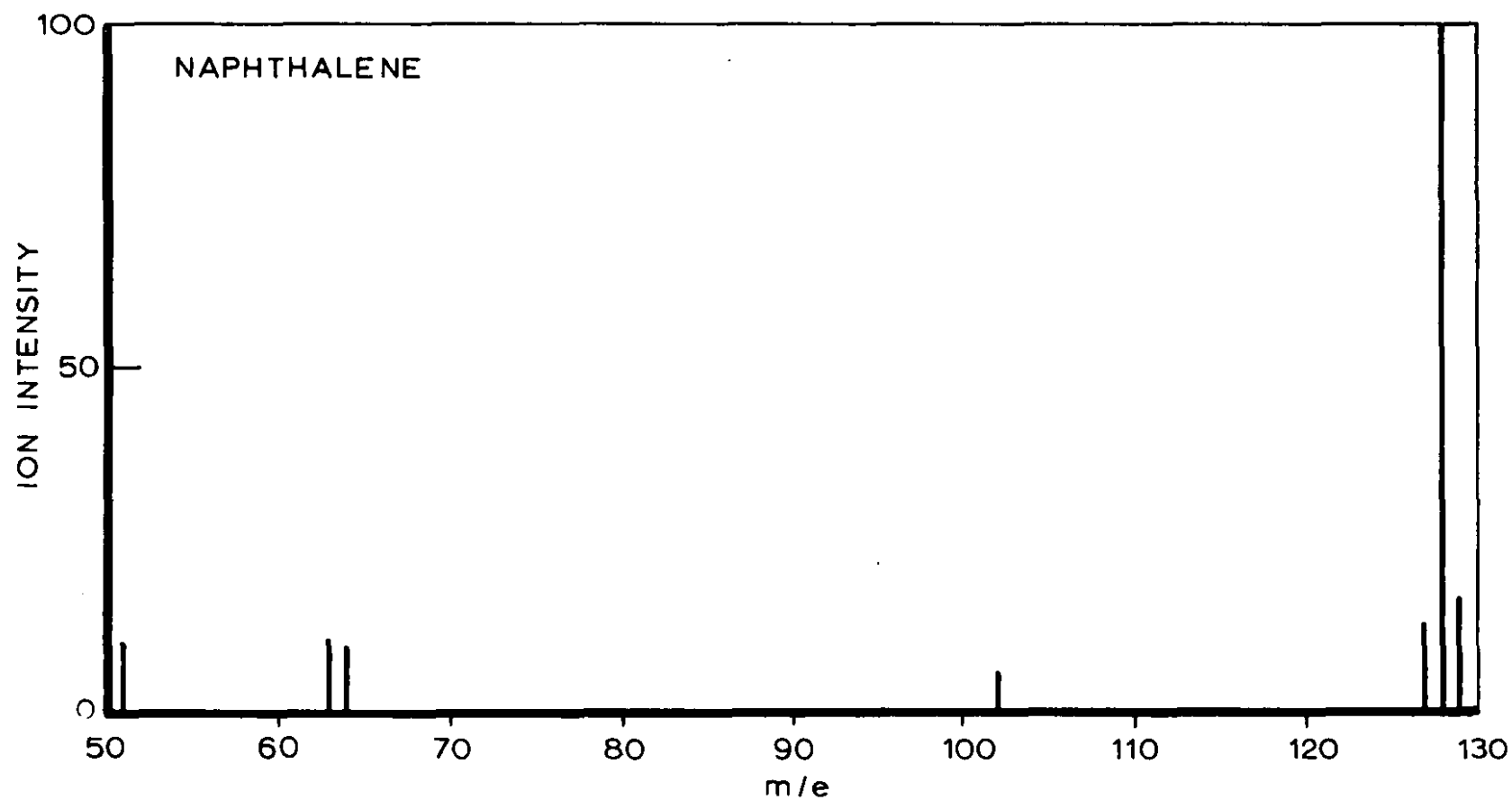


FIG. 38. MASS SPECTRUM OF PEAK 75 FROM SILICONE GREASE RANGE 10. FAST LEAK.

