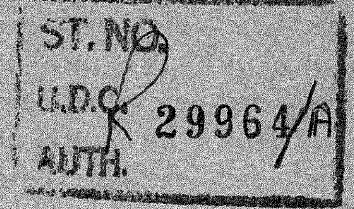


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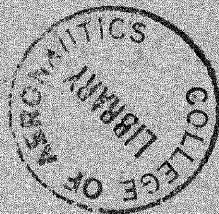


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SOME ASPECTS OF THE THERMAL DEGRADATION  
OF EPOXIDE RESINS

by

J. M. Stuart and D. A. Smith



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DEPARTMENT OF MATERIALS

Some aspects of the thermal degradation

of epoxide resins

Part 1

- by -

J.M. Stuart and D.A. Smith

S U M M A R Y

This Note contains a review of previous work in the field of pyrolytic degradation of epoxide resins, and a description of the development of an instrument for this purpose, using the principle of gas chromatography. The method depends on the pyrolysis of the material using an electrically heated filament, the difficulties of this method are critically examined, and attempts to overcome them described. The pyrolytic degradation in a nitrogen atmosphere, of unhardened epoxide resin was investigated, likewise the degradation of resin hardened with 1:2 diamino ethane and triethylene-tetramine, is described. An attempt has been made to explain, in terms of possible degradation reactions, the actual compounds detected in the pyrolytic break-down.



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## Some aspects of the thermal degradation of high polymers

### Introduction

Epoxide resins are now widely used thermosetting polymers noted for such useful properties as versatility, good mechanical and electrical properties, chemical resistance and good adhesive properties. The most commonly used polymers are based on the diglycidyl ether of 2,2'-bis(p-phenylol) propane. Various cross-linked systems are formed by reaction of this material with several types of polyfunctional materials known as hardeners. Well known types of hardener are aliphatic amines, amides, aromatic amines, acid anhydrides and dicarboxylic acids.

Epoxide resins are frequently used in high temperature applications such as electrical insulators, and it is of interest to have some insight into the nature of the reactions whereby these materials degrade in such conditions.

One successful method of examining polymer degradation is to pyrolyse a small quantity of material and analyse the volatile degradation products by gas chromatography. This system appears to be one of the most efficient methods of obtaining direct information on polymer degradation and has been chosen as the basis of our method of study. The best model for a method appeared to be that of Barlow, Lehrle and Robb<sup>6</sup>; this method was modified in the various ways described in this Note. The modified method was used to examine the thermal degradation of a resin of known chemical structure supplied by CIBA (ARL) Ltd.; in the following states: unhardened, hardened by 1:2 diamino ethane and hardened by a commercial aliphatic amine hardener supplied by CIBA (ARL) Ltd. The chemical nature of the commercial materials was divulged by CIBA (ARL) Ltd., for which we would like to express our thanks.

### Historical survey

#### Development of experimental methods of pyrolysis using gas chromatography

The pyrolytic degradation of polymers using gas chromatography to analyse the breakdown products was originally described by Davison, Slaney and Wragg<sup>1</sup>; Haslam, Hamilton and Jeffs<sup>2</sup>; de Angelis Ippoliti and Spina<sup>3</sup> and Parriss and Holland<sup>4</sup>. Parriss and Holland injected the decomposition products straight into the gas stream entering the gas chromatography column, while de Angelis had an intermediate gas burette, which does not appear to have been entirely satisfactory. Direct coupling of the pyrolysis unit to a chromatography unit is described by Ridell and Strutz<sup>5</sup>.

Improved techniques of examining polymer decomposition by this method are described by Barlow, Lehrle and Robb<sup>6</sup>. In their work the sample was placed on a filament in the carrier gas stream, the filament then being

heated for 10 to 20 seconds and the degradation products swept directly into the chromatographic column. At lower filament temperatures there was only partial degradation of the sample, so that part of the sample remained and could be degraded subsequently by means of a pulse at a higher temperature. These workers were thus able to subject the polymer sample to an ascending stepped series of temperatures. The sample weights were of the order of 2mg. A special timing device was described which ensured that the duration of the electric pulse was pre-determined. The temperature of the filament was calibrated against the supply volts. Up to 700°C this was done using the known melting points of standard organic and inorganic compounds; above 700°C an optical pyrometer was used. One of the features of this work is that a serious attempt was made to specify the temperature of pyrolysis. Various thermoplastic materials were examined, such as poly-vinyl chloride-vinyl acetate co-polymers and methyl methacrylate-styrene copolymers. The degradation products were successfully identified from the peaks obtained using gas chromatography and the results agreed well with what is known about the decomposition of these materials when degraded by other methods. It was found that although pyrolysis products were first detected at temperatures above the maximum utilisation temperatures of the polymers, these temperatures were an indication of the relative stability of the polymers. The gas-chromatography unit was one constructed by the authors.

Szymanski, Salinas and Kwitowski<sup>7</sup> pyrolysed material in a vacuum and then introduced pyrolysates into the gas chromatograph column as a second operation. They compared this method with the technique of pyrolysing the material in the usual way in the carrier gas system. Using a poly-rethane sample there were marked differences between the two methods. A technique of mixing Plaskon metal with the polymer sample is also described. This was to overcome problems caused by the poor thermal conductivity of polymers.

Straightforward use of the pyrolysis method simply for identification or 'finger printing' of polymers is described by Hewitt and Whitham.<sup>8</sup> They used the technique of pyrolysing straight into the carrier gas stream and describe the results for a number of acrylic and vinylic polymers. The polymer was dropped into a heated chamber. The application of 'finger-print' methods of a similar kind for criminological identification of polymers is described by Nelson, Yee and Kirk.<sup>9</sup> A very large range of polymers was investigated and characterised as 'finger-prints'.

Virus<sup>10</sup> describes a similar system of pyrolysis straight into the gas chromatography column, but he also measured the temperature of the pyrolysis wire directly using a thermocouple. 'Finger-print' pyrograms are quoted for a number of materials, including silicone resins, butadiene-styrene copolymers and butadieneacrylonitrile-styrene copolymers.

The use of a small boat, instead of a filament, for pyrolysis is described by Lehmann and Brauer<sup>11</sup> and Nelson and Kirk.<sup>12</sup> An alternative system

of injecting the polymer into a heated steel tube is described, apart from Hewitt and Whitham<sup>8</sup>, by Legate and Burnham<sup>13</sup> and also by Smith, G.G., Wetzel and Koster<sup>14</sup>.

Ettre and Varadi<sup>15</sup> compare the three methods of flash filament pyrolysis, use of a small boat in a furnace, and injection of polymer into a heated chamber.

They object to flash filament pyrolysis on the ground:

- a) that the polymer has to be dissolved and then coated on the filament. The dissolved form, they consider, may not decompose in the same way as the undissolved form. The amount cannot be weighed, nor the residue examined. The glowing wire may catalyse certain decompositions.
- b) The difficulties of analysis by the boat system are considered to be its slow rate of heating up. Thus the sample ascends slowly through a whole series of temperatures before reaching a desired temperature. Products of pyrolysis at the lower temperature, which have not escaped, may thus undergo secondary reaction. Thus a distorted picture of pyrolysis may be obtained.
- c) The difficulties of the heated chamber system are considered to be the difficulty of changing temperature and devising a satisfactory system of injecting the material.

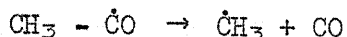
The system of pyrolysis that they describe consists essentially of a small boat, in which 12 to 13 mg of polymer are placed, which is rapidly pushed, using a magnetic piston, into a heated portion of the combustion tube. The boat can be withdrawn after a set time and provision is made for the use of several boats, without breaking down the apparatus. Carrier gas flows over the boats, into the gas chromatography unit during combustion. Nitrocellulose, poly n butyl methacrylate and poly vinyl alcohol were examined according to this procedure. The method of Ettre and Varadi is the basis of the Perkin Elmer pyrolysis unit.

