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The thermal degradation of epoxy resins IV

The thermal degradation of polypyromellitimides II

- by -

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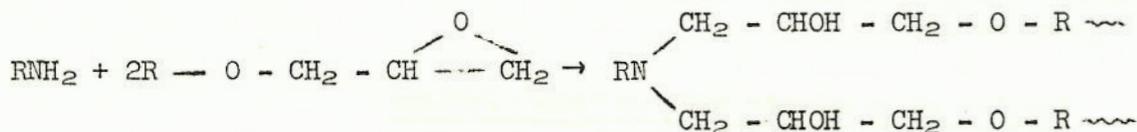
The thermal degradation of epoxy resins IV

A summary of work carried out between 1st September, 1967 and 1st March, 1968 on the thermal degradation of the resin hardener systems DDM/EP274, DDM/KOPOX171, PA/EP274, PA/KOPOX171, THPA/EP274, PMDA/EP274.

1. In a previous report (1) it was suggested that acetone and acetaldehyde may be liberated from the structure - CH₂ - CO - CH₂ -, which could be formed by dehydrogenation of the normal cured structure - CH₂ - CHO - CH₂ -.

This dehydrogenation reaction might be catalysed by the nichrome filament which is used to pyrolyse the resin samples, (1) and some work has been carried out to establish whether this is the case or not.

Calibration curves have been obtained for acetone and acetaldehyde using column DE104 (2) at 50°C and 40 ml/min of nitrogen. The amounts of acetone and acetaldehyde detected on complete pyrolysis of samples of DDM/EP274 at 700°C under the same operating conditions indicate that about 5.5% of all - CH₂ - CHO - CH₂ - groups yield acetaldehyde and 0.75% yield acetone. It has already been established that 50% of these groups yield water (1). These percentages are based on the assumption that the resin is cured 100% by the reaction:



Although this is not actually the case, these figures may be compared with those obtained for pyrolysis of DDM/EP274 samples in a small porcelain boat instead of on the nichrome filament. Unfortunately the results from the porcelain boat pyrolysis are not available yet and so no conclusion can be reached on the question of catalytic dehydrogenation by the nichrome filament.

2. 'New' Resin Hardener Systems

Pyrolysis work has been carried out on a number of 'new' resin hardener systems, namely DDM/KOPOX171, PA/KOPOX171, THPA/EP274, PMDA/EP274. The reason for using KOPOX171, a triglycidyl ether of diphenyl, is that it has been found to have particularly good ablative properties when cured with certain acid anhydrides, (3) (4) and is therefore interesting in the context of the present work. Tetrahydrophthalic anhydride (THPA) and pyromellitic dianhydride (PMDA) are being used as curing agents because these two compounds are to be used in the C¹⁴ work.

The new resin hardener systems were prepared in the following way:

THPA/EP274

2g. of EP274 were mixed with 0.8g. (85% of the stoichiometric amount) of THPA and 0.036g. of NNdimethyl aniline. The mixture was heated and stirred

until a clear homogeneous solution was obtained. This system was cured for 40 hours at 120°C, and 6 hours at 200°C.

PMDA/EP274

4g. of EP274 were melted in a small petri dish on a hot plate and PMDA was added with stirring. It was found that the EP274 would not dissolve more than about 70% of the stoichiometric amount of PMDA. The solution turned bright yellow as PMDA was added - this seems to be a characteristic of PMDA solutions. The system was cured 2 hours at 200°C, no catalyst was required as PMDA is much more reactive than THPA.

DIM/KOPOX171

0.57g. of DIM (85% of stoichiometric) were stirred into 2g. of hot KOPOX171 to give a clear homogeneous solution. The system was cured for 5 hours at 120°C.

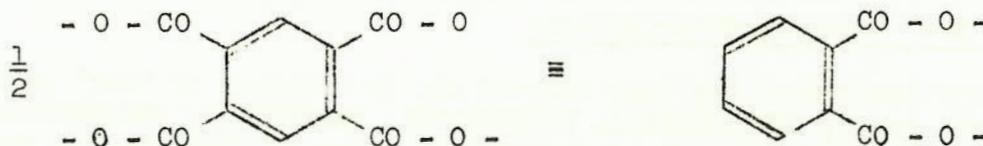
PA/KOPOX171

0.85g. of PA (85% of stoichiometric) were stirred into 2g. of hot KOPOX171 to give a clear homogeneous solution. The system was cured for 24 hours at 120°C.

3. Results of pyrolysis work on 'new' systems

The pyrograms obtained for THPA/EP274 are very similar to those of PA/EP274 as may be expected (Figs. 1 and 2).

The pyrograms of PMDA/EP274 (Figs. 3-6) show that more CO and CO₂ are evolved from this system than from the other anhydride cured resins. The reason for this is not immediately obvious; it would be expected that



as far as CO and CO₂ yield is concerned.

Another interesting feature of the PMDA/EP274 pyrograms is that benzene and toluene do not appear to be degradation products, and only small quantities of phenol are liberated. This suggests that the PMDA tends to stabilise the aromatic part of the resin in some way, probably by forming a more stable 'char'. This is of interest in connection with the pyrolytic behaviour of the polyimides which are based on PMDA and form extremely stable 'chars'.

The KOPOX171 resins are also interesting in that they yield very little in the way of volatile aromatic products (Figs. 7 and 8). A study of the high boiling degradation products which condense on the walls of the pyrolysis tube, and some approximate weight loss measurements will be made on these resins in the near future. The resin hardener systems THPA/KOPOX171 and PMDA/KOPOX171 and another epoxide ERE 1359, (the diglycidyl ether of resorcinol) will also be studied.

Development of the C¹⁴ work

It was expected that C¹⁴ work would be in progress by January 1968 but unfortunately the scintillation counter head unit (1) which was ordered from Nuclear Enterprises in August 1967 is still not completed. The development of this instrument has proved more difficult than the Company anticipated, particularly with respect to high temperature operation.

The electronics for the /radiogaschromatograph' are complete, the following description of their operation refers to Fig. 9.

This instrument is intended to drive a chart recorder with events/sec. data obtained from the scintillation detector. The instrument also integrates the total count in each radioactive peak of the chromatogram and displays the number digitally. By interposing a suitable voltage-to-frequency converter between the input of this instrument and a conventional chromatograph detector having a voltage output, the peak integration facility would be available for conventional gas chromatography.

Pulses arising from events in the detector head are fed via the 'UP' gate into the REVERSIBLE COUNTER and at the end of each 1 sec. period the count is transferred to STORE 1 which drives the CHART RECORDER via the DIGITAL-TO-ANALOGUE CONVERTER, producing a deflection proportional to the number of events in that one second period. This reading is held until STORE 1 is set to count for the next 1 sec. period, thus a histogram type record is produced on the chart.

At the same time as the store is loaded (i.e. at the end of a 1 sec. period) the UP/DOWN STORE is set to 'down' which isolates the counter from the data source and connects it to CLOCK 1. This causes the counter to count down towards zero at 10⁶ p.p.s. (pulses per sec.). When zero is detected the UP/DOWN STORE is reset to 'up' and the next counting period begins. The capacity of the counter is 255 so that the maximum time required for reset is 1/4 millise., giving a negligible error in the 1 sec. gating periods.

