THE COLLEGE OF AERONAUTICS

DEPARTMENT OF MATERIALS

The pyrolytic degradation of epoxy resins

in nitrogen at 400 to 700°C

- by -

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SYNOPSIS

The thermal degradation of a bisphenol-A based epoxy resin (EP 274) cured with 4,4'-diaminodiphenyl methane (DDM) and with phthalic anhydride (PA) was studied using pyrolysis gas chromatography. Conclusive evidence for some of the degradation mechanisms of these resins was obtained by pyrolysing samples containing various ^{14}C labelled groups and analysing the products using a combined gas chromatography and radiochemical technique.

Acknowledgements

Introduction

In a review of work on the thermal degradation of epoxy resins carried out before mid 1966[1], the authors concluded that despite the considerable amount of work that had been done in this field, there was still relatively little known about the mechanisms of the thermal breakdown of this important class of polymers.

Since that time a number of papers have been published that contribute to the understanding of the thermal degradation of these resins[2-6]. Probably the most significant of these is the paper by Bowen[2] which describes the use of a combination of thermogravimetric and radioisotope techniques to study the thermal breakdown of a variety of ^{14}C-labelled epoxy resins.

The aim of the present work was to establish the principle degradation mechanisms of aromatic amine and anhydride cured resins using a combination of pyrolysis gas chromatography and ^{14}C tracer techniques. The resin/hardener systems studied were similar to those used by Bowen and consequently it has proved possible to interpret some of his findings in more detail.

Materials

EP274. An epoxy resin known as EP274 was used throughout this work. It was supplied by CIBA (A.R.L.) Ltd. as 'almost pure' diglycidyl ether of bisphenol A (I), a white waxy solid melting at 42°C. It was recrystallised from absolute alcohol and vacuum dried before use. Elemental analysis for (I) requires:
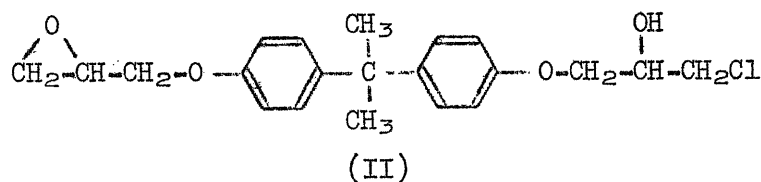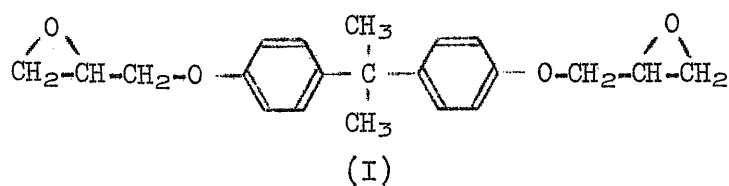
C, 74.1%; H, 7.1%; O, 18.8%.

found for EP274: C, 73.9%; H, 7.0%; Cl, 0.23%; O, by difference, 18.9%.
Assuming that chlorine occurs as shown in structure (II), the amount
found in EP274 (0.23%) suggests that the sample of EP274 consisted of 98%
structure (I) and 2% structure (II).

(I)

(II)

4,4'-Diaminodiphenylmethane (DDM) was obtained in a 'pure' form from
Koch-Light Laboratories Ltd. This material (mp. 88-89°C) was recrystallised
from benzene and vacuum dried to a melting point of 90-91°C. It was kept
in well sealed bottles in the dark to minimise the discolouration which
occurs on exposure to light and oxygen.

Phthalic anhydride (PA) was obtained from May and Baker Ltd. in a pure form
(mp. 132°C). Further purification was considered to be unnecessary; the
sample was stored in a desiccator over phosphorous pentoxide to minimise
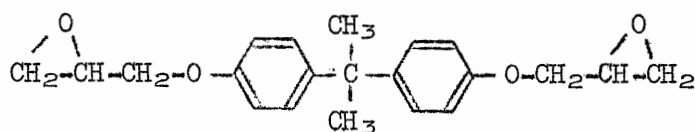reaction with atmospheric moisture.

[14]C-labelled compounds

The ^{14}C-labelled epoxides (III) and (IV) were prepared in these
laboratories from appropriately labelled acetone (III) and phenol (IV),
supplied by the Radiochemical Centre, Amersham, Bucks. Experimental details
appear in the literature[7,8]

C* denotes ^{14}C
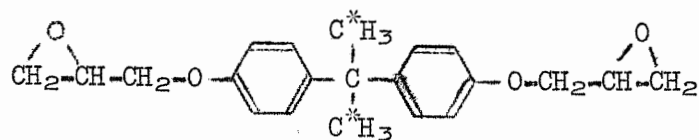
Specific activity: 1.1 µc/g. (III)

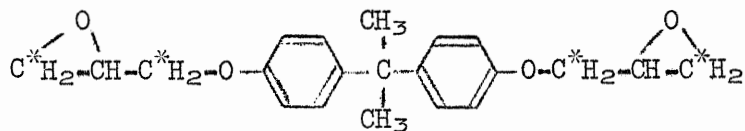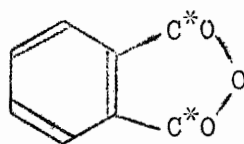Specific activity: 1.2 µc/g (IV)

The labelled epoxides (V) and (VI) and the labelled phthalic anhydride (VII) were obtained from Dr. D.O. Bowen of The Dow Chemical Co., Freeport, Texas. The labelled DDM (VIII) was prepared by Yarsley Research Laboratories, Chessington, Surrey.
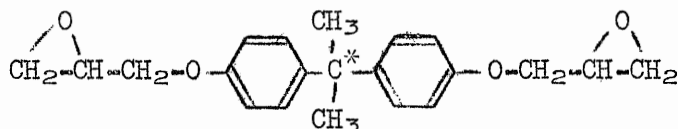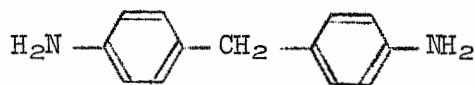

Specific activity 4.0 µc/g. (V)

Specific activity 20 µc/g.   (VI)

Specific activity: 4.9 µc/g.   (VII)

$$H_2N - \langle\bigcirc\rangle - CH_2 - \langle\bigcirc\rangle - NH_2$$

Specific activity: 3.8 µc/g (VIII)

Experimental

Preparation of cured resins

EP274/DDM. The resin EP274 and hardener DDM were mixed together in
stoichiometric proportions at 100°C. When a homogeneous solution had
been obtained it was placed in a vacuum desiccator for 3 hours for degassing.
The resin was then cured for 16 hr. at 55°C, 2 hr. at 125°C and 2 hr. at 175°C.
Cured resins were prepared from (III), (IV), (V) and (VI) and DDM and from
EP274 and (VIII) in the same way.

