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DEPARTMENT OF MATERIALS

The thermal degradation of epoxy resins II

- by -

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Progress report:

A summary of work carried out between 1st October, 1966 and 1st March, 1967.

Introduction

The work in this period may be divided conveniently into two parts, (i) pyrolysis/gas chromatography work on two model hardener/resin systems (PA/EP274 and DDM/EP274), and (ii) preliminary preparative work for the C^{14} tracer work outlined in the previous report.

(i) Pyrolysis/gas chromatography

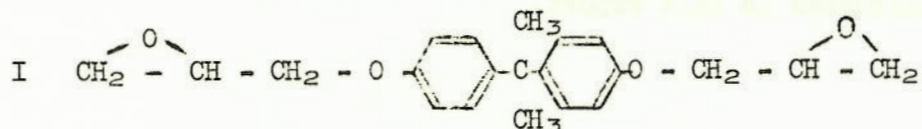
Technique. All the pyrolysis work to date has been carried out in a nitrogen atmosphere on an electrically heated nichrome filament. The filament is housed in a glass tube which is built into a Perkin Elmer 452 gas chromatograph, so that degradation products which are volatile at the chromatograph oven temperature are swept into the column and separated.

To obtain the pyrolysis temperature a calibrated thermocouple of 0.004" chrome/amul wires was spot-welded to the midpoint of the filament; the temperature of the filament was then correlated with the current supplied to it for given carrier-gas flow rates and oven temperatures. (A fixed gas flow rate of 40 ml/minute has been used for all work to date).

The standard detector in the Perkin Elmer 452 is a thermal conductivity cell, hence both positive and negative peaks appear on the chromatograms. This factor caused some difficulties in previous work (1), (2) because it was not always easy to differentiate between 'peaks' and 'troughs' on chromatograms where complete separation was not achieved, (See Figs. 5 and 6). By using a wider variety of columns and oven temperatures, however, it has proved possible to separate and identify almost all the major degradation products of the two resin/hardener systems being studied.

Materials

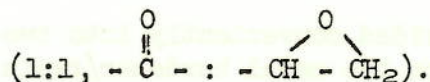
The epoxide being used is the pure diglycidyl ether of bisphenol A (I), it was supplied by CIBA (A.R.L.) Ltd., under the name EP274. It is a white waxy solid melting at 42°C.



This epoxide has been cured with pure diamino diphenyl methane (DDM),

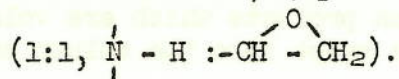
mp. 90°C, to form the resin referred to as DDM/EP274 and with pure phthalic anhydride (PA), mp 132°C, to form the resin PA/EP274. The cured resins were prepared in the following way:

PA/EP 274. The epoxide and phthalic anhydride were mixed together at 130°C in the ratio 100/43 parts by weight



When a homogeneous mixture was obtained it was poured into a mould and maintained at 130°C in a thermostated oven for 24 hours. The oven temperature was raised to 175°C for a further 5 hours before removing the sample.

DDM/EP274. The epoxide and diamino diphenylmethane were mixed together at 100°C in the ratio 100/27 parts by weight



When a homogeneous mixture had been obtained it was cooled to room temperature and placed under vacuum for a period of 3 hours to remove entrapped air. The material was then poured into a mould and cured for:

- 16 hours at 55°C
- 2 hours at 125°C
- 2 hours at 175°C

Chromatograph Columns

Silica Gel. 2 metres, stainless steel column, 1/4" O.D., packed with 30-60 mesh silica gel. Best results obtained at 50°C.

DE102. 2 metres, stainless steel column, 1/4" O.D., packed with Apiezon L/60-80 mesh Chromosorb P, 10/90. Best results (for phenol and cresols) obtained at 150°C.

DE104. 2 metres, stainless steel column, 1/4" O.D., packed with 7, 8-Benzoquinoline/60-80 mesh Chromosorb P, 15/85. Best results (for volatile compounds) obtained at 50°C.

Several other columns have been used with varying degrees of success, they will not be discussed in this report.

Results and Discussion

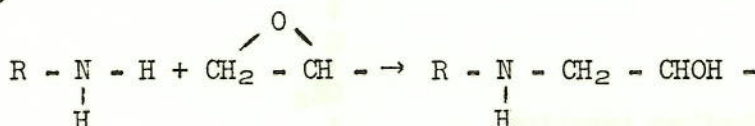
Pyrolysis of the following compounds has been studied: EP274, DDM, PA, bisphenol A, cured resin DDM/EP274 and cured resin PA/EP274. It will be seen from the accompanying chromatograms (Figs. 1 - 6) that the three columns when used at the optimum temperatures separate different fractions of the degradation products. The involatile products which remain in the pyrolysis tube as a tar were not examined but previous workers (2) have partially analysed them via thin layer chromatography and I/R spectroscopy.

The reproducibility of the chromatograms was very good. Chromatograms of EP274, DDM, PA and bisphenol A pyrolysis products were not very informative as these compounds tended to distill from the nicrome filament and condense on the sides of the pyrolysis tube before any degradation occurred. The major degradation products of PA/EP274 and DDM/EP274 have been identified by their retention times and confirmed in some cases by their I/R spectra. It is hoped that I/R spectra will be obtained for all the major peaks in due course, but the technique that has been used so far is not suitable for volatile products.

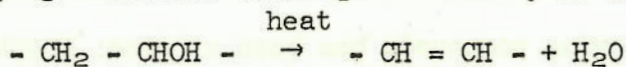
Samples for I/R analysis are obtained in the following manner. The desired product is collected as it emerges from the chromatograph column on finely ground, dried, KBr crystals. The KBr (100-200 mg.) is contained in a length (1") of 1/4" O.D. glass tubing which is plugged at one end with glass wool, and fitted with a very short piece of silicone rubber tubing at the other, the rubber tubing being a close fit on the exit port of the chromatograph. When a 'peak' has been collected the KBr is transferred to an agate mortar and ground to distribute the compound evenly in the crystals. These are then placed in a die which is evacuated for 5 - 10 minutes and then subjected to a pressure of 10 tons/sq.in. for 2 minutes to form a thin KBr disc suitable for I/R work.

Having identified the major degradation products of the two resins it is interesting to compare them. It can be seen from Figs. 1, 2, 5 and 6 that the most notable difference lies in the relatively large amount of water evolved from DDM/EP274. It is well established that anhydride cured resins exhibit greater thermal stability than amine cured resins. Fig. 7 shows that DDM/EP274 loses significant amounts of water before any other degradation occurs, while Fig. 8 shows that PA/EP274 loses minute quantities of water under similar conditions.

