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LEVEL II

**THERMAL DEGRADATION PRODUCTS
OF THPOH-NH₃ TREATED COTTON**

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The controlled pyrolysis of a particular flame retardant treated cotton fabric has been examined and the chemical composition of several main pyrolysis products have been investigated. Treated cotton fabric (VEE 4253/THPOH-NH ₃ process) was pyrolyzed under controlled laboratory conditions and the thermolysis products were investigated. The amount of volatilized products ranged from 50 to 60% and consisted of an unusually large proportion of solid material. This material was found to contain levoglucosan along with polymeric substances presumed to originate from incomplete degradation of the flame retardant.			

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polymer. The liquid portion of the pyrolysis product was separated into components, which were characterized by GC, GC-FTIR and NMR. Positive identification was made for levoglucosenone, 2-furaldehyde, 5-methyl-2-furaldehyde, and 2-furyl methyl ketone. Several additional components were tentatively identified. The composition of the pyrolyzate from this particular fire retardant treated cotton is compared with the results of pyrolysis studies on similarly treated cotton materials. The potential toxicity of the components are briefly discussed.



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THERMAL DEGRADATION PRODUCTS OF THPOH-NH₃ TREATED COTTON

INTRODUCTION

When flame retardant treated cotton is thermally degraded either by burning or under controlled pyrolysis, a complex sequence of reactions occurs and numerous pyrolysis products are formed. The quantity and composition of these products are of interest because of the possible formation of toxic substances and because they relate to studies on the mechanisms of flame retardant action.

Phosphorus-containing compounds are extremely important for the flame retardant treatment of cotton. The effectiveness of the flame retardant treatment often is enhanced by inclusion of certain nitrogen compounds, which react with the phosphorus flame retardant and thus immobilize it on the fabric. A beneficial synergistic effect frequently results from the combination of both phosphorus and nitrogen moieties in the same flame-retardant matrix.

The mechanisms of flame retardant action for these compounds are extremely complex, and comprehensive explanations for all of the processes occurring during thermal degradation have yet to be made. However, a rudimentary explanation for the mode of action of phosphorus flame retardants on cotton can be proposed. The initial reaction involves a thermal decomposition of the retardant to give phosphoric and polyphosphoric acids. These non-volatile acids catalyze a sequence of condensed phase dehydration reactions in the cellulose chains. The decomposition may proceed either by an acid catalyzed carbonium ion mechanism or by

phosphorylation of the glucose units that form the cellulose chain. These reactions promote the production of carbonaceous char and decrease the amount of volatile combustible material which is formed.

The present investigation involves a limited evaluation of the pyrolysis products that result from thermal degradation of cotton fabrics which had been treated with a flame retardant by the THPOH-NH₃ process.

Since military personnel may use treated cotton fabric of this type in an enclosed environment, it was of interest to examine briefly the pyrolysis products of this particular fabric sample. However, an extensive investigation of the pyrolysis products would require resources beyond those presently available. The results of this investigation are compared with pyrolysis studies on similarly treated cotton textiles to determine the potential for production of toxic products, and to suggest the mechanism of thermal breakdown.

EXPERIMENTAL

Fabric Description:

Unfinished cotton sateen Mil C-43122 0.28 kg/m² (8.2 oz/yd²) treated with THPS and ammonia (THPOH-NH₃ cure process) was manufactured by Cotton Incorporated, Raleigh, North Carolina. The treated fabric weighed 0.34 kg/m² (10 oz/yd²) and was labeled with the file code VEE4253.

Pyrolysis Apparatus and General Procedure:

A Lindberg tube furnace (tube opening; 34 cm long by 29 mm diameter) was used for pyrolyzing the fabric. Samples of fabric weighing 2-10g

were rolled up and inserted into Pyrex tubes sealed at one end (30 cm long by 22 mm I.D.). The exit end of the sealed tube was bent about 30° and led into a dry-ice-cooled collection trap. Pyrolyses were conducted by inserting the fabric-filled tube into the preheated furnace. The pyrolysis products were collected over a period of 15 to 40 minutes. At the end of each run the carbonaceous residue left in the tube was removed and weighed. The difference between this weight and the original fabric weight was recorded as the total amount of volatilized product.

