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The thermal degradation of epoxy resins III
The thermal degradation of polypyromellitimides I

- by -

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The thermal degradation of epoxy resins III

A summary of work carried out between 1st March and 1st September, 1967 on the thermal degradation of the resin/hardener systems DDM/EP274 and PA/EP274.

1. Further pyrolysis/gas chromatography work has been carried out on the resin/hardener systems DDM/EP274 and PA/EP274. Pyrolysis products from these resins identified in previous work are listed in Table I. Possible mechanisms for the formation of each of these products may be postulated, and where possible, further work has been carried out to provide evidence for or against the various mechanisms.

Table I

Products of Pyrolytic Degradation of Epoxy Resins at 750°C in a Nitrogen Atmosphere

DDM/EP274

Hydrogen (a)
Carbon monoxide (c)
Methane (b)
Carbon dioxide (c)
Acetaldehyde (a)
Acetone (b)
Water (a)
Benzene (c)
Toluene (c)
Phenol (a)
O-Cresol (c)
p-cresol (c)

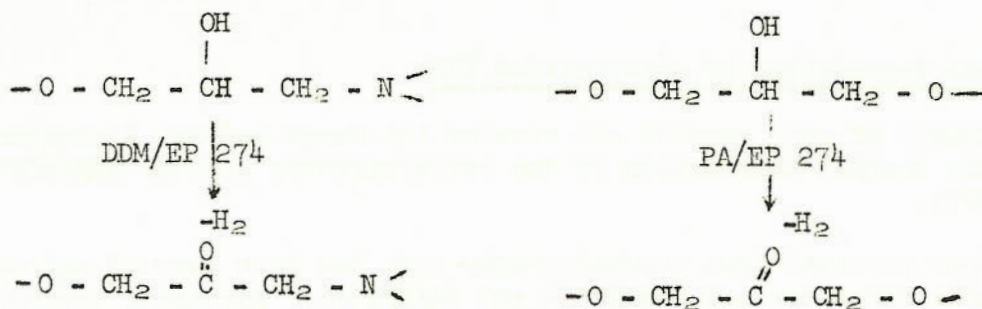
PA/EP274

Hydrogen (a)
Carbon monoxide (c)
Methane (b)
Carbon dioxide (b)
Acetaldehyde (a)
Acetone (a)
Water (a)
Benzene (a)
Toluene (c)
Phenol (a)
O-Cresol (c)
Phthalic anhydride (a)

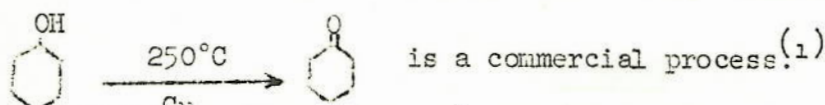
(a) = major, (b) = secondary, (c) = minor importance of degradation product.

It should be noted that, where temperatures are quoted for the formation of particular degradation products, these represent the temperatures at which detectable quantities of the products are formed within 30 seconds, and not the temperatures at which the products actually begin to be formed. For example no degradation products are detectable (after 30 sec.) at 300°C, but it is well known that epoxy resins begin to degrade at 200-250°C.

Hydrogen. It is probable that hydrogen liberated at temperatures between 400 and 500°C (Figs. 1 - 6) is formed by dehydrogenation of secondary hydroxyl groupings in the cured resins:



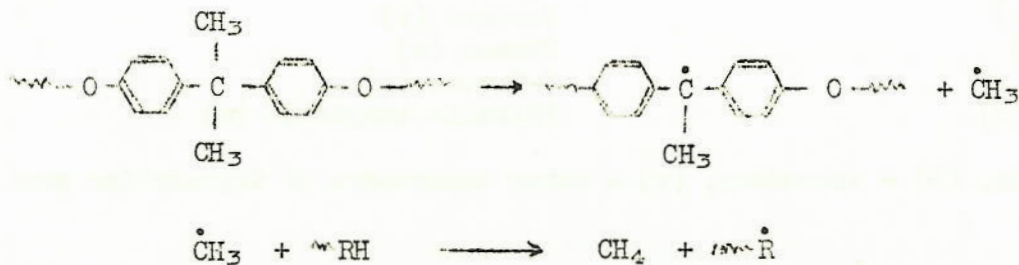
This reaction could be catalysed by the nichrome filament since



At higher temperatures H₂ may be eliminated from aromatic structures to leave a network of carbon rings which probably constitute the carbonaceous part of the residue found on the filament after 'complete' pyrolysis.

Carbon monoxide is a minor degradation product of both resin/hardener systems (Figs. 1 and 2). Other workers have suggested mechanisms for its formation^(2,3) but it is to be hoped that the C¹⁴ work will pin point its origin in PA/EP274 at least.

Methane. Although other workers⁽²⁾ have postulated mechanisms for the formation of methane, they are too complex to account for the relatively large quantities of methane liberated at temperatures between 400°C and 500°C by both resin systems. The following mechanism seems far more likely;

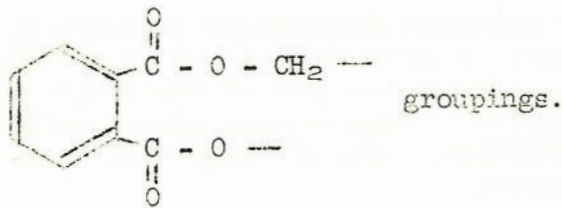


This has been substantiated by pyrolysing a sample of bisphenol A and passing the products through a silica gel column; peaks corresponding to hydrogen and methane were recorded, (Fig. 7). (It has since been noted that Davis and Golden⁽⁴⁾ suggest the same mechanism for the formation of methane from a polycarbonate).

Carbon dioxide

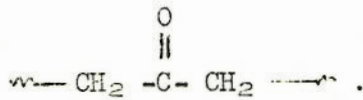
(a) DDM/EP274. The small quantities of CO₂ formed on pyrolysis of DDM/EP274 may result from oxidative attack by oxygen dissolved in the resin.