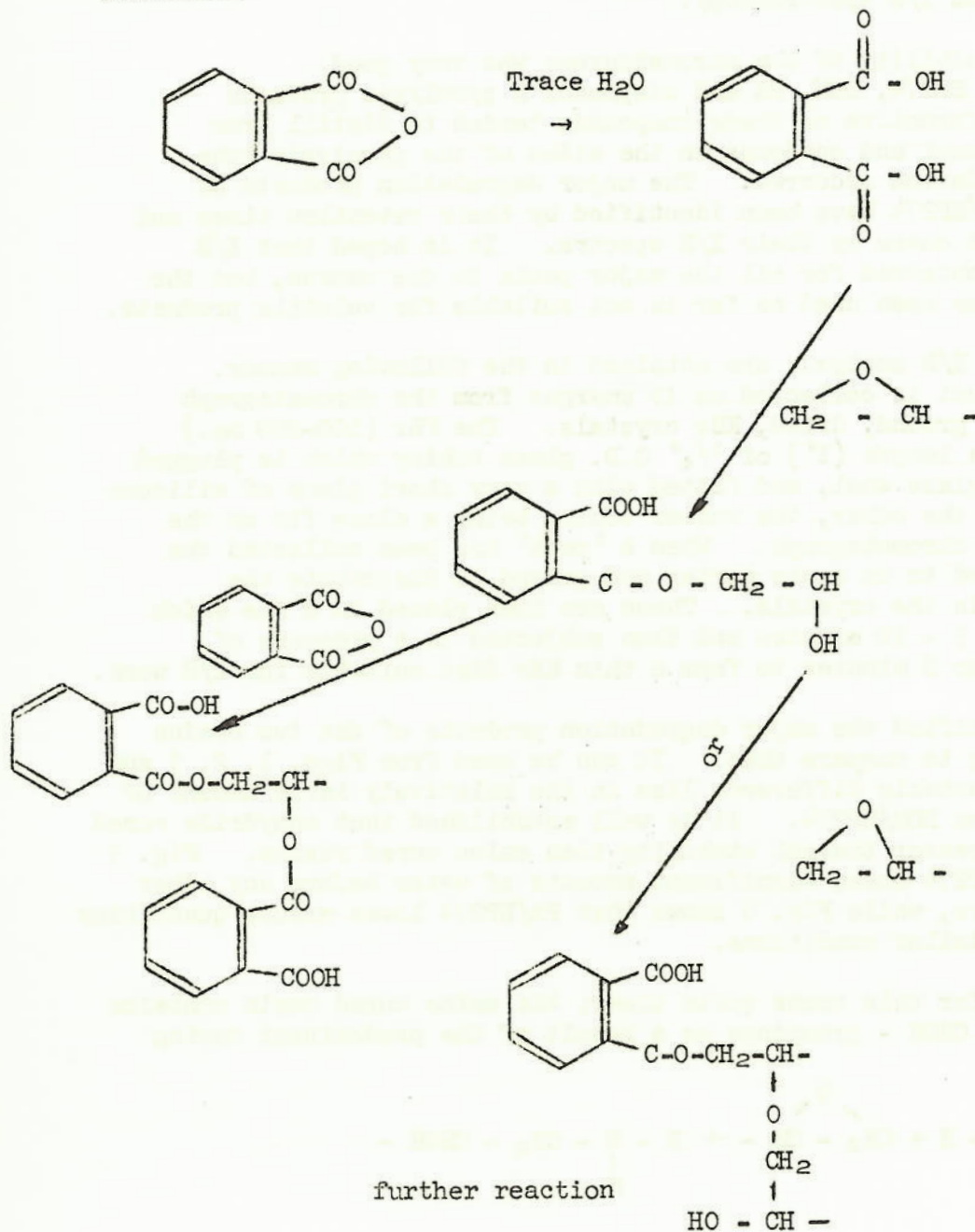
The reason for this seems quite clear: the amine cured resin contains numerous - CH₂ - CHOH - groupings as a result of the predominant curing mechanism;



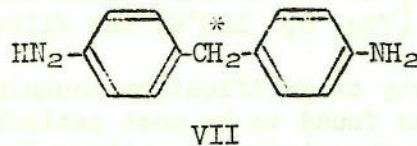
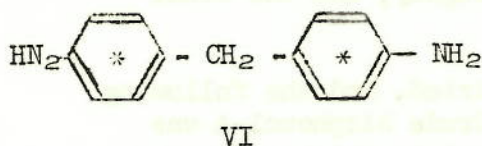
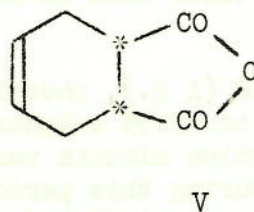
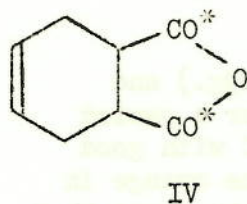
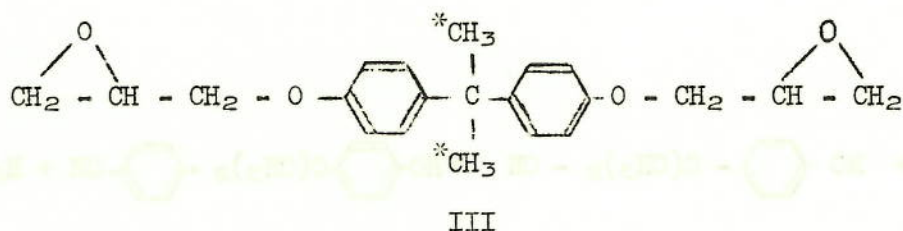
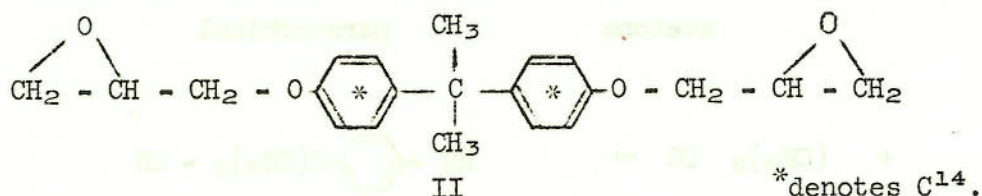
This grouping will lose water quite readily at high temperatures



there are indications that this dehydration reaction begins at temperatures as low as 150°C and it may be of value to study changes in amine cured resins at temperatures in this region. The anhydride cured resins on the other hand can lose little water because they contain very few -CH-CHOH- groupings, free -OH groups being consumed in the predominant curing reactions:



It is possible to postulate mechanisms by which other degradation products are formed, but (as suggested in the previous report) if identical resins are prepared labelled with C^{14} in different places, and if the activity of the pyrolysis products of these resins is determined it should be possible to obtain conclusive evidence for particular degradation reaction schemes. Preparative work is therefore being carried out with a view to preparing the following C^{14} labelled compounds.



