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# Pyrolysis-Gas Chromatography as a Tool for Studying the Degradation of Ablative Plastics

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## SUMMARY

Pyrolysis-gas chromatography has been used to locate the degradation front in pieces of typical phenolic ablative materials. This technique gives quantitative results for per cent phenolic resin versus distance normal to the surface. The charred material is carefully machined so as to remove successive 0.020-in. cuts starting with the charred face of the material. Each cut is then analyzed by the combined techniques of pyrolysis and gas chromatography. A plot of per cent phenolic resin versus distance from the undecomposed back face gives a profile of the degree of degradation of the ablative plastic. Samples are weighed on the pyrolysis ribbon before and after pyrolysis giving total per cent volatiles. Divergence of the per cent volatiles and per cent phenolic resin curves near the charred surface of the material is due to the presence of the pyrolysis products near the surface.

## INTRODUCTION

Ablative plastic thermal protection systems for ballistic missile and satellite re-entry vehicles have been used successfully for many years. Continued

interest exists in improving the materials used as mission requirements are expended and increased performance is demanded. Proper characterization and evaluation of the physicochemical properties of these materials are essential if improved materials are to be developed.

The purpose of this paper is to describe a pyrolysis-gas chromatography technique that has proved useful for the accurate location of the degradation front and which provides quantitative results on the degree of polymer degradation.

The thermal performance of charring ablative plastics is measured in terms of recession, char thickness, and degradation depth. On black ablative material such as carbon and graphite-phenolics, the zone of degradation is not clearly observable. By observation the very porous surface zone was considered to be char, and the zone between char and virgin material was called the zone of degradation.

Several techniques have been utilized to locate these zones. In the scribe technique a sharp point is drawn across the virgin/char surface. The depth of the marks is used to indicate the degraded zone. Subsequent analysis showed the degraded zone to have been underestimated. Another method that has been used is the density profile. The machining of a geometrical volume of a charred sample and the repeated grinding and measurement of the piece establish the char density profile through the material.

Until the development of the pyrolysis-gas chromatography technique, a dye penetrant test was used as a visual aid. The porosity of the degraded material allows a penetrant to seep into the sample. An absorbent developer draws out the dye and indicates the areas of porosity. The dye penetrant indications correlated well with the measured density profile. The chief disadvantage with this method lies in the fact that penetration is a function of time, and results are subject to interpretation by the technician performing the test.

The pyrolysis-gas chromatography technique described in this paper accurately locates the degradation front and, in addition, gives quantitative results for per cent phenolic resin versus distance normal to the back face of the material.

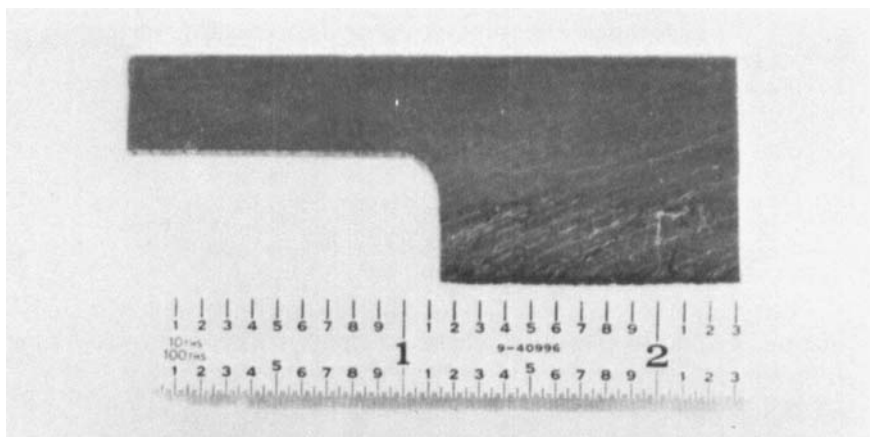
## EXPERIMENTAL

An F&M model 810 dual-column gas chromatograph, equipped with dual hydrogen flame detectors, and a Barber-Colman model 5180 pyrolyzer were used in this investigation. Pyrolysis is performed on a small platinum

ribbon contained in a pyrolysis chamber of only 1-cc volume. Half-milligram samples are weighed directly onto the platinum ribbon using a Cahn gram electrobalance.