EP274/PA. The resin EP274 and hardener PA were mixed together at 130-140°C
using 85% of the stoichiometric amount of anhydride. When a homogeneous
solution had been obtained it was cured at 130°C for 24 hrs and then at
175°C for 5 hr. Cured resins were prepared from (III), (IV), (V) and (VI)
and PA and from EP274 and (VII) in the same way.

Combined pyrolysis and radio-gas chromatography

Samples of the various cured resins were pyrolysed at temperatures
between 400 and 700°C on an electrically heated nichrome filament. The
filament was housed in a pyrex glass tube which was built into a Perkin Elmer
452 gas chromatograph so that degradation products that were volatile at the
chromatograph oven temperature were swept into the column and separated.
Nitrogen was used as the carrier gas (and atmosphere for pyrolysis)
throughout this work, and since the chromatograph was fitted with a thermal

conductivity detector the peaks recorded on the 'pyrograms' were +'ve or

-'ve depending on their thermal conductivity relative to that of nitrogen

at the oven temperature.

The sample size was varied between 5 and 50 mg. depending on the

specific activity of the resin and on the degradation products being

studied.   It was found that varying the sample size in this range, did

not significantly alter the relative amounts of the degradation products

formed at a given pyrolysis temperature.   Presumably this was because

no radical change in the geometry of the system was involved.   It should

be stressed however that the results of this type of work are highly

dependant on the heating method used[9],[10], and in some cases catalytic

degradation is a complicating factor.

The separated degradation products were identified by comparing their

retention times with those of known compounds, and where possible, by trapping

them individually on KBr crystals, recording their I/R spectra and

comparing these with the spectra of known compounds.

When ^{14}C-labelled resins were pyrolysed the separated products were

burnt to CO_2 and water by passing them through cupric oxide heated to $700°C$.

The gas stream was then passed through a scintillation detector which

consisted of a glass spiral packed with scintillation grade authracene

crystals viewed by a photomultiplier tube.   When a radioactive peak

passed through the spiral, the weak β emission from the ^{14}C caused

scintillations in the authracene which were detected by the photomultiplier.

Events per second data from the photomultiplier tube were amplified and

passed to an integrator unit which was designed to drive a chart recorder

and to integrate each radioactive peak and display the total digitally.

Pyrolysis of a ^{14}C-labelled sample therefore gave the usual 'pyrogram' and a 'radio-pyrogram' on which the activity of each peak could be recorded. A more detailed description of this apparatus may be found in the literature[11].

In those cases where the specific activity of the resin was rather low (resin IV) the detector was not sufficiently sensitive to record active peaks of minor degradation products. Consequently the separated products from these resins were condensed and collected separately in a suitable scintillator solution (0.5% Butyl P.B.D. in redistilled A.R. toluene) contained in counting bottles. These samples were then counted using normal liquid scintillation counting techniques.

Results

The volatile degradation products identified on pyrolysis of the cured resins EP274/DDM and EP274/PA (at temperatures between 400 and 700°C in nitrogen) are listed in Tables I and II, and some typical pyrograms are shown in Figs. 1-5.

It should be noted that although degradation products are assigned to the pyrolysis temperatures, it does not mean that these are the only degradation products formed at those temperatures, but that these were the products formed in sufficient quantities during the pyrolysis time of 30 sec. to be detected by our equipment. For example, no degradation products were detected after pyrolysis for 30 sec. at 350°C, but it is well known that if an epoxy resin is maintained at 350°C in an inert atmosphere considerable degradation does occur[4].

The results of the work with ^{14}C-labelled resins are summarised in Table III and some typical pyrograms and radiopyrograms are shown in Figs. 6-9.

Table I

Degradation products of EP274/DDM at pyrolysis temperatures between 400 and 700°C in nitorgen.

PYROLYSIS TEMPERATURES			
400°C	500°C	600°C	700°C
Hydrogen	Hydrogen	Hydrogen	Hydrogen
Methane	Carbon monoxide	Carbon monoxide	Carbon monoxide
Water	Methane	Methane	Methane
	Carbon dioxide	Carbon dioxide	Carbon dioxide
	Acetaldehyde	Formaldehyde?	Formaldehyde?
	Water	Acetaldehyde	Acetaldehyde
	Phenol	Water	Unknown
		Phenol	Acetone
		O-Cresol	Water
			Benzene
			Toluene
			Unknown
			Phenol
			O-Cresol
			P-Cresol
			Higher phenols

Table II

Degradation products of EP274/PA at pyrolysis temperatures between 400 and 700°C in nitrogen.

PYROLYSIS TEMPERATURES			
400°C	500°C	600°C	700°C
Hydrogen	Hydrogen	Hydrogen	Hydrogen
Methane	Carbon monoxide	Carbon monoxide	Carbon monoxide
Carbon dioxide	Methane	Methane	Methane
Water	Carbon dioxide	Carbon dioxide	Carbon dioxide
	Acetone	Acetaldehyde	Formaldehyde?
	Water	Acetone	Acetaldehyde
	Phthalic anhydride	Water	Unknown
		Phenol	Acetone
		Phthalic anhydride	Water
			Benzene
			Toluene
			Unknown
			Unknown
			Phenol
			O-Cresol
			Unknown
			Phthalic Anhydride

Table III

Volatile radioactive degradation products of ^{14}C-labelled resins.