(b) PA/EP274 yields fairly large quantities of CO₂ which must originate from

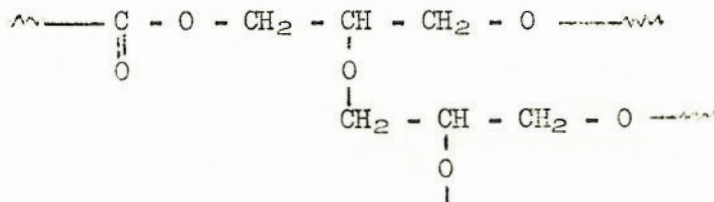


Acetaldehyde and Acetone

Once the proposed dehydrogenation reaction has occurred, acetaldehyde and acetone are expected breakdown products of the structure

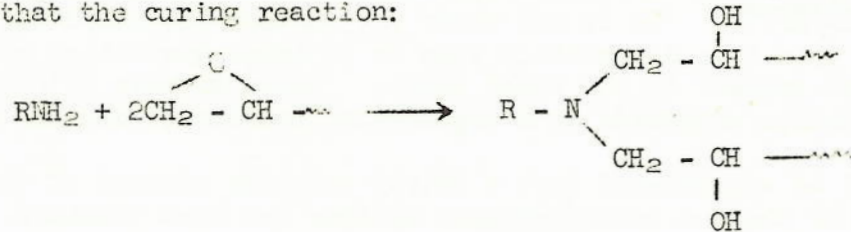


This is probably the sole source of acetone and acetaldehyde in DDM/EP274, but PA/EP274 contains structures such as;



which may also be expected to yield acetone and acetaldehyde.

Water. It is assumed that water splits out of the -O - CH₂ - CHOH - CH₂ - structures; this means that there is competition between the dehydrogenation and dehydration reactions. By calibrating the water peak obtained on separating pyrolysis products with column DE104 (7,8 Benzoquinoline) it has been established that, on complete pyrolysis, DDM/EP274 yields about 50% of the maximum theoretical amount of water. This result was calculated assuming that the curing reaction:

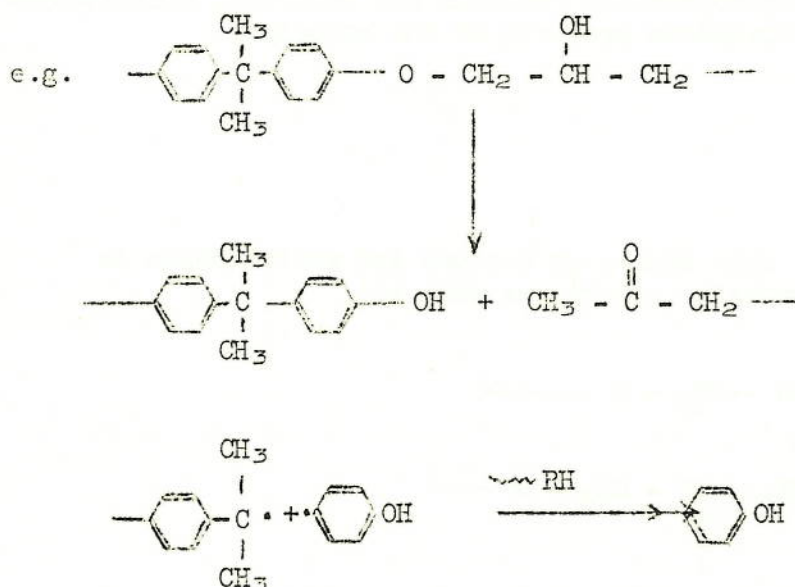


is stoichiometric. In reality this is not the case, and it is therefore likely that rather more than 50% of - CH₂ - CHOH - CH₂ - groups are dehydrated

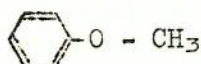
The remaining -CHOH- groups are probably dehydrogenated by the pyrolysis technique, but this may not be so in the absence of the 'hot wire'.

Benzene and Toluene may be regarded as secondary degradation products - they do not appear in significant quantities below 700°C (Figs. 5 and 6). Both compounds could originate from the bisphenol-A part of the resin structure or from the DDM part of DDM/EP274. Some benzene almost certainly comes from the phthalic anhydride in PA/EP274. The C¹⁴ work will throw more light on the origin of these products.

Phenol is a major degradation product of both resin/hardener systems, and undoubtedly comes from the bisphenol-A part of the network:



O- and p-cresols may be formed by rearrangement of fragments such as

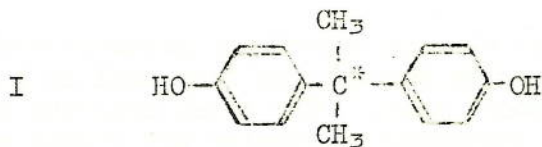


Phthalic anhydride has recently been identified as a major degradation product of PA/EP274. It is not clear yet whether the anhydride is regenerated by a true degradation step or if large quantities of unreacted anhydride are present in the cured resin. Other workers (5)(6) have reported phthalic anhydride as a degradation product of similar resins.

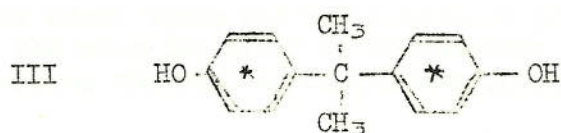
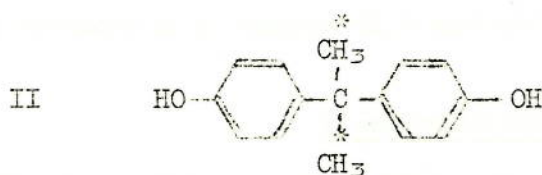
It will be appreciated that a fairly complete picture of the thermal degradation of the two resin/hardener systems has been obtained. The fate of the DDM segments of DDM/EP274 is still unknown but this should be established by the C¹⁴ work.