The work of Feuerberg and Weigel<sup>16</sup> also shows a movement away from the flash filament pyrolysis technique. The authors consider the pyrolysis of 1 to 10 mg of material, though giving a fundamental picture of a certain kind of chemical reaction, may not be a guide to how the material would behave under more realistic conditions. This is particularly true of materials containing fillers etc. Polymer was ground to a powder and quantities between 50 mg and 1 g were placed in a tube, which was inserted in a special oven at 620°C. The tube was then subjected to a powerful stream of compressed air. Pyrolysis products were condensed in cooled traps and then injected in the usual way into the gas chromatography apparatus.

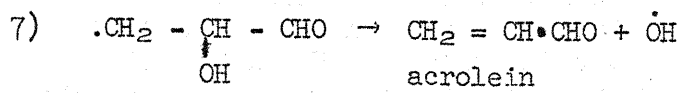
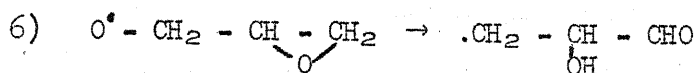
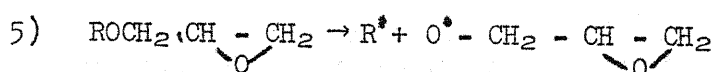
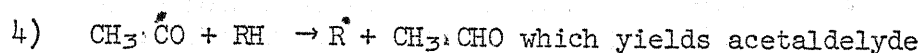
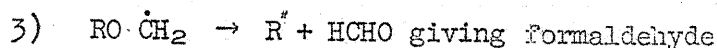
A number of vinylic and cellulosic materials were examined in this way.



2) The acetyl radical decomposes:-



The methyl radical abstracts hydrogen from the polymer giving methane



Thus according to this scheme one would expect formaldehyde, acetaldehyde and acrolein to be degradation products.

H.C. Anderson reports further effects on the thermal degradation of epoxide resins hardened by methyl nadic anhydride, maleic anhydride m-phenylene diamine, reacted with the diglycidyl ether of bis phenol A and also resins formed by the reaction of methyl nadic anhydride and m-phenylene-diamine with resorcinol diglycidyl ether.<sup>23</sup> This was done by thermogravimetric analysis in vacuo. Polymers incorporating methyl nadic anhydride decomposed in two stages whereas those based on m-phenylene diamine or maleic anhydride degraded in only one stage. This is attributed to de-carboxylation of the ester groups in the materials using methyl nadic anhydride.

The effect on certain mechanical and electrical properties of epoxy resins by continued ageing at 200°C is reported by Lemon.<sup>24</sup>

A detailed study of the degradation of epoxy resins is reported by Lieng-Huang Lee<sup>25,26</sup>. Two types of resin were examined, conventional bis-phenol A resins and epoxytated novolaks. Several anhydrides and methylene di-aniline were used as curing agents. Chlorine contents on the cured systems are also quoted.

Four methods of analysis of the materials are described:

- 1) Thermogravimetric analysis,
- 2) Differential thermal analysis
- 3) Vapour-phase chromatography
- 4) Mass-spectrometry of the low boiling pyrolyzates (below 120°C).



DTA showed that the epoxide reacts at 300-380°C. This may be isomerisation of the epoxide group or etherification of the epoxide group with the hydroxyl groups on the polymer chain.

Pyrolysis of both cured and uncured resins were conducted at 350°C and 450°C, pyrolysis for providing mass-spectrometry specimens was conducted at 475°C.

The uncured novolak resin gave, on pyrolysis at 450°C toluene, ethane, allyl chloride, and water.

On pyrolysis at 350°C the uncured, short chain, material based on the diglycidyl ether of bis-phenol A yielded toluene, water, and methyl cyclopentadiene. The higher boiling portions at 475°C contained phenols, cresols, iso propyl phenol, isopropenyl phenol and bisphenol A.

A long chain version of the bisphenol A type resin gave at 350°C water, toluene, carbon dioxide and acetaldehyde. At 450°C Lee obtained toluene, water, methyl chloride, acetaldehyde and carbon dioxide.

Analysis of the pyrolysis of the hardened epoxytated novolak at 350°C is quoted, it was noteworthy that no fragments from the methylene dianiline were identified.

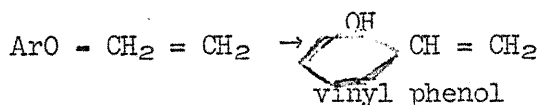
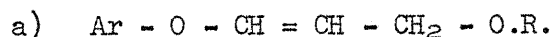
The short-chain bis-phenol A, based epoxide cured with methylene dianiline yielded at 350°C merely water. At 450°C methyl cyclopentadiene, carbon monoxide, water, carbon dioxide, acetaldehyde, methyl chloride and methane were identified. Again the residues of the amine curing agent were not identified.

Similar data are quoted for the anhydride cured materials.

Several degradation mechanisms are proposed, as Lee does not agree with Neiman's schemes. The ideas are based on the data in Hurd's monograph on the pyrolysis of ethers.

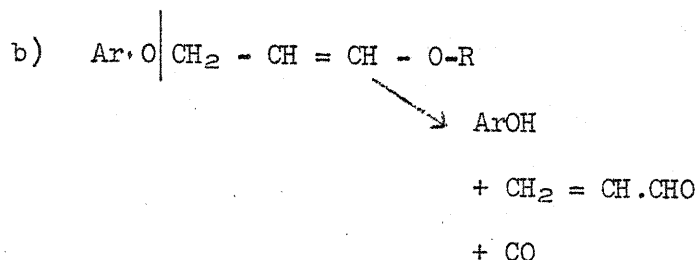
In scheme I Lee proposes the residual epoxide groups isomerise into aldehydes. This should yield propionaldehyde or possibly ethane and carbon monoxide.

In scheme II the residual epoxide is supposed to etherify or polymerise to 1,3 diethers, the ether may cleave in three different ways:-



Vinyl phenol may polymerise or cross-link.





The above route involves the cleavage of the unsaturated ether between the phenoxy oxygen and the allylic carbon. The major products should be phenols, acrolein (or ethylene) and carbon monoxide.

c) This represents a case where both groups attached to the etheric oxygen are phenyl.



Here one gets allyl phenols, or propyl or iso propyl phenols by the Claisen rearrangement. These materials may decompose and give allene, which may further demerise and cyclise into methyl cyclopentadiene.

The third scheme concerns 1,2,3 triethers which may be common in cured systems. These should yield acrolein, acetaldehyde, formaldehyde and acetone or propylene in the volatiles. Lee expects methane, ethylene or hydrogen to be the secondary decomposition products.

If the epoxy resin is oxidised during cure the oxidised segments may yield an unsaturated acid, or vinyl phenols, these in turn may decompose and yield carbon dioxide.

In Lee's work most of the identification of breakdown products was done by mass-spectrometry.

Madorsky and Strauss<sup>28</sup> have also examined the stability of several thermoset plastics at high temperatures. Here several polyesters, epoxy, phenolic and silicone polymers were pyrolysed in a vacuum at 360, 500, 800 and 1200°C. The volatiles were collected in traps and fractionated. The lighter fractions were analysed by mass spectrometry and the heavier materials by microcryoscopy. The carbonised residues were weighed as estimates of resin stability. Activation energies of thermal degradation were also discussed.

Discussion and summary of previous work

Methods of pyrolysis

Two main methods of pyrolysing the polymers for gas chromatography appear in the literature, these are the electrically heated filament method and the use of a boat inside a combustion chamber. Opinion seems divided on the merits of these two methods. Criticism may be levelled at the filament method on the grounds:-

- 1) that the metal of the filament exerts a catalytic effect on the reaction, or catalyses secondary reactions.
- 2) that it is not easy to weigh the amount of material placed on the filament, and even less easy to estimate the weight of tarry solid residues left behind after pyrolysis.
- 3) that reaction takes place first on that part of the film of polymer next to the heated metal and that decomposition products may undergo secondary reaction as they diffuse out of the polymer. This might also cause some change in the chemical nature of the polymer, due to the secondary reaction.
- 4) that materials deposited on the wire by solution evaporation may differ from the original materials, and the degradation products contain solvent fragments.