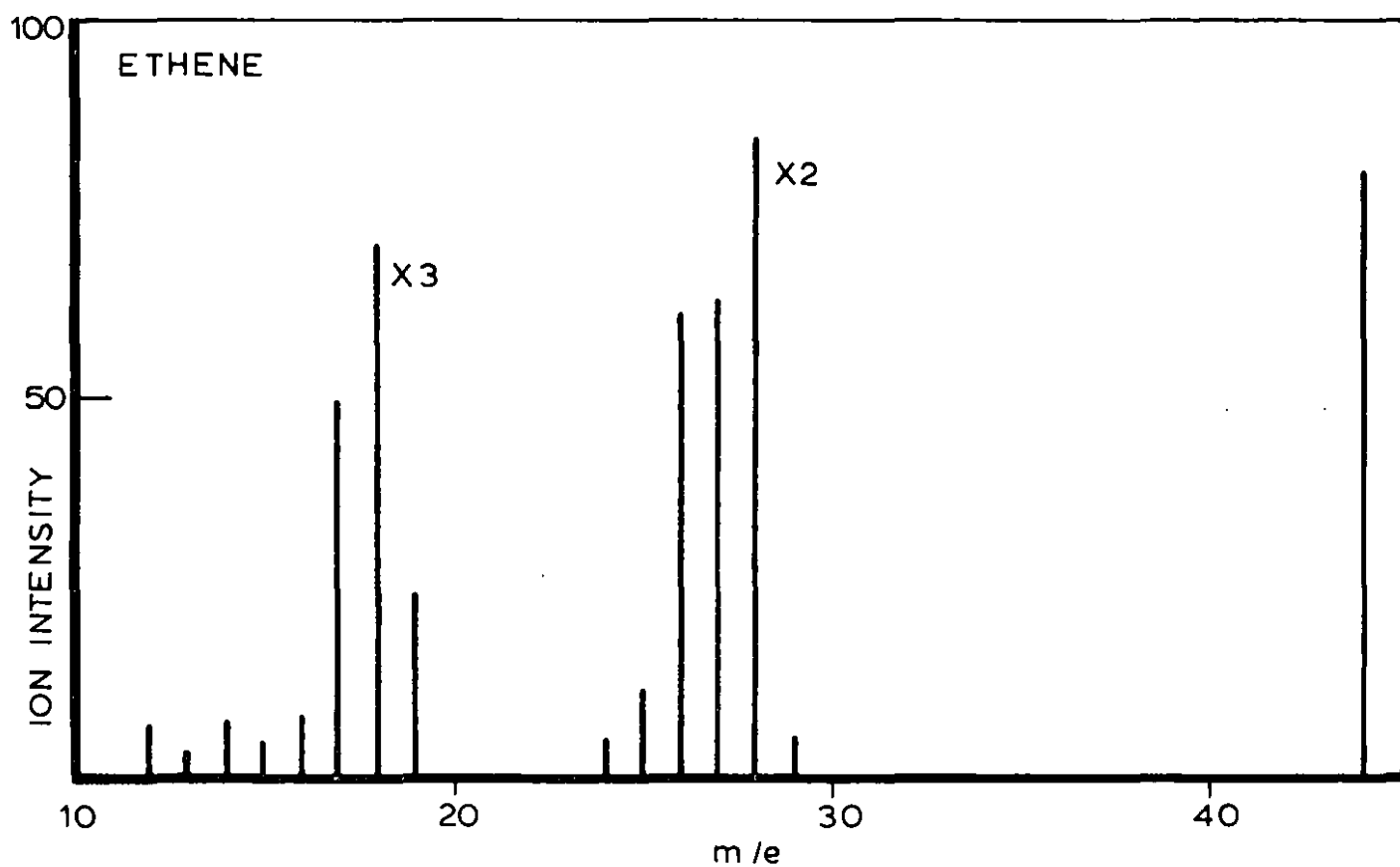


FIG. 39. MASS SPECTRUM OF PEAK a FROM PORAPAK. RANGE 2.5. FAST LEAK.