The pyrolysis chamber is sealed by compression of an O-ring between the pyrolyzer body and the cover glass. The whole unit is heated by a cartridge heater to prevent condensation of the pyrolysis gases. The pyrolysis chamber is flushed with nitrogen carrier gas for 1 min before pyrolysis to ensure an inert atmosphere.

The material to be analyzed is carefully machined so as to remove successive 0.020-in. cuts, starting with the charred face of the material (Fig. 1). Each cut is then analyzed by the combined techniques of pyrolysis and gas chromatography.



**Fig. 1.** Section of carbon phenolic pipe after machining off 0.020-in. cuts for pyrolysis-gas chromatography analysis.

The ribbon is electrically heated from ambient temperature to 1000°C in 1.5 sec in a flowing nitrogen atmosphere. Samples are held at this temperature for 15 sec while pyrolysis products are swept by the nitrogen into the gas chromatograph for separation and quantitative analysis (Fig. 2). After pyrolysis each sample is reweighed on the ribbon. This gives per cent volatiles for each cut.

## CONDITIONS:

DETECTOR - FLAME IONIZATION  
 COLUMN - 10 FT. DI-ISO-DECYL PHTHALATE 10%  
 ON CHROMOSORB 60/80 MESH  
 CARRIER - NITROGEN 60 CC/MIN  
 TEMPERATURE - 165 °C ISOTHERMAL

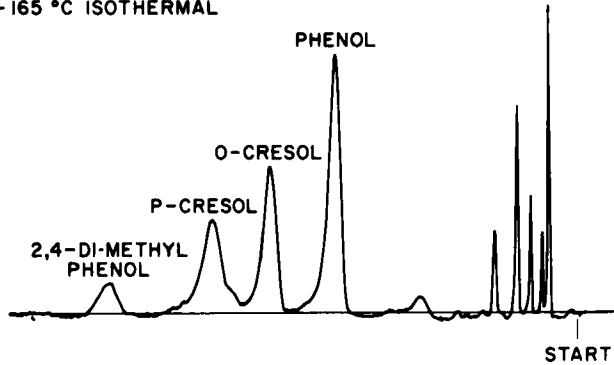


Fig. 2. Pyrogram of phenolic resin 91LP.

## RESULTS

The per cent phenolic resin in each cut is determined from a previously prepared calibration curve (Fig. 3) and is plotted as a function of distance from the back face of the material. The resultant curve clearly shows the zones of charring, partial degradation, and virgin material (Figs. 4-6). Comparison of several curves indicates that the slope of the curve at the inflection point is a function of the heat flux experienced by the material during re-entry heating. The curves thus determined agree very well with char density data, dye penetrant data, and REKAP† analysis (Fig. 6). REKAP, the analytical charring ablator model, is used to evaluate test data. The independently measured reaction rate constants and material properties are used to develop the ablation performance model for each material. Through the use of ground and flight test data, the REKAP program has been calibrated and verified for a wide range of ablative materials.

Divergence of the per cent volatiles and per cent phenolic resin curves near the surface of the material (Fig. 7) is due to the presence of the

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†Reaction Kinetics Ablation Programs.