Since the number of pulses required to bring the counter back to zero equals the number reached when counting data pulses, there is at the output of the DOWN GATE, during the resetting phase, a train of that number of pulses. This is used to drive the DECIMAL COUNTER via the INTEGRATE GATE which is controlled by the THRESHOLD DETECTOR. If the present threshold is reached or passed by the data count the reset pulse train is fed into the DECIMAL COUNTER and added to the number already there, but if the threshold is

not reached the reset pulse train does not enter the DECIMAL COUNTER.

During a radioactive chromatogram peak the threshold will be reached during every data count, allowing the count total to accumulate in the counter.

When at the end of the peak the threshold is not reached the DISPLAY CONTROL is armed and the INTEGRATE GATE is closed. The DISPLAY CONTROL causes STORE 2 to hold the number reached by the counter, and the counter is reset to zero ready for the next peak. The DIGITAL DISPLAY shows the number held in the store. In this way the total count for each peak is displayed until the next total has been accumulated, and may be noted on the recorder chart or otherwise.

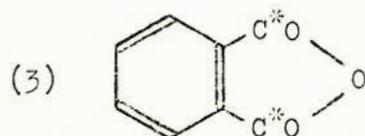
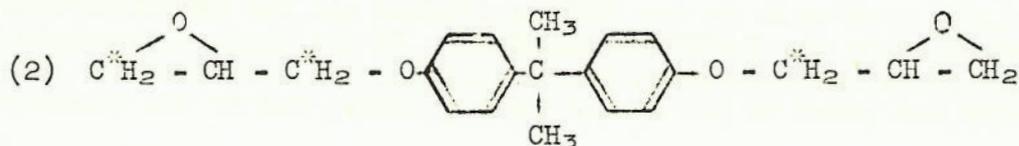
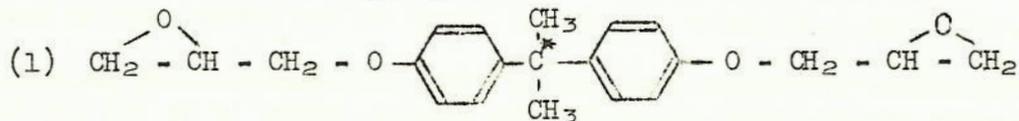
The effects of overflow in the two counters have been considered and measures taken to prevent the generation of wrong data. A signal is produced if the REVERSIBLE COUNTER reaches full scale which isolates the counter input thus storing full scale in the counter. At the end of the 1 sec. period this count is transferred in the normal way to STORE 1 producing full scale deflection on the chart recorder. In addition a warning light shows that an overflow has occurred.

An overflow in the DECIMAL COUNTER produces a carry signal which sets a store so connected that when the count next reaches 8000 the input is isolated, locking the counter at that number. When the display is set a warning light is also set if an overflow has occurred. The display is therefore interpreted as follows:

<u>Display</u>	<u>Overflow</u>	<u>Time Count</u>
< 9999	No	As display
< 8000	Yes	As display + 10,000
8000	Yes	≥ 18,000

C¹⁴ Labelled Components

The following C¹⁴ labelled compounds have been obtained from Dr. D.O Bowen of Dow Chemicals, Freeport, Texas.



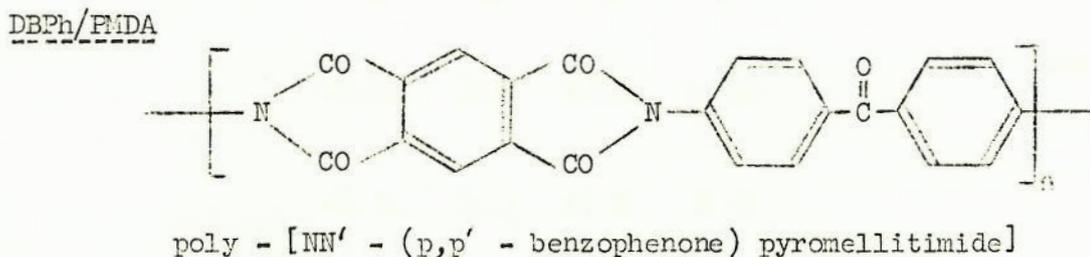
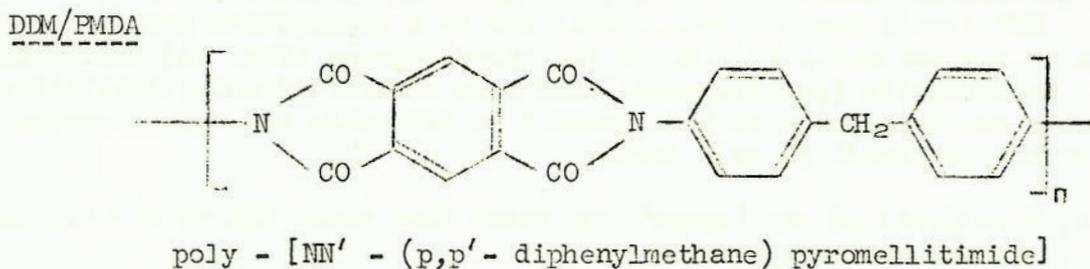
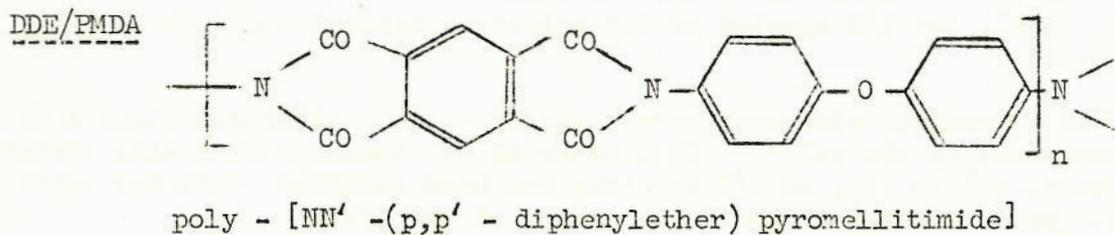
and also samples of (1) and (2) cured with DDM, with PA, and with (3).

Samples of C¹⁴ labelled acetone and phenol have been used to prepare labelled bisphenol A's (1), and labelled DDM, THPA, and PMDA are being prepared by Yarsley Research Laboratories.

The Thermal Degradation of Polypyromellitides II

A summary of work carried out between 1st September 1967 and 1st March 1968 on the polyimides DDE/PMDA, DDM/PMDA and DBPh/PMDA .

Pyrolysis work has been carried out on three different aromatic polyimides:



Pyrolyses have been carried out on 5-20 mg. samples at 700°C in N₂. Approximate weight loss experiments show that on complete pyrolysis the polyimides lose about 40% by weight. Volatile pyrolysis products have been identified by gas chromatography and infra red spectrometry. Typical gas chromatograms are shown in Figs. 10-12. The volatile degradation products identified for the three polyimides are listed below.

DDE/PMDA	hydrogen, carbon monoxide, methane, carbon dioxide, X (possibly HCN), water, benzene, phenol, benzonitrile.
DIM/PMDA	hydrogen, carbon monoxide, methane, carbon dioxide, X (possibly HCN), water, benzene, toluene, benzonitrile.
DBPh/PMDA	hydrogen, carbon monoxide, methane, carbon dioxide, X (possibly HCN), water, benzene, benzonitrile.

The high boiling degradation products from the polyimides which condense on the walls of the pyrolysis tube were dissolved in acetone and transferred to an agate mortar. The acetone was evaporated and the 'tar' was ground with dry KBr and pressed into discs; the I/R spectra of these 'tars' are shown in Figs. 16-18, the I/R spectra of the original polyimides are shown in Figs. 13-15.