(ii) Preparative Work

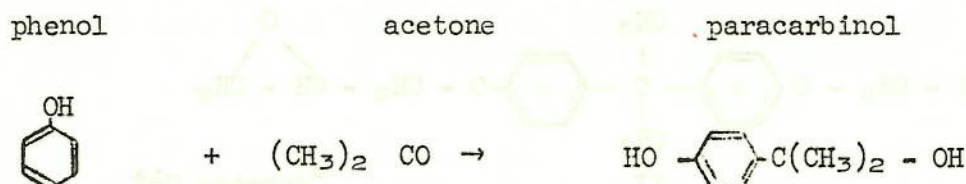
Preparation of II and III

The preparation of II and III involves two separate reactions, namely the preparation of bisphenol-A from acetone and phenol, (both of which may be purchased C^{14} labelled) and the preparation of the diglycidyl ether (EP274 in fact) from bisphenol-A and epichlorohydrin. (It would be interesting to use C^{14} labelled epichlorohydrin but this is not obtainable 'ready made' and would possibly be difficult to prepare in the laboratory).

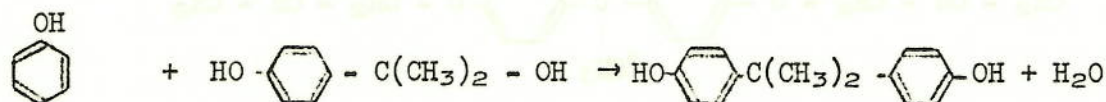
Preparation of Bisphenol A.

The mechanism of bisphenol A formation has been discussed by Schnell and Krimm (3) and by De Jong and Demethos (4). The addition of phenol to acetone is the rate determining step:

First step:



Second step:



Reaction conditions were taken from an example given by De Jong and Demethos (4).

85% Thioglycolic acid (1 g.), phenol (94g.), acetone (29g.) and toluene (3g.) were added to 72.5% sulphuric acid (450g.) over a period of 20 minutes. The reaction mixture was maintained at 40°C with good stirring for 3 hours. During this period the mixture became orange in colour and bisphenol-A was precipitated. The reaction mixture was then poured into 3 litres of cold water stirred thoroughly, and the crude bisphenol-A (70g. mp. 120°C) was filtered off.

A variety of purification techniques were tried, and the following procedure was found to be most satisfactory. Crude bisphenol-A was dissolved in the minimum quantity of cold methanol to which a few grams of decolourising charcoal were added. The mixture was refluxed for a few minutes, filtered, and the colourless filtrate was poured into 3 litres of cold water with good stirring. The bisphenol-A (mp. 149-153) was filtered off, dried in the oven at 110°C, and finally recrystallised from toluene to give bright crystals melting at 153-156°C. (Literature melting point 154 - 157°C).

Preparation of bisphenol-A diglycidyl ether

The diglycidyl ether of bisphenol-A was prepared by a method described in the literature (5).

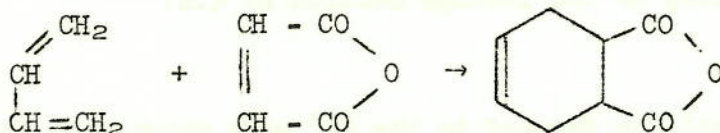
Bisphenol-A (22.8g.) and epichlorohydrin (185g.) were placed in a flask

fitted with stirrer, thermometer, reflux condenser, and dropping funnel and heated to 100°C. This temperature was maintained while 20 mls of 40% sodium hydroxide solution were added over a period of 2 hours. Excess epichlorohydrin was then distilled off under atmospheric pressure at first, and then under reduced pressure down to 1 mm.Hg and up to 160°C.

The residue consisting of salt and ether product was agitated with iso-butyl methyl ketone (40g.) and water (125g.) at room temperature. The diglycidyl ether dissolved in the ketone and the salt in the water, the aqueous layer was discarded and the organic layer was stirred with 50% sodium hydroxide solution (100 ml.) at 80°C for 1 hour to remove combined chlorine. The mixture was cooled and separated. The aqueous layer was discarded and the organic layer stirred with 2% sodium dihydrogen phosphate solution (50 ml.) at room temperature to neutralise residual caustic. The mixture was separated and the aqueous layer discarded. The organic layer was washed with distilled water and then distilled to remove iso-butyl methyl ketone (bp. 114°C) and any traces of water, up to 140°C and then down to 0.2 mm.Hg. when the diglycidyl ether began to distill. It proved impossible to distill the ether from the existing equipment without causing degradation and the product was set aside for purification at a later date. A portion of the ether - which is a brownish-yellow semi-solid at room temperature - was cured with DDM. A few milligrams of the cured resin were pyrolysed and gave chromatograms similar to DDM/EP274.

Preparation of IV and V

The preparation of IV and V has not been attempted so far but should present no problems once a supply of butadiene has been obtained. The Diels-Alder reaction between butadiene and maleic anhydride in benzene at 100°C is claimed to be quantitative.



Maleic anhydride may be purchased labelled with C¹⁴ in the 1,4 or 2,3 positions.

Preparation of VI and VII

4,4'-Diamino diphenyl methane may be prepared from formaldehyde and aniline (both of which are obtainable C¹⁴ labelled) by a condensation reaction in acid conditions. The first attempts at preparing this compound by a method described in the patent literature (6) gave extremely poor yields. The method described by Fedotova et al. (7) has proved more satisfactory.

36% hydrochloric acid (90 ml), distilled water (200 ml.) and aniline (102g.) were placed in a 3 necked flask fitted with stirrer, reflux condenser, and thermometer. The flask and contents were cooled in ice-water to 13-15°C while 40.5 ml of 37% formaldehyde solution were added with vigorous stirring. The ice-water bath was removed and the reaction temperature was increased to 40°C. This temperature was maintained for 1 hour and then increased to 50°C for a further 4 hours. The reaction mixture was then treated with 10% sodium hydroxide solution until weakly alkaline; crude 4,4'-diamino diphenyl methane was precipitated. The crude product was filtered off, dried, and set aside for purification by distillation and recrystallisation.