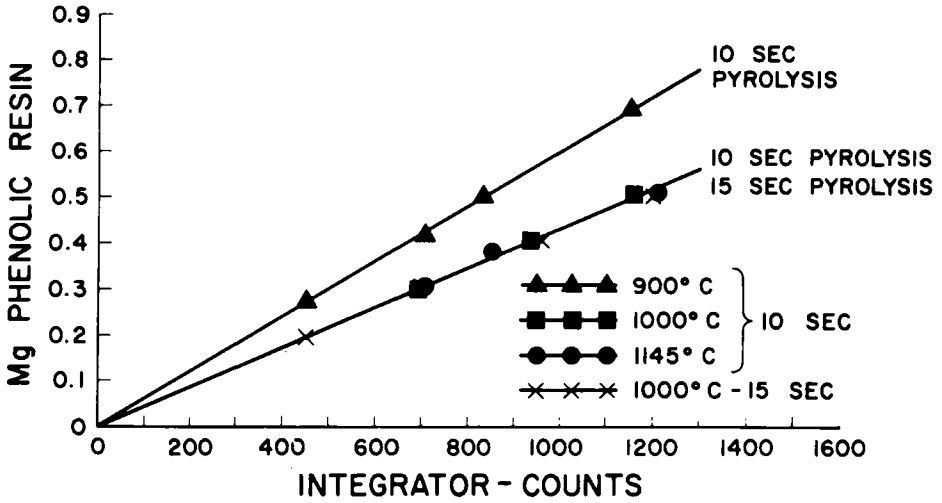


Fig. 3. Phenolic resin calibration versus temperature and time.

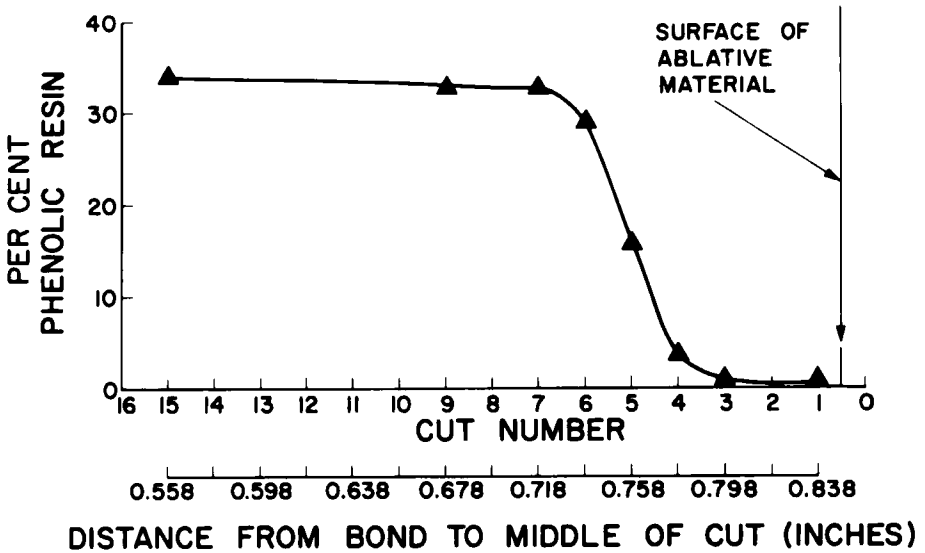


Fig. 4. Per cent phenolic resin versus distance from back face of heat shield.

COMPARISON OF PYROLYSIS & DYE PENETRANT TECHNIQUES

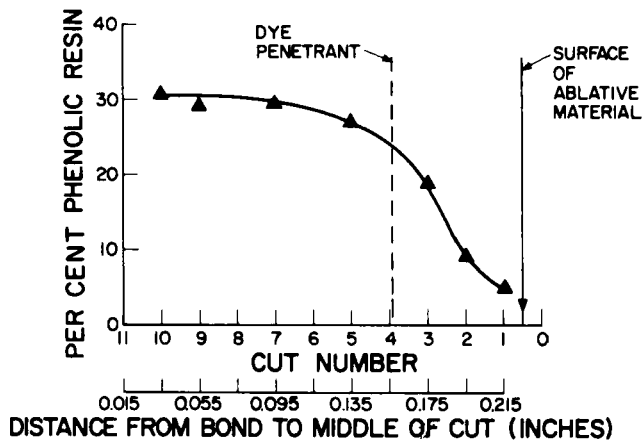


Fig. 5. Per cent phenolic resin versus distance from back face of heat shield.