After extraction with acetone the pyrolysis tube still contained a white solid condensed on the walls. This material is insoluble in a wide variety of solvents, and so far, no I/R spectrum has been obtained. It was noted that this product forms in the early stages of pyrolysis.

The predominant odour of the volatile pyrolysis products is that of a cyanide. HCN itself has not been identified as a degradation product (by us) but there is one unidentified peak on the chromatograms (Fig. 11) which might be HCN. Benzonitrile (phenylcyanide) has been identified and quantitative measurements are being made on this product to determine how much nitrogen is lost by the polyimide in this form.

C, H, N analysis of the 'chars' indicates that about 30% of the nitrogen is lost, a typical analysis gave:

	C	H	N	O
Theoretical				
Original	69.11	2.62	7.33	20.94
DDE/PMDA				
DDE/PMDA				
'Char'	78.8	2.79	5.87	11.54

The I/R spectrum of a typical 'char' is shown in Fig. 19.

The amount of benzonitrile found is not enough to account for such a large drop in nitrogen content and it seems likely that some HCN is formed.

The major degradation products are CO and CO₂. The pyrograms suggest that far more CO₂ than CO is formed but it is not easy to interpret the peak areas quantitatively (Fig. 10) Bruck, (5)(6)(7) and Heacock and Berr (8), found more CO than CO₂ however, and it is therefore of importance to establish the true CO/CO₂ ratio and to determine whether the variation in this ratio is

a function of method of pyrolysis, method of analysis or method of preparation of the polyimides.

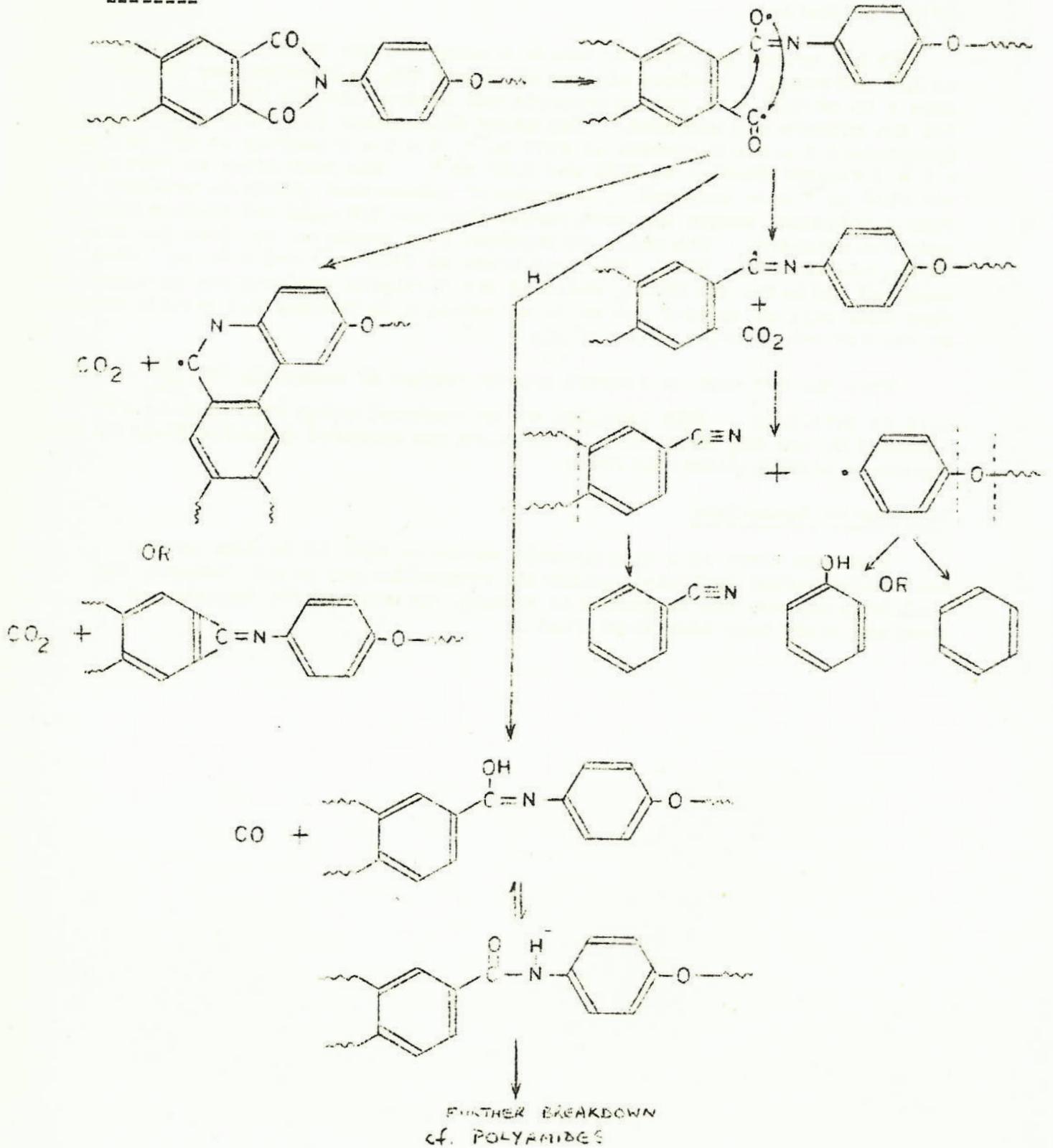
It has proved possible to obtain a value for the CO/CO₂ ratio using an I/R technique. A known mixture of CO and CO₂ in nitrogen was passed into a 10 cm cell with sodium chloride end windows and the I/R spectrum for the mixture was recorded. The major absorptions (Fig. 20) are the anti-symmetrical O = C = O stretch at 2349 cm⁻¹, O = C = O bending at 667 cm⁻¹ and a C ≡ O stretch doublet at 2184 and 2125 cm⁻¹. The peak areas at 2349 cm⁻¹ and 2184 cm⁻¹ were compared. A sample of unseparated pyrolysis products from a polyimide sample was then passed into the I/R cell and another I/R spectrum recorded. The major absorptions were identical to those for the CO/CO₂ mixture (Fig. 21). The peak areas at 2349 cm⁻¹ and 2184 cm⁻¹ were compared and hence the CO/CO₂ ratio of the pyrolysis products was obtained. More work will be carried out on this technique in future, but results obtained so far indicate a molar ratio of $\frac{\text{CO}}{\text{CO}_2} \approx 1.7$.

When the C¹⁴ work is started another method of measuring the $\frac{\text{CO}}{\text{CO}_2}$ ratio will be available. PMDA labelled at the carbonyl group will produce C¹⁴ labelled CO and CO₂ which will be detected and measured quantitatively by the equipment already described above.

Degradation Mechanisms

Although there is a considerable amount of work to be done on the polyimides before definite degradation mechanisms can be put forward, the following schemes are suggested to account for some of the degradation products which have been identified.

DDE/PMDA



Preparative

Since it will be necessary to prepare polyimides for the C¹⁴ work a 'dummy run' has been carried out on the preparation of DDM/PMDA. The product obtained was of rather low molecular weight and films cast from DMF solution became brittle on curing. Otherwise the sample was satisfactory as the I/R spectra (Figs. 22-24) show. Fig. 22 shows the spectrum for the polyamic acid, Fig. 23 is the spectrum for the same sample after 1 hour at 250°C and Fig. 24 is for a sample cured for 2 days at 120°C plus 14 minutes at 400°C (in air). It is interesting to compare Fig. 24 with Fig. 15, clearly $-\text{CH}_2-$ $\xrightarrow[\text{air}]{400^\circ\text{C}}$ $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$ without causing any other

significant changes.