Criticism 1 was to some extent countered by Barlow, Lehrle and Robb<sup>6</sup> who sputtered gold onto a nichrome wire, and found the presence of gold had no effect on the rate of degradation of polymethyl meth acrylate. This does not settle the issue for all reactions, but suggests the catalytic question may not be so important as might be supposed. This is nevertheless a valid criticism.

Criticism 2 is valid, especially with regard to the question of tarry residues. It is felt that the filament method is in any case not the method for studying weightloss phenomena, which are better studied by thermogravimetric analysis.

Criticism 3 may be countered by placing a piece of solid polymer in the curved end of the filament so that the external surface of the polymer is in contact with the heated metal surface. The decomposition products are thus formed on the surface of the polymer and will rapidly diffuse into the surrounding gas. The rate of heat up of the polymer is extremely rapid; it may be supposed that the interior of the piece of polymer is not heated due to the poor thermal conductivity of polymeric materials.

Other methods seemed, in our opinion, to contain far more real dangers of giving secondary reactions of the degradation products and thus obscuring the picture of the degradation reactions.

Criticism 4 may be valid, but using a portion of solid material, mounted as described above, this difficulty may be avoided.

The use of boats inside a heated chamber introduces the problem of relatively slow rates of heating. The composition of the degradation products may reflect heating up to a certain temperature rather than degradation at a certain temperature. The inner portions of the polymer specimen may now become hot enough to degrade and the whole complex question of diffusion of degradation products through the specimen, and their secondary reactions is now raised. It was for this reason that we preferred the filament method for our analysis of epoxide degradation reactions.

Some work has been described on injecting the polymer into a heated steel chamber, which contains flowing carrier gas. Difficulties here would be:

- 1) though the temperature of the chamber wall may be accurately known one could not be very sure of pyrolysis temperature,
- 2) there will be a finite time to pyrolyse the polymer specimen, this will be incorporated in the retention time of any compounds evolved, and this pyrolysis time will be unknown. When model compounds are injected they will have an evaporation time (depending on quantity) which will also be part of the retention time. Some trouble in identifying compounds by the use of retention times of model compounds might be anticipated. The great difficulty here is that the chamber, due to its bulk, must be heated throughout the process, thus once the polymer is introduced all of it must be burned up, the time of this will be a variable, difficult to determine.

Nevertheless we feel a serious comparison of this method with the filament method might well be attempted.

- 3) It is difficult to change the chamber temperature quickly.

A weakness of much of all the work, particularly by the filament method, has been lack of temperature measurement, though this was described by Barlow, Lehrle and Robb<sup>6</sup> and by Virus<sup>10</sup>. In our work we have attempted to investigate the problem of temperature, in order to evaluate the effect of temperature on the reaction.

Once pyrolysis has taken place most workers arrange for carrier-gas to be swept as quickly as possible into the heated column of the gas chromatography apparatus. A real difficulty here is that high-boiling degradation products may condense before they reach the column.

A few workers<sup>3,7,16</sup> actually condense the degradation products and then pump these into the gas chromatography unit in a separate operation. In the pyrolysis of a large (say 0.1g) specimen of polymer there may be some virtue

in this operation, because it would not be desirable to force a large quantity of material, over a long time, through the column. In the pyrolysis of a few milligrams of material this step would not appear to be necessary, and might lead to losses of material.

Very few workers divulge much detail on how the final peaks of the chromatography traces are identified and related to known chemical compounds. Presumably model compounds have been used, and the peaks identified by retention times.

#### Discussion of the relation of our method of pyrolysis with previous work

In the light of the above discussion it was considered that though the system of Barlow, Lehrle and Robb<sup>6</sup> was most suitable, it would be advantageous to pay more attention to temperature measurement and the problem of comparing retention times with those of model compounds.

Barlow, Lehrle and Robb<sup>6</sup> coated their electric filament, or placed solid bodies in a coil of wire. In our case the small piece of polymer was placed in the bend of the nichrome filament ( $\frac{1}{8}$ "  $\times$  .005") consequently the polymer is in contact with this wire. In step-wise filament heating two possible problems arise:-

- a) diffusion of pyrolysis products into the gas stream, this is presumably along the polymer metal interface. There is the possibility of secondary reactions during this process.
- b) After the first heating of the filament there may be a layer of tarry material between the filament and the resin surface. Unless this tar is of extremely low thermal conductivity one cannot be sure of the temperature of the resin surface, as opposed to the temperature of the tar. This trouble will increase as the number of filament heatings increases.

In our method, although we cannot be completely sure on the first point, the width of the filament was not great, and in any case there would not be continuous contact along the metal - resin interface.

If the second point were valid, degradation of the tar would not be expected necessarily to follow the same course as degradation of the resin. If so, the pyrograms would change with increasing temperature; in fact however the basic pattern of the pyrogram did not change with temperature, suggesting that in all cases the actual resin was being pyrolysed, and not some partially degraded tarry material.

We have attempted to adapt one of the standard Perkin-Elmer Gas Chromatography units to give as direct a gas entry as possible into the column, so that pyrolysis took place in the oven of the chromatography unit, and the danger of condensation of high boilers was minimised.

In work up to the present time the actual identification of degradation products presents some difficulty. Identification using a model compound's retention time under one set of conditions is not good enough in our opinion. Two compounds may show the same retention times under one set of conditions, under other conditions this may not be the case. Thus quoting retention times under one set of column and temperature conditions is not even a probable, but merely a speculative identification. We have attempted a more critical investigation of this question, and also that of the difficulty of relating, in a flowing gas stream, the retention times of model compounds, to retention times of degradation products. To our knowledge this has not been discussed previously.

The use of infra-red spectroscopy or mass spectrometry on the gases (after emerging from the column) is also possible,<sup>29</sup> but as the quantities of material may be very small, and their identity uncertain, it is possible that other difficulties will appear using these methods. In many cases identification may not be as positive as could be desired.

#### Degradation mechanisms

Three authors have considered the degradation reactions of epoxides; they have used a variety of methods of analysis, including quasi distillation methods, differential thermal analysis and gas chromatography. These are Anderson<sup>18, 19</sup>, Neimann et al.<sup>17, 20, 21, 22</sup> and Lee<sup>25, 26</sup>. Discussion on the proposed schemes is deferred to a later section of this Note where it is convenient to compare them with some postulates of our own.

#### Experimental

##### Instruments

The gas chromatograph used was a slightly modified version of a standard Perkin-Elmer Model 452. The injection block normally used in these instruments had been removed to allow glass units of our own design to be connected to the column within the oven thus avoiding condensation of low boiling-point materials. This was made possible by a port in the side of the instrument (Fig. 1) through which the glass units could be inserted and connected directly onto the column by means of a short piece of silicone rubber tubing. Preliminary tests had showed that this tubing did not give 'noise' at the temperatures used in these experiments.

Also incorporated externally on the side of the instrument was a fast action needle valve enabling the carrier gas to be switched on and off in a time very short compared with pyrolysis times. This meant that the carrier gas stream was diverted out of the side of the instrument's oven, through the needle valve and into the glass units where the gas would sweep any compounds produced there directly into the column.

Apart from these modifications the instrument remained unchanged. The column temperature was controlled by an oven unit capable of reaching temperatures in slight excess of 225°C with a thermostating system capable of holding the selected temperature constant to within 0.05°C. Reproducibility of temperature could be achieved to within 0.25°C.

Two standard Perkin-Elmer columns were used. Type 'O' column was a silicone grease on an inert dust and Type 'R' was polypropylene glycol on an inert dust.

The instrument incorporated a standard hot wire detector operating a pen recorder in the usual way.

