

The Pyrolysis of Wool and the Action of Flame Retardants

PETER E. INGHAM, *Wool Research Organisation of N.Z. (Inc.),
Christchurch, New Zealand*

Synopsis

The thermal degradation of untreated wool and wool treated with a number of flame retardants has been studied in a variety of atmospheres using thermogravimetric analysis and pyrolysis-gas chromatography. The major products of pyrolysis have been identified and their amounts determined. Gas evolution curves have been determined for the main light gases evolved.

INTRODUCTION

In order to develop better flame retardants for wool fabrics, it is useful to know more about the processes occurring during the combustion of wool and how flame retardants alter these processes.

Extensive literature exists on the elucidation of the mechanisms of thermal degradation and the roles of flame retardants for cellulose. In general, an effective flame retardant for cellulose increases the amount of water produced and the amount of char remaining, while decreasing the yield of flammable volatiles. Ideally, decomposition should proceed via a dehydration mechanism to yield only carbon and water. Reid et al.^{1,2} postulated that an effective flame retardant acted as a Lewis acid at or near the combustion temperature to alter the course and speed of the reactions involved. They found that the decomposition of cotton was accelerated and the gas production decreased by a flame retardant. The flammable gases were produced at a lower temperature for flame-proof cotton, probably below their ignition temperature. It was later shown³⁻⁵ that the same nonoxidative mechanism operates in the pyrolysis of cellulose under all conditions.

Little work has been carried out on the thermal behavior of wool at the temperatures of ignition or combustion; most workers have been concerned with the thermal effects occurring below 200°C. Koroskys⁶ reported the evolution of carbon monoxide and dioxide, hydrogen sulfide, hydrogen cyanide, nitric oxide, nitrogen dioxide, and acrylonitrile as combustion products from wool. Hiramatsu⁷ identified a large number of organic products from the pyrolysis of wool between 400° and 800°C by mass spectroscopy. Haase and Rau⁸ and Gokcen and Cates⁹ have used pyrolysis-gas chromatography as a method of identifying wool and other fibers.

This study was undertaken to provide a similar basic background for wool flammability as exists for cotton, bearing in mind the extra complexity of the structure of wool does not permit such a complete analysis as is possible for cotton. Pyrolysis-gas chromatography (PGC) and thermogravimetric analysis (TGA) were used to investigate and compare the thermal behaviors of untreated and flame retardant-treated wool.

EXPERIMENTAL

Apparatus

Thermogravimetric analyses were carried out with an apparatus developed from an Aminco differential thermal analyzer (DTA) and a Cahn gram electrobalance. The Aminco DTA furnace was inverted and the sample was threaded onto a 0.1-mm platinum wire hanging down into the furnace from the Cahn balance. A sample size of approximately 40 mg was used for each run except where stated otherwise. A gas flow of nitrogen, oxygen, or air was introduced into the furnace at a flow rate of 60 ml/min. The linear temperature programmer of the Aminco thermoanalyzer was used to provide a uniform heating rate of 6.0°C/min. The sample weight was read manually from the balance and plotted against the temperature. The furnace temperature readout was provided by a calibrated Chromel-Alumel thermocouple on the furnace wall adjacent to the sample.

To check the effect of buoyancy and thermal convection currents on the sample, runs were conducted with glass wool and asbestos fiber to simulate the bulk of the wool sample. The increase in apparent weight in each case was less than 0.5%, and these effects were therefore neglected.

The thermograms showed that the loss of regain water was complete by 100° and they were therefore scaled to a zero weight loss at 100°C.*

The infrared spectra of char samples were run with a Beckman IR 8 spectrophotometer using the KBr disc method.¹⁰

The pyrolyzer used was a Hamilton pyrolysis sampling device. This consists of a Vycor processing tube which passes through three zones: (1) a room temperature region where the sample may be held while purging air from the system; (2) a furnace zone, variable up to 800°, into which the sample is dropped for pyrolysis; and (3) an oven zone, variable up to 300°, where the vapors are held. From the oven, the processing tube connects directly with a heated (up to 300°) stainless steel line terminating in a needle which is inserted directly into the gas chromatograph (GC) inlet septum.

Two main methods of operation were used: fixed mode and successive mode pyrolyses. In the former, a sample of approximately 1 mg in a small quartz capillary was used. The sample was placed in the room temperature region of the processing tube and purged of air for 5 min, after which

* All temperatures are in degrees centigrade.

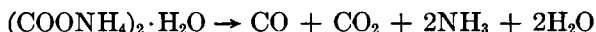
the needle was inserted into the GC septum. With the purge valve off, the sample was slid into the furnace by tilting the furnace assembly. After 60 sec of pyrolysis, the sample was returned to the room temperature region and the sample introduction valve was opened to enable the pyrolysis vapors to be swept into the GC column. In a successive mode pyrolysis, a sample size of approximately 4 mg was used. The sample was purged as before, the furnace temperature set to 100°, and the sample slid into the furnace for 60 sec of pyrolysis. This procedure was repeated on the same sample with the furnace temperature increased in 20° steps up to 600°. Thus, pyrograms were obtained for each 20° temperature interval.

The gas chromatograph used was a Varian 1200. A thermal conductivity detector was used throughout. Columns used were: (i) 2 m × 4 mm I.D. of Porapak Q with 3% polyethylenimine; (ii) 2 m × 4 mm I.D. of Chromasorb W with 20% polyethylene glycol 1500; (iii) 2 m × 4 mm I.D. of 85% molecular sieve 13X and 15% molecular sieve 5A preceded by a 0.6 m × 4 mm I.D. column of silica gel.

All column packings used were 80/100 mesh. For quantitative results, the peaks were calibrated by pyrolyzing weighed milligram quantities of ammonium hydrogen carbonate and ammonium oxalate. Ammonium hydrogen carbonate was found to decompose according to the equation



and ammonium oxalate, according to



The amounts of hydrogen sulfide and methane evolved were determined by the use of thermal conductivity weighting factors¹¹ knowing the detector response and weight factors for the other light gases. The amount of hydrogen cyanide was determined on the Chromasorb column by calibration with injections of dried liquid hydrogen cyanide. The amounts of carbon monoxide and methane were determined on the molecular sieve column.