Conclusion

Provided the C¹⁴ work does not suffer further delays, it should be possible to present fairly detailed descriptions of the mechanisms of the thermal degradation of epoxy resins and aromatic polyimides (in nitrogen) in the next report.

References

- (1) CoA Memo. No. 132.
- (2) CoA Memo. No. 122.
- (3) G.J. Fleming, NOLTR 67-40.
- (4) G.J. Fleming, NOLTR 66-124.
- (5) S.D. Bruck, Polymer, 5, 435, (1964).
- (6) S.D. Bruck, Polymer, 6, 49, (1965).
- (7) S.D. Bruck, Polymer, 6, 319, (1965).
- (8) J.F. Heacock and C.E. Berr, S.P.E. Trans., 105, April 1965.

Key to Figures

1. Sample: THPA/EP274 Pyrolysis Temp: 700°C Oven Temp: 50°C Column: DE 104
2. Sample: PA/EP274 Pyrolysis Temp: 750°C Oven Temp: 50°C Column: DE 104
3. Sample: PMDA/EP274 Pyrolysis Temp: 700°C Oven Temp: 50°C Column Silica Gel
4. Sample: PMDA/EP274 Pyrolysis Temp: 700°C Oven Temp: 50°C Column DE 104
5. Sample: PMDA/EP274 Pyrolysis Temp: 700°C Oven Temp: 150°C Column DE 102
6. Sample: PMDA/EP274 Step Burn 305°C 400°C 700°C Oven Temp: 50°C
Column DE 104
7. Sample: DDM/KOPOX 171 Pyrolysis Temp: 500°C Oven Temp: 150°C Column: DE 102
8. Sample: PA/KOPOX 171 Pyrolysis Temp: 500°C Oven Temp: 150°C Column: DE 102
9. Counter and Integrator for Radiogaschromatograph.
10. Sample: DDE/PMDA Pyrolysis Temp: 700°C Oven Temp: 50°C Column: Silica Gel
11. Sample: DDE/PMDA Pyrolysis Temp: 700°C Oven Temp: 50°C Column: DE 104
12. Sample: DDE/PMDA Pyrolysis Temp: 700°C Oven Temp: 150°C Column: DE 102
13. Infra-red absorption spectrum of polyimide DDE/PMDA
14. Infra-red absorption spectrum of polyimide DIM/PMDA
15. Infra-red absorption spectrum of polyimide DBPh/PMDA
16. Infra-red absorption spectrum of DDE/PMDA 'Tar'
17. Infra-red absorption spectrum of DDM/PMDA 'Tar'
18. Infra-red absorption spectrum of DBPh/PMDA 'Tar'
19. Infra-red absorption spectrum of polyimide 'Char'
20. Infra-red absorption spectrum of known CO/CO₂ mixture
21. Infra-red absorption spectrum of polyimide pyrolysis products
22. Infra-red absorption spectrum of DIM/PMDA polyamic acid
23. As Fig. 22 cured for 1 hour at 250°C
24. As Fig. 22 cured for 2 days at 120°C plus 14 minutes at 400°C in air.

SAMPLE : THPA/EP274
PYROLYSIS TEMP : 700°C
OVEN TEMP : 50°C
COLUMN : DE 104

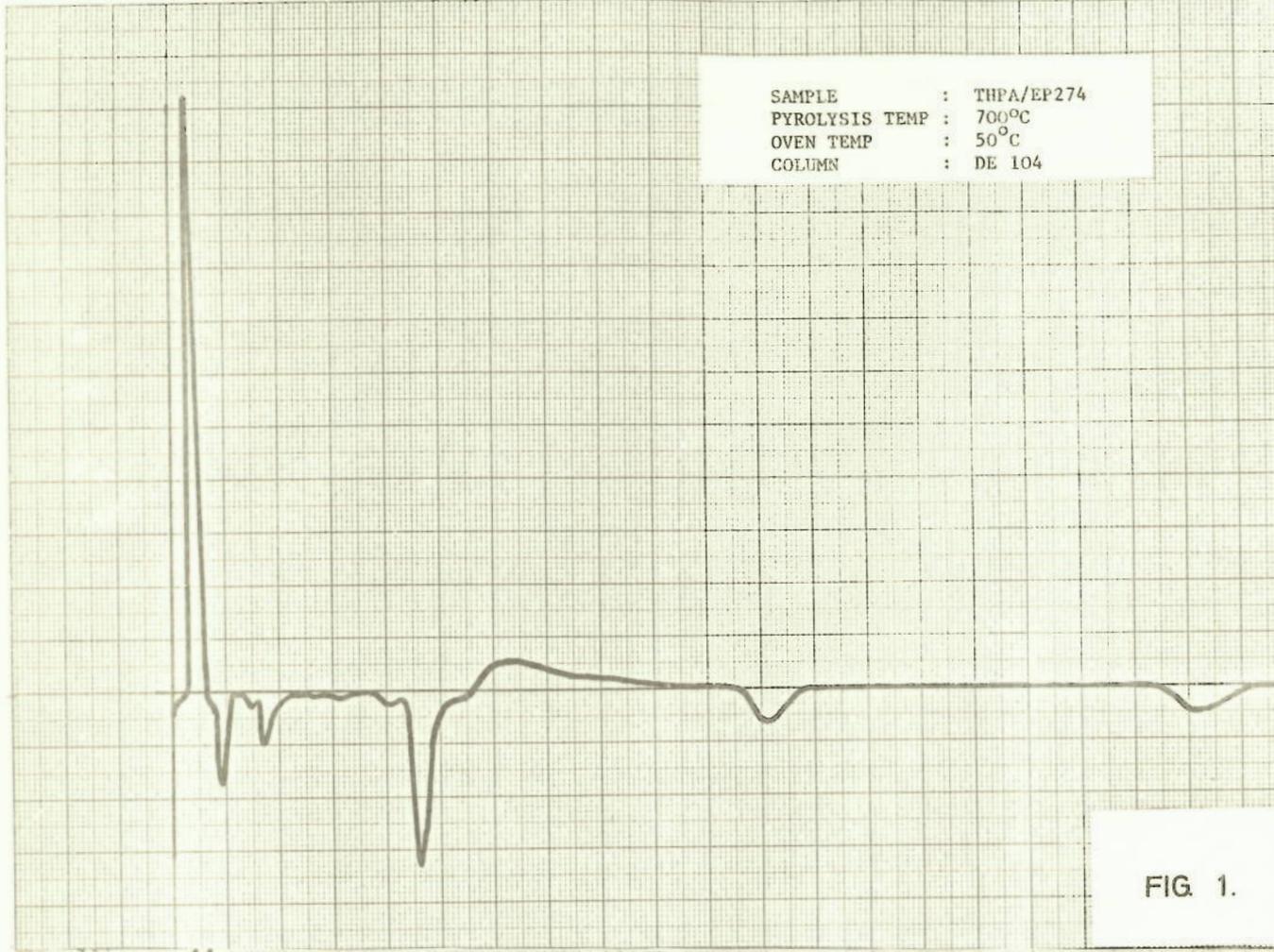
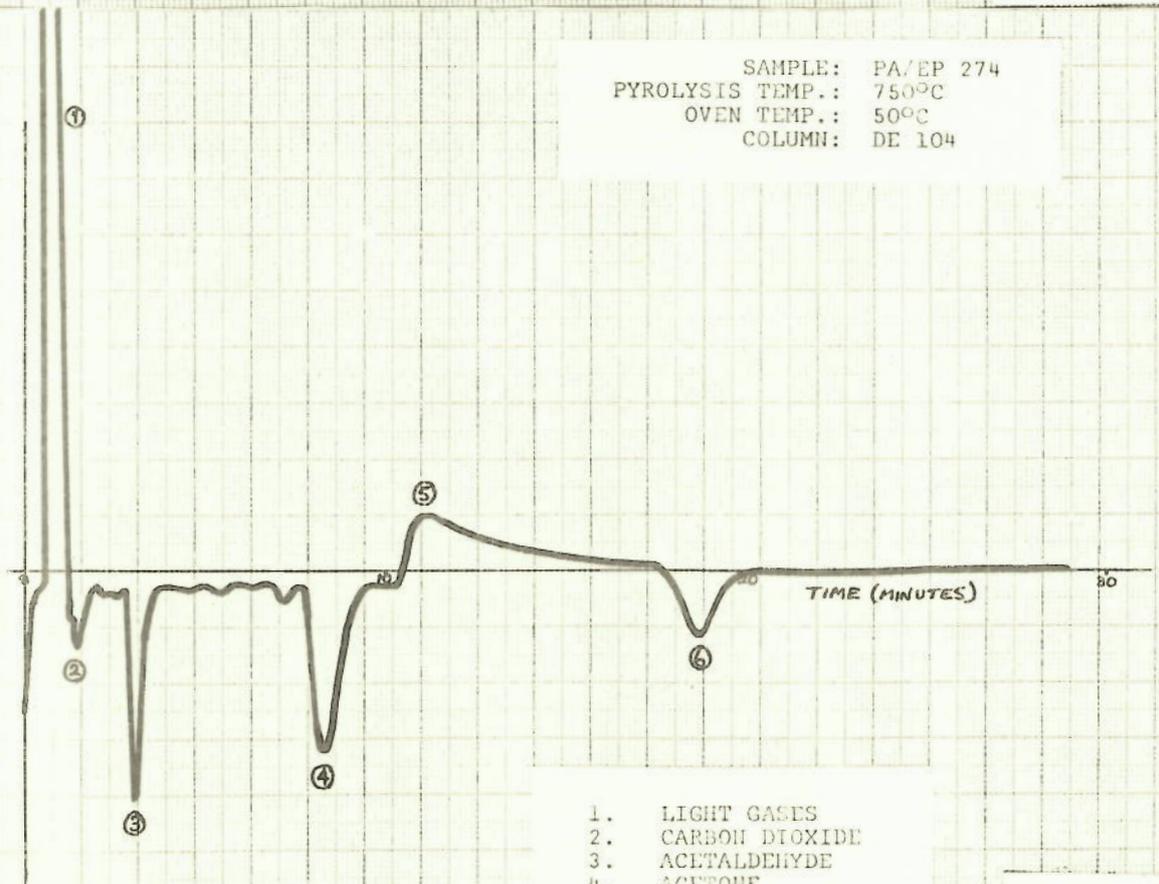