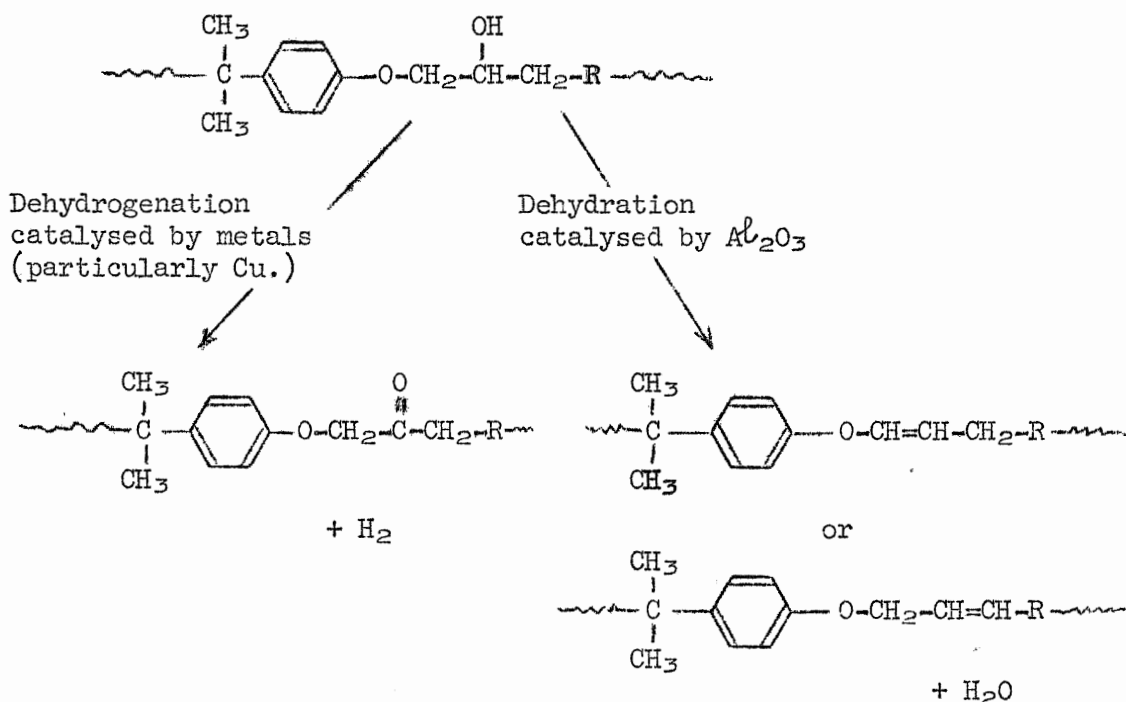| Resin	Volatile radioactive degradation products
III/DM III/PA	Methane
IV/DDM	Phenol, O-Cresol, p-Cresol (benezene, toluene?)
V/DDM V/PA	Methane, higher phenols.
VI/DDM VI/PA	Methane, Ethylene, Acetaldehyde, Acetone.
EP274/VII	Carbon monoxide, Carbon dioxide, Phthalic anhydride.
EP274/VIII	None (benezene, toluene?)

Discussion

The results of this work provide sufficient information for a fairly detailed picture of the thermal breakdown of these aromatic amine and anhydride cured epoxy resins to be given.

In the early stages of degradation, at the lowest temperature studied, the predominant breakdown mechanisms are clearly 'non chain-scission' reactions leading to the formation of hydrogen, methane and water. At higher temperatures degradation products resulting from the breakdown of the aliphatic part of the resins appear in large quantities together with some primary breakdown products of the aromatic entities. At the highest pyrolysis temperatures studied secondary breakdown products of the aromatic parts of the resins are formed in addition to all the other products. The mechanisms of the various stages of degradation may be discussed in some detail.

Non chain-scission reactions

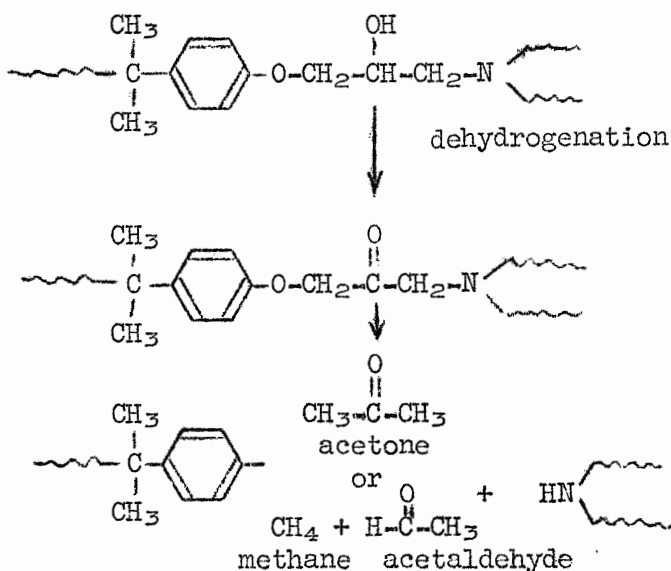### (i) Dehydration and dehydrogenation

The most important non scission reactions occurring in these resins are the competing dehydration and dehydrogenation reactions associated with the secondary alcohol groups in the cured resin structures. (The cured resin structures are shown in Figs. 10 and 11). The relative extents to which these reactions occur are dependant on the pyrolysis technique:

$$\sim\sim\sim\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\!\!-\!\!\bigcirc\!\!-\!O\!-\!CH_2\!-\!\overset{\displaystyle OH}{\overset{|}{CH}}\!-\!CH_2\!-\!R\sim\sim$$

Dehydrogenation   Dehydration
catalysed by metals   catalysed by Al_2O_3
(particularly Cu.)

$$\sim\sim\sim\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\!\!-\!\!\bigcirc\!\!-\!O\!-\!CH_2\!-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!CH_2\!-\!R\sim\sim$$

$+\ H_2$

$$\sim\sim\sim\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\!\!-\!\!\bigcirc\!\!-\!O\!-\!CH\!=\!CH\!-\!CH_2\!-\!R\sim\sim$$

or

$$\sim\sim\sim\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\!\!-\!\!\bigcirc\!\!-\!O\!-\!CH_2\!-\!CH\!=\!CH\!-\!R\sim\sim$$
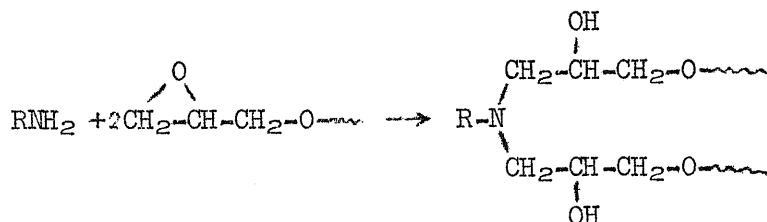
$+\ H_2O$

When hot wire pyrolysis is used it is likely that the dehydrogenation reaction is catalysed, pyrolysis in a porcelain boat on the other hand would favour the dehydration reaction.

This effect has been demonstrated by comparing the quantities of acetone and acetaldehyde liberated on complete pyrolysis of samples of EP274/DDM, (a) on the nichrome filament and (b) in a porcelain boat. The quantities of acetone and acetaldehyde represent the extent of dehydrogenation because:

$$\sim\sim\sim\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\!\!-\!\!\bigcirc\!\!-\!O\!-\!CH_2\!-\!\overset{\displaystyle OH}{\overset{|}{CH}}\!-\!CH_2\!-\!N\!\!\!<$$

$\downarrow$ dehydrogenation

$$\sim\sim\sim\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\!\!-\!\!\bigcirc\!\!-\!O\!-\!CH_2\!-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!CH_2\!-\!N\!\!\!<$$

$\downarrow$

$$\sim\sim\sim\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\!\!-\!\!\bigcirc\!\!-\!$$

$$\overset{\displaystyle O}{\overset{\|}{CH_3\!-\!C\!-\!CH_3}}$$
acetone

or

$$CH_4 + H\!-\!\overset{O}{\overset{\|}{C}}\!-\!CH_3$$

$+\ HN\!\!\!<$

methane   acetaldehyde

The results are listed in Table IV, they show that the hot wire technique

yields about 100 times more acetaldehyde and 20 times more acetone than

the porcelain boat method, and thus underline the fact that degradation

mechanisms are sometimes a function of pyrolysis technique.