Materials

The fabric used throughout was unraised, undyed, unbleached blanket material of 370 g/m² made of New Zealand crossbred 48/50s wool. Phosphoric acid was applied at different levels of add-on by wetting out the fabric in various concentrations of phosphoric acid for 2 hr, then drying. The ammonium salts were applied by wetting out the fabric in solutions of ammonium dihydrogen phosphate or ammonium sulfamate to a 100% wet add-on and drying to give a solids add-on of around 10% on wool weight. Tris(1-aziridinyl)phosphine oxide (APO) was applied by the method of Simpson.¹² A solution of 8:50:2 parts by volume of 80% APO solution: water:boron trifluoride (35% solution in methanol) was applied to the fabric to give a wet add-on of 100%. The sample was dried at 100–105° for 10 min to give a dry add-on of 11.8%.

RESULTS AND DISCUSSION

TGA

The thermogravimetric curves for untreated wool (Fig. 1) show that after the loss of regain water, the initial decomposition begins at approx. 210° in air, oxygen, or nitrogen atmospheres. The curves for air and nitrogen show an initial decomposition from 210° to 290°, followed by a region of uniform rate of weight loss from 290° to 340°. In nitrogen, the rate then decreases to a lower and approximately uniform rate up to 700°, while in air the rate increases and a major weight loss begins at about 440°. The rate later decreases until at 620° all the sample has been volatilized. In oxygen, a sudden, rapid weight loss occurred at 240°, while at 385° there was an explosion probably due to the ignition of flammable, volatile products.

The TGA curves of phosphoric acid-treated fabric and phosphoric acid itself in a nitrogen atmosphere are shown in Figure 2, and in air in Figure 3. Phosphoric acid is an extremely effective flame-proofing agent for wool, even at low levels of add-on (i.e., around 2%), but it is not wash fast. In nitrogen, two main effects are observed compared with untreated wool: the decomposition temperature is lowered and the weight loss is decreased. Both of these effects depend on the level of add-on. At 400°, the weight loss was 49.2% for the untreated control, 42.8% for wool with 6.2% phosphoric acid, and 39.0% with 12.0% phosphoric acid. It should be noted, however, that some part of the weight of the residues of the treated samples may be attributable to the flame retardant itself or its degradation products.

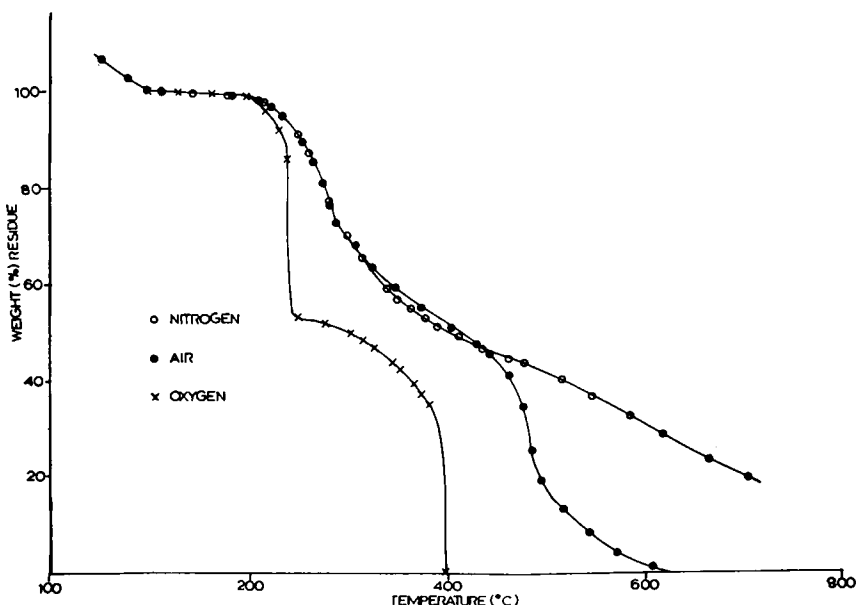


Fig. 1. Thermogravimetric curves for untreated wool.

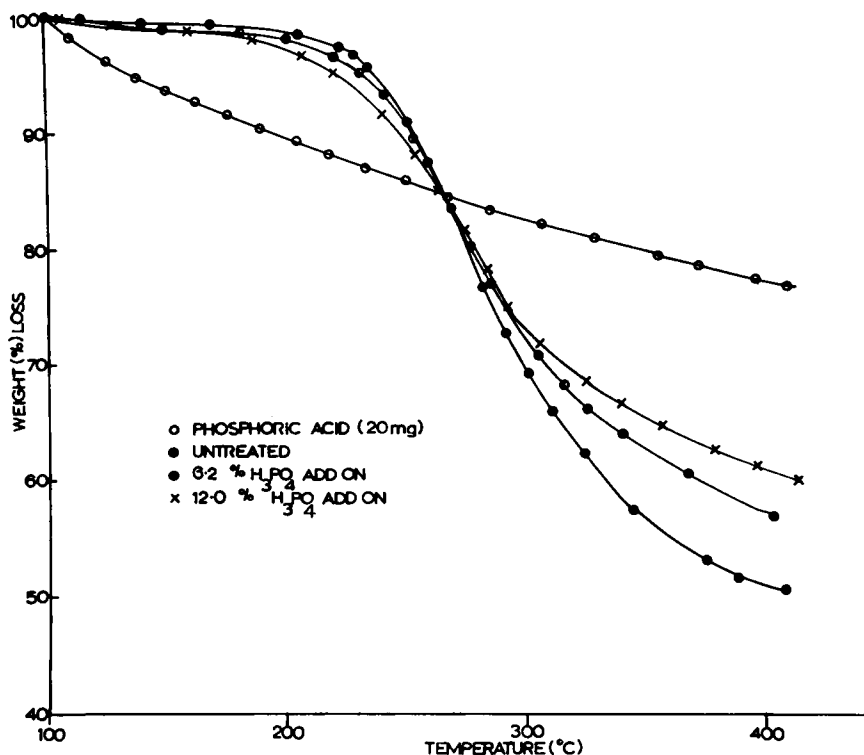


Fig. 2. Thermogravimetric curves for phosphoric acid, untreated wool, and phosphoric acid-treated wool heated in nitrogen.

In air, the curves follow the same general shape up to 400°, with a lower decomposition temperature and a higher residual char for the flame-proof samples. The most striking effect of the flame retardant is the decrease in the rate and extent of weight loss beginning at 440° compared with an untreated sample in air. Thus, at 600° the residue is 37% for 12.0% add-on, 22% for 6.2% add-on, and 1.3% for the untreated control. Since this weight loss at 440° occurs in air but not in nitrogen, it is probably due to an oxidative process which is suppressed by the phosphoric acid flame retardant. The same effects, i.e., earlier decomposition, lower weight loss, and suppression of the weight loss at 440° in air, are seen for all the flame retardants examined. Figures 4 and 5 show the thermograms in air and nitrogen for fabric treated with ammonium dihydrogen phosphate and APO, respectively.