Measurement of C¹⁴ in the gas chromatograph effluent

When the C¹⁴ work was suggested it was intended that C¹⁴ in the gas chromatograph effluent should be detected by passage through a glass scintillator flow cell housed above a suitable photomultiplier tube. In order to ensure a low background count rate the photomultiplier tube must be kept cool, subsequently when hot gas containing organic vapours is passing through the cell, fogging and condensation problems are likely to arise.

One way of overcoming this difficulty is to burn all carbon containing compounds in the gas stream to CO₂ and then cool the gas stream before passing it through the flow cell. This technique would no doubt present some problems and it has been decided that the development of a flow counting technique should be continued by another member of the department. In the meantime compounds emerging from the chromatograph will be collected separately by bubbling them into cold scintillator solution (Butyl P.B.D. in toluene), and counted on automatic liquid scintillation counting equipment at Queen Elizabeth College, London. The use of this equipment was kindly offered to us by Dr. G. Ayrey of the Isotope Section at Q.E.

Future Work

The next few months will be devoted to the C¹⁴ work which will include considerations of the effect of sample size and geometry on degradation products. Pyrolysis of the resin formed by curing EP274 with cis Δ 4-tetrahydrophthalic anhydride will also be studied. When this programme is completed consideration will have to be given to further work. The programme could be extended to include a wider variety of epoxide resins, but it might be of more value to move to quite different polymers.

References

1. Stuart, J.M., and Smith, D.A., J. Appl. Polymer Sci., 9, 3195, (1965).
2. Keenan, M.A., unpublished work.

3. Schnell, H., and Krimm, H., *Angew. Chem.* 75, 662, (1963)
4. De Jong, J.I., and Demethers, F.H.D., *Recueil*, 84, 460, (1965).
5. U.S. Patent 2,841,595.
6. British Patent 970,779.
7. Fedotova, O., *Zhur. obshchei Khim.*, 27, 775, (1957).

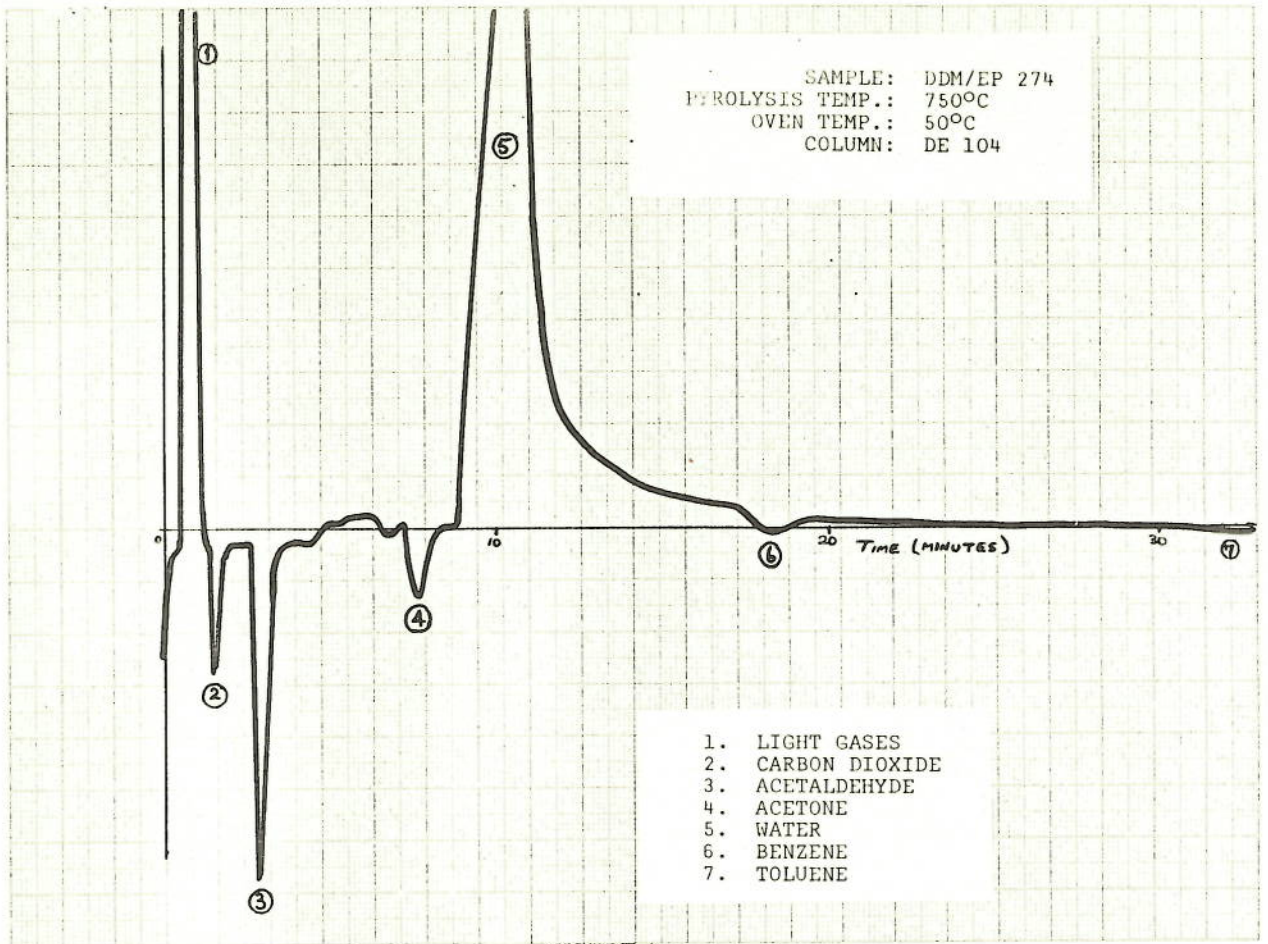


FIGURE 1.