Quantitative measurements of the water formed on complete pyrolysis

of EP274/DDM samples on the nichrome filament indicate that about 50% of

all the secondary alcohol groups undergo dehydration. This result was

obtained by assuming that the curing reaction:

$$RNH_2 + 2CH_2-CH-CH_2-O\text{---} \longrightarrow R-N \begin{cases} CH_2-CH-CH_2-O\text{---} \\ \quad\quad\ |\ OH \\ CH_2-CH-CH_2-O\text{---} \\ \quad\quad\ |\ OH \end{cases}$$

in stoichiometric. (In fact about 90% of the epoxy groups react in this

way). Most of the other secondary alcohol groups are probably dehydrogenated;

at least 25% of these yield acetone or acetaldhyde and methane and others

probably give methane and carbon monoxide or formaldehyde, but these products

are discussed in more detail under chain-scission reactions.

Table IV

Comparison of 'hot wire' and 'porcelain boat'

pyrolyses of EP274/DDM at 700°C in N_2.

	Nichrome filament	Porcelain boat
Samples wt.mg.	19.65	1.9
wt.CH_3CHO mg.	0.226	0.14×10^{-3}
% wt.CH_3CHO	1.15	0.01
Wt.$(CH_3)_2CO$ mg.	0.039	0.13×10^{-3}
% wt.$(CH_3)_2CO$	0.20	0.01
Ratio $\frac{CH_3CHO}{(CH_3)_2CO}$	5.8	1.1

(ii) Other non chain-scission reactions

Methane: It has already been noted that methane is a product of the breakdown

of the aliphatic parts of the cured resin, but since relatively large

quantities of methane are liberated before any other chain scission products

it seems likely that the following mechanism is responsible for the formation

of methane at the lower degradation temperatures;
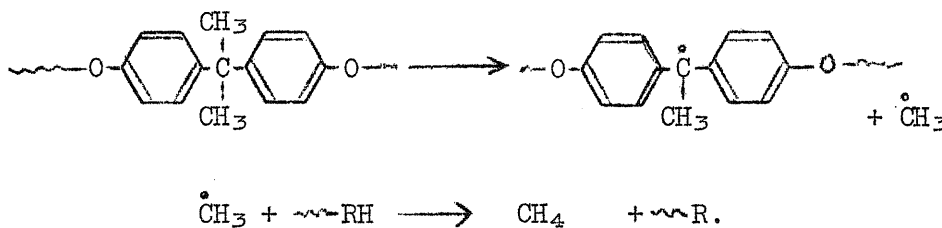
The fact that the cured resins III/DDM and III/PA both gave [14]CH_4 confirmed

that this reaction does occur.

Carbon dioxide: In the early stages of the degradation of anhydride cured resins, some CO_2 may result from decarboxylation of unreacted carboxyl groups.

Hydrogen: In addition to the dehydrogenation reaction discussed above, hydrogen may also be stripped from aromatic nuclei at temperatures above 600°C.

Chain Scission reactions

### (i) Primary chain scission products

The primary chain scission products result from the breakdown of the aliphatic segments of the cured resin structures and from the initial stages of breakdown of the aromatic segments.

Following dehydration or dehydrogenation the aliphatic segments break down into methane and ethylene (and possibly propylene) or acetone, acetaldehyde and methane (and probably carbon monoxide and formaldehyde):

$$
\begin{array}{c}
\text{OH} \\
| \\
\text{---CH}_2\text{-CH-CH}_2\text{---}
\end{array}
$$

$H_2O +$ ---CH=CH-CH$_2$ ---

$H.\downarrow$

possibly CH_2=CH-CH$_3$

mainly CH_4

some CH_2=CH$_2$ } See Fig.1

---CH$_2$-$\overset{\overset{O}{\|}}{C}$-CH$_2$--- $+H_2$

$\downarrow$

CH_3-$\overset{\overset{O}{\|}}{C}$-CH$_3$

or $CH_3CHO + CH_4$

or $2CH_4 + CO$ or H_2CO
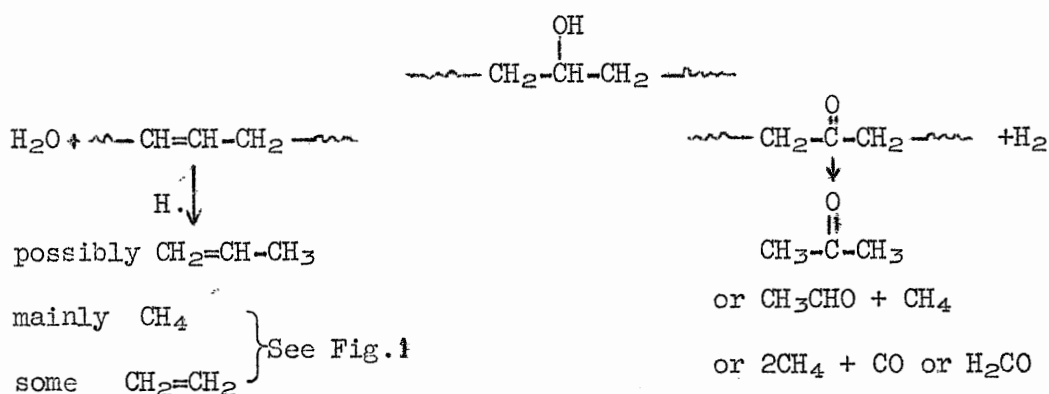
These mechanisms were confirmed by the fact that pyrolysis of

the cured resins VI/DDM and VI/PA yielded ^{14}C labelled methane, ethylene,

acetaldehyde, and acetone (Figs. 6 and 7).

The initial stage of the breakdown of the aromatic segments of these

resins produces phenol which originated from the bisphenol-A structures:
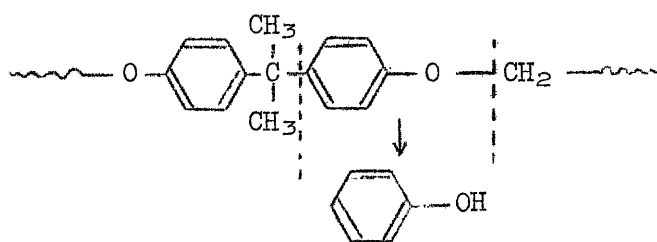
This was confirmed by the identification of ^{14}C labelled phenol in the

pyrolysis products of the resin IV/DDM.