The carrier gas was supplied to the instrument at a pressure of approximately 25 p.s.i. The flow rate of the carrier gas was controlled by adjusting the pressure regulator incorporated in the machine. This flow rate was measured by a soap-bubble flowmeter. For a given column temperature a fixed volume of gas is required to elute a specific component; increasing the gas flow will therefore shorten the time required for the component to reach the detector, but resolution may be impaired. Initial experiments showed that a flow rate of 40 mls per minute gave suitable resolution for a wide range of components and temperatures and therefore this rate was adopted throughout.

#### Injection systems

Having removed the conventional injection block three units were built for the purpose of injecting components into the column, a pyrolysing unit for the cured resins, a hypodermic/septum device for liquids and solutions of model compounds and a gas burette for gases and vapours.

##### 1. Pyrolysis unit

The unit (Fig. 3) consisted of a nichrome filament, previously rolled to a flat cross section of  $\frac{1}{8}$ " , welded in the form of a loop between two rigid nichrome rods. The two rods led out of a glass container via rubber bungs and were connected into an electrical circuit (Fig. 1). The rubber bungs gave no 'noise'. On passing a current through the system the filament acted as a resistance heater and pyrolysed samples previously mounted in the loop. To obtain the temperature of the filament, a small thermocouple of 0.004" chrome/amul wires was spot welded onto the middle point of the filament loop and by this means the temperature of the filament was directly correlated with the current supplied to it for any set of gas and oven conditions. The filament unit mounted in its glass container was connected to the gas chromatogram so that the carrier gas would sweep past the filament. The carrier gas would take with it any vapours or gases, resulting from pyrolysis, into the column where separation would take place. As a check on the accuracy of the thermocouple and bridge several compounds of known melting point, such as diphenyl urea, and sodium chloride were placed on the filament. The temperature, as recorded by the thermocouple, corresponded to these melting points to within  $\pm 5^\circ\text{C}$ .

It was clear that the temperature of the wire would be affected by the flow of gas, and by the oven temperature of the instrument, thus several calibrations of temperature against current in the filament were undertaken to account for burning under flowing gas conditions ('dynamic conditions') and stationary gas conditions ('static conditions'). It was hoped by these means to obtain true filament temperatures.

Because all the above experiments were performed on uncoated wire it was considered a coating of resin might alter the temperature of the wire, due to thermal insulation. The filament was thus coated with unhardened resin MY750 and tested, under static conditions, in the normal pyrolysing position in the apparatus. Temperatures, as measured by the attached thermocouple, still corresponded to the voltage calibration data, thus suggesting that no effective thermal insulation had occurred. Later on, solid polymer was placed in the fold of the loop, secured by fine wire, and the question of thermal insulation was not so pertinent. After all checks and calibrations were performed, the current was normally taken as indicative of temperature, using calibration charts.

## 2. Hypodermic injection unit (Fig. 4)

Liquids and solutions of compounds were injected into the gas stream of the chromatogram by means of a micro-litre hypodermic syringe piercing a rubber septum mounted into a glass unit. (Fig. 4). The liquid, entering the heated glass tube inside the instrument oven, evaporated and the vapours entered the column in the usual way.

## 3. Gas injection unit (Fig. 5)

Model gases (produced by a variety of reactions, e.g. Grignard compounds and water, were generated into the gas burette (fig. 5), through a two-way valve. The gas could then be fed into the chromatograph by allowing a head of mercury to displace a known volume of gas into the carrier gas stream at a controlled rate. The efficiency of this system was assessed by comparing retention times of ether liquid (using standard conditions) and ether vapour using the gas burette. Close agreement was obtained.

## Carrier gas

Preliminary experiments with helium and nitrogen showed that because of its high thermal conductivity helium led to greater sensitivity than nitrogen but had the disadvantage of cooling the pyrolysing filament to such a degree that high pyrolysing temperatures were difficult to achieve. It was for practical reasons therefore that white spot nitrogen was chosen as the carrier gas and was used throughout the main experiments. However by using nitrogen as a carrier, it may be noted that any nitrogen produced during pyrolysis would not be detected and that air would be recorded as only oxygen.

The specification of 'white spot' nitrogen is a maximum 500 p.p.m. impurity.



## Methods and procedure

### 1. Pyrolysis of materials

To pyrolyse unhardened liquid resins or liquid amine curing agents the burner filament was dipped into the substance and the excess fluid allowed to drain off, whilst for solid and hardened resins a small particle of the material (0.01 - 0.02 gms) was carefully wired onto the loop of the filament. The burner filament was then inserted into its glass container which in turn was connected to the column of the gas chromatogram.

To pyrolyse a substance at a specific temperature a predetermined current was passed through the filament. The products of pyrolysis were then passed through the column resulting in a peak (or peaks) being plotted on the recorder. Temperatures were raised, using the same specimen of polymer, according to a 'step-wise' sequence.

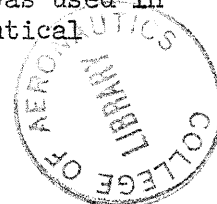
### 2. Model compounds

Model or known compounds were introduced into the column in small quantities by the use of the hypodermic system or the gas burette system. It was noted that when certain liquid models were injected into a flowing or dynamic gas stream their retention times varied with the amount used. This was found to be due to a finite evaporation time not normally encountered when using the conventional injection-block system, where evaporation is considered to be instantaneous. It was also found that the gas burette could not be used with a flowing gas stream, because the carrier gas pressure was far in excess of the burette pressure resulting in the model gas being forced back into the burette.

### Standardised method of introducing compounds into column

To overcome the above mentioned practical difficulties the following method was devised. The flow of carrier gas was turned off at the snap-action valve and after a pause of 10 seconds to allow the carrier gas pressure to fall, the compound was injected either by hypodermic syringe or by gas burette. This was followed by a further pause of 30 seconds to allow for evaporation (found by experiment to be the optimum time), after which the carrier gas was switched on and the retention times of substances timed from that moment. In order that the pyrolysis of materials should conform as closely as possible to the above conditions, the following procedure was adopted. A pause of 10 seconds after switching the gas off was followed by a period of burning. This was followed by a further pause, timed to give an overall total of 40 seconds, (e.g. 10 seconds pause, 5 seconds burning period, 25 seconds pause) before switching on the gas. Retention times were estimated from the moment of turning on the gas. The burning time was achieved using a switch and stop watch.

To check the accuracy of this method of introduction, ether was used in all three units as a vapour or a liquid and was found to have identical



retention times for all three, regardless of quantity.

#### Experimental results

The materials chosen for pyrolysis were supplied by CIBA (A.R.L.) Ltd. and were standard commercial products. The epoxide system used was based on Araldite MY750 resin cured with an amine hardener Araldite HY951. The formulation used was 100 p.b.w. MY750 to 10 p.b.w. HY951, these two components were thoroughly mixed together and cured for 12 hours at 50°C to ensure a fully crosslinked polymer.

The resulting polymer was then degraded by pyrolysis under a variety of conditions (Table 1) and the products analysed in the gas chromatograph. The peaks resulting from these products were recorded and the retention time of the major ones noted and compared with retention times of models.

Also pyrolysed for purposes of comparison were unhardened MY750, HY951, and MY750 hardened with 1:2 diaminoethane.

HY951 is substantially tri-ethylene tetra amine, resin MY750 is substantially the diglycidyl ether of bis phenol A having an average epoxy content of 5.2 eq/Kg.

#### General observations

The following are some general observations made on the traces produced by the degradation products of the pyrolysis of MY750/HY951 under the conditions stated in Table 1.

- 1) Using either column at any given oven temperature there is a marked increase in peak heights recorded once the pyrolysing temperature is in excess of 450-500°C. An example of this is given in Trace No. 1. Below 400°C relatively small amounts of material are evolved.
- 2) On increasing the pyrolysing temperatures above 500°C the 'patterns' and retention times of the peaks do not alter but the peak heights do increase, thus showing that larger amounts of the same components are given off at the higher temperatures. (See Trace No. 1).
- 3) More peaks (or components) are obtained using high oven temperatures. This may be explained by high boiling point materials condensing and not passing through the column at low oven temperatures. (Traces 2,3,4,5).
- 4) After pyrolysing either hardened or unhardened resins there always remained behind on the burner a relatively large amount of carbonaceous material.
- 5) The breakdown pattern using Hardener 1:2 diamino ethane was similar to the above.