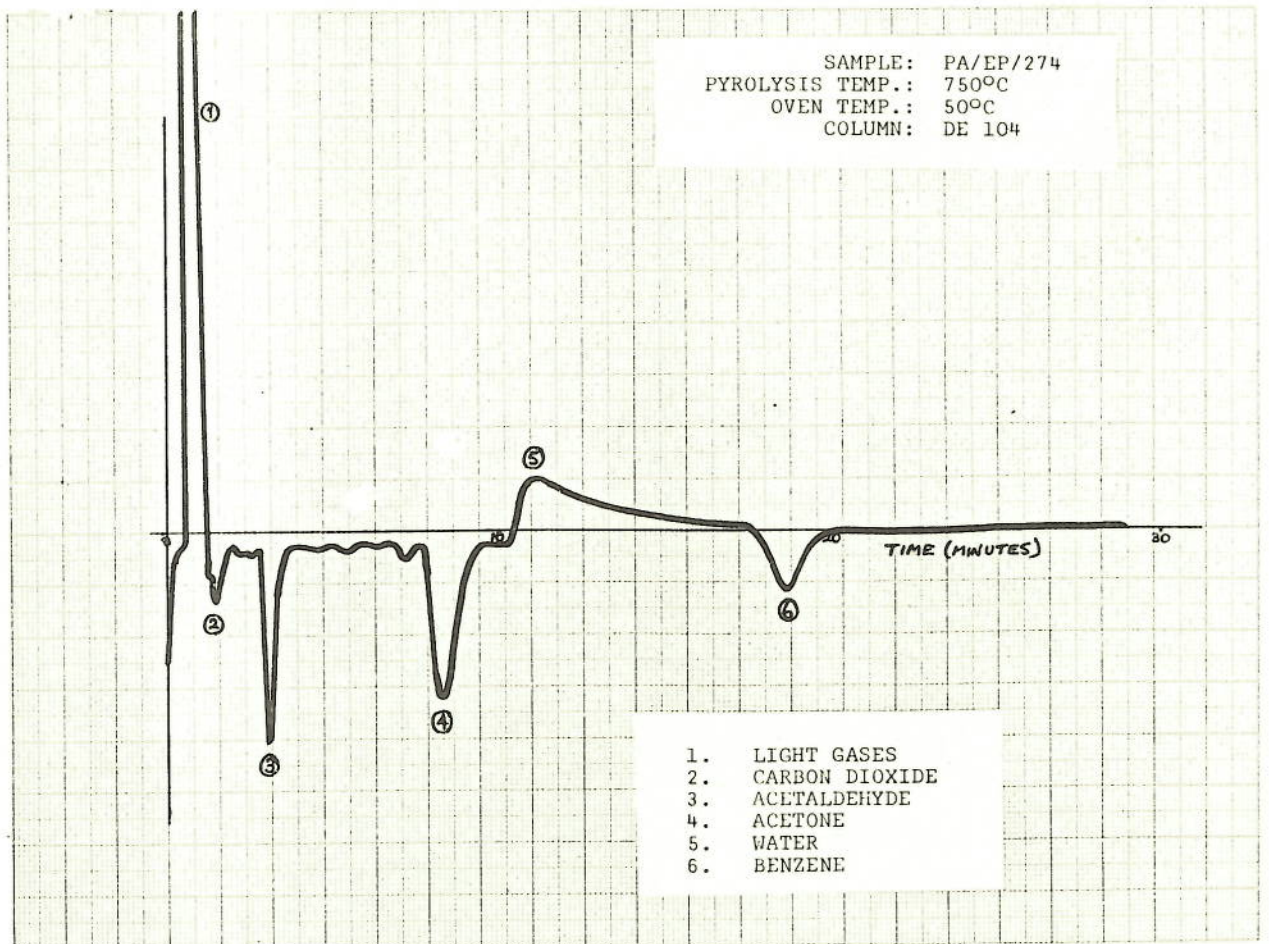


FIGURE 2

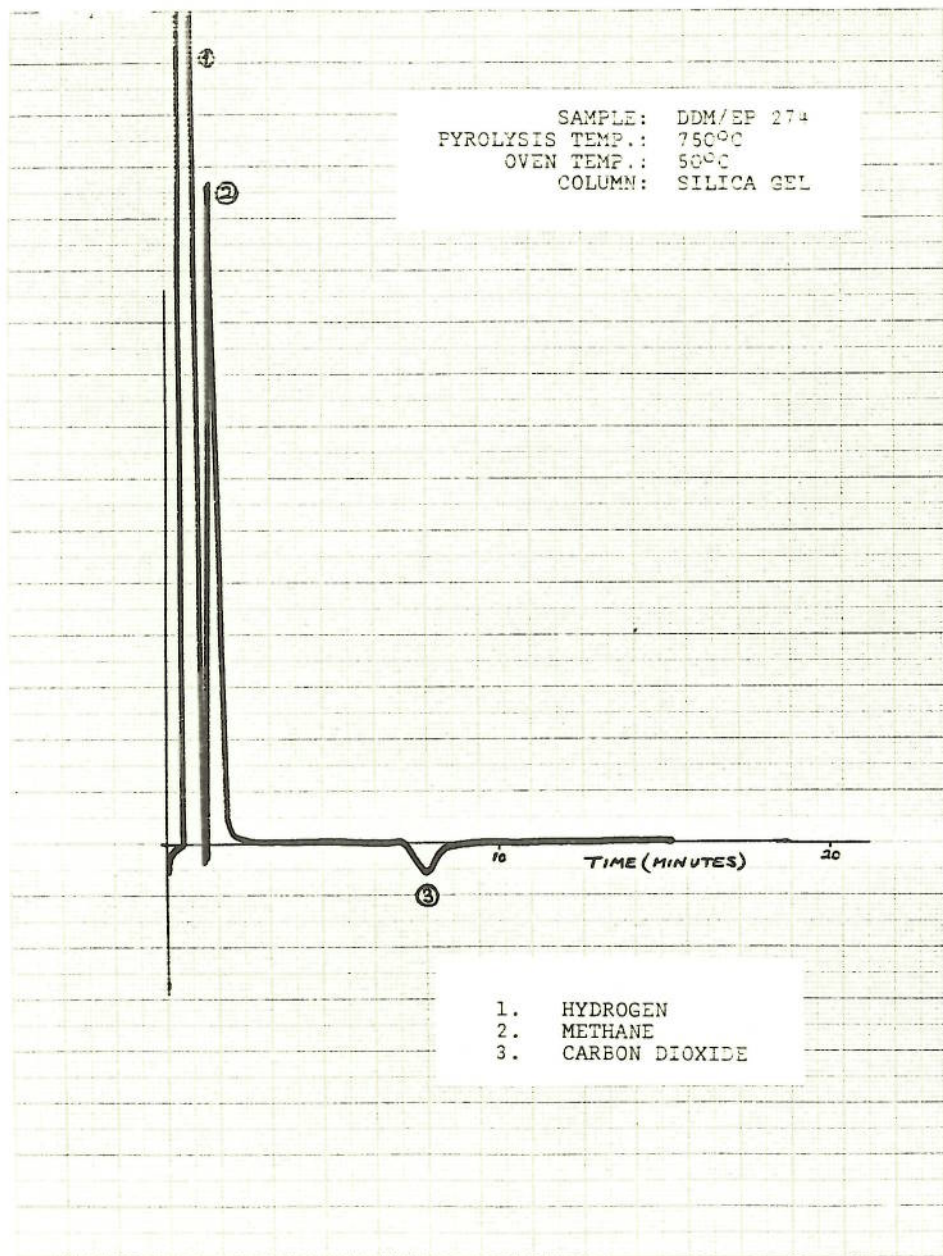


FIGURE 3