Phthalic anhydride was regenerated in large quantities on pyrolysis

of EP274/PA at temperatures of 500°C and above together with carbon monoxide

and carbon dioxide. The PA cured resins also gave off larger quantities

of benzene than the DDM cured resins. The following mechanisms account

for these findings:
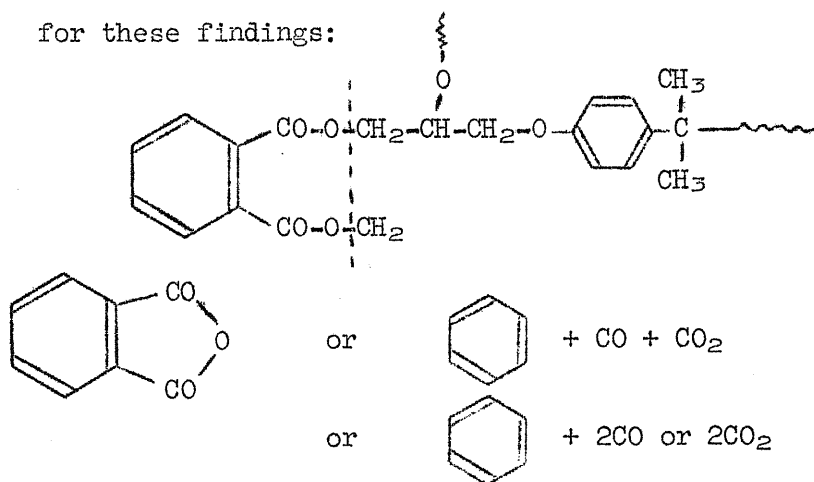
Pyrolysis of EP274/VII gave ^{14}C-labelled CO, CO_2 and phthalic anhydride as

would be expected (Figs. 8 and 9).

(ii) Further chain scission products

The degradation products which only occur in detectable quantities at the higher pyrolysis temperatures are benzene, toluene, O- and p-cresols, higher phenols and some unidentified products. In general these may be accounted for by further breakdown or rearrangement of the aromatic segments of the resins. The cresols and higher phenols originate from the bisphenol A structures, but benzene and toluene may originate from any of the aromatic nuclei. Pyrolysis of EP274/VIII did not give any positive evidence on the fate of the DDM; slight activity was noted in the benzene and toluene from this resin but clearly the bulk of the DDM remained in the high boiling tars.

Differences between aromatic amine and anhydride cured resins

The principle differences in the thermal degradation patterns of the anhydride and amine cured resins are;

(i) Amine cured resins contain many more $-CH_2-CHOH-CH_2$ groupings (Figs. 10 and 11) than the anhydride cured resins and consequently yield more water and hydrogen. Since the dehydration and dehydrogenation reactions occur at relatively low temperatures the amine cured resins show more weight loss at these temperatures and therefore appear to have inferior thermal stability to the anhydride resins.

(ii) When chain scission occurs the anhydride cured resins tend to regenerate the hardener and CO and CO_2 in large quantities. The amine hardeners do not appear to be regenerated but their fate has not been clearly established.

(iii) The aliphatic segments of the amine cured resins yield more acetaldehyde

than acetone whereas the reverse is true for the anhydride cured resins. This may be due to a preferential rupture of the C-N bond in the case of the amine cured resins leading to acetaldehyde:

$$\text{~~~~ O-CH}_2\text{-C-CH}_2\text{- N} \overset{\text{O}}{\overset{\|}{}}$$
$$\downarrow \quad 2\text{H.}$$
$$\text{~~~ O-CH}_2\text{-C-CH}_3 + \text{HN}$$
$$2\text{H.} \downarrow$$
$$\text{~~~ O-CH}_3 + \text{HCOCH}_3$$
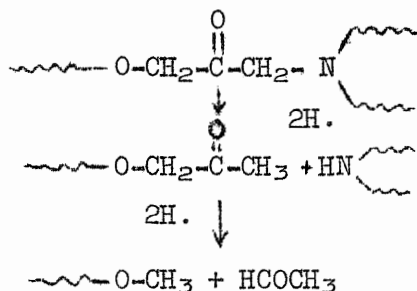
The anhydride system is symmetrical and may tend to break symmetrically:

$$\text{~~~ O - CH}_2 - \overset{\text{O}}{\overset{\|}{\text{C}}} - \text{CH}_2 - \text{O ~~~}$$
$$\downarrow 4\text{H.}$$
$$\text{~~~ OH + CH}_3\text{-C-CH}_3 \quad + \quad \text{HO ~~~}$$
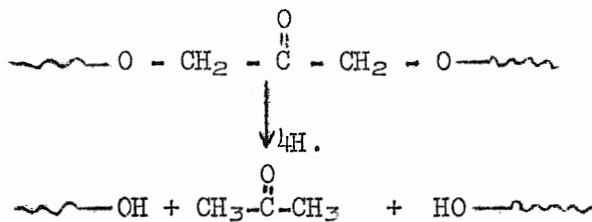
Conclusion

The number of degradation products of a hardened epoxy resin is sufficiently large for the origin of particular fragments to be in doubt. The use of ^{14}C labelling techniques has made it possible to pin point the origin of most of these degradation products.

Figure Captions
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Fig. No.

1.   Pyrogram of EP274/PA.   Pyrolysis temp: 700°C.   Column:

        Silica gel.   Oven temp: 50°C.   Carrier gas: N_2, 40 ml/min.

2.   Pyrogram of EP274/DDM.   Pyrolysis temp: 700°C.   Column: 7,8-

        Benzoquinoline/Chromosorb P, 15/85.   Oven temp: 50°C.

        Carrier gas: N_2, 40 ml/min.

3.   Pyrogram of EP274/PA.   Pyrolysis temp: 700°C.   Column: 7,8-

        Benzoquinoline/Chromosorb P, 15/85.   Oven temp: 50°C.

        Carrier gas: N_2, 40 ml/min.

4.   Pyrogram of EP274/PA.   Pyrolysis temp: 700°C.   Column:

        Apiezon L/Chromosorb P, 10/90.   Oven temp: 150°C.

        Carrier gas: N_2, 40 ml/min.

5.   Pyrogram of EP274/DDM.   Pyrolysis temp: 700°C.

        Column: Apiezon L/Chromosorb P, 10/90.   Oven temp: 150°C.

        Carrier gas: N_2, 40 ml/min.

6.   Radiopyrogram of VI/PA.   Pyrolysis temp: 700°C.   Column:

        Silica gel.   Oven temp: 50°C.   Carrier gas: N_2, 30 ml/min.

7.   Radiopyrogram of VI/PA.   Pyrolysis temp: 700°C.   Column:

        7,8-Benzoquinoline/Chromosorb P, 15/85.   Oven temp: 50°C.

        Carrier gas: N_2, 20 ml/min.