2. Preparation of C¹⁴ compounds

Compounds I, II and III have been prepared by techniques described in the previous report. These are to be converted into the corresponding



*Denotes C¹⁴



diglycidyl ethers, but so far, attempts at this conversion have failed at the final distillation stage. It is hoped that some help will be forthcoming from CIBA (ARL) with this preparation.

The preparation of IV and V are being contracted out.



3. Development of apparatus for detecting C¹⁴ in the gas chromatograph effluent.

After negotiations with Nuclear Enterprises (G.B.) Ltd., an order for the modified NE 5504, scintillation counter head unit, (Fig. 8) has been placed.

The effluent from the gas chromatograph will pass directly into the

heated flow cell (through a short heated pipe if necessary). Decay of C^{14} labelled compounds in the cell give rise to scintillations in the glass scintillator base of the flow cell. These 'light flashes' will be detected by the photomultiplier (P.M.) tube, the signal will be amplified and passed to the electronics.

Events detected by the P.M. tube will be summed and recorded every 1.0 sec., thus an active compound passing through the flow cell in 1 minute, say, will be recorded as a fairly smooth peak. The total activity of a given radioactive peak will also be displayed by summing all events occurring during the time when the count rate is above the background level.

A full description of the electronics will appear in a separate CofA memo.

The Thermal Degradation of Polypyromellitimides I

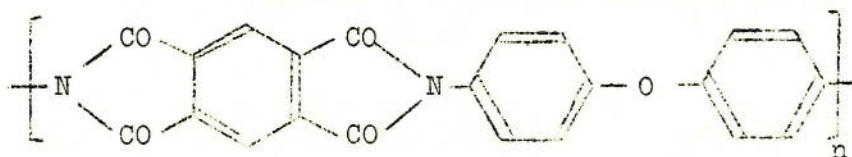
It has been decided to continue the work on the pyrolysis of polymers with a study of the thermal degradation of polypyromellitimides (polyimides).

The C^{14} tracer techniques being developed for the epoxy resin work will be applicable to polyimides. The preparation of these polymers has been described in a number of papers (7)(8), and should not present serious problems.

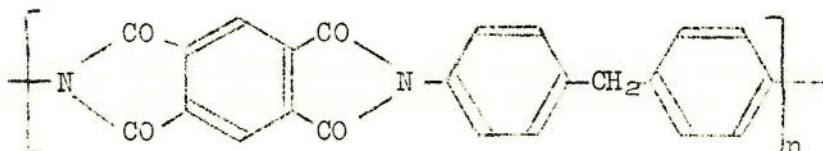
The thermal degradation of polyimides has not been extensively reported in the literature as yet. The papers which have been published (9)(10)(11) (12)(13) have not dealt with degradation mechanisms in any detail.

Samples of the four following polyimides have been supplied by Dr. W.W. Wright (R.A.E. Farnborough):

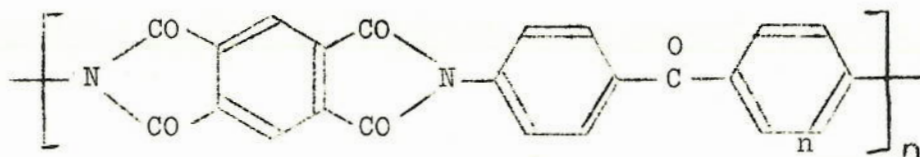
I poly-[NN'-(p,p'-diphenylether) pyromellitimide] (DDE/PMDA)



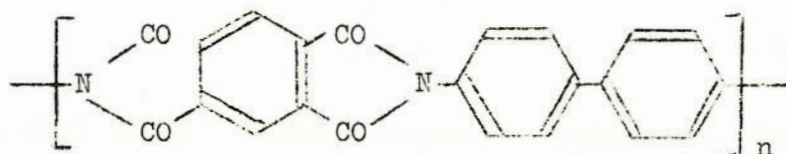
II poly-[NN'-(p,p'-diphenyl methane) pyromellitimide] (DDM/PMDA)



III poly-[N,N'-(p,p'-benzophenone) pyromellitimide] (DBPL/PMDA)



IV poly-[N,N'-(p,p'-diphenyl) pyromellitimide] (PPD/PMDA)



Preliminary Experimental Work

Infra red spectra of the polyimide samples have been recorded and assignments made for most of the major absorptions.

It is doubtful whether any estimate of uncyclised material present in the polyimides can be made by I/R work alone, but in studying degradation mechanisms it will be important to determine the effects of uncyclised units.

Pyrolysis/gas chromatography

Polyimide samples have been pyrolyzed at 700°C on the electrically heated nichrome filament described in previous work. Degradation products have been separated on the same three columns used for the epoxy resin work - silica gel, 7,8-benzo-quinoline and Apiezon L. The latter two columns have not proved very satisfactory in that there appear to be several degradation products which 'tail' badly. A Porapak column will be tried in future.

On complete pyrolysis at 700°C (in N₂) the polyimides show a weight loss of about 40%. The amount of 'tar' which condenses on the walls of the pyrolysis tube is small compared with that observed for epoxy resins. The tars are being collected for further study. The carbonaceous residues have also been retained for C,H,N analysis.

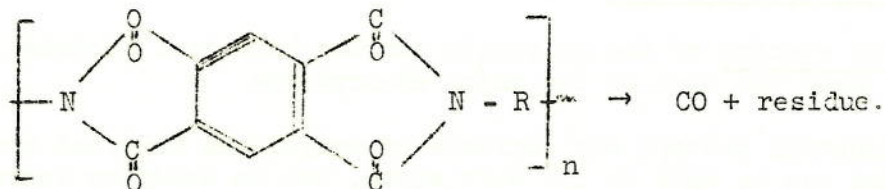
Pyrolysis products identified to date are listed in Table 2.