A sample with a 7% add-on of sulfuric acid exhibited the earlier initial decomposition temperature, but thereafter the thermograms in both nitrogen and air were almost identical with those for untreated wool. Sulfuric acid does not produce any appreciable degree of flame retardance when applied to wool.

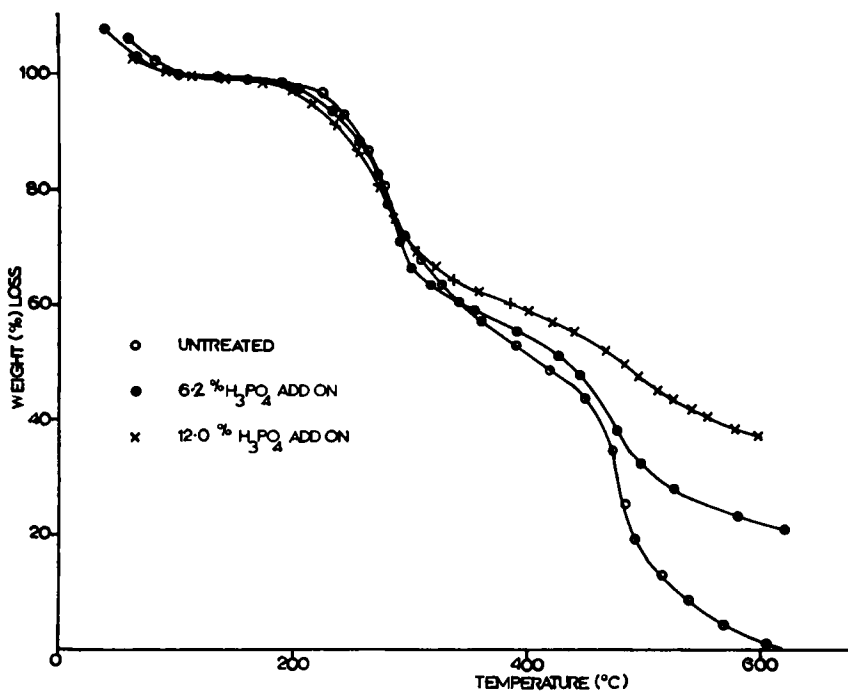


Fig. 3. Thermogravimetric curves for phosphoric acid-treated wool heated in air.

Isothermal TGA

The curves of isothermal runs at various temperatures around the initial decomposition temperature are shown in Figure 6. The results are scaled to show a 100% weight retention at zero time.

At 202°, after loss of regain water, there is a slow, linear weight loss of 0.045%/min. Most of this loss may be attributed to degradation of the most labile side chain and terminal amine and carboxylic acid groups as ammonia and carbon dioxide. At successively higher temperatures, the initial rate of weight loss increases, and the respective steady-state rates after 50 min are 0.055%/min at 220°, 0.061%/min at 236°, and 0.077%/min at 250°.

The effect of a flame retardant is shown by the curve for wool containing 12.0% phosphoric acid heated at 236°. Compared with the untreated sample, the initial weight loss is smaller, and after 50 min the weight loss is 0.061%/min compared with 0.068%/min for an untreated sample at the same temperature.

Distribution of the Flame Retardant

To ascertain the distribution of a flame retardant between the solid char and the volatile products, samples of woolen blanket material with a 7.3% phosphoric acid add-on were heated in the TGA furnace at 6.0°/min in

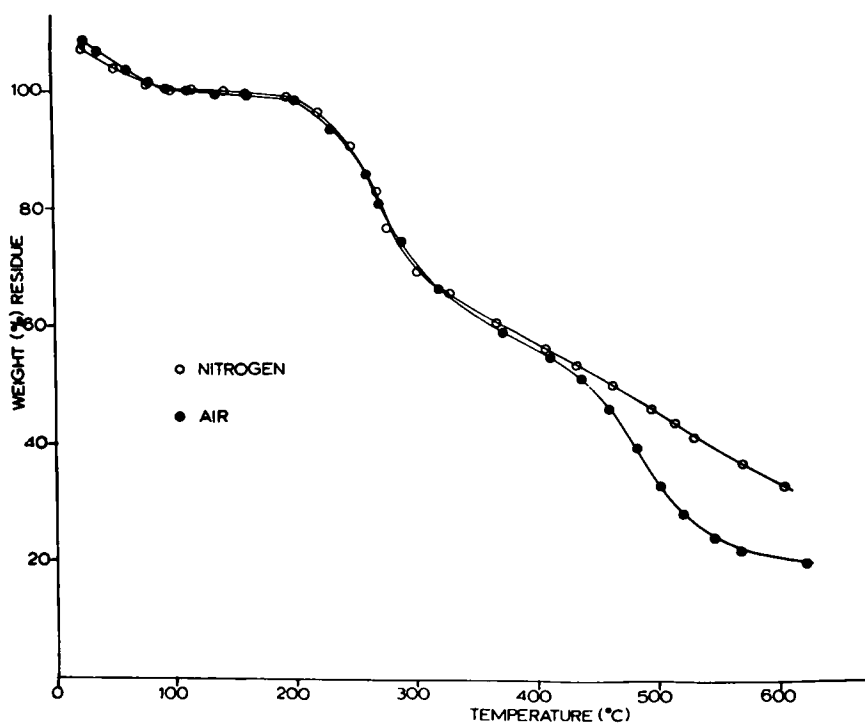


Fig. 4. Thermogravimetric curves for wool with 6.1% add-on of ammonium dihydrogen phosphate.

air. At selected points along the TGA curve, heating was stopped by removing the sample from the furnace. Phosphorus analyses were carried out on the charred samples, with the results given in Table I.

