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THE THERMAL DEGRADATION OF EPOXY RESINS (V)

by

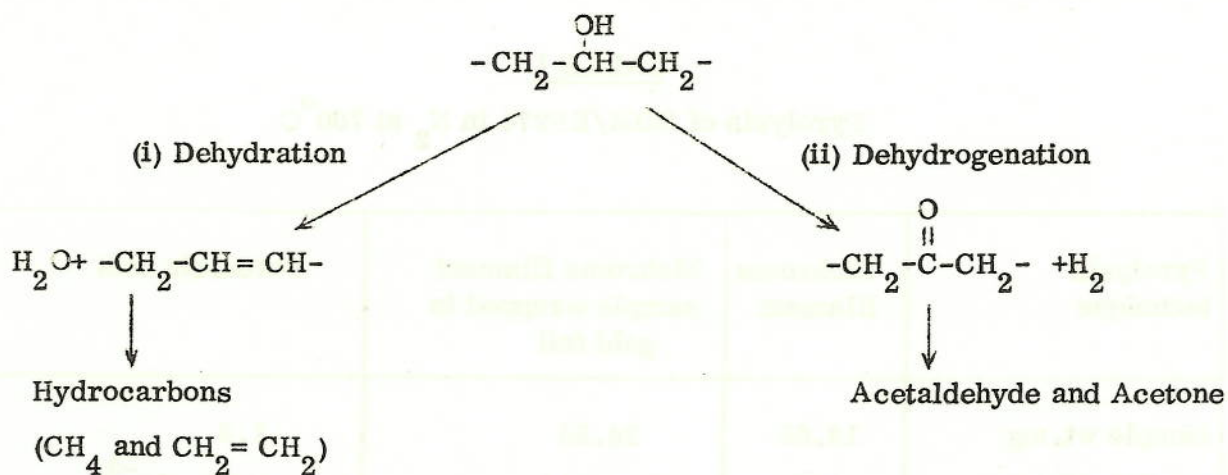
D. P. Bishop

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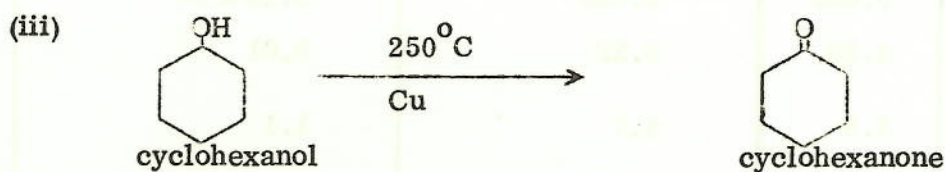
A summary of work carried out between March 1968 and August 1968 on the resin hardener systems DDM/EP274, PA/EP274, LY558/HT973, EP274/Synolide 960, and CY175/HT907/DY065.

1. Problems of Catalysis in the Breakdown of DDM/EP274

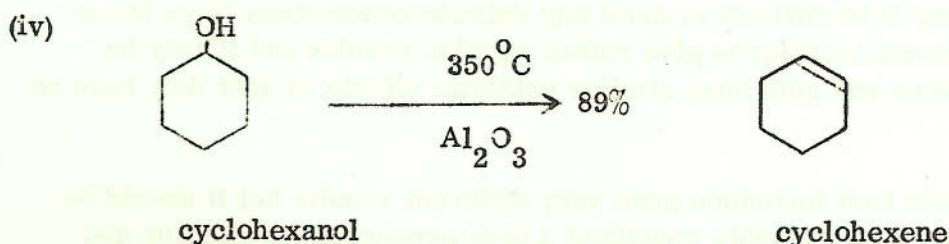
In previous reports (1) (2) the breakdown of $-\text{CH}_2-\text{CHOH}-\text{CH}_2-$ groups which occur in cured epoxy resins, has been discussed in terms of two mechanisms:



These mechanisms are both well known reactions of alcohols, for example,



is a commercial process, and



is a common laboratory preparation.