TABLE 2

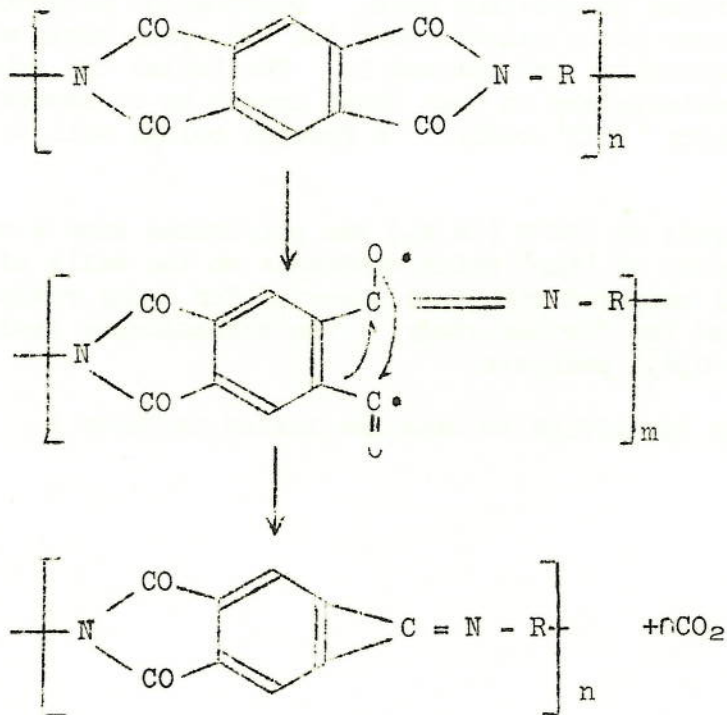
Products of Pyrolytic Degradation of Polyimides at 700°C in a Nitrogen Atmosphere

Hydrogen
Carbon monoxide
Carbon dioxide
Ammonia (?)
Water
Benzene
Phenol (?)

The major degradation product is carbon dioxide. Bruck (10) suggests that carbon monoxide should be the major degradation product:



The mechanism suggested by Cotter and Dine-Hart for the dissociation of phthalanil under electron-impact (14) seems likely to account for the formation of carbon dioxide.



References

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14. Cotter, J.L., and Dine-Hart, R.A. R.A.E. Tech. Report No. 66254.