Chromatography:

Thin layer chromatography was performed with Whatman MK6F silica gel coated glass plates with fluorescent indicator. Whatman KC₁₈ reversed-phase thin layer plates were also used. In addition to the fluorescent indicator present in the plates, visualization was aided by iodine absorption.

A Waters Associates ALC 201 liquid chromatograph with a Partisil PXS (25 cm x 10 mm O.D.) column and a Perkin-Elmer LC-55 variable wavelength detector was used for liquid chromatography. Gas chromatography was carried out with a F and M 5750 Research Chromatograph equipped with thermal conductivity detector and dual 180 cm x 10 mm, 5% Tergitol NPX columns.

Spectrometry:

Preliminary separation and identification of some of the pyrolysis products was made with a Nicolet FT-IR in conjunction with a Sadtler

CIRA GC-IR cell operated in the stopped-flow mode. The gas chromatograph in this system used a 180 cm x 10 mm, 3% OV-17 column operated isothermally at 220°C. Perkin-Elmer 521 and Nicolet FT-IR spectrophotometers were used for both transmission and attenuated total reflectance (ATR).

A JEOL 100 MHz NMR spectrometer was used for the proton magnetic resonance spectra. Chemical shifts are reported as parts per million relative to tetramethylsilane.

RESULTS AND DISCUSSION

The THPOH-NH₃ Process for Cotton:

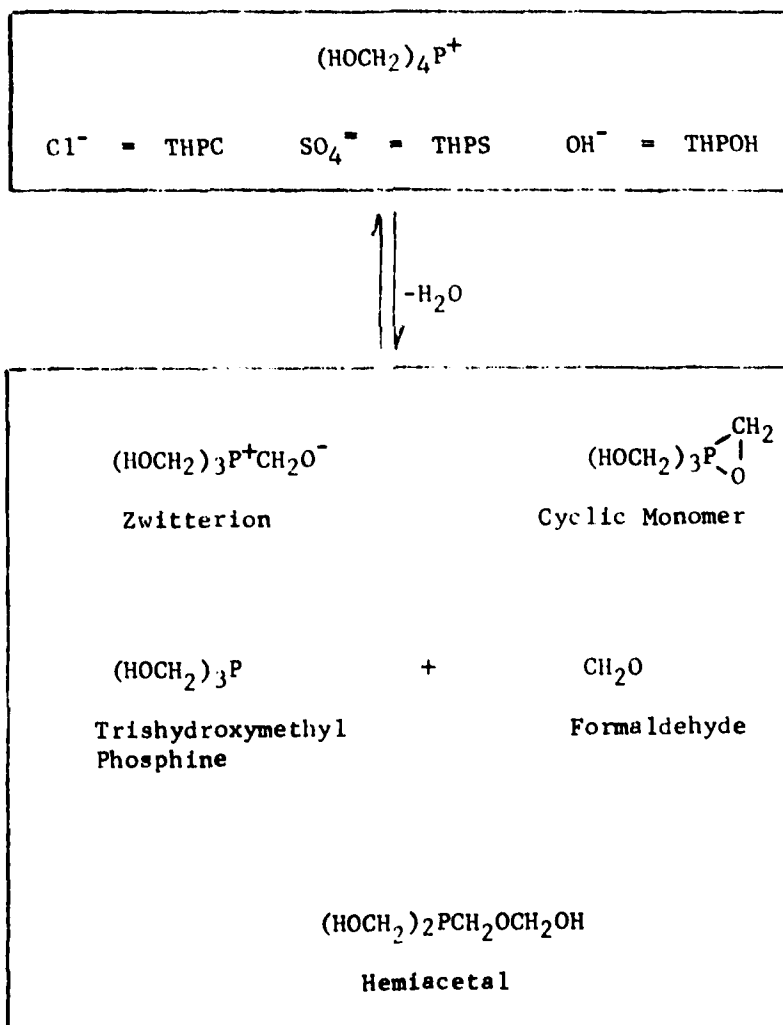
Tetrakis(hydroxymethyl)phosphonium salts form the basis for some of the most frequently used flame retardant treatments for cotton. In the treatment procedure, a solution of the phosphonium salt, commonly used as the chloride (THPC) or the sulfate (THPS), is adjusted to pH 7.0-7.5 by addition of aqueous sodium hydroxide to form a solution of what is generally regarded as tetrakis(hydroxymethyl)phosphonium hydroxide (THPCM). This solution is applied to the cotton textile and then insolubilized by a crosslinking reaction involving various basic nitrogen-containing compounds. In the present case the fabric was treated with neutralized THPS and cross linked with ammonia.