8.   Radiopyrogram of EP274/VII.   Pyrolysis temp: 700°C.

        Column: Silica gel.   Oven temp: 50°C.   Carrier gas: N_2,

        40 ml/min.

9.   Radiopyrogram of EP274/VII.   Pyrolysis temp: 700°C.

Column: Apiezon L/Chromosorb P, 10/90.   Oven temp: 200°C.

Carrier gas: N₂, 30 ml/min.

1. D.P. Bishop, D.A. Smith, Ind. Eng. Chem. 59, Aug. 1967, 32-39.

2. D.O. Bowen, Modern Plastics, Aug. 1967, 127-164.

3. M.A. Keenan, D.A. Smith, J. Appl. Polymer Sci., 11, 1009-1026, (1967).

4. J.C. Patterson-Jones, D.A. Smith, J. Appl. Polymer Sci., 12, 1601-1620(1967).

5. G.J.Fleming, J. Appl. Polymer Sci., 10, 1813-1830, (1966).

6. E.S. Freeman, A.J. Becker, J. Appl. Polymer Sci., 2829-2851 (1968).

7. de Jong, Demethers, Rec. Trav. Chim. 84, 460, (1965).

8. U.S. Patent 3, 142, 688.

9. R.L. Levy, J. Gas Chromatography, March, 1967, p. 107.

10. F. Farré-Ruis, G. Guiochon, Anal. Chem., 40, 998, (1968).