SAMPLE: DDM/EP 274

COLUMN: SILICA GEL

OVEN TEMP: 50°C

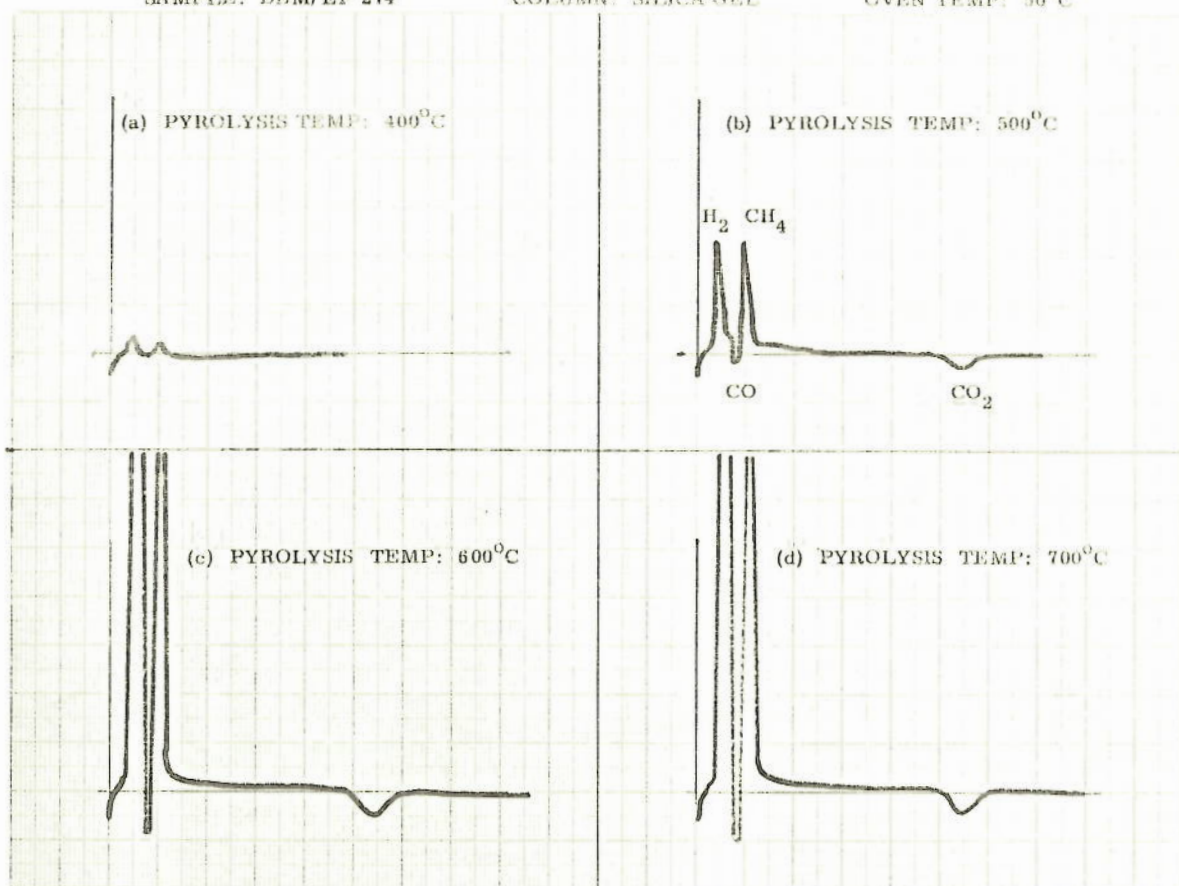


FIGURE 1

SAMPLE: PA/EP 274

COLUMN: SILICA GEL