Various aspects of the chemistry of THPOH flame retardant treatments have been investigated ^{1,2,3} and the situation is more complex than it

1. M. Grayson, J. Am. Chem. Soc. 1963, 85, 79.
2. W. J. Vullo, J. Org. Chem. 1968, 33, 3665.
3. W. A. Reeves, D. J. Daigle, D. J. Donaldson and G. L. Drake Jr., Textile Chemist and Colorist 1970, 2, 283.

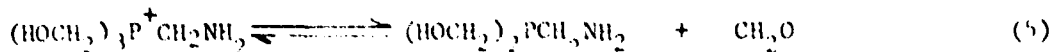
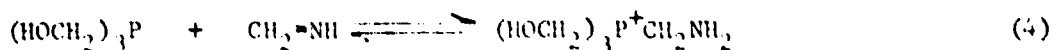
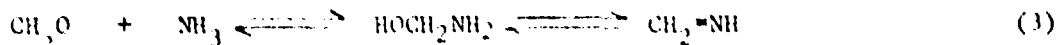
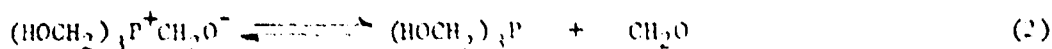
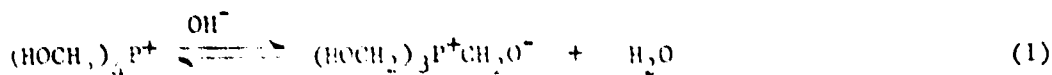
might initially appear. Although THPOH is often represented as the reactive component in the treatment solution, the actual composition of this solution is somewhat different. A series of reversible reactions can be proposed to account for the various species present in the neutralized phosphonium salt solution (SCHEME I).

SCHEME I



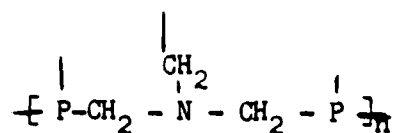
Granzow⁴ has studied the kinetics of the crosslinking reactions of tetrakis(hydroxymethyl)phosphonium salts with urea. His conclusions can be extended to account for the crosslinking reactions that occur when ammonia is used with the phosphonium salts. These reactions are depicted in SCHEME II.

SCHEME II

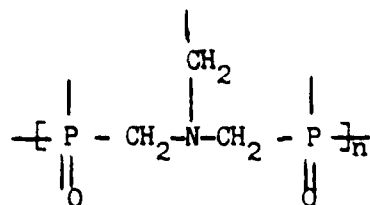


In the presence of base, a proton is abstracted from the phosphonium salt, eq. (1), and the reaction then proceeds via eq. (2) to form tris(hydroxymethyl)phosphine and formaldehyde. Reaction of formaldehyde with ammonia in eq. (3) gives an imine intermediate. This intermediate reacts with tris(hydroxymethyl)phosphine in eq. (4) to yield an amino-methyl tris(hydroxymethyl)phosphonium salt. Another proton is then abstracted from this phosphonium compound in eq. (5) and the sequence represented by equations (1) through (4) is repeated to give a crosslinked polymer with the following generalized structure:

4. A. G. Granzow, J. Am. Chem. Soc. 1977, 99, 2648.



A final step in the flame retardant treatment process generally involves oxidation of the crosslinked polymer to yield a phosphine oxide:



Preparative Pyrolysis:

Pyrolyses of THPOH-NH₃ cured cotton fabric (VEE 4253) were run in air both at atmospheric pressure and under vacuum. The flame retardant treatment decreased the amount of volatile tars produced during thermal degradation and diminished the quantity of this fraction available for investigation. When the pyrolysis was run under vacuum, slightly more of the volatile tars were isolated. As a result, most of the preparative pyrolysis runs were carried out under reduced pressure. The compositions of the products from either the atmospheric pressure runs or the reduced pressure runs were essentially the same according to comparative gas and liquid chromatography. Data for a number of preparative pyrolysis runs on fabric VEE 4253 are presented in Table 1.