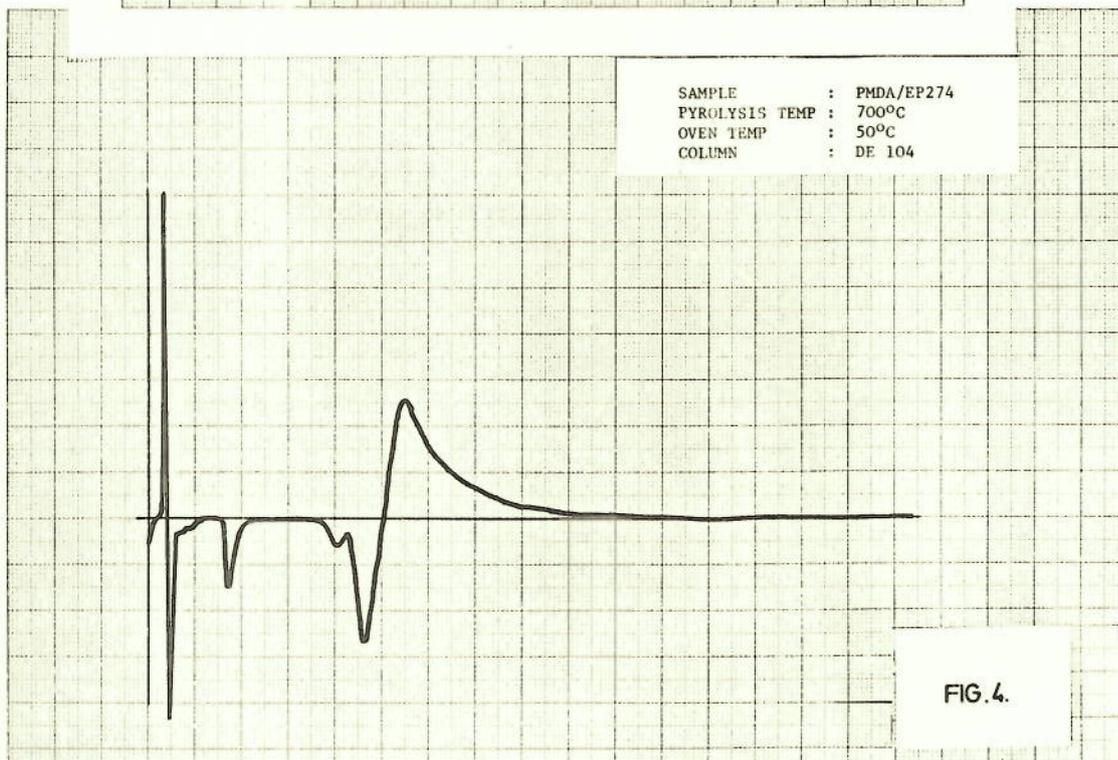
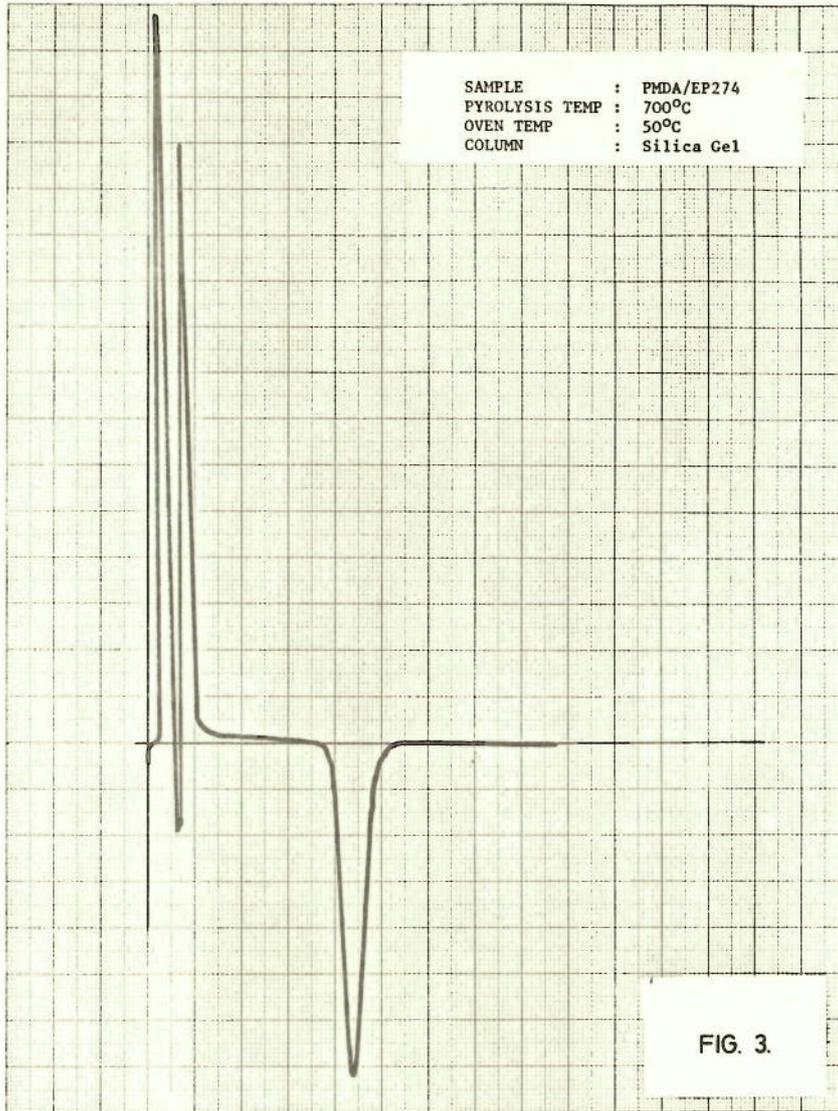
FIG. 1.