It can be seen that the charred fabric retains nearly all of the total phosphorus, suggesting that phosphoric acid acts as a flame retardant primarily in the solid phase. In a similar series of analyses for tetrakis(hydroxylmethyl)phosphonium chloride in cotton twill and for phosphorylated cotton sheeting, Stansbury and Hoffpauir¹³ found the charred fabrics con-

TABLE I
Distribution of Phosphorus in Char

Temp. of heating, °C	P in char, %	P based on original dry weight, %
Unheated control	2.30	2.30
180	2.32	2.30
210	2.41	2.33
250	2.54	2.29
287	3.15	2.30
330	3.92	2.52
400	3.92	2.29

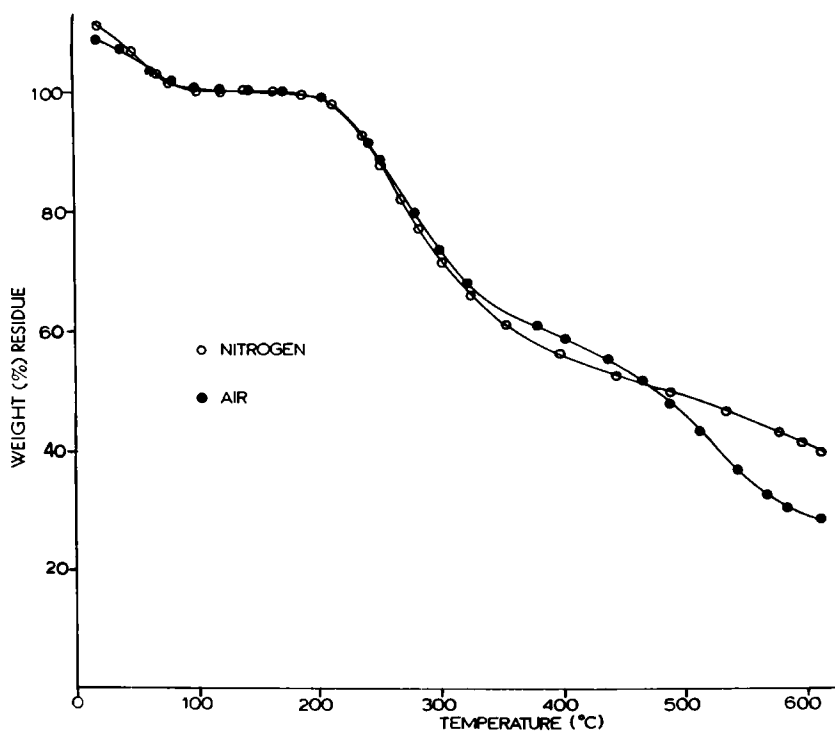


Fig. 5. Thermogravimetric curves for wool with add-on of 11.8% of tris(1-aziridinyl)-phosphine oxide.

tained 95.6% and 97.5%, respectively, of the total phosphorus after being heated at 400°.

Infrared Analysis of Char

Samples of untreated fabric were heated in the TGA apparatus as for the phosphorus analyses, from room temperature to 220°, 260°, 300°, and 400° in air. The spectra are shown in Figure 7. The amide A and B peaks at 2.99 μm and 3.26 μm (a Fermi resonance of N—H and C \equiv N stretching and N—H bending) and the N—H bending frequency at 6.58 μm showed a reduction in intensity, as would be expected with increasing loss of ammonia from the char. The CH₂— and CH₃— stretching modes at 3.39, 3.42, and 3.50 μm did not show much reduction in intensity until 400°, indicating that the evolution of volatile hydrocarbons commences only at higher temperatures. The carbonyl stretching frequency at 6.13 μm shows less reduction in intensity, but by 400° the maximum absorption is at 6.25 μm , suggesting the formation of C=C. At 300° and 400°, a new peak at 4.35 μm appears, possibly due to C \equiv N stretch.

Pyrolysis-Gas Chromatography

Figure 8 shows the chromatogram of untreated wool pyrolyzed in helium at 550°. The main products identified are carbon monoxide, methane,

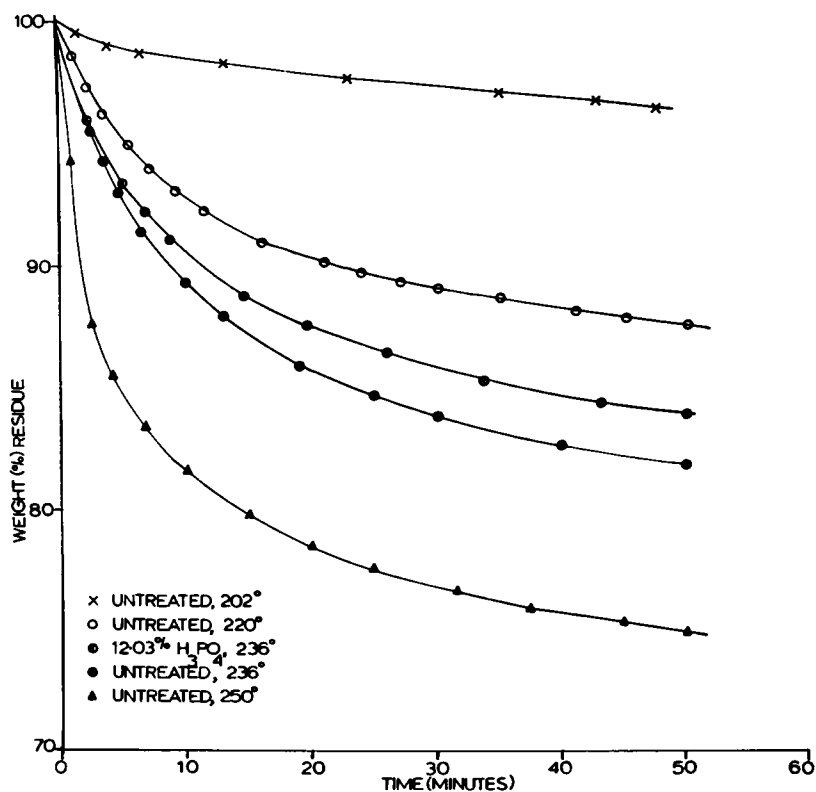


Fig. 6. Isothermal thermogravimetric curves for untreated and phosphoric acid-treated wool.