Table 1

Pyrolysing conditions for the degradation of MY750/HY951.

Range setting 1. Detector Supply setting 2.

Column designation	Oven temperature °C	Pyrolysing temperature °C	Pyrolysing time secs.
0	200	400	5
		500	5
		600	5
		700	5
		800	5
		800	10
0	150	350	5
		450	5
		550	5
		650	5
		750	5
		750	10
0	100	200	5
		300	5
		400	5
		500	5
		600	5
		700	10
0	50	700	5
		700	10
R	Series repeated as above		

### Use of model compounds

Having recorded and timed the major peaks for the pyrolysed resin under a variety of conditions, (Table 1) model compounds of suspected breakdown products were introduced into the columns by the methods stated. If the retention time of a model compound corresponded with that of a major peak in the breakdown products, then the model would be tried under a variety of oven temperature conditions and columns identical to those used for the degradation of polymer. If the model's retention time always corresponded to the unknown peak under all practical conditions it was assumed that the unknown peak was produced by the same chemical as the model and the model compound was listed as a highly probable breakdown product.

Certain model compounds could not, however, be tested under a wide variety of conditions, (e.g. phenyl glycidyl ether) because its high boiling point, only produced a peak when passed through a column running at an oven temperature of 200°C. Therefore this retention time could only be matched against pyrolysis products that had been passed through a column at the same high oven temperature. Such compounds thus identified were listed as probable, and could only be checked over a narrow range of conditions.

Model compounds found to correspond to an unknown peak only under one set of conditions were termed speculative.

Model compounds of suspected breakdown products that were tested and found not to correspond with any given peak produced by pyrolysis were said to be undetected and listed as such. A full list appears as Table 2 but no such distinction has been made between compounds when labelling example traces 2,3,4 and 5.

### Thermal degradation

#### Discussion

The compounds that have been identified are classified in three categories, highly probable, probable and speculative. Only those peaks which correspond to model compounds over a wide variety of conditions were deemed highly probable. According to the degree of correspondence, other materials were classified as probable or merely speculative.

There are two main theories of thermal epoxide degradation; that due to Neimann, et al<sup>22</sup> and that due to Lee<sup>25,26</sup>. (See section on Historical Survey). Neimann's theory would explain the presence of aldehydes, such as formaldehyde, acetaldehyde and acrolein, these are not however, according to our analysis, the major decomposition products, although the presence of formaldehyde is probable. Our evidence thus leads us to agree with Lee, that Neimann's scheme does not go far in explaining the presence of many of the compounds identified.

Table 2

MY750/HY951

Highly probable

Hydrogen  
Carbon dioxide  
Benzene  
Toluene  
Phenol  
Mixed xylenes  
Mixed cresols.

Probable

Formaldehyde  
Acetaldehyde  
Phenyl glycidyl ether

Speculative

Carbon monoxide  
Methane  
Propane  
Acetone  
Methyl cyclo pentadiene  
2: isopropyl phenol

Undetected

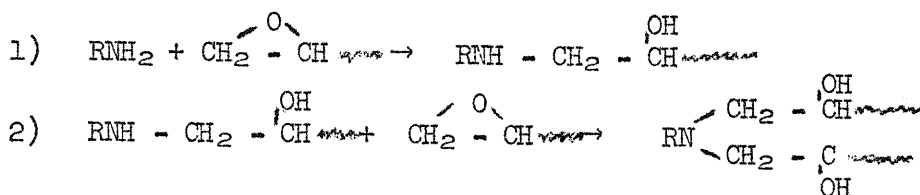
Ammonia  
Ether  
Methyl ethyl ketone  
Anisole  
Phenetole  
Piperazine  
Bisphenol A  
HY 951 (used as model)

The schemes put forward by Lee merit detailed discussion.

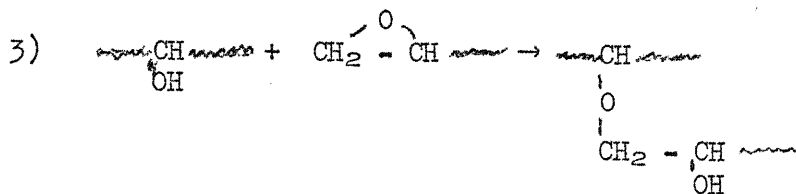
Scheme I

Here Lee follows Anderson in postulating the isomerisation of residual epoxide groups to give several aldehydes. Of these we believe formaldehyde to be a probable decomposition product, but the small quantities suggest, certainly in the cured resin, that this is a secondary reaction. This would be expected. Lee's other schemes all depend on an initial attack on the ether groups.

Scheme II is also based on the attack on ether groups formed from the polymerisation of epoxide groups to form ethers, several forms of cleavage of these ethers are described giving rise to carbon monoxide, vinyl phenol, acrolein, ethylene, and allyl phenols and isopropenyl phenols. He also predicts allene, and its dimerisation and cyclisation product, methyl cyclopentadiene. In work of this kind it would be rash to deny categorically the presence of these materials amongst the decomposition products, in our opinion only carbon monoxide of these is an important breakdown product. In materials cured by primary and secondary amine hardeners the most important reactions are:-



and reactions of hydroxyls, so formed, with epoxides



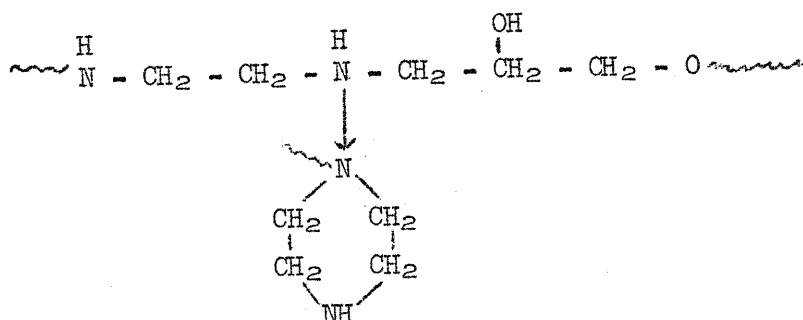
The third reaction will yield ether links, but there is evidence to suggest that this third reaction hardly proceeds at all in the presence of primary and secondary amines.<sup>27</sup> Reaction of epoxide groups with epoxide groups is in competition with the reaction of epoxide and amine groups, and one would suppose that this reaction also would not proceed to any great extent. There are of course ether groups already existing and these may break down in ways similar to those suggested by Lee.

In Scheme III Lee suggests that residual epoxide groups will form 1,2,3 triethers and claims this is the most predominant species in the cured epoxide resin. In amine cured systems this may be doubted. As a result of this it is claimed that these tri-ethers will decompose to give acrolein, acetaldehyde, formaldehyde acetone and propylene, with methane, ethylene and hydrogen as secondary products.

Formaldehyde is probable and some of the other primary materials possible. However, we believe hydrogen to be given off in high yield. The considerable proportion of hydrogen present does not seem to be explained entirely by the above degradation scheme.

It will be noted that Lee could find no trace of nitrogen compounds derived from his aromatic amine hardeners. It was noted in our work with aliphatic hardeners that there were no nitrogenous residues of amine hardeners, as far as could be ascertained.

It was suggested that piperazine and substituted piperazines could be formed as follows:-



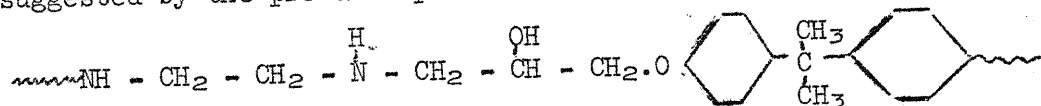
There was, however, no evidence that this occurred.