It was suggested (1) that the dehydrogenation reaction (ii) may be catalysed by the hot nichrome filament when cured epoxy resins are pyrolysed by this technique (cf. (iii)). In order to investigate this possibility, quantitative measurements on the amounts of acetone and acetaldehyde formed have been made using three different pyrolysis techniques.

Samples of DDM/EP274 were pyrolysed in nitrogen at 700°C,

- (a) on the nichrome filament
- (b) on the nichrome filament with the sample wrapped in gold foil, and
- (c) in a porcelain boat in a small furnace.

The results of this work are listed in Table I.

TABLE I
Pyrolysis of DDM/EP274 in N₂ at 700°C

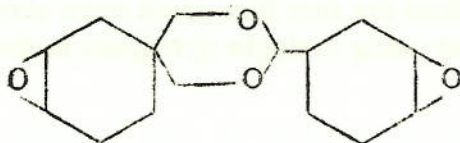
Pyrolysis technique	Nichrome filament	Nichrome filament sample wrapped in gold foil	Porcelain boat
Sample wt. mg	19.65	24.55	1.9
Wt. CH ₃ CHO mg	0.226	0.254	0.14 x 10 ⁻³
%wt. CH ₃ CHO	1.15	1.03	0.01
Wt. (CH ₃) ₂ CO mg	0.039	0.055	0.13 x 10 ⁻³
%wt. (CH ₃) ₂ CO	0.20	0.22	0.01
Ratio: $\frac{\text{CH}_3\text{CHO}}{(\text{CH}_3)_2\text{CO}}$	5.8	4.7	1.1

Unfortunately it is difficult to draw any definite conclusions from these results. The two filament techniques give rather similar results and it may be said that either nichrome and gold have similar catalytic effects or that they have no catalytic effect.

The porcelain boat technique gave very different results but it should be noted that the porcelain boat probably contained a high percentage of alumina and hence the dehydration reaction (i) would almost certainly be favoured (cf. (iv)). The

CY175/HT907/DY065

CY 175 is a cycloaliphatic type epoxy resin of structure:



The recommended curing agent is hexahydro phthalic anhydride (HT 907) with accelerator DY065. (No details of DY065 are available.) 4 g. of Cy175, 3 g. of HT 907 and 0.25g. of DY065 were heated to 80° C and mixed thoroughly. Curing was carried out for 3 hrs at 80° C and 6 hrs at 120° C.

Pyrolysis work on these systems has not been started yet.

Conclusion 14 Work

(i) Modifications to the NE5504 head unit

The 'special' NE5504 head unit (1) was ordered from Nuclear Enterprises Ltd. in August 1967, it was delivered in April 1968, about four months behind schedule.

The unit was required to detect C¹⁴ in a gas stream with 20-30% efficiency. Preliminary tests indicated that this requirement could not be met, and it transpired that Nuclear Enterprises had not tested the instrument with C¹⁴ in a gas stream!

It was considered that the unit should be returned to the makers to be modified to give the required performance. In view of the inordinately long time taken to produce the unsatisfactory unit however, it was felt that modifications would be better carried out in these laboratories.

The original design for the heat unit is shown in CoA memo. No.132, Fig.8. The E.M.I. 6097S photomultiplier tube is quite suitable for the present work. It may normally be operated at cathode to anode voltages of up to 2200V, and E.M.I. describe a suitable dynode chain for the tube in their literature. The dynode chain fitted by Nuclear Enterprises restricted the maximum working voltage of the tube to 1250V. The scintillations produced in organic phosphors by the weak β emission from C¹⁴ are of such low intensity that this P.M. tube, when working at 1250V, gives insufficient gain for the pulses to be recognised in the output signal from the tube. The dynode chain was therefore replaced by the one recommended by E.M.I.

Apart from having low light output, the scintillations produced by C¹⁴ in organic phosphors are short lived; they have decay times ranging from a few nanosec. to 100 nanosec., depending on the phosphor. If the P.M. tube and amplification system are to produce pulses corresponding to these scintillations it is essential that they should both have fast rise times.