SAMPLE: PA/EP 274
PYROLYSIS TEMP.: 750°C
OVEN TEMP.: 50°C
COLUMN: DE 104



1. LIGHT GASES
2. CARBON DIOXIDE
3. ACETALDEHYDE
4. ACETONE
5. WATER
6. BENZENE

FIG. 2.



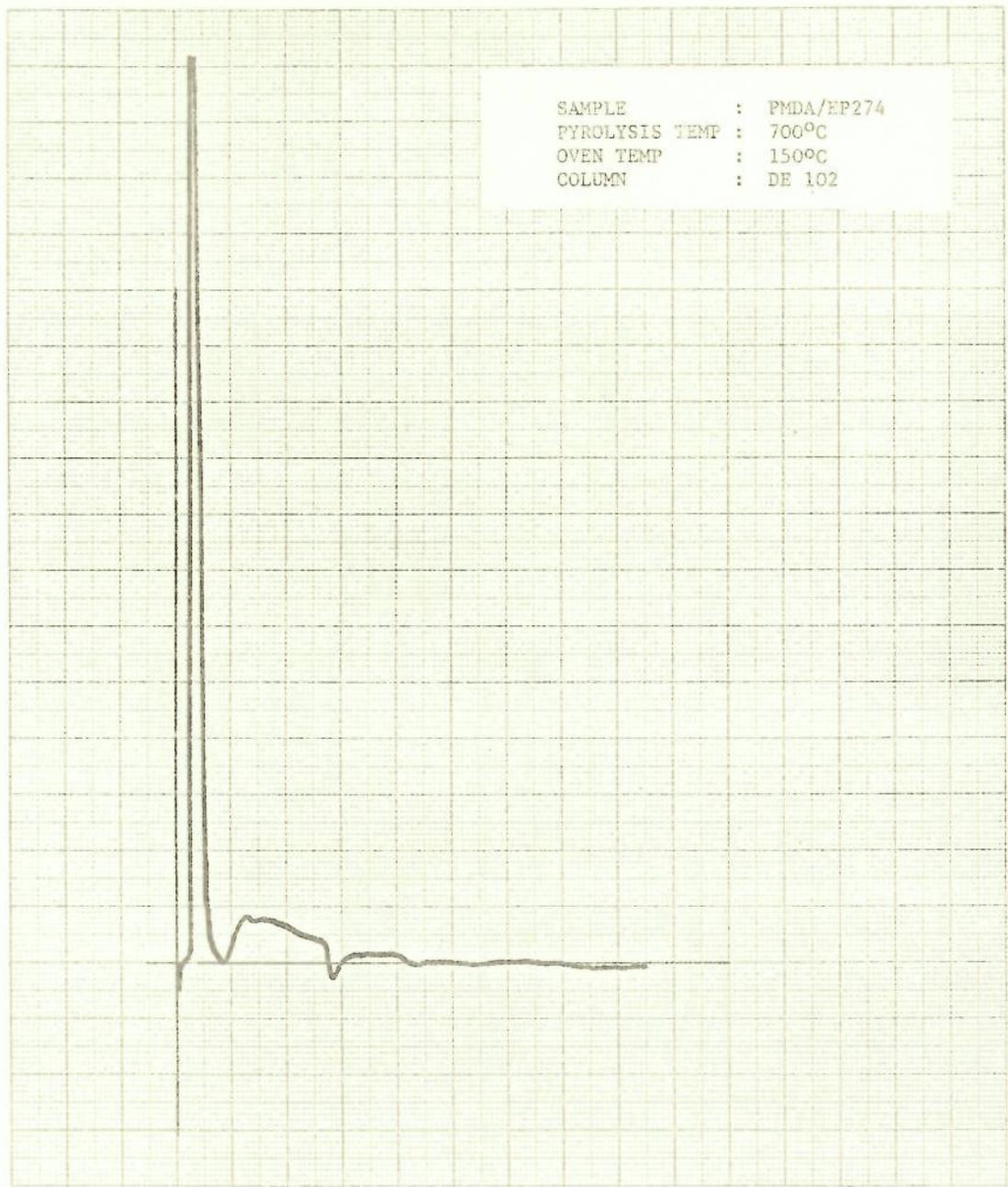


FIG. 5.