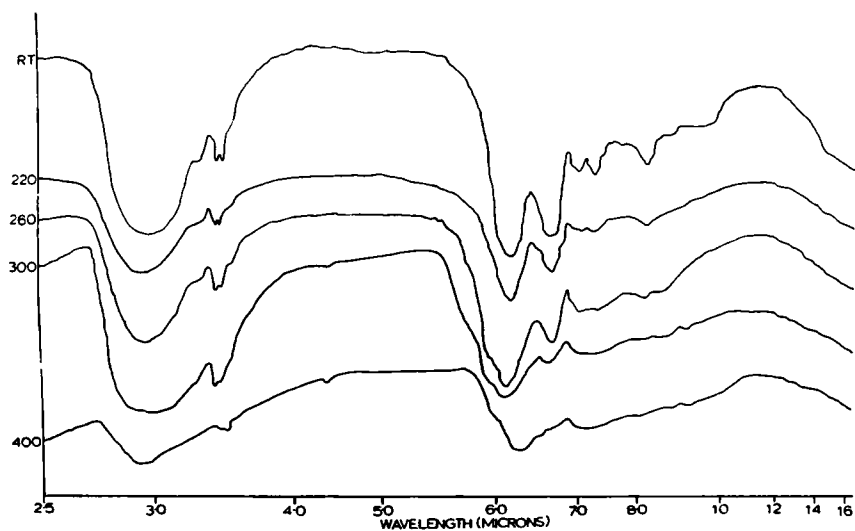


Fig. 7. Infrared spectra of wool after heating in TGA furnace in air from room temperature to 220°, 260°, 300°, and 400° at a heating rate of 6°/min.

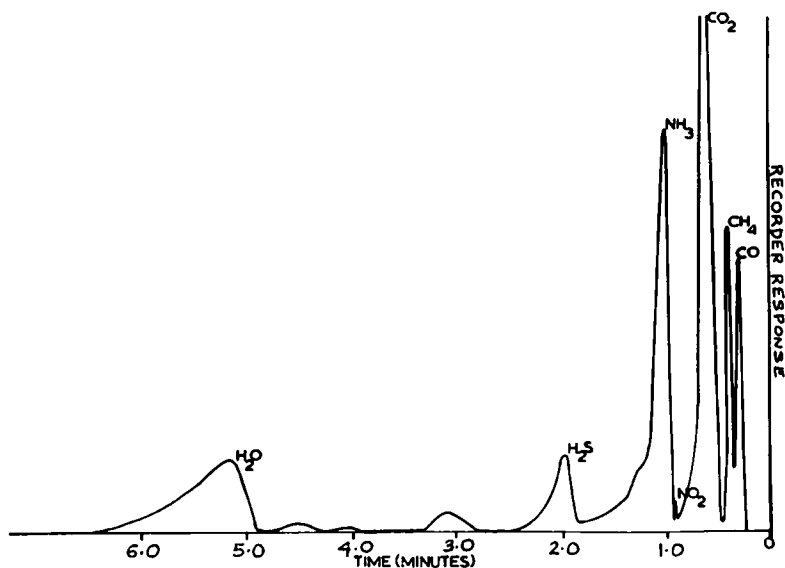


Fig. 8. Pyrogram of light gases from pyrolysis of 1 mg of untreated wool for 60 sec at 550°; pyrolysis oven, 200°; heated line, 250°. GC conditions: column i; He flow rate, 12 ml/min; column temperature, 75° (isothermal); detector 200 mA, 220°; injector, 220°.

carbon dioxide, ammonia, hydrogen sulfide, and water. The peaks were identified by retention times at three different column temperatures and in some cases by infrared spectral analysis of the pyrolysis gases collected from the pyrolysis unit in an IR gas cell.

No new products were observed in the pyrolysis of flame retardant-treated wools as compared with untreated wool. The main differences noted were in the relative amounts of the products, particularly water. The results of quantitative measurement of the main gases evolved during pyrolysis in helium are shown in Table II. Because hydrogen cyanide had a similar retention time to water on the Porapak column, it was determined on the Chromasorb + polyethylene glycol column (column ii).

TABLE II
Total Amount of Light Gases Evolved during Pyrolysis in Helium*

	Gases evolved, μ moles/mg					
	CO ₂	NH ₃	H ₂ O	H ₂ S	HCN	CO
Untreated wool	3.12	4.27	3.40	0.81	0.21	0.48
Wool + 7.0% H ₃ PO ₄	2.53	4.39	5.89			
Wool + 6.1% NH ₄ H ₂ PO ₄	3.08	3.90	5.43			
Wool + 14.0% NH ₄ SO ₃ NH ₄	2.86	4.14	6.84			
Wool + 1.2% TiO ₂	3.31	3.74	5.12			

* Values given are the averages of a minimum of six pyrolyses on approx. 1-mg samples which had been dried for 48 hr in vacuo over P₂O₅. Pyrolysis conditions: 60 sec at 550°.

As well as carbon monoxide and methane, small amounts of oxygen and nitrogen were separated by the molecular sieve column during pyrolyses in helium (Fig. 9). These may be due to some residual air in the fiber which was not removed by purging, or they may be pyrolysis products. Neither nitric oxide nor sulfur monoxide was detected from any sample.

Pyrolyses in air gave results identical within experimental error with those in helium for carbon monoxide, methane, carbon dioxide, ammonia, hydrogen sulfide, hydrogen cyanide, and water, for all temperatures of pyrolysis.

At high column temperatures and high detector attenuation, a pyrogram of organic pyrolysis products was obtained. With a Porapak Q + 3% polyethylenimine column run isothermally at 185°, over twenty peaks could be separated, ranging from the light gases to high molecular weight constituents of the tar produced by pyrolysis. The pyrogram of the organic products from untreated wool is shown in Figure 10. In view of its complexity, little attempt was made to identify most of the peaks, but peak no. 7 was tentatively identified by retention times as ethylamine. Hiramatsu⁷ identified C, H, and O compounds such as methane, acetylene, ethylene, ethane, propylene, propane, butene, butane, methanol, ethanol, acetone, acetic acid, methyl ethyl ketone, furan, acetaldehyde, methylfuran, di-

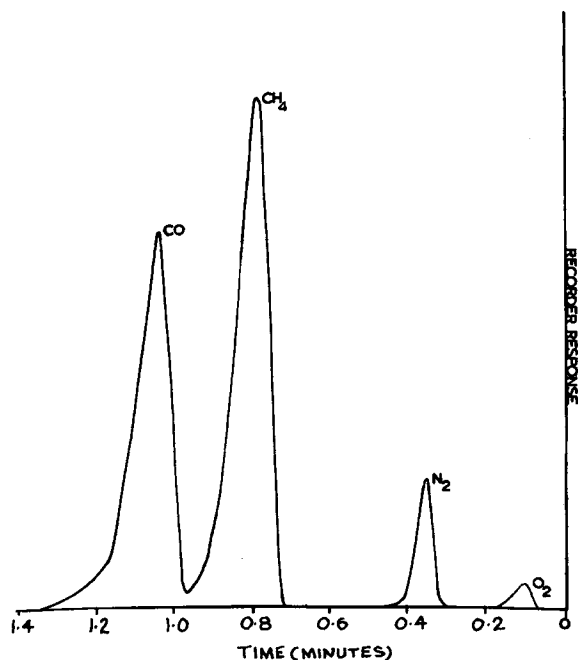


Fig. 9. Pyrogram from molecular sieve column. Pyrolysis conditions: furnace, 550°; oven, 200°; heated line, 250°; pyrolysis for 60 sec. GC conditions: column iii; He flow rate, 40 ml/min; column at room temperature (isothermal); detector 200 mA, 200°; injector, 220°.