OVEN TEMP: 50°C

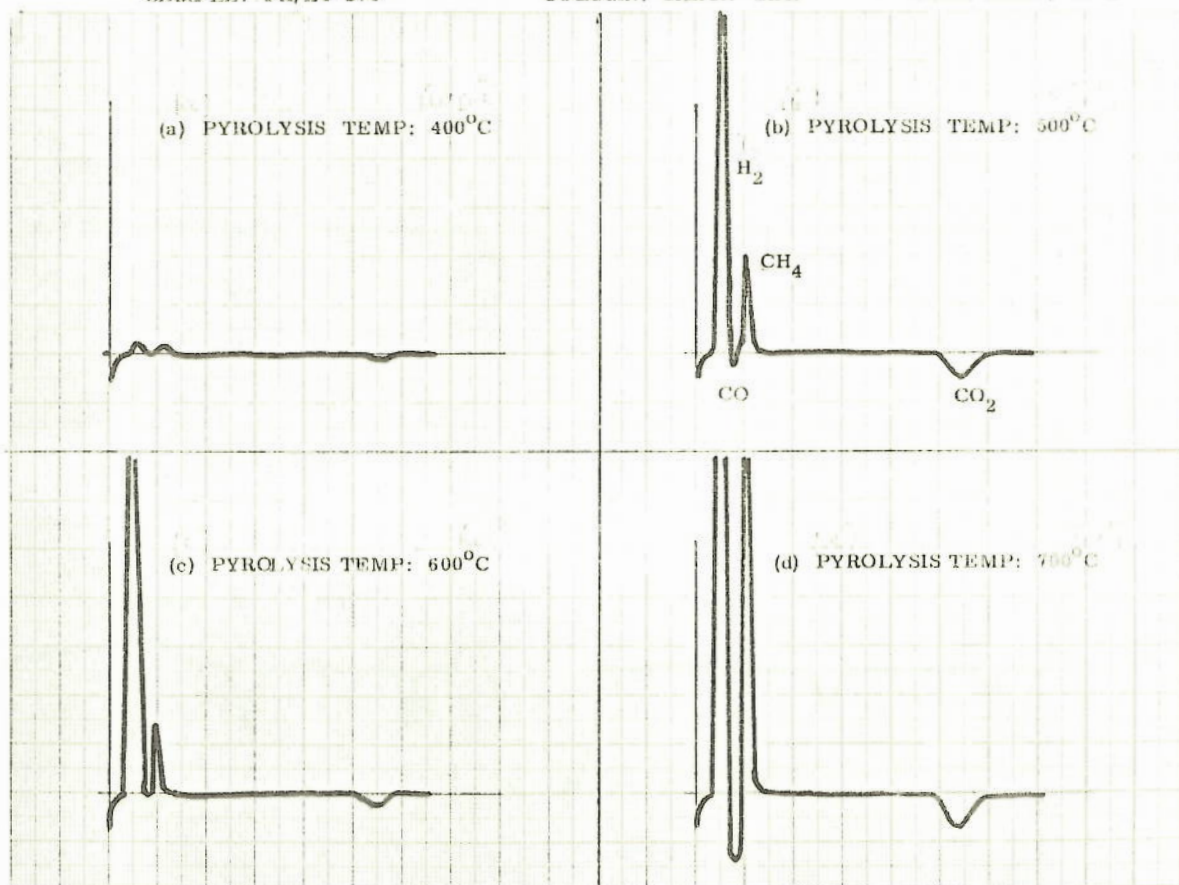


FIGURE 2

SAMPLE: DDM EP274 COLUMN: DE 104 OVEN TEMP: 50°C

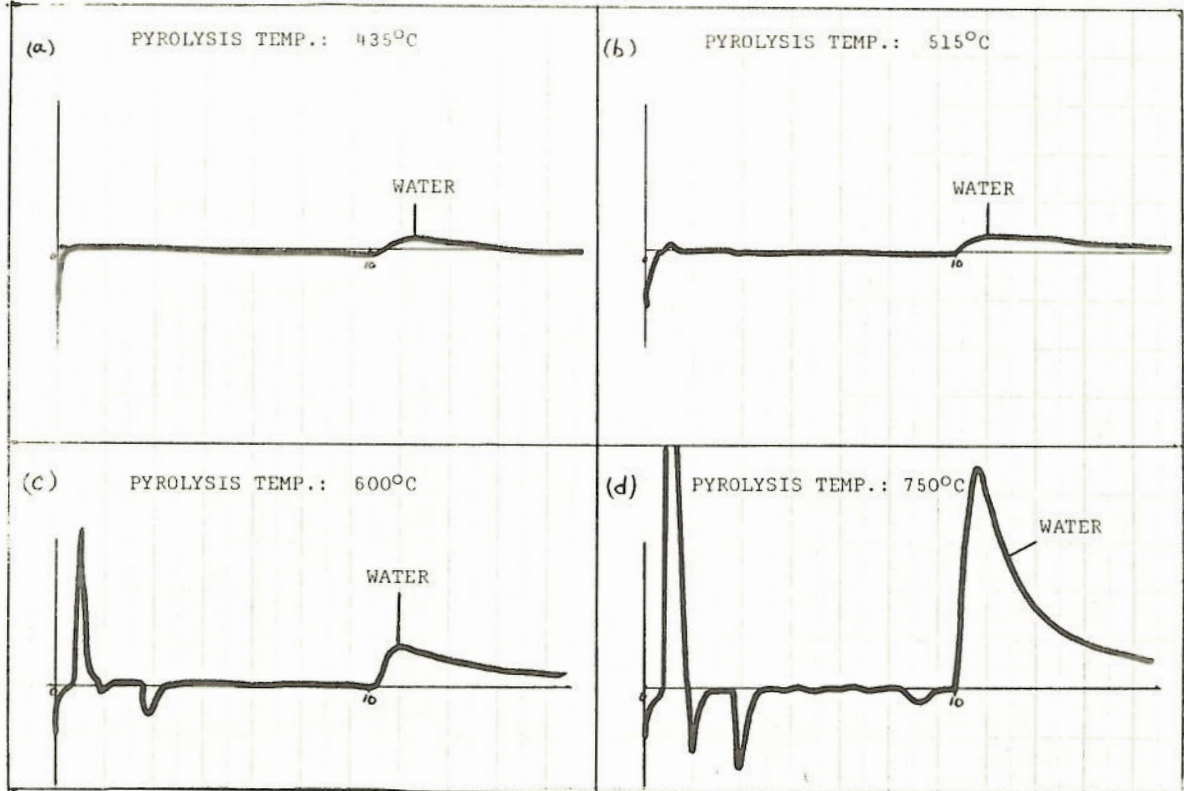