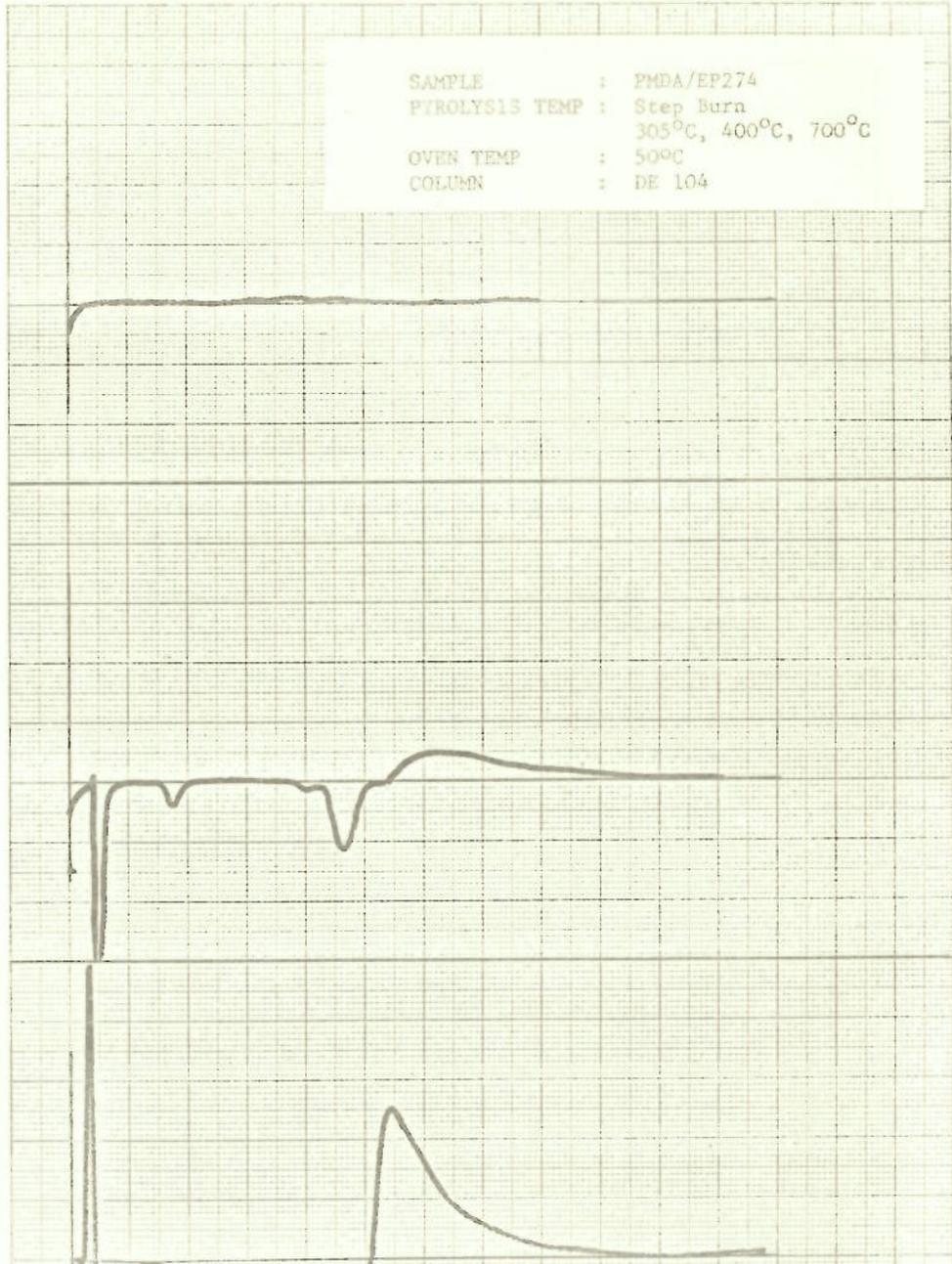


FIG. 6

SAMPLE : DDM/KOPOX171
 PYROLYSIS TEMP : 500°C
 OVEN TEMP : 150°C
 COLUMN : DE 102

SAMPLE : PA/KOPOX171
 PYROLYSIS TEMP : 500°C
 OVEN TEMP : 150°C
 COLUMN : DE 102

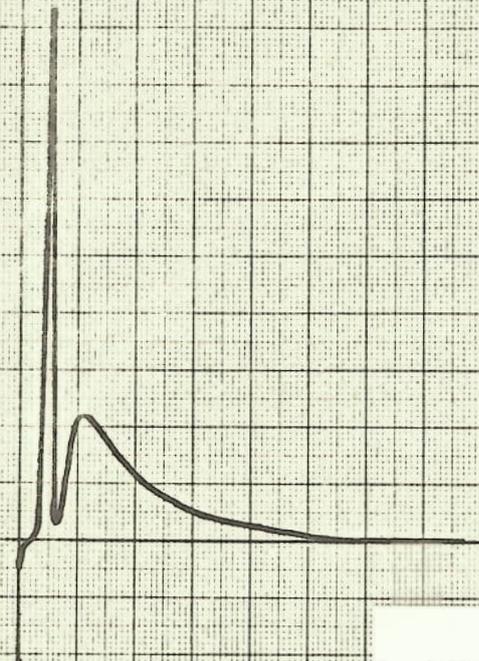


FIG. 7.

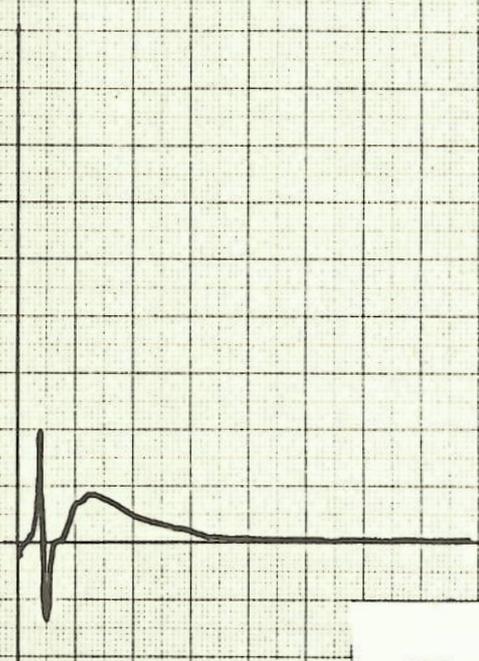


FIG. 8.