11. D.P. Bishop, B.R. Moffitt, D.A. Smith, J. Gas Chromatography, in press.

FIG.1

FIG. 2
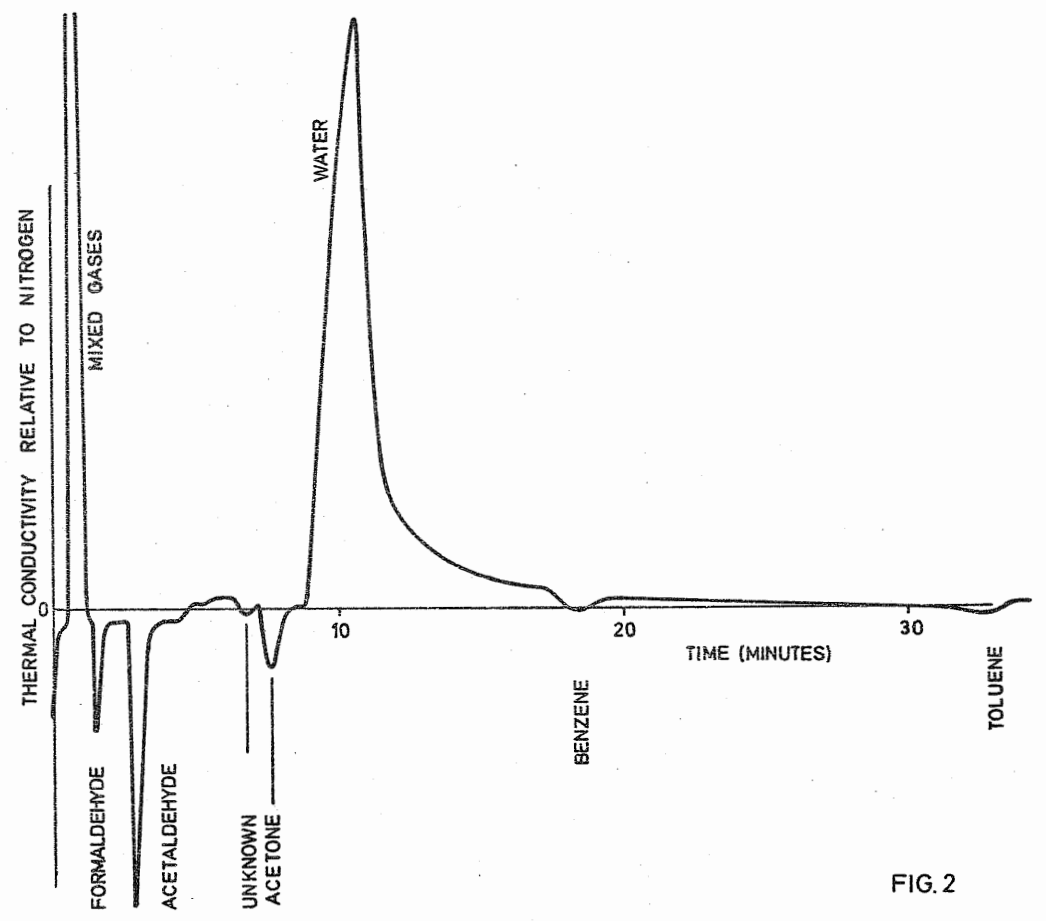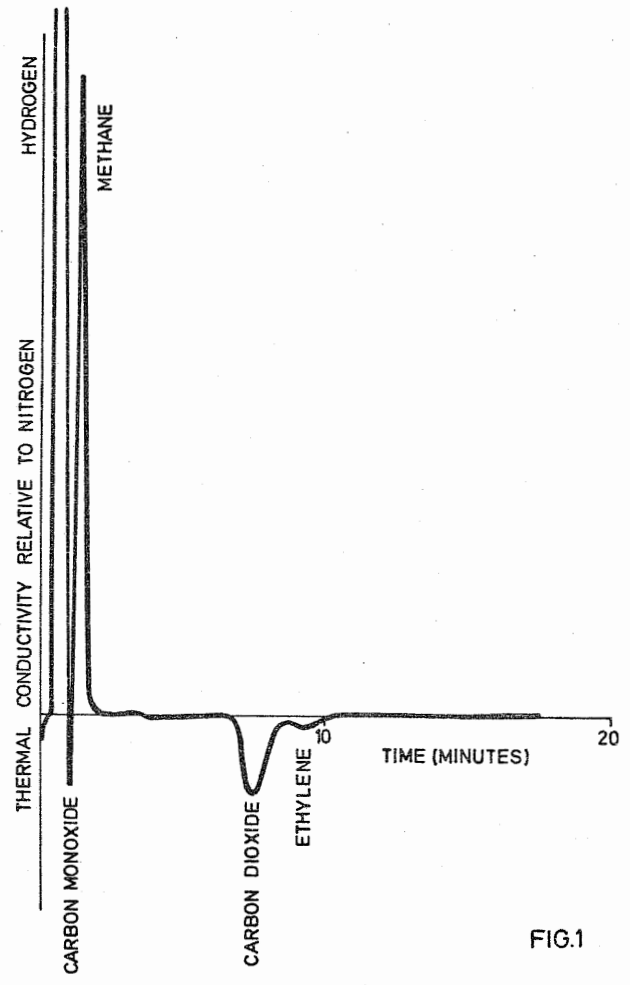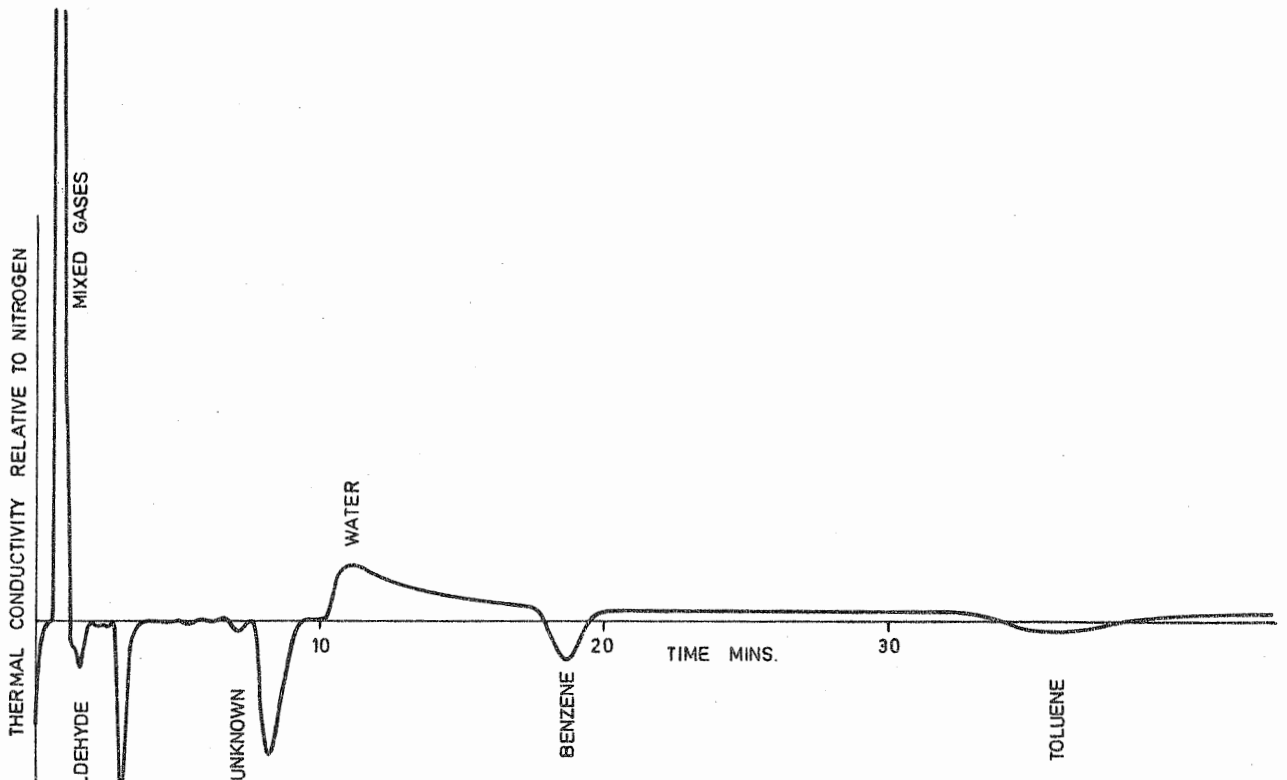
FIG.3
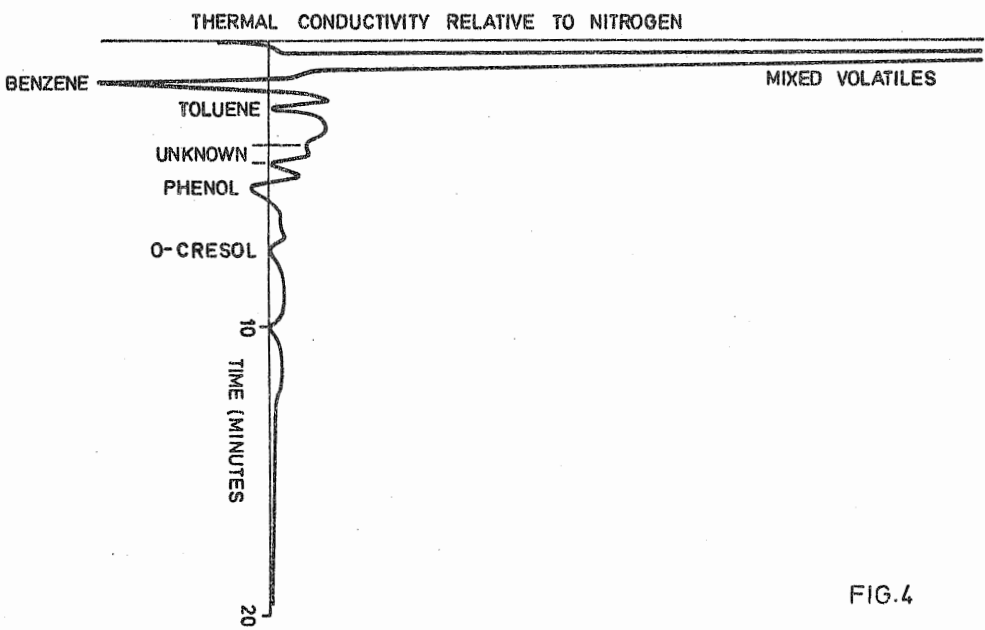
FIG.4
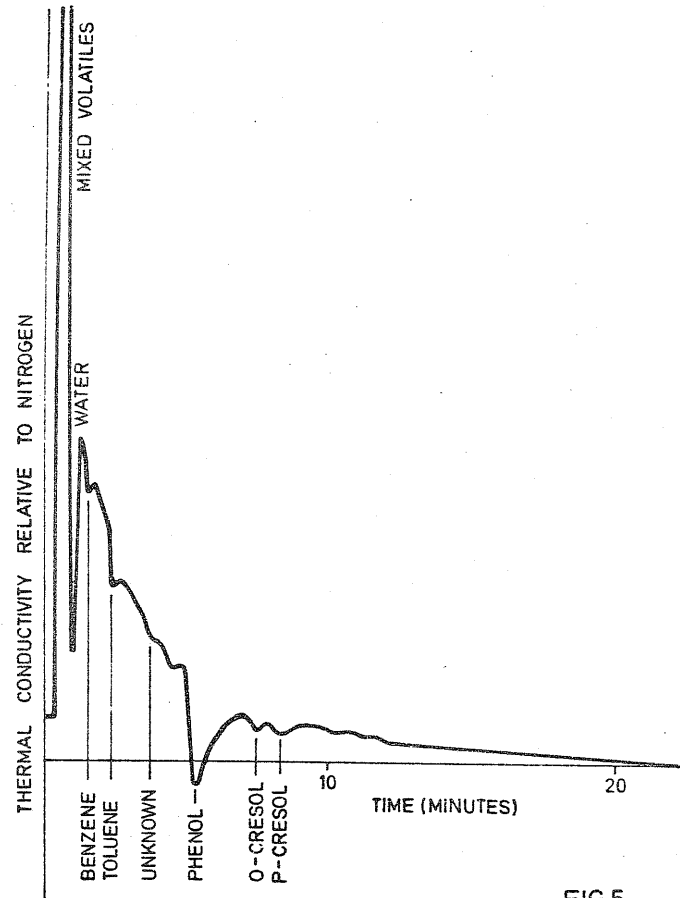
FIG.5
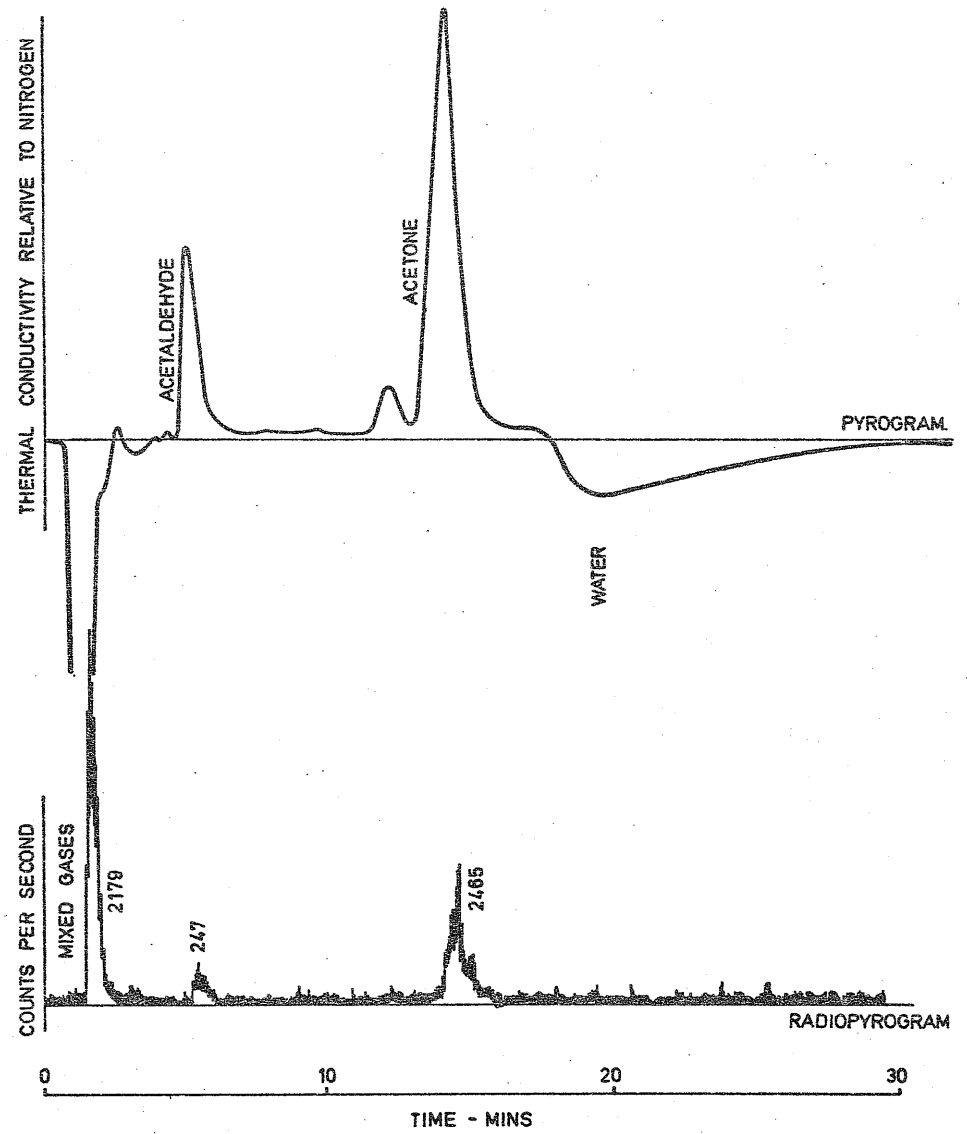
FIG. 6
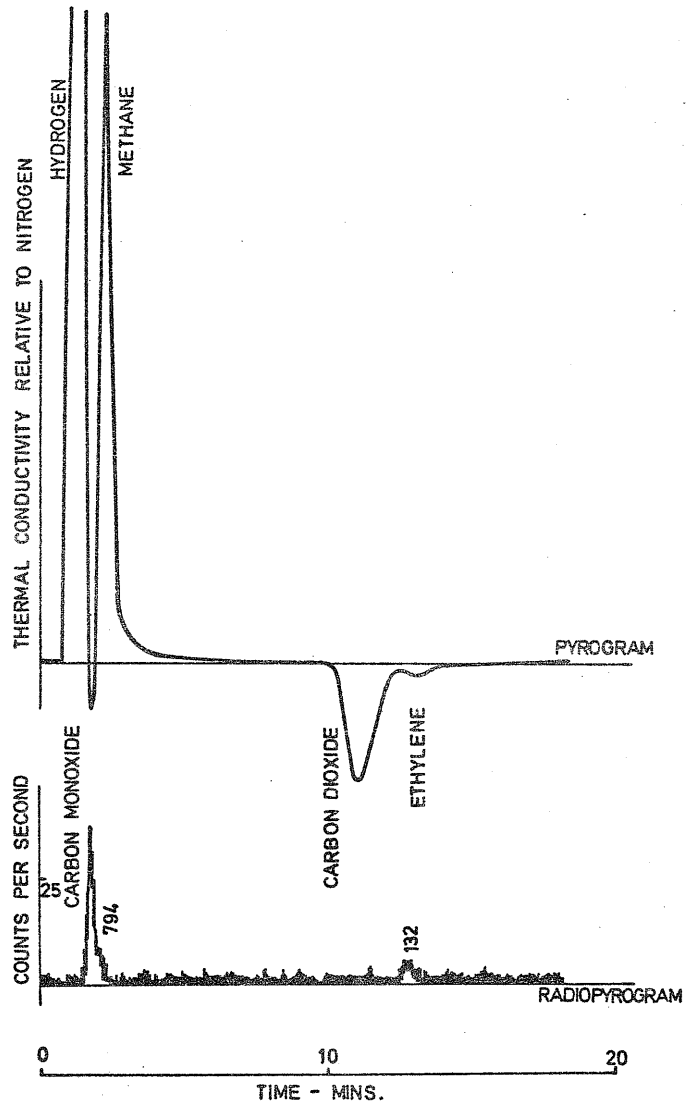
FIG.7

FIG. 8

FIG.9

FIG.10

FIG.11