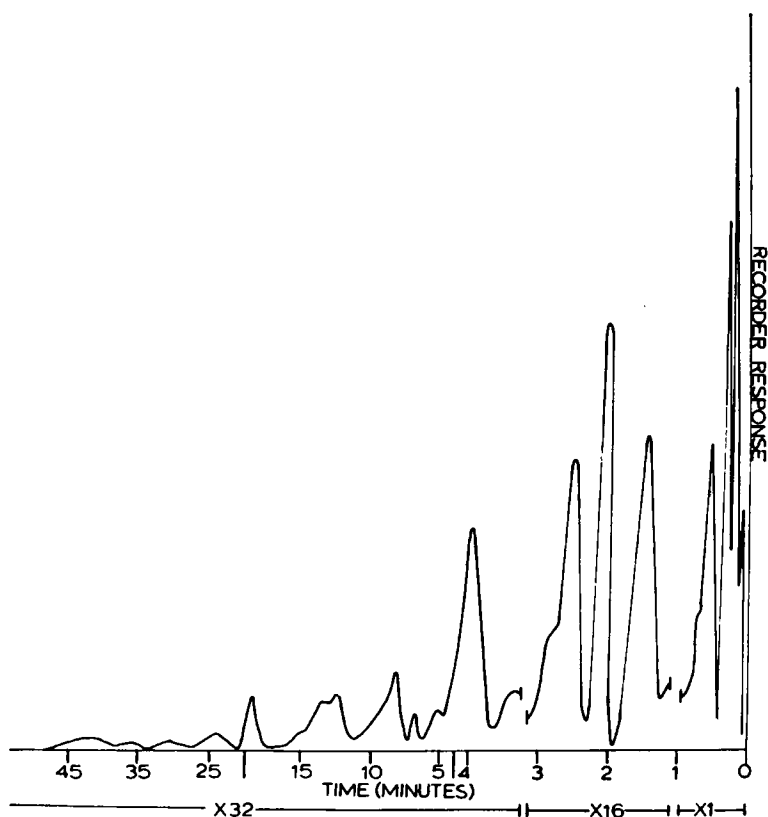


Fig. 10. Pyrogram of organic products from untreated wool. Pyrolysis conditions: furnace, 550°; oven, 220°; heated line, 250°; pyrolysis for 60 sec. GC conditions: column i; He flow rate, 10 ml/min; column temperature, 185° (isothermal); detector 250 mA, 200°; injector, 200°.

methylfuran, benzene, and toluene by mass-spectrometric analysis of the volatile products obtained from the pyrolysis of the wool at 800°.

The pyrograms of the organic pyrolysis products of the flameproofed samples are qualitatively identical with that for untreated wool, but quantitative measurements of peak areas from pyrolysis of weighed samples showed a 20–25% reduction in area for flameproofed samples. Thus, as well as increasing the amount of water evolved, a flame retardant also decreases the yield of flammable, volatile organic products.

The pyrograms in air of treated and untreated samples are identical with those in helium at all temperatures up to approximately 450°, indicating that at lower temperatures the mechanism of pyrolysis is thermolytic rather than oxidative. At temperatures of 500° and over, the pyrogram of the organic products changes completely and consists only of two small peaks at retention times of 2.0 and 3.9 min, with a few low trace peaks at longer retention times. Visual observation of the pyrolysis of a 1-mg sam-

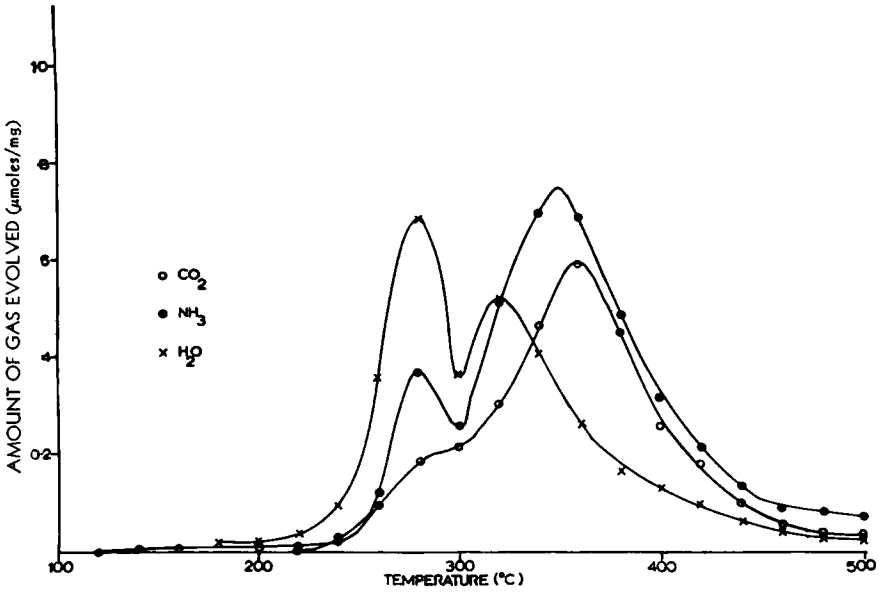


Fig. 11. Gas evolution curves for untreated wool.