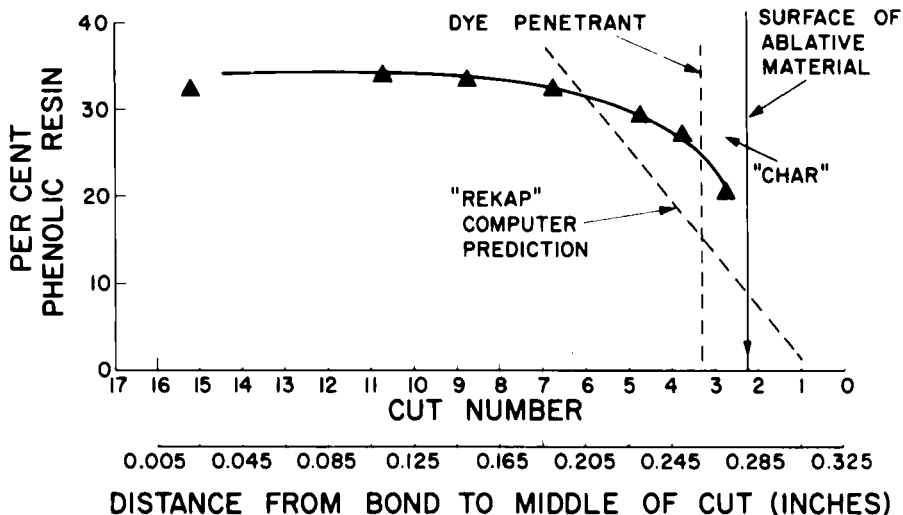


Fig. 6. Per cent phenolic resin versus distance from back face of heat shield.

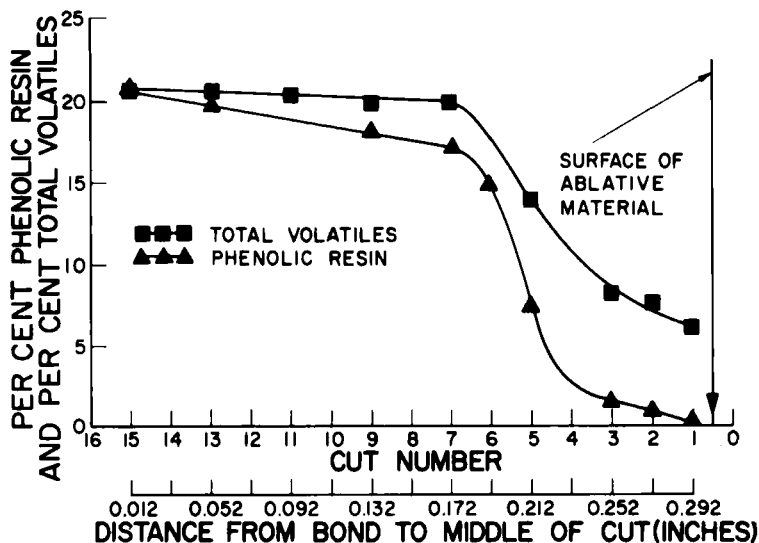


Fig. 7. Per cent phenolic resin and per cent volatiles versus distance from back face of heat shield.

degradation products of heating re-entry which have been absorbed by the active carbon of the carbon char. These degradation products are clearly shown by the chromatograms (Fig. 8) to be quite different from those due to heating at the relatively low temperature of 1000°C used for pyrolysis-gas chromatography analysis. The products shown in Fig. 8 were desorbed from the active char at a temperature of only 400°C. The phenol peak on the chromatogram is used as the indicator of virgin phenolic resin although other products, such as o- or p-cresol, have been used. The phenol peak decreases as samples are taken closer to the surface, indicative of degradation of the resin (Fig. 9), but at the same time there is a marked increase in the number and quantity of low-molecular-weight species. The identity of these low-molecular-weight compounds is important since these compounds represent the actual degradation products due to conditions of re-entry heat, surface pressure, environment, etc. A complete analysis of these products should give much-needed information about actual degradation products, average molecular weight, and  $\Delta H$  values for ablative plastics under various environmental conditions.