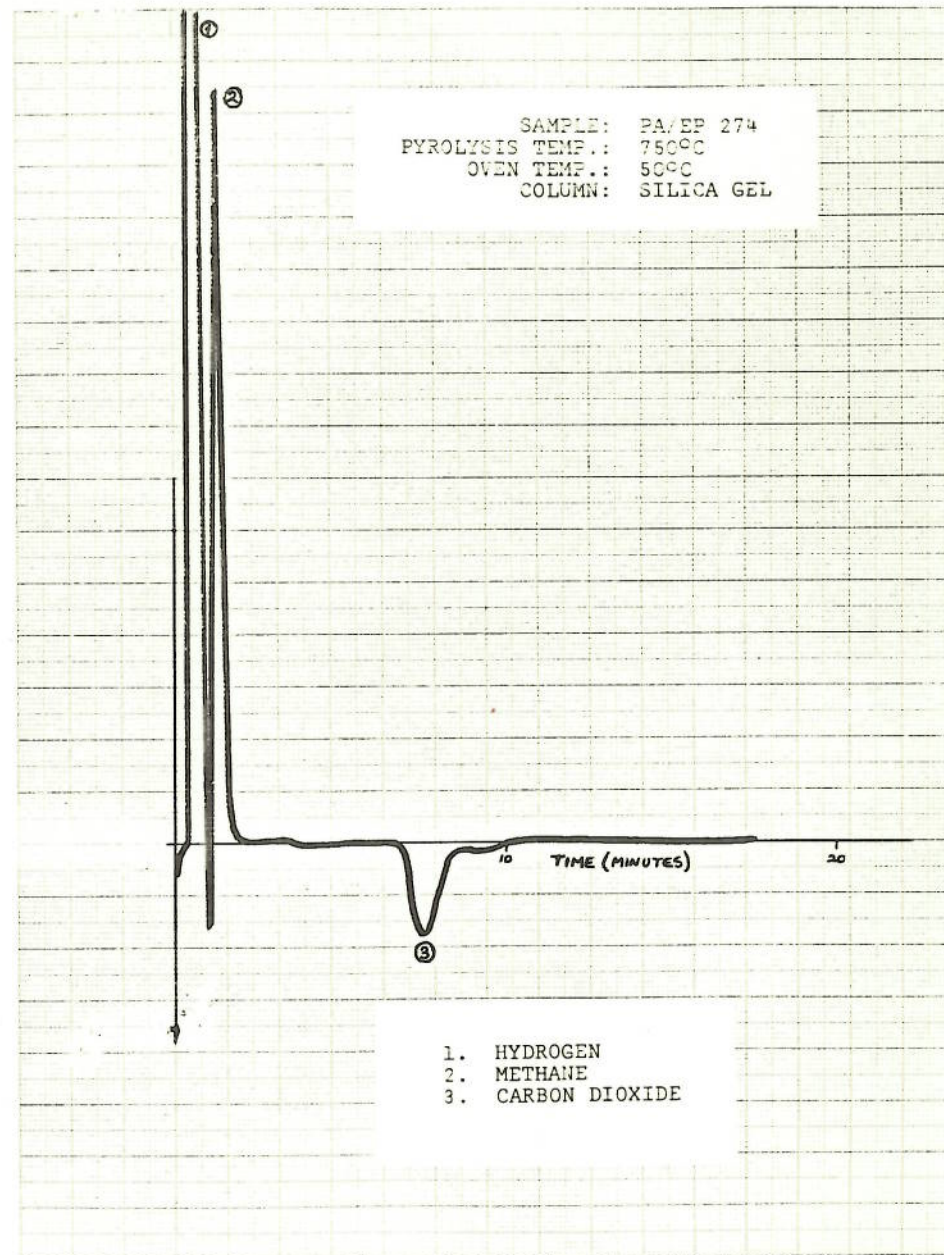


FIGURE 4

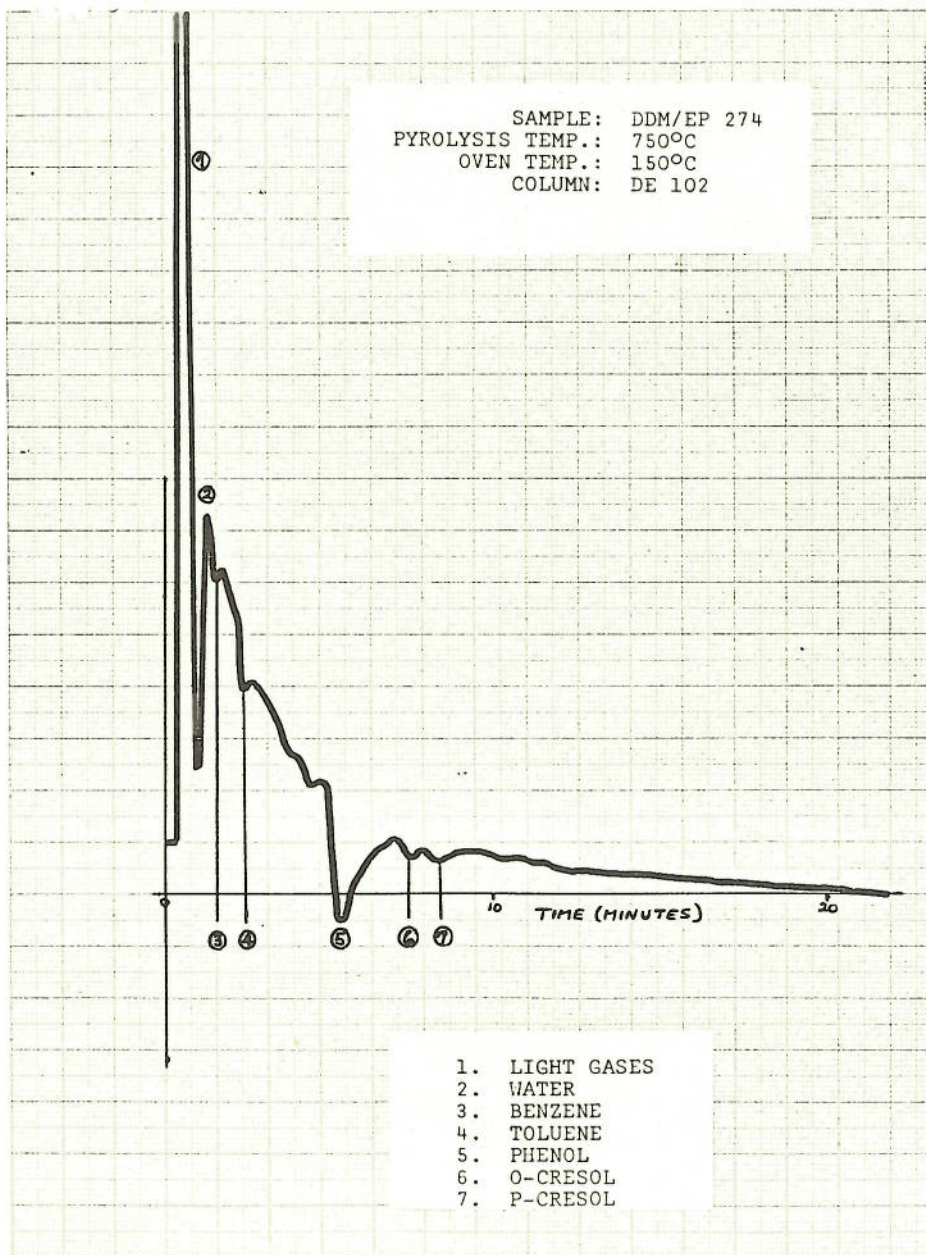


FIGURE 5

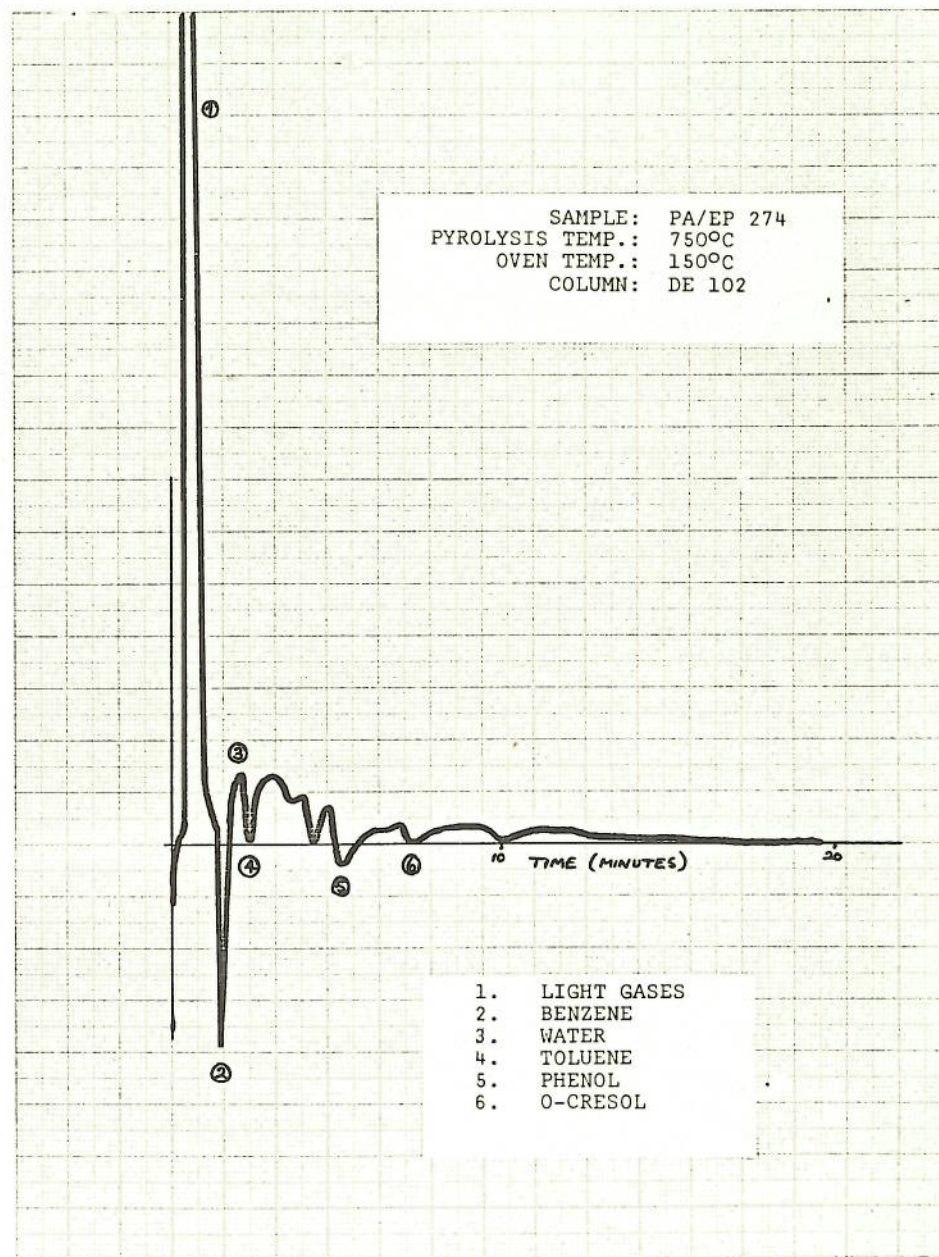