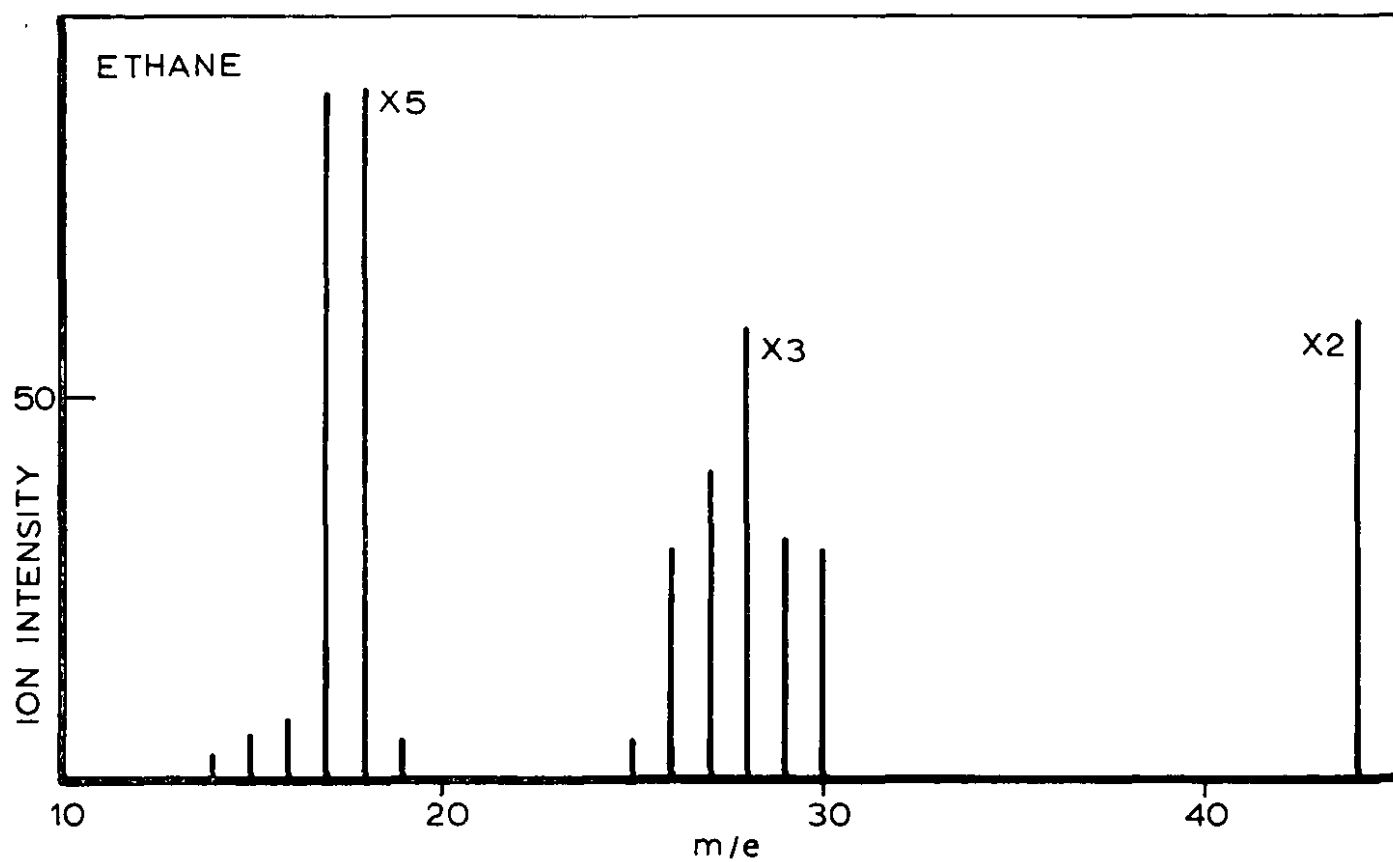


FIG. 40. MASS SPECTRUM OF PEAK b. FROM PORAPAK. RANGE 100. FAST LEAK.