It is barely possible that these sections of the polymer decompose to give nitrogen, which would not be detected, but this seems a very unlikely explanation. It is more probable that nitrogenous materials may be found in the tarry non-volatile residues, which were not examined. Amine hardeners are certainly not regenerated as such by any simple reversible mechanism.

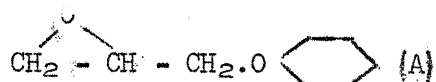
In addition to the reactions proposed by Lee the following additional ones may be postulated:-

1) Direct loss of hydrogen from the aromatic and aliphatic portions of the chain, the carbon-containing residues possibly condensing to structures containing fused benzene rings in some sort of quasi-graphite structure. It appears that hydrogen is one of the most important decomposition products, appearing fairly sharply between 400°C and 500°C.

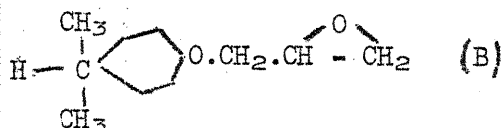
2) Chain scission occurs at other points than the ether links, this is suggested by the probable presence of phenyl glycidyl ether.



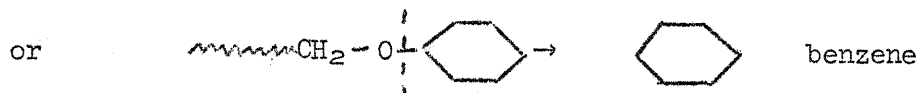
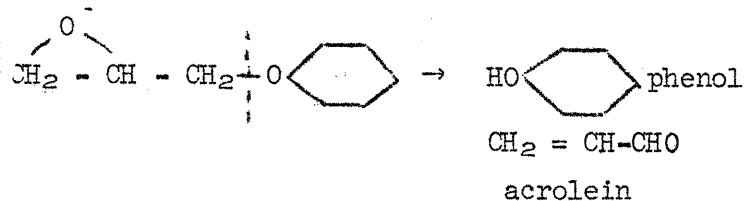
giving



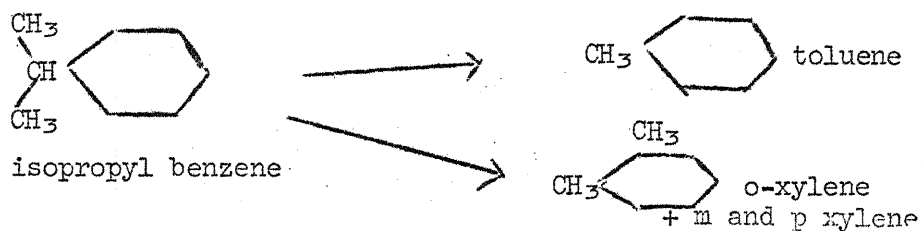
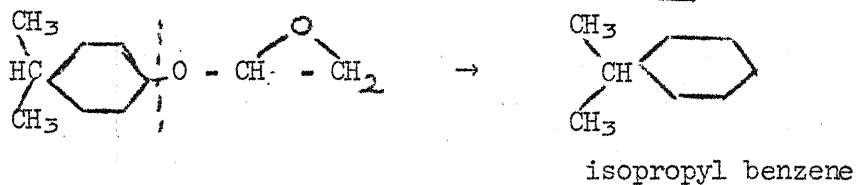
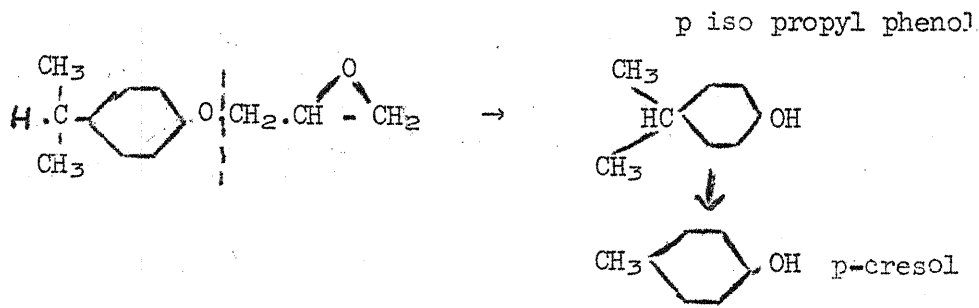
There would also be molecules such as



Further scission at the ether group may now occur to (A) thus:



Decomposition of (B) may follow similar lines



The above reactions may be supposed to proceed by free radical mechanisms.



3) The reactions of Lee and Anderson may be accepted as explaining carbon monoxide, and probably the dioxide, and also the various aldehydic products and the speculative presence of methyl cyclo-pentadiene.

The above revised degradation schemes appear to explain most of the compounds identified in the breakdown reaction. The most outstanding difficulty is the absence of nitrogen compounds that could have been derived from the aliphatic amine hardener, triethylene tetramine.

#### Suggestions for future work

The most difficult problem outstanding is the question of what happens to the amine hardeners on pyrolysis. The only fact that we can be sure of is that they are not regenerated as such by any simple reversible mechanism. It is difficult to accept the idea that nitrogen gas is evolved as such, but this must be checked, using helium as carrier gas. It is also known that the nitrogen function does not appear as ammonia or piperazine.

Studies on a number of amine hardeners, if the theories are correct, should yield substantially the same picture as described in this Note, pyrolysis using several aromatic amine hardeners must therefore be attempted. Logical departures from the bis-phenol A structure to phenolic Novolak based resins should give marked changes, whereas using different hardeners should not. Some of Lee's existing work supports this hypothesis, but much amplification is needed.

In our opinion it may be worth while investigating the tarry residues deposited on the glass wall of the pyrolysis tube. These may be dissolved in a suitable solvent and infra-red analysis may at least reveal the presence of nitrogen functions.

On a broader level it is certain that the question of the pyrolysis method is still very open. Although we have attempted to obtain conditions where secondary reactions are reduced to a minimum, the whole question of whether degradation products are partly a function of pyrolysis method requires further investigation. Feuerberg and Weigel<sup>16</sup> have, in fact, gone back to pyrolysis of quite large quantities of material, even up to 1g. From a practical point of view the pyrolysis of a large quantity of material may yield more useful information. It is conceivable that some method could be devised for pyrolysing larger quantities of material and using preparative scale chromatography; in this way some of the degradation products could be identified as such, using more conventional methods.

It will have been noted that the method described in this Note gives little information on the degradation of the polymer that may occur between say, 150°C and 400°C. It is in this region that few volatile degradation products are evolved. Nevertheless we may suppose that polymer chains are breaking down into shorter lengths. It is proposed to initiate a new line of investigation using differential thermal analysis to investigate this question.

Acknowledgements

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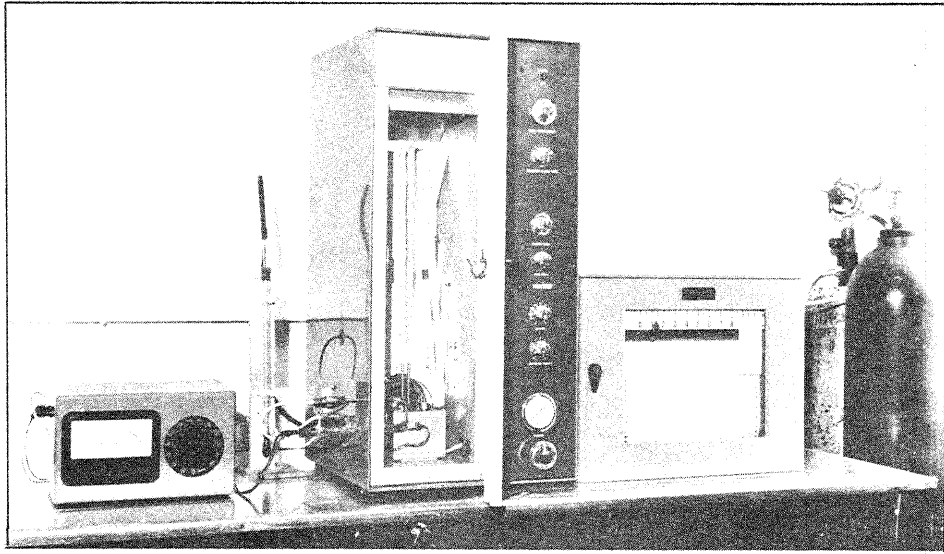