FIGURE 6

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

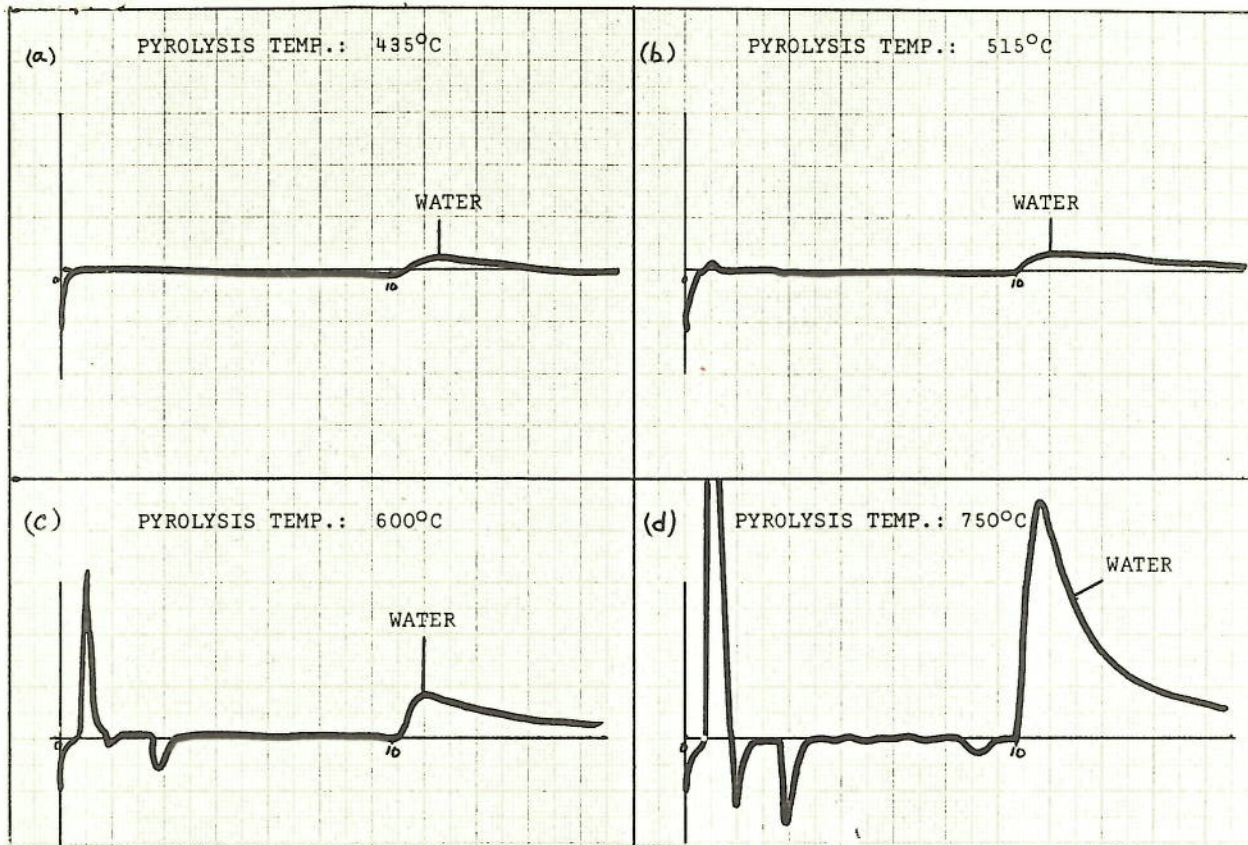