FIG. 3

SAMPLE: PA/EP274 COLUMN: DE 104 OVEN TEMP: 50°C

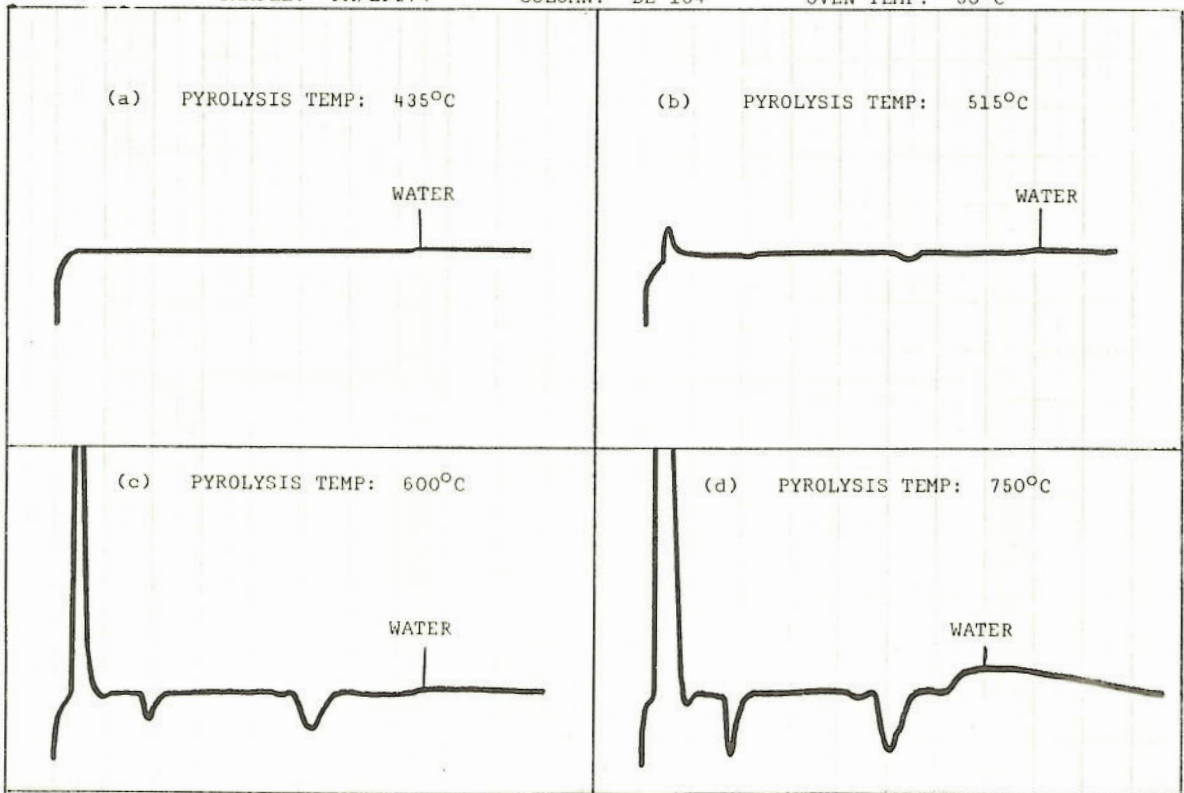


FIG. 4

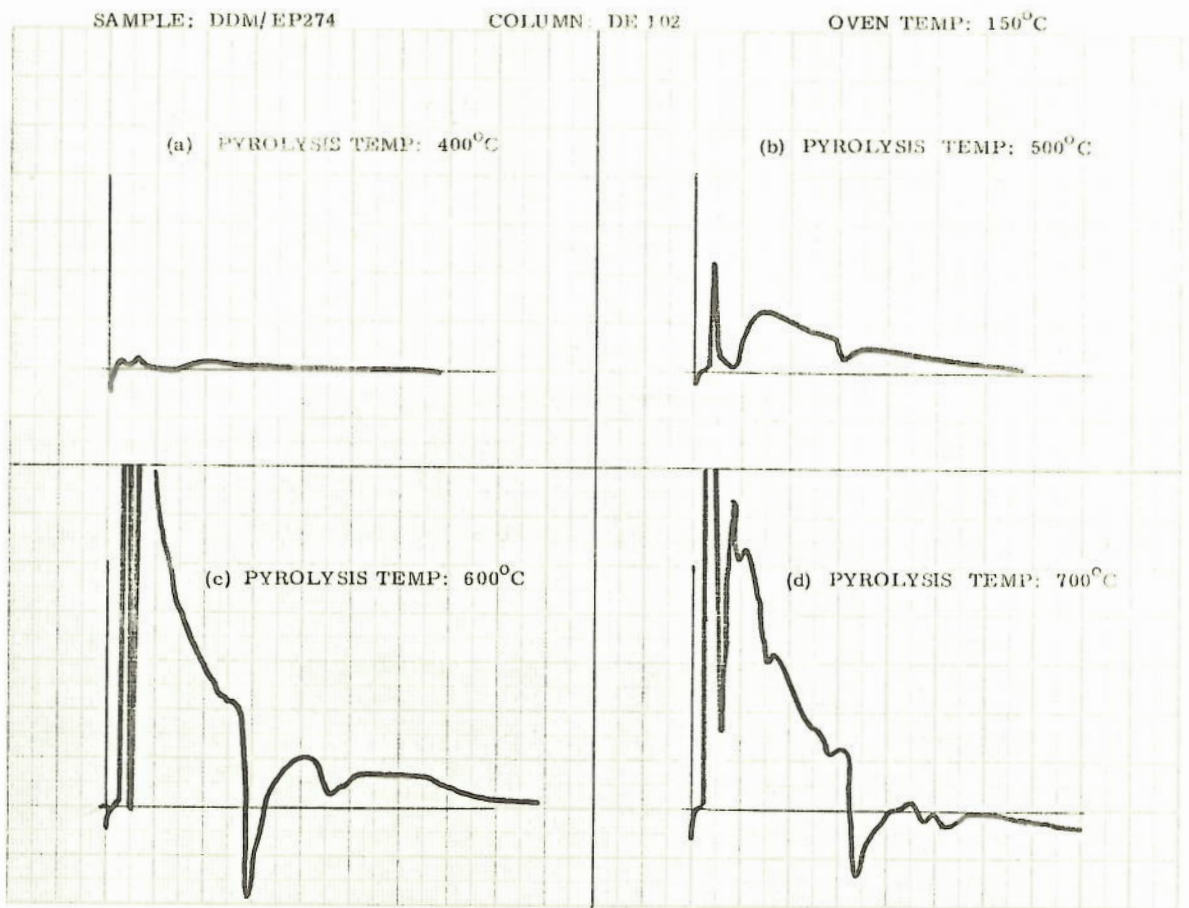


FIGURE 5