The P.M. tube has a rise time of 7 nanosec. which is quite satisfactory, and the preamplifier fitted by Nuclear Enterprises had a rise time of 75 nanosec. This would have been acceptable, but the way in which the preamplifier was used in the head unit increased its effective rise time to about 10μ sec. which meant that it was hardly responding to pulses from the P.M. tube. This preamplifier was discarded and replaced by one having a rise time (as used in the head unit) of 20 nanosec.

At this stage the head unit worked well as a liquid scintillation counter; samples of C^{14} labelled acetone in a suitable phosphor (5% Butyl P.B.D. in redistilled A.R. toluene) were counted with 65% efficiency.

When the flow cell was used for counting C^{14} labelled acetone however no sensible results could be obtained. It was found that the glass scintillator base plate of the flow cell gave an extremely high background count when the P.M. tube was operated at voltages suitable for detecting scintillations arising from C^{14} decay. No satisfactory explanation for this phenomenon can be given.

The original flow cell was discarded and the top section of the head unit was modified to take a redesigned cell.

The new flow cell consists of a pyrex glass spiral (30 cm. of 0.3 c.m. I.D. tubing) loosely packed with scintillation grade anthracene crystals. A plane mirror is mounted above the spiral to reflect scintillations occurring near the top surface of the spiral into the light pipe, and hence to the photo cathode of the P.M. tube. A highly polished brass collar surrounds the spiral and mirror, and the enclosure thus formed is filled with an optically clear grade of silicone oil. The function of this oil is to give optical contact between the glass spiral and the top of the light pipe, and also to make thermal contact between the brass collar and the spiral. The original heating coil fits neatly round the brass collar.

In this extensively modified form the head unit was found to detect C^{14} labelled acetone in the gas chromatograph effluent with about 20% efficiency with the P.M. tube operating at 1400V. Trials were made with the gas chromatograph oven at 50 C and the flow cell at room temperature. No work has been attempted with the flow cell at high temperatures.

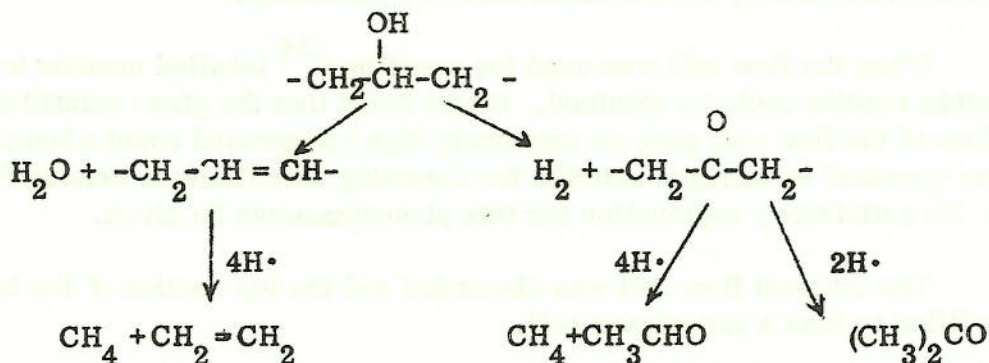
2. Thermal Degradation of C^{14} Labelled PA/EP274

A study of the volatile pyrolysis products of two differently labelled PA/EP274's has been made. These cured resins were labelled at

- I the phthallic anhydride carbonyl groups,
- II the 1,3 positions of the EP274 glycidyl groups.

The pyrograms and corresponding 'radio-pyrograms' for these resins are shown in Figs. 1-4. These results will not be discussed in detail in this report, but it will be seen, that to a large extent, they confirm degradation mechanisms postulated in CoA Memo.No.132.

The formation of methane from the 1,3 —glycidyl groups in EP274 was not considered before, but clearly (Figs. 3 and 4) it is a major reaction:



A number of other C¹⁴ labelled resins are currently being studied, and it is expected that the labelled compounds being prepared by Yarsley Research Laboratories Ltd. will be ready by mid-September 1968.