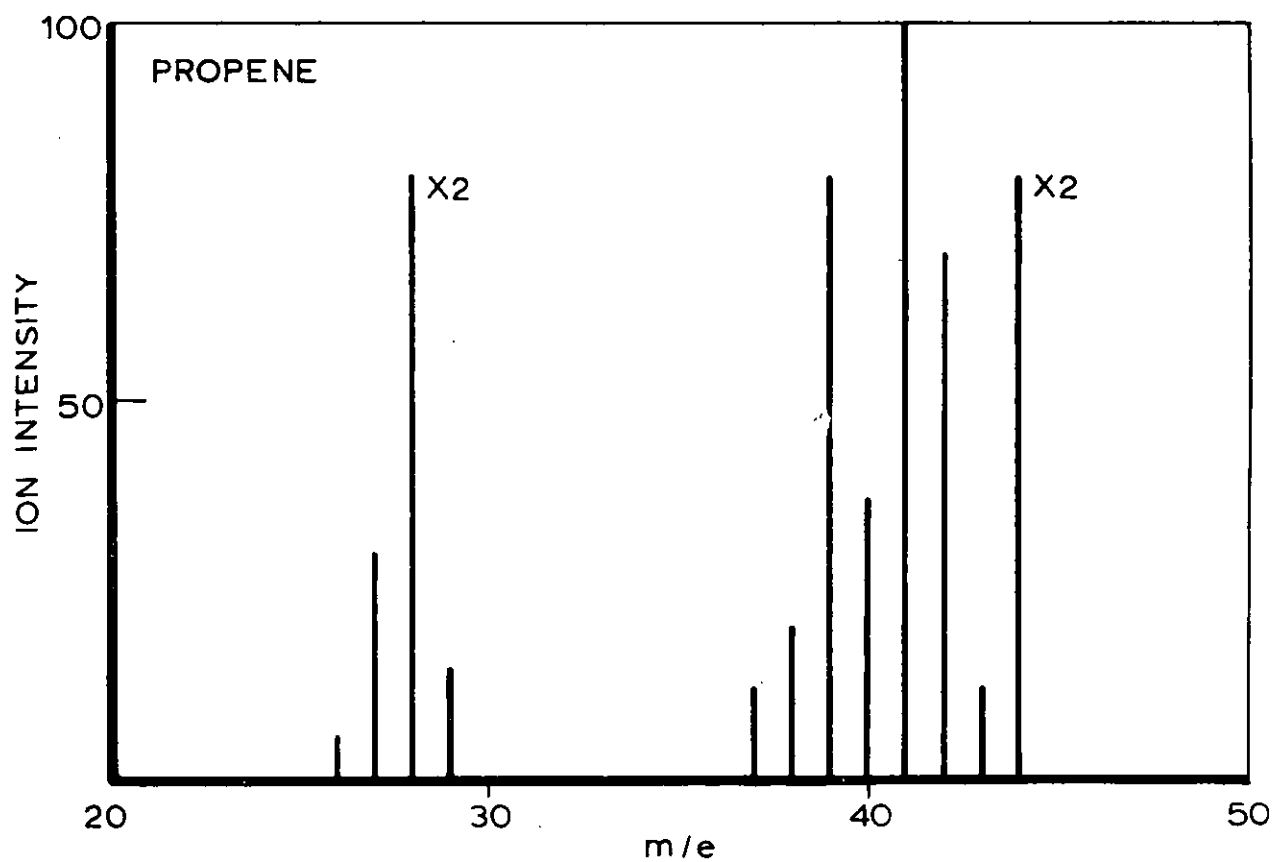


FIG. 41. MASS SPECTRUM OF PEAK d. FROM PORAPAK. RANGE 25. FAST LEAK

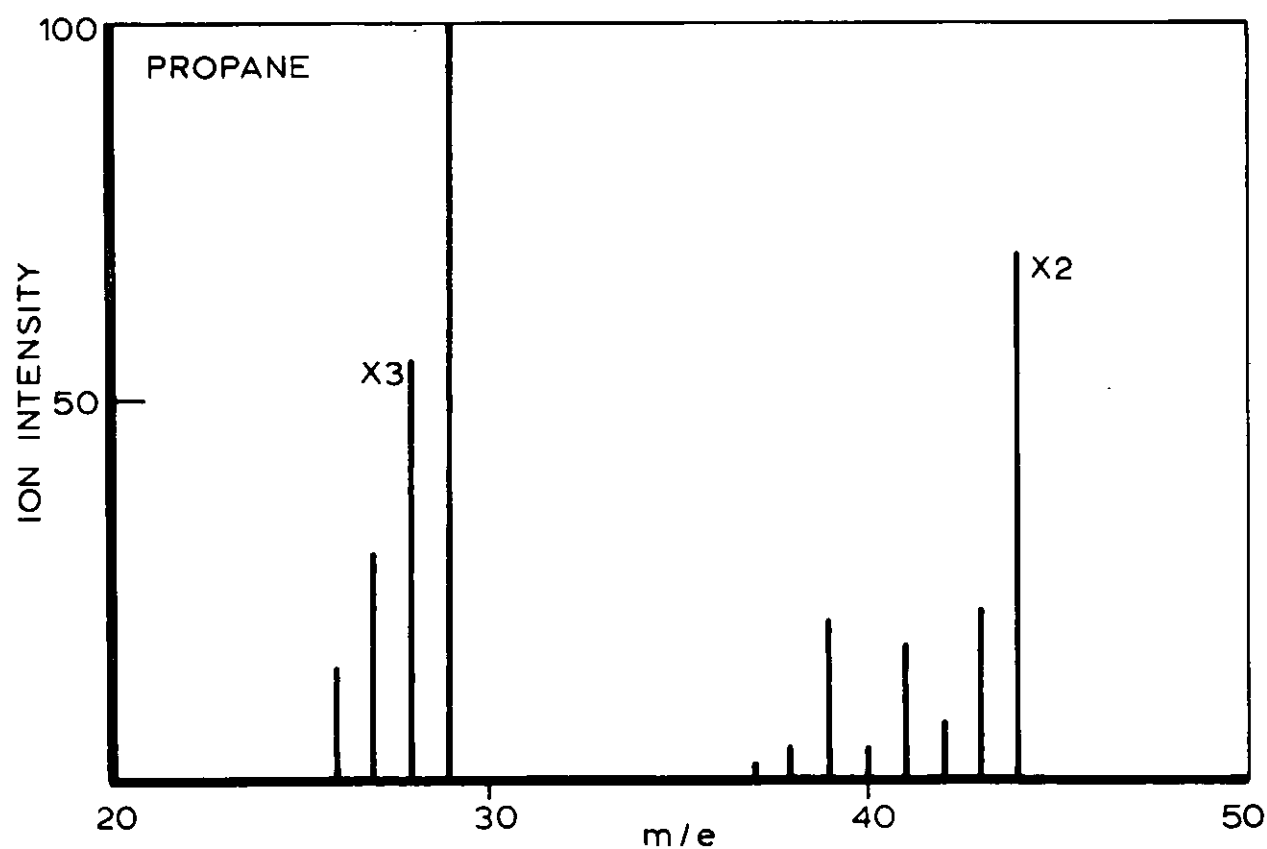


FIG. 42. MASS SPECTRUM OF PEAK e. FROM PORAPAK. RANGE 25. FAST LEAK.