FIGURE 7

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

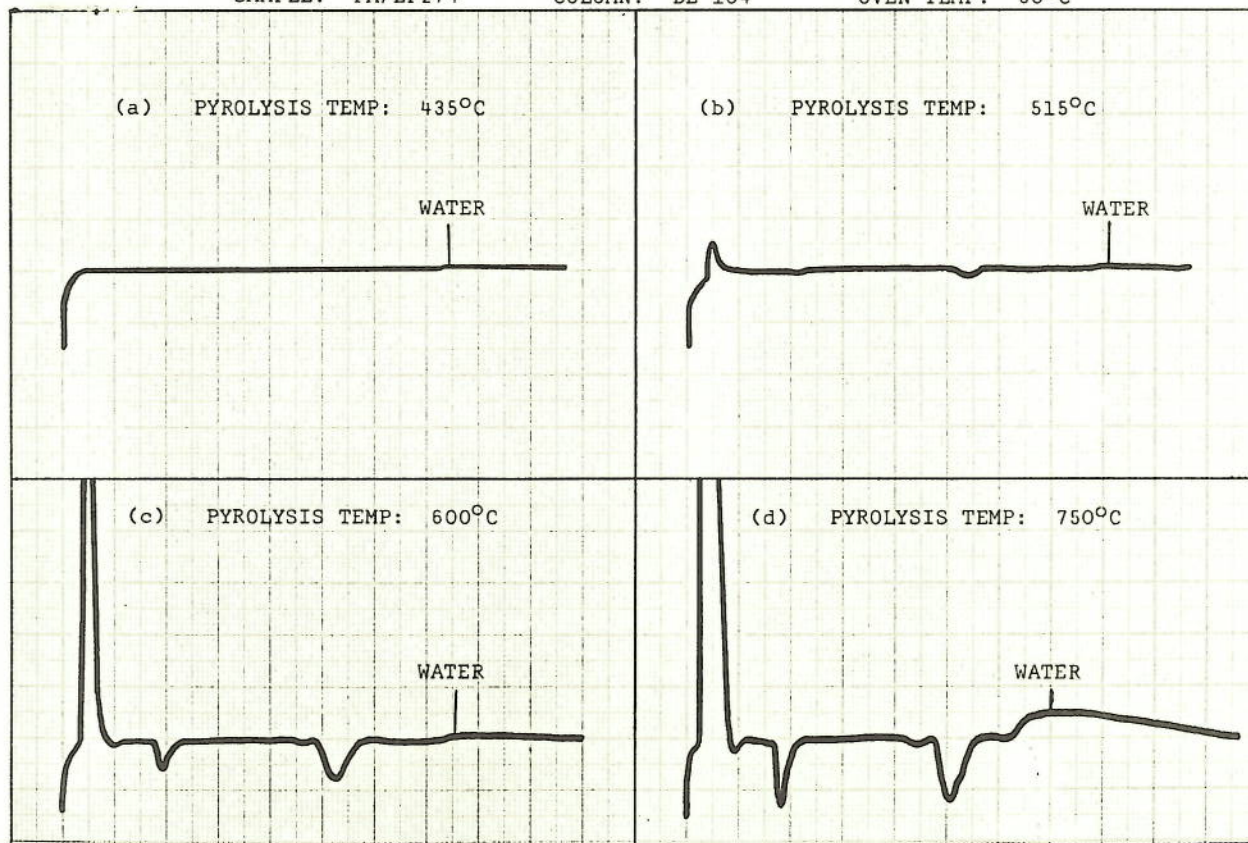


FIGURE 8