Fig. 1

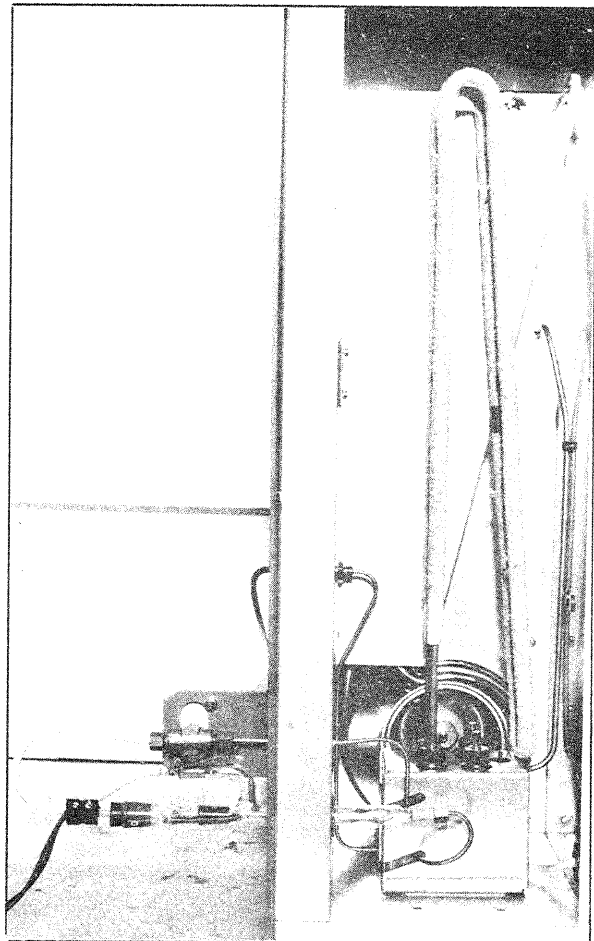


Fig. 2



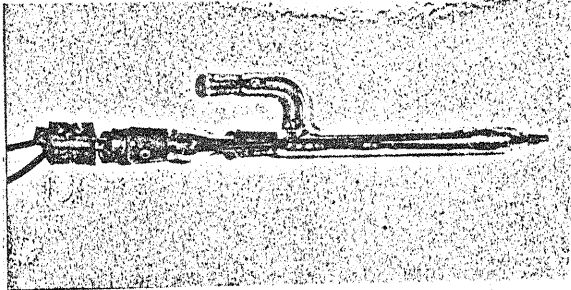


Fig. 3 Pyrolysis unit

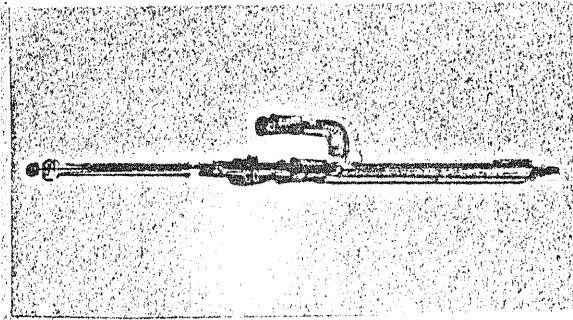


Fig. 4 Hypodermic injection unit

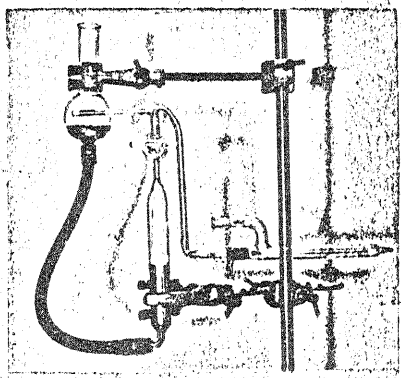
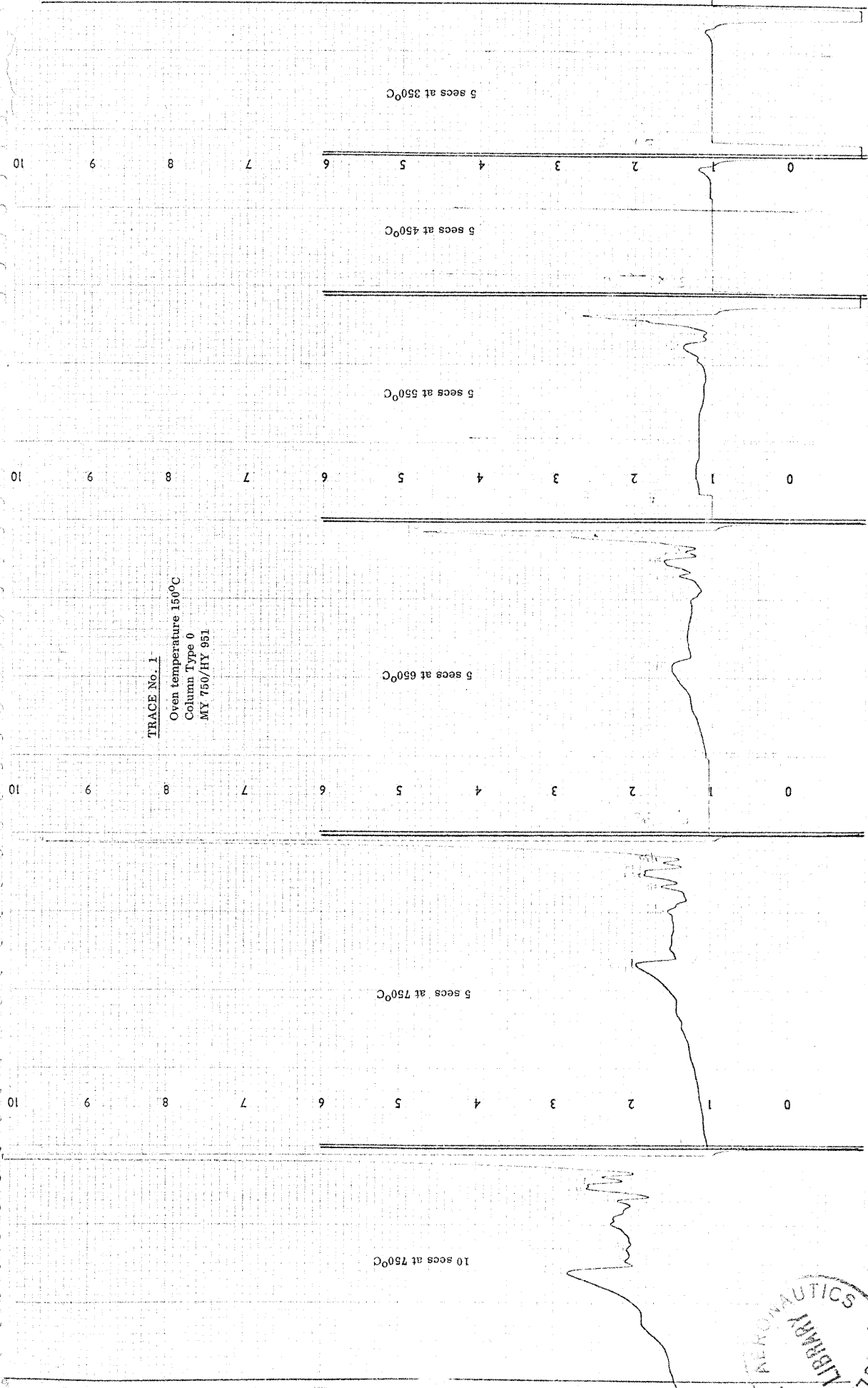
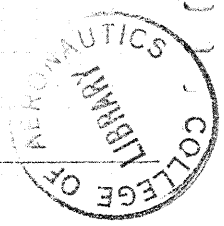
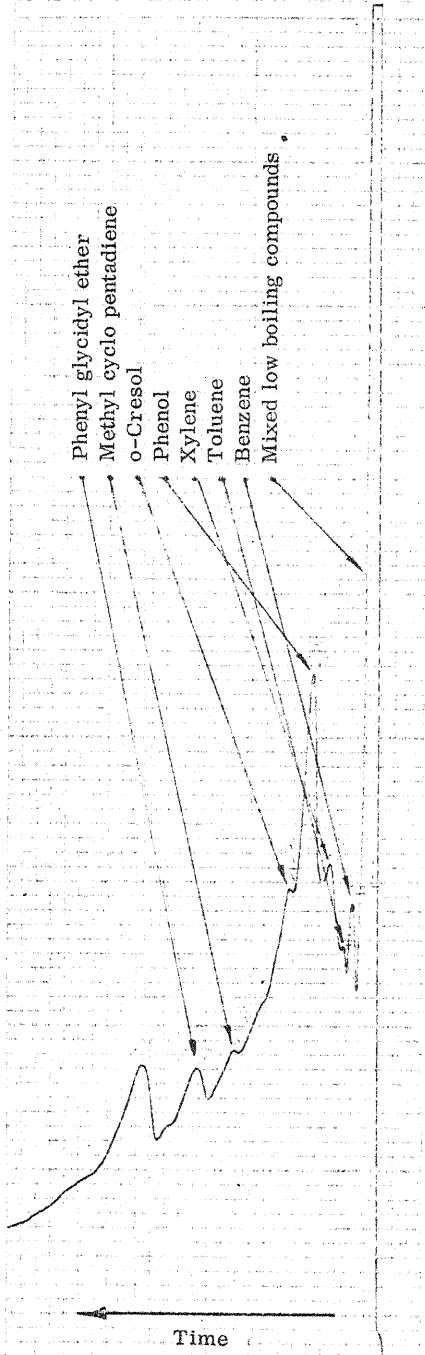