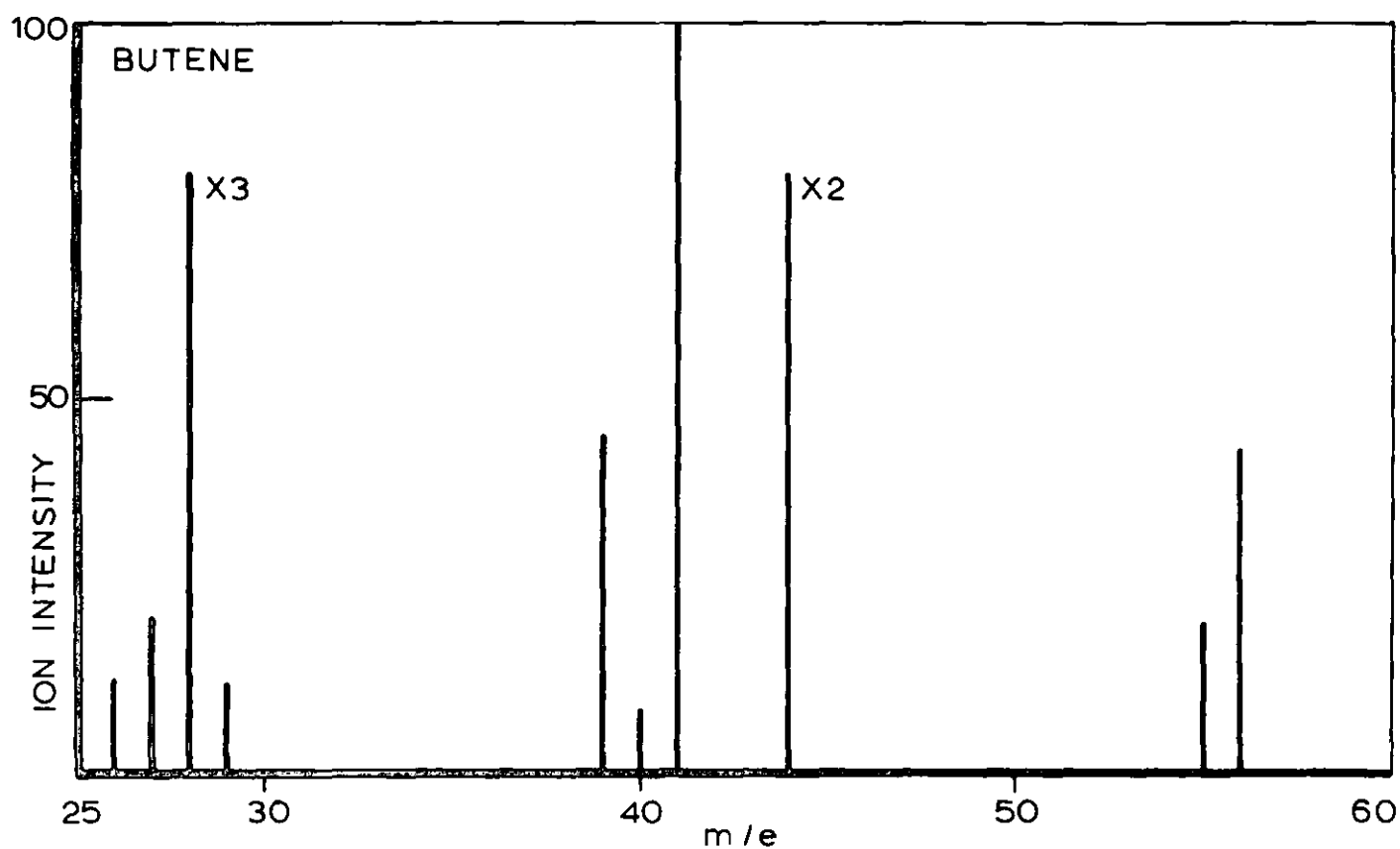


FIG. 43. MASS SPECTRUM OF PEAK j.
FROM PORAPAK. RANGE 25. FAST LEAK.