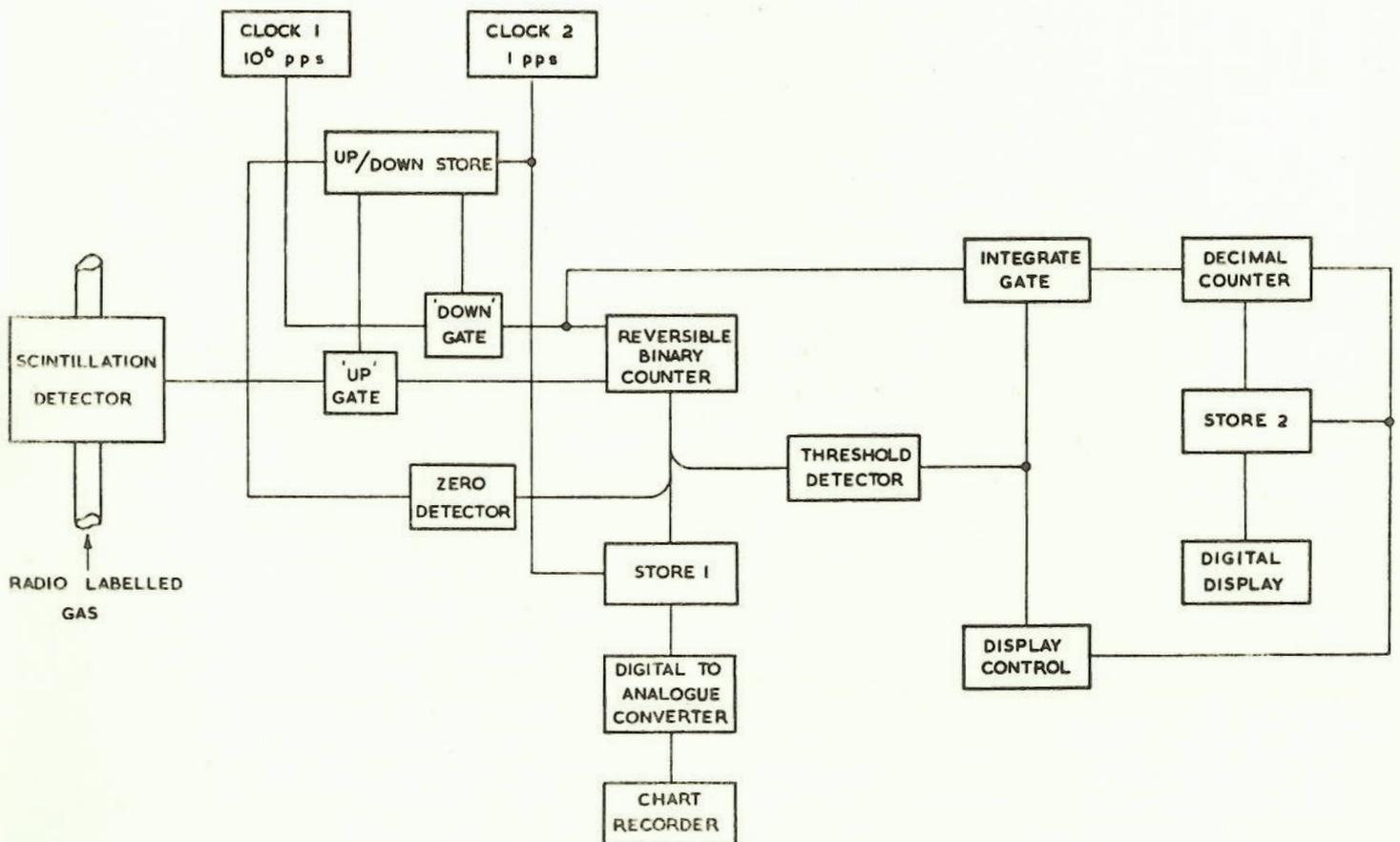


FIG. 9.

SAMPLE : DDE/PMDA
PYROLYSIS TEMP : 700°C
OVEN TEMP : 50°C
COLUMN : Silica Gel

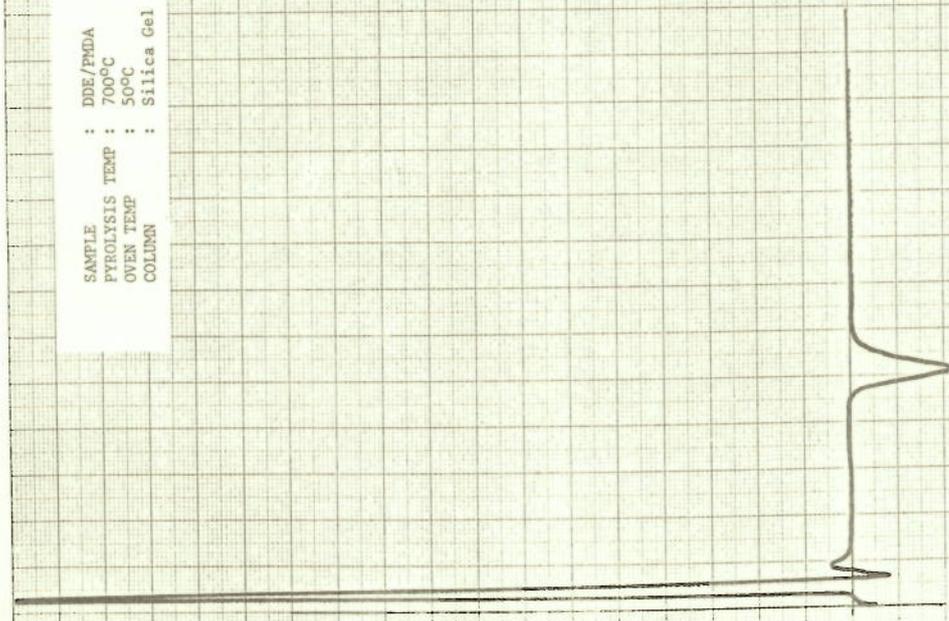


FIG. 10.

SAMPLE : DDE/PMDA
PYROLYSIS TEMP : 700°C
OVEN TEMP : 50°C
COLUMN : DE 104

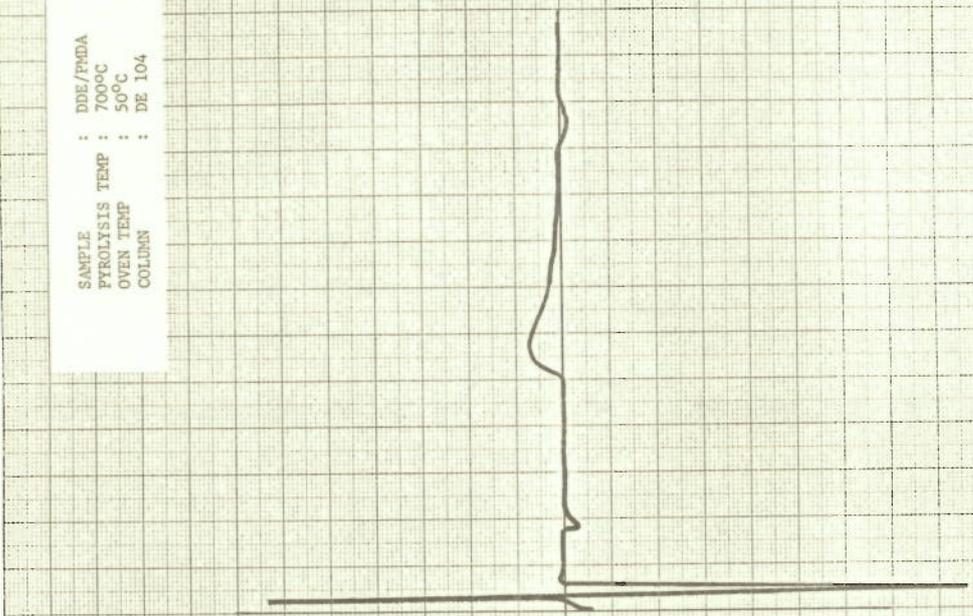


FIG. 11.

SAMPLE : DDE/PMDA
PYROLYSIS TEMP : 700°C
OVEN TEMP : 150°C
COLUMN : DE 102

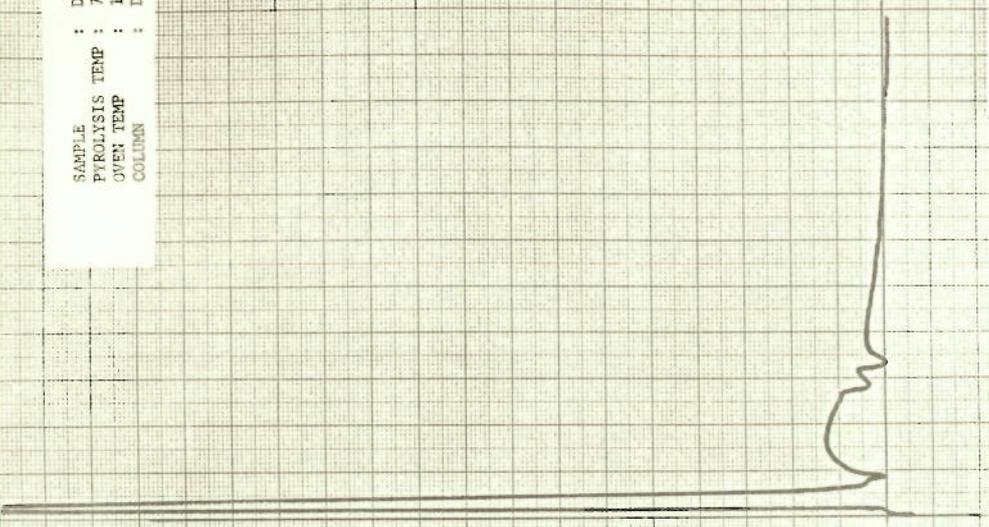


FIG. 12.