No work has been carried out on the thermal degradation of polyimides since March 1968.

REFERENCES

- (1) CoA Memo.No.132.
- (2) CoA Memo.No.149.

ACKNOWLEDGEMENTS

The author wishes to thank Mr. Knight of R.A.E., Farnborough for carrying out the DDM/EP274 'boat burn', and Mr. B.R. Moffitt of the Instrumentation Department, College of Aeronautics, for his invaluable help in modifying the NE5504 head unit.

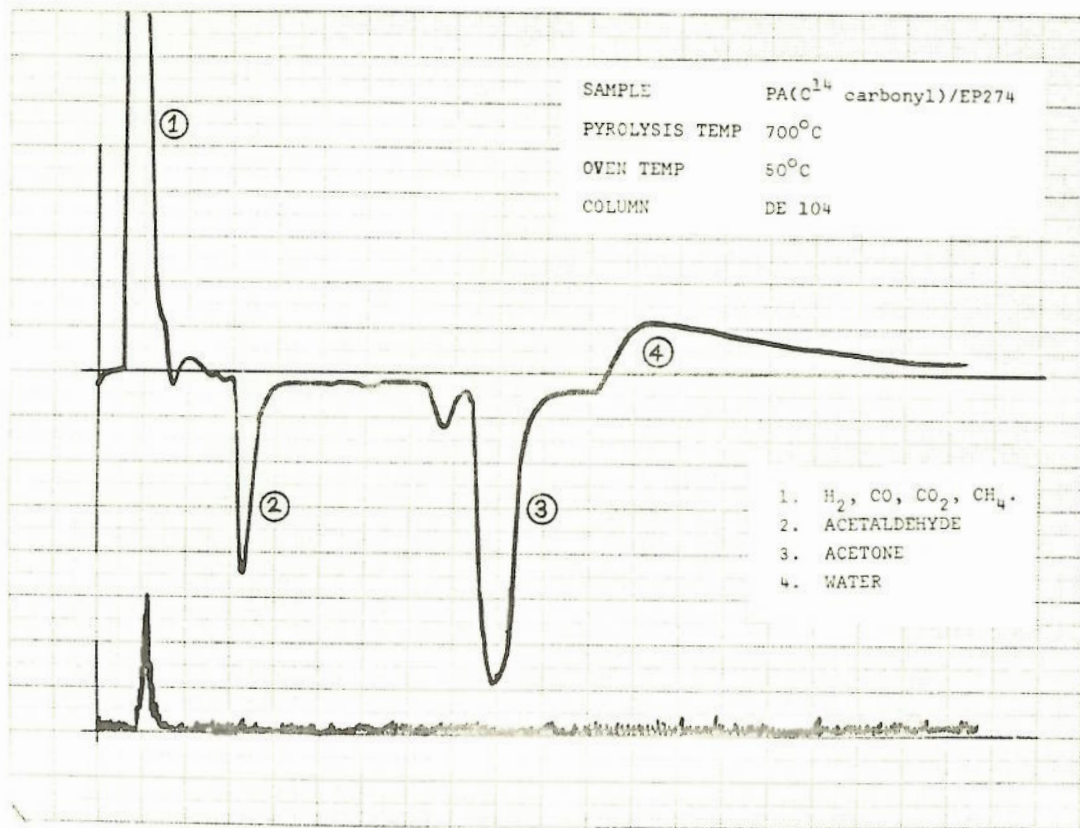


FIGURE 1

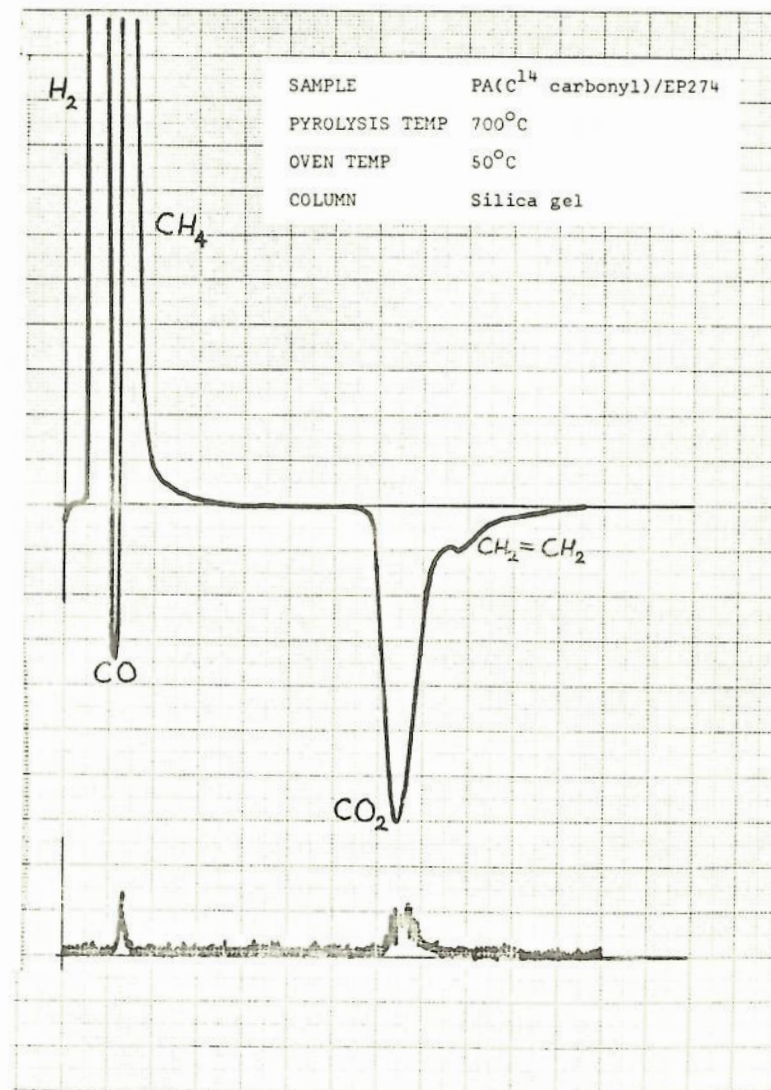


FIGURE 2

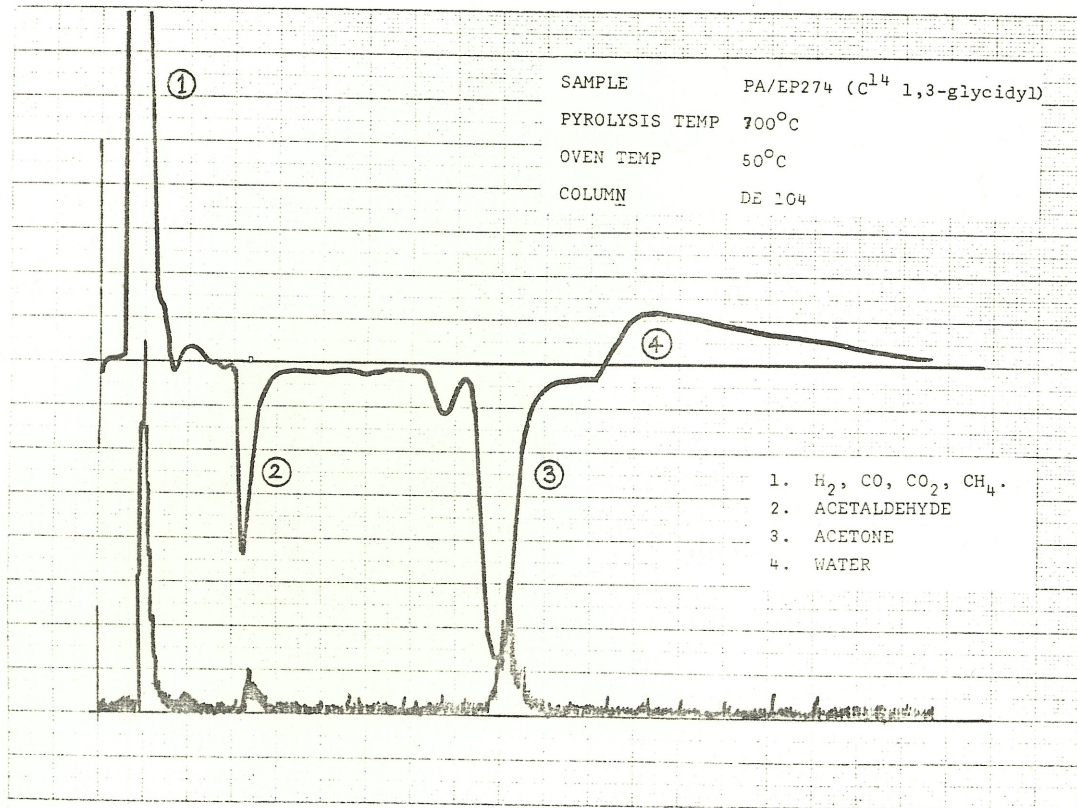


FIGURE 3.

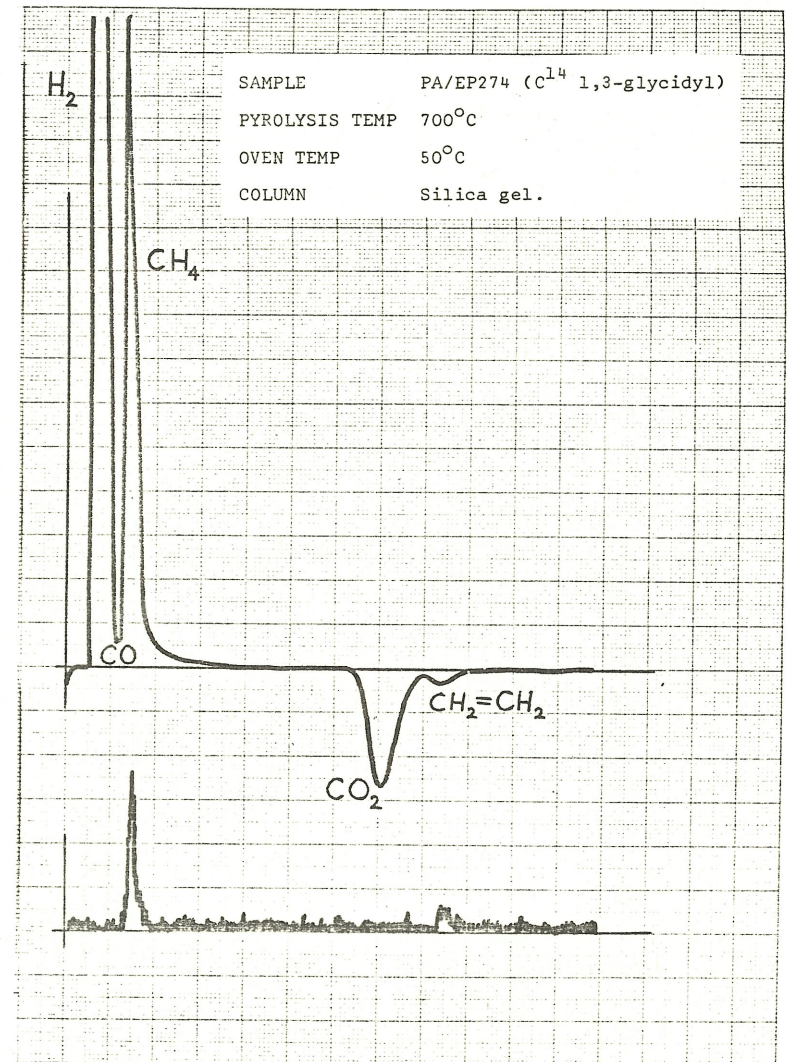


FIGURE 4.