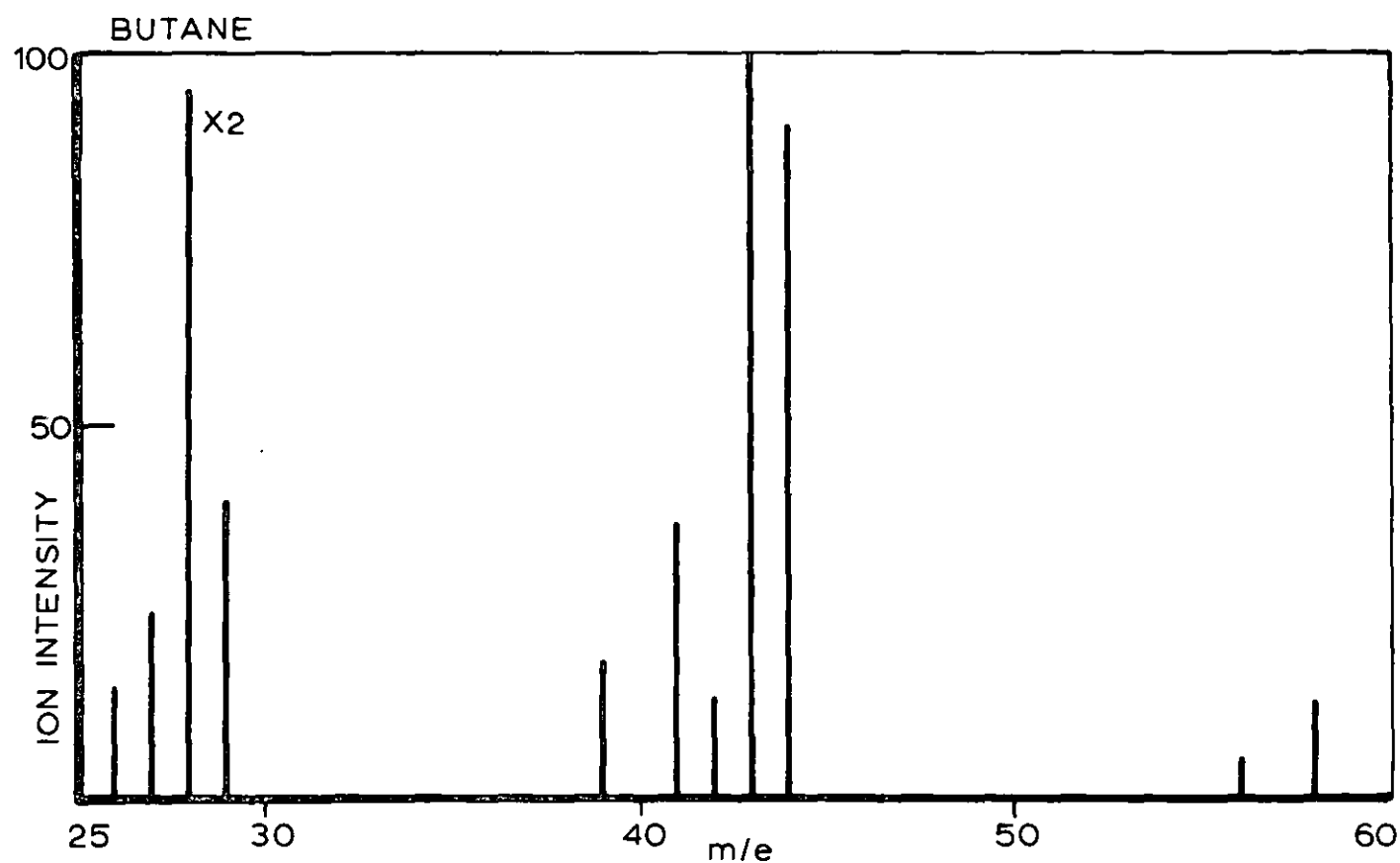


FIG. 44. MASS SPECTRUM OF PEAK k.
FROM PORAPAK. RANGE 25. FAST LEAK.