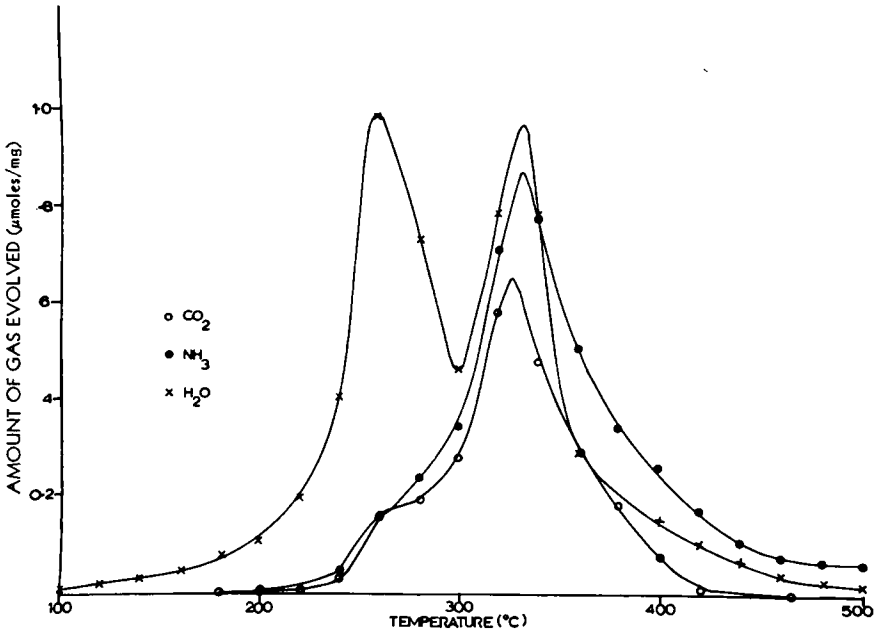


Fig. 12. Gas evolution curves for wool with 7.0% phosphoric acid add-on.

ple in air at 500° or over showed the immediate formation of a dense, pale-yellow smoke in the pyrolysis tube which condensed in 2-3 sec to a viscous yellow tar on the cold region of the tube. Thus, it appears as if there is a

critical temperature at which nearly all the volatile organic products oxidize to form a viscous tar. This oxidation of organic products corresponds to the region of rapid weight loss from 460° to 500° in the TGA thermogram of untreated wool heated in air.

Successive Mode Pyrolyses

In an attempt to measure the temperatures of evolution of the main gases and relate these to the TGA curves, a series of successive mode pyrolyses was carried out. The results for untreated wool and some flameproof treatments are shown in Figures 11 to 14.

For untreated wool, the gas evolution curve for ammonia has a small maximum at 280° with the main peak at 350°. The first peak is likely to be ammonia derived from terminal amine and side-chain amine and amide groups of lysine, arginine, asparagine, and glutamine, while the main peak is likely to be ammonia produced from hydrogen abstraction reactions following fragmentation of the main peptide chain. A similar pattern is seen for the carbon dioxide evolution curve in which the first peak corresponds to gas produced from decarboxylation of terminal carboxylic and side-chain carboxylic acid groups of aspartic and glutamic acids, and the main peak at 360° is from carbon dioxide produced after peptide chain fragmentation. The evolution curve for water shows a larger initial peak at 280°, with a second smaller peak at 320°.

The gas evolution curves for hydrogen cyanide, hydrogen sulfide, meth-

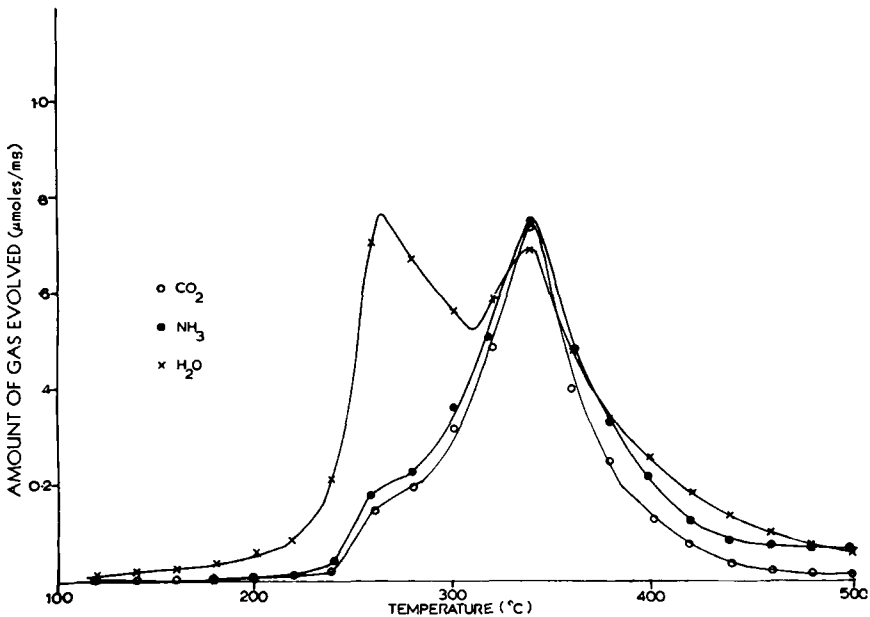


Fig. 13. Gas evolution curves for wool with 6.1% ammonium dihydrogen phosphate add-on.

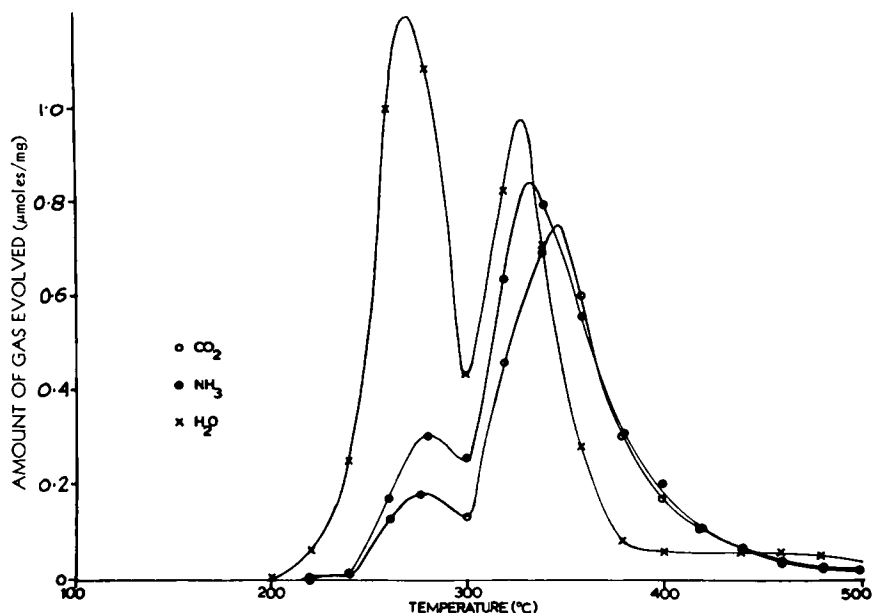


Fig. 14. Gas evolution curves for wool with 14.3% ammonium sulfamate add-on.

ane, and carbon monoxide are shown in Figure 15. Hydrogen sulfide is released almost entirely between 240° and 300°, with a maximum at 265°. This agrees generally with the results of Felix et al.¹⁴ who, in a TGA study of wool, attributed an endotherm at 230° to disruption of the disulfide linkages. The slow heating rate of 3–4°/min used by Felix et al. would cause a lower peak temperature than the effective 20°/min heating rate used in this work. Carbon monoxide is evolved over a wide temperature region, with a maximum at 420°, while the evolution of methane builds up gradually to reach a maximum at 580°. A small amount of hydrogen cyanide is produced between 310° and 450°, with a maximum at 345°.