Fig. 5 Gas injection unit



TRACE No. 1  
 Oven temperature 150°C  
 Column Type 0  
 MY 750/HY 951



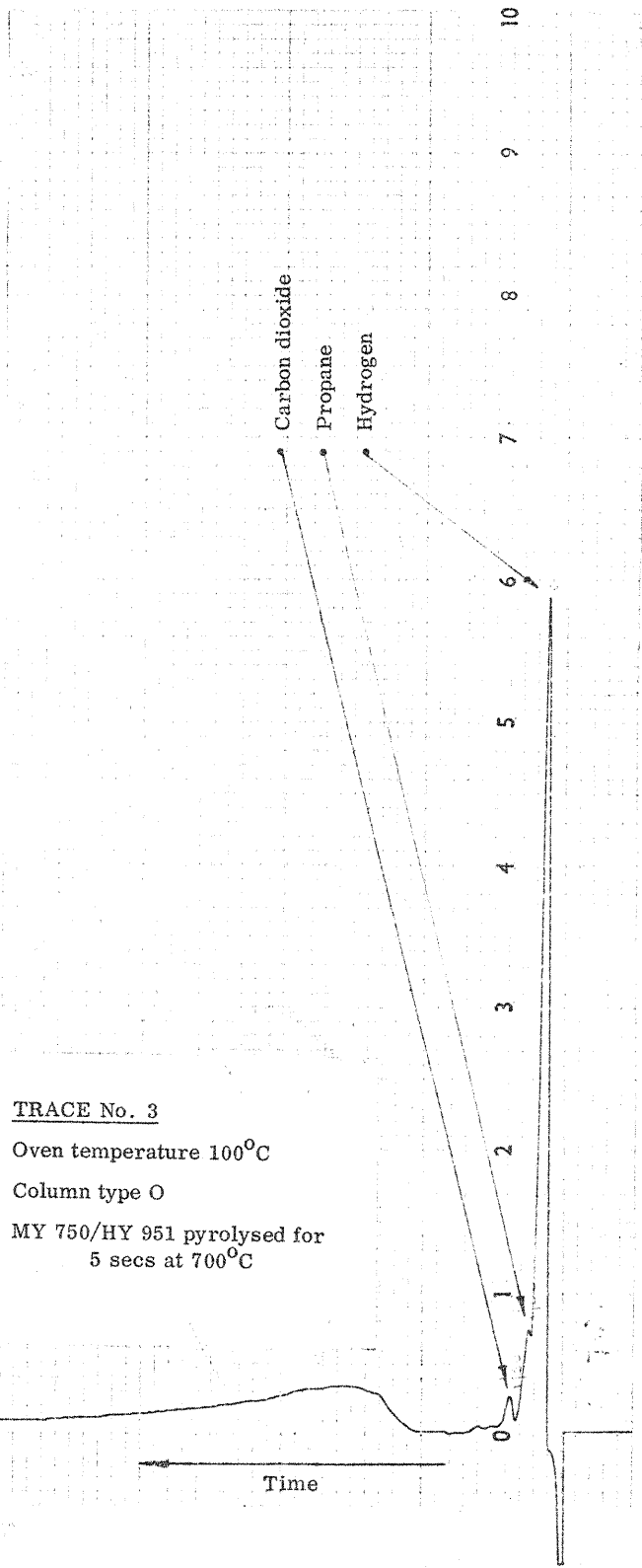


TRACE No. 2

Oven temperature 200°C

Column type O

MY 750/HY 96 Pyrolysed for 10 secs at 800°C



TRACE No. 3

Oven temperature 100°C

Column type O

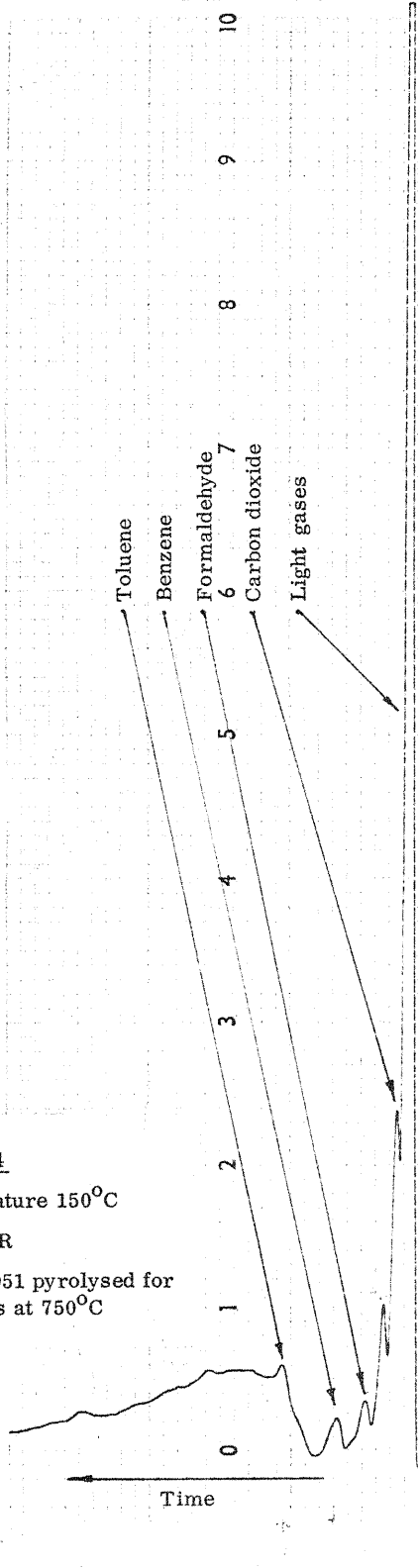
MY 750/HY 951 pyrolysed for 5 secs at 700°C

TRACE No. 4

Oven temperature 150°C

Column type R

MY 750/HY 951 pyrolysed for  
5 secs at 750°C



TRACE No. 5

Oven temperature 50°C

Column type R

MY 750/HY 951 pyrolysed for  
10 secs at 700°C