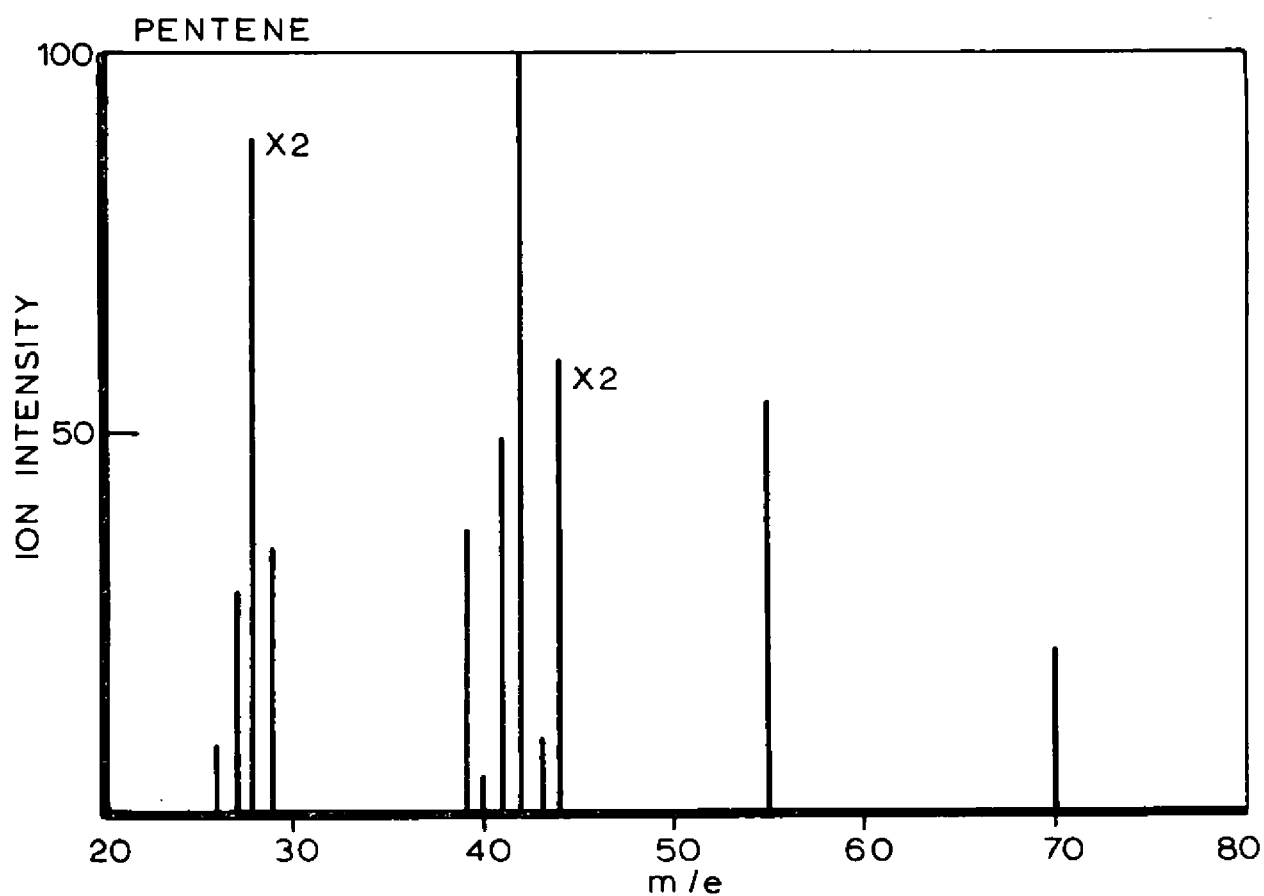


FIG. 45. MASS SPECTRUM OF PEAK q FROM PORAPAK. RANGE 25. FAST LEAK.