PRODUCTS DESORBED BY HEATING TO APPROXIMATELY 400°C

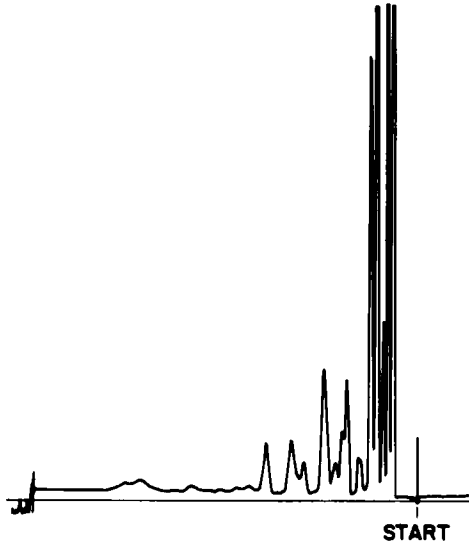


Fig. 8. Low-molecular-weight products of re-entry heating absorbed onto char.

AN INCREASE IN THE NUMBER OF LOW MOLECULAR WEIGHT PRODUCTS

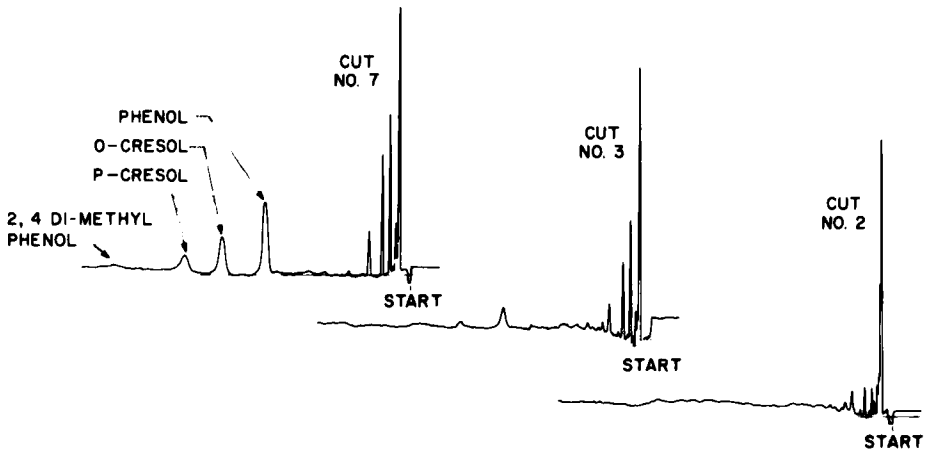


Fig. 9. Pyrograms showing disappearance of phenol peak.

## ACKNOWLEDGMENT

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## REFERENCES

- [1] J. Janak, *Preprints, Third Symposium on Gas Chromatography, June 8-10, 1960, Edinburgh, Scotland*, Butterworths, London, 1960, Paper Y-233-Y-244.
- [2] E. M. Barrall, II, R. S. Porter, and J. F. Johnson, "Effect of Pyrolysis Temperature and Sample Size on the Pyrolysis Gas Chromatograms of Polymers," presented at the California Section, Am. Chem. Soc. Meeting-in-Miniature, University of California, Berkeley, December 17-18, 1962.
- [3] D. F. Nelson, J. L. Yee, and P. L. Kirk, *Microchem. J.*, **6**, 225-231 (1962).
- [4] S. G. Perry, *J. Gas Chromatog.*, **2** (2), 54-59 (1964).
- [5] G. C. Hesitt and B. T. Whitham, *Analyst*, **86**, 643-652 (1961).
- [6] H. W. Lochte, E. L. Strauss, and R. T. Conley, *J. Appl. Polymer Sci.*, **9**, 2799-2810 (1965).
- [7] E. Weber, General Electric Co. GE RSD TDM-8151-035, September 1964.
- [8] R. A. Sheridan, General Electric Co. GE RSD TDM-8151-048, March 1965.

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