The curves for the flameproofed samples all show a similar general pattern. The greatest difference seen in comparison with untreated wool is the greatly increased area of the second water peak, which occurs at a higher temperature so as almost to envelop the main-chain degradation region in which most of the ammonia and carbon dioxide are produced. The amount of water evolved below 300° is also increased, but to a lesser extent. The increased earlier weight loss observed for flameproof samples accounts for this larger and earlier evolution of the first water peak.

SUMMARY AND CONCLUSIONS

TGA and PGC have been used to study the thermal degradation of untreated wool and wool treated with some flame retardants. The TGA curves for all the effective flame retardants tested show the same general

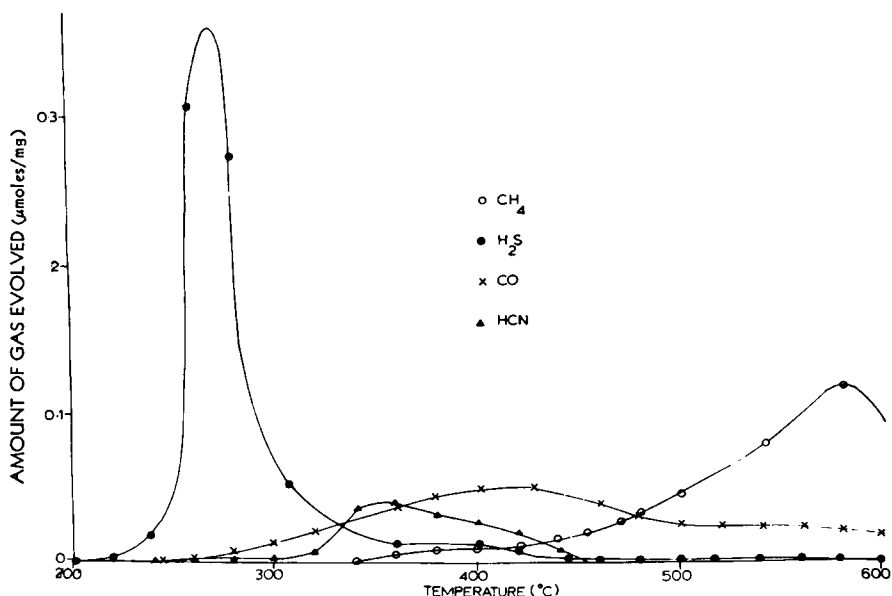


Fig. 15. Gas evolution curves for some of the minor gases from untreated wool.

effects, i.e., an earlier decomposition temperature and a larger amount of char remaining. Runs in air also show that the flame retardant suppresses a weight loss beginning at 440° which corresponds to an oxidative process. The earlier onset of decomposition appears to be acid catalyzed, as wool treated with sulfuric acid also degrades at a lower temperature, but this acid does not alter the processes occurring at and above 440°. In particular, the presence of sulfuric acid neither increases the weight of the residual char nor significantly increases the flame-resistance of the wool.

PGC indicated an earlier and increased evolution of water vapor, thus providing a probable explanation of the earlier weight loss. In the presence of a flame retardant, wool produces an extra 1.0 mmole of water per gram of wool in the peak below 300°, which may be derived from the hydroxyl groups of serine and threonine (9.7% and 7.0%, respectively by weight of the amino acids present) in a similar manner to the postulated mechanism of protonation of the much more numerous hydroxyl groups in cellulose. Although wool has a much more complex structure than cellulose, the similarity in the overall changes in the pyrolytic behavior produced by a flame retardant (i.e., earlier decomposition temperature, increased char, and large increase in the amount of water) and that efficient flame retardants for cotton are also effective when applied to wool suggest that a similar mechanism may operate in the cases of wool and cellulose.

PGC also showed a large preponderance of carbon dioxide, ammonia, and water over other pyrolysis products. Significant amounts of hydrogen sulfide, methane, carbon monoxide, and hydrogen cyanide were identified

and measured. A large number of trace amounts of organic products were detected. These showed a 20–25% reduction for wool treated with a flame retardant.

The advice of, and helpful discussions with, Dr. W. S. Simpson and Dr. A. J. McKinnon are gratefully acknowledged, as is the experimental assistance of Mrs. J. M. Archer and Miss M. A. Burrows. Mr. D. D. Haden performed the analyses.

References

1. H. A. Shuyten, J. W. Weaver, and J. D. Reid, *Advan. Chem. Ser.*, **9**, 7 (1954).
2. H. A. Shuyten, J. W. Weaver, and J. D. Reid, *Ind. Eng. Chem.*, **47**, 1433 (1955).
3. R. F. Schwenker, Jr. and E. Pascu, *Ind. Eng. Chem., Chem. Eng. Data*, **2**, 83 (1957).
4. R. F. Schwenker, Jr., and E. Pascu, *Ind. Eng. Chem.*, **50**, 91 (1958).
5. S. L. Madorsky, V. E. Hart, and S. Straus, *J. Res. Nat. Bur. Stand.*, **56**, 343 (1956).
6. M. J. Koroskys, *Amer. Dyest. Rep.*, **58** (6), 15 (1969).
7. K. Hiramatsu, *Mass Spectrosc.* (Japan), **14**, 285 (1966).
8. H. Haase and J. Rau, *Melliand Textilber.*, **47**, 434 (1966).
9. U. Gokcen and D. M. Cates, *Appl. Polym. Symposia*, **2**, 15 (1966).
10. R. T. O'Connor, E. F. Du Pre, and E. R. McCall, *Anal. Chem.*, **29**, 998 (1957).
11. W. A. Dietz, *J. Gas Chromatogr.*, **5**, 68 (1967).
12. W. S. Simpson, Wool Research Org., August 1970.
13. M. F. Stansbury and C. L. Hoffpauir, *Amer. Dyest. Rep.*, **44**, 33 (1955).
14. W. D. Felix, M. A. McDowall, and M. Eyring, *Text. Res. J.*, **33**, 465 (1963).

Received May 27, 1971.

Revised July 30, 1971.