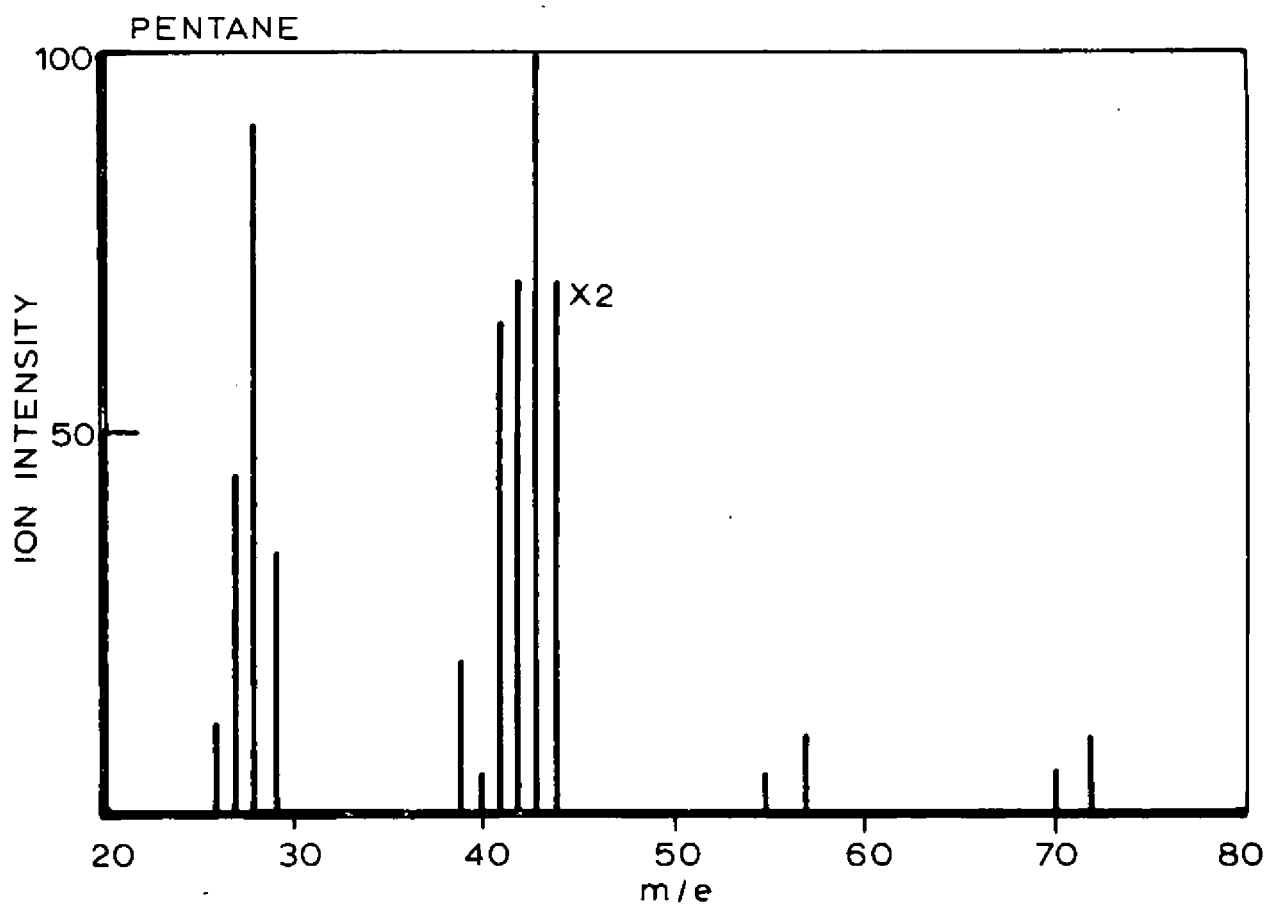


FIG. 46. MASS SPECTRUM OF PEAK r FROM PORAPAK. RANGE 25. FAST LEAK.