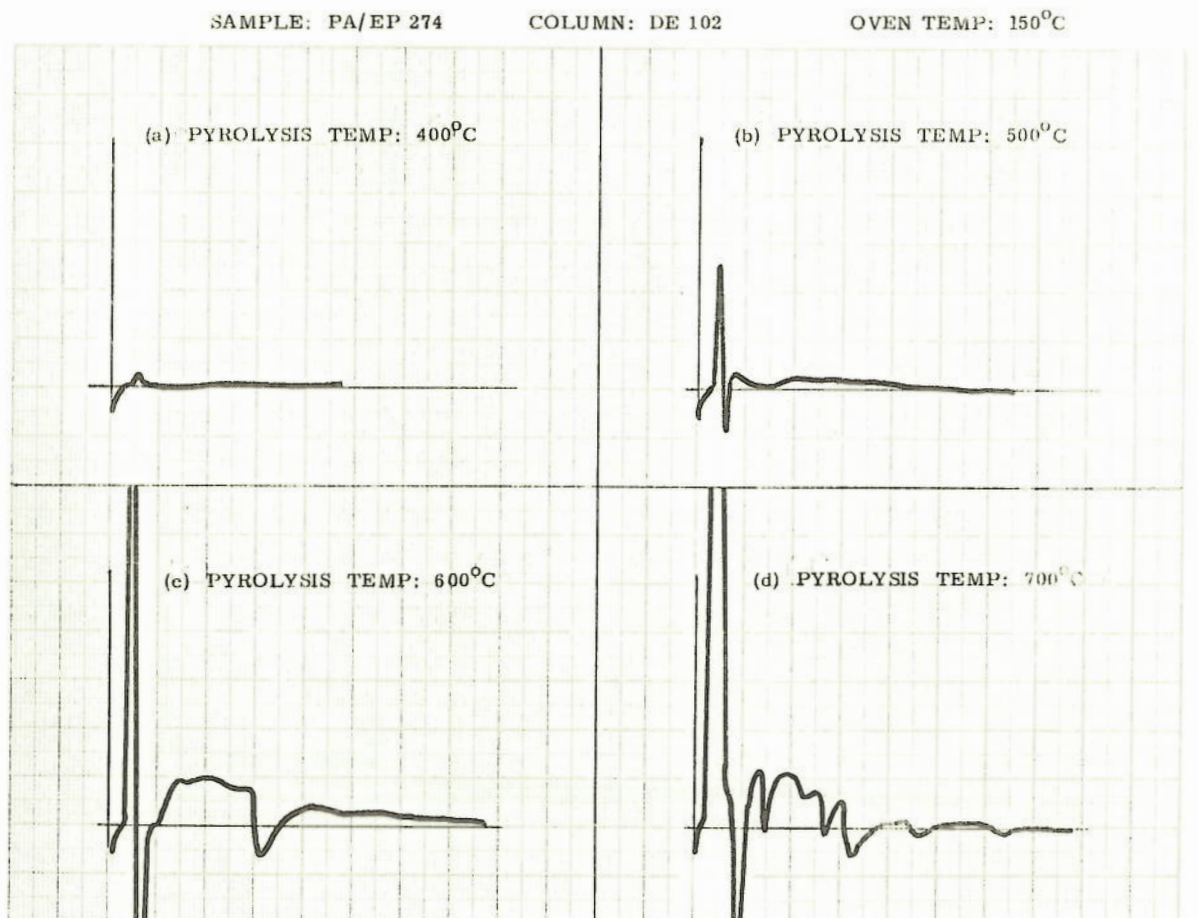


FIGURE 6

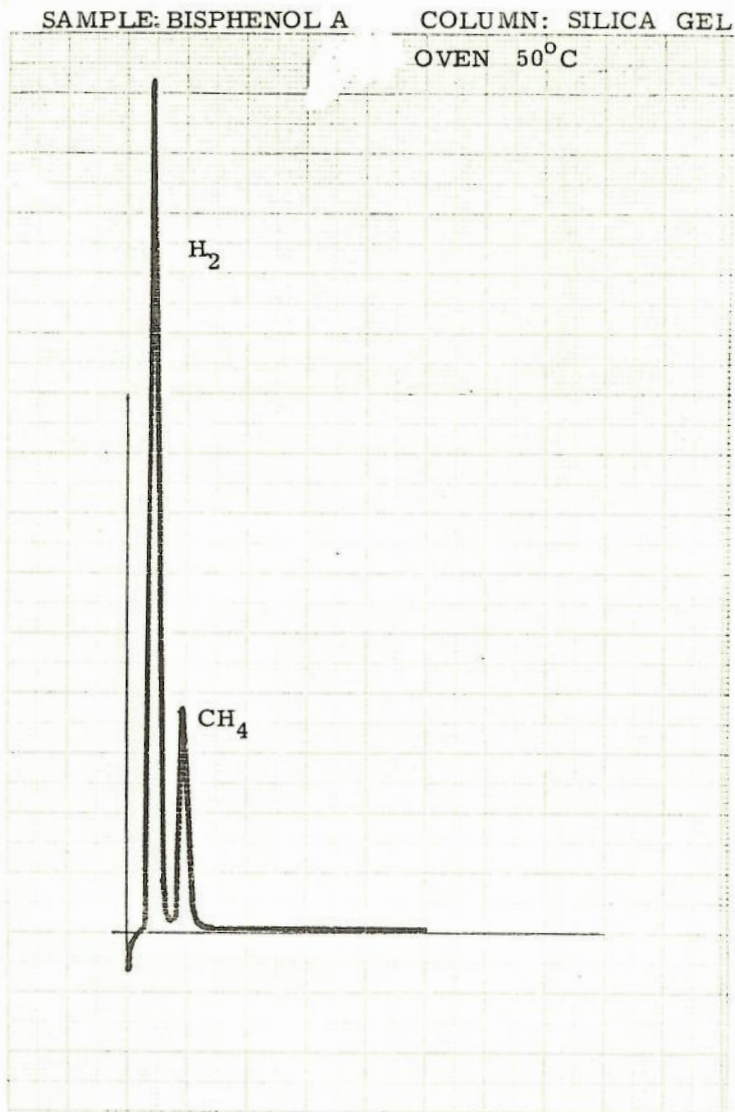


FIGURE 7

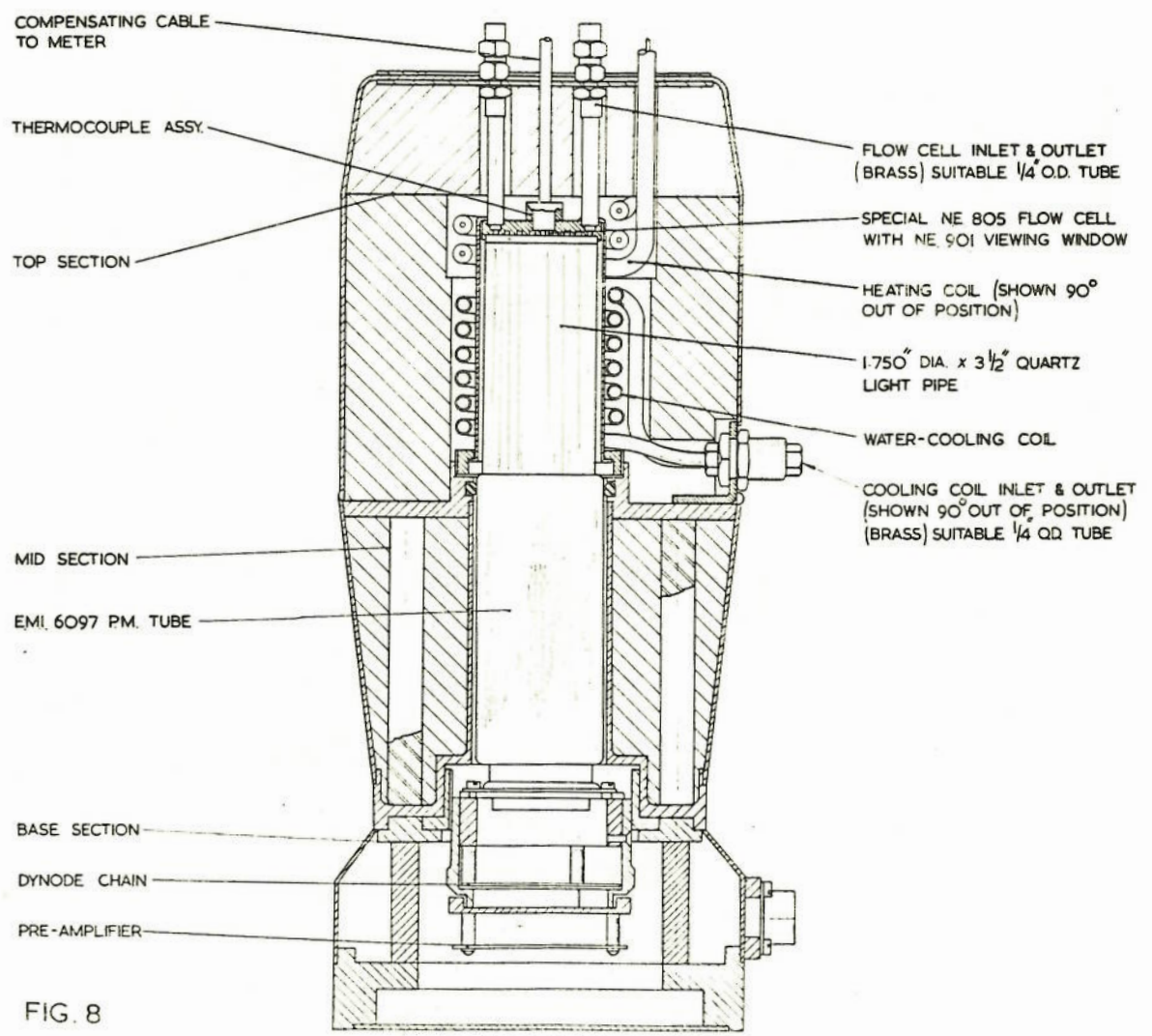


FIG. 8