Table 1
Pyrolysis of Fabric VEE 4253

Temperature °C	Pressure mm	Initial Fabric Weight g	Residue Weight g	Residue %	Volatile %
340-350°	160	20.8	8.5	41	59
340-350°	160	19.3	7.8	40	60
325°	1.0	8.6	2.4	28	72
325°	1.0	8.7	3.0	35	66
325°	1.0	8.6	2.6	30	70
325°	1.0	9.4	3.3	35	65
325°	1.0	10.7	4.2	39	61

The values given in Table 1 for the initial fabric weight were obtained on material which had not been previously conditioned to standard humidity, and some fluctuations in sample weight due to differences in initial moisture content are to be expected. Very little difference was found in the weight losses for samples run at the two different reduced pressures. These pressure readings represent values that were obtained at the start of the pyrolysis run before the tubes were heated in the furnace. Within minutes after the tubes were inserted into the furnace a vigorous reaction ensued. Volatiles and particulate matter were rapidly ejected from the pyrolysis region. The violence of the vaporization reaction tended to overpower the vacuum system, which caused the pressure during this stage of reaction to attain a nearly constant value regardless of the value at the start or completion of a run. The quantitative aspects of the pyrolysis

reaction including the effect of pressure on the amount of volatile material are more effectively investigated by thermal gravimetric analysis.^{5,6}

The Char Residue:

After the pyrolysis reaction was completed, a black char remained in the tube. This material still retained the original fabric structure, was surprisingly flexible, and had sufficient strength to remain intact while being handled.

A sodium fusion test for elements was run on a portion of the black char. Both phosphorus and nitrogen were strongly detected as their phosphomolybdate and ferrocyanide precipitates, respectively. When the char was extracted with boiling water, an acidic solution with pH 3 was obtained. The solution gave a positive phosphomolybdate test and presumably contains some phosphoric acid arising from the thermally degraded flame retardant polymer. These aqueous extracts may also contain soluble fragments from the original crosslinked polymer as well as phosphorylated glucose units. Granzow⁷ has postulated the formation of phosphoramidates during the pyrolysis of cellulose which had been treated with phosphonium salts. These may also be present in the char. The char was extracted several times with boiling water until the extracts were neutral. The extracted

5. J.A. Sousa, G.J. Caldarella, J.F. Roach, L.A. Levasseur and D.E. Remy, Tech. Report in preparation 1979.

6. B.F. Gilliland and B.F. Smith, J. App. Poly. Sci., 1972, 16, 1801.

7. A. Granzow, Acc. of Chem. Res., 1978, 11, 177.

char was fused with sodium, and positive tests for both phosphorus and nitrogen were still observed.

The Condensed Pyrolyzates:

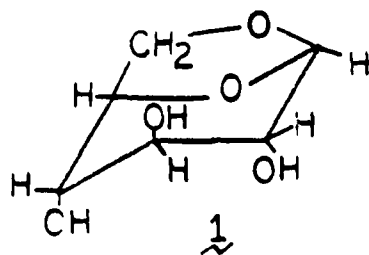
The volatiles from the pyrolysis were collected in a dry ice acetone cooled trap as a yellow-brown solid. When the trap was allowed to warm to room temperature, a brown slurry resulted. The slurry was separated into three main fractions, which are discussed separately in the following sections:

1. Solid Fraction. Approximately 23% of the collected volatile residue was obtained as a brown solid. Since this solid could not be subsequently volatilized, it was probably carried over as an aerosol during the vigorous thermal decomposition of the flame retarded cotton. The solid was moderately soluble in dilute ammonium hydroxide solution and was chromatographed on thin layer (silica gel/n-propyl alcohol, NH_4OH , H_2O /6:2:1). The chromatogram was poorly resolved possibly due to the presence of a complex mixture of oligomeric and polymeric substances in the fraction. Both phosphorus and nitrogen were detected in the solid fraction, which may indicate that a large portion of this material is composed of fragments from the original crosslinked fire retardant polymer. If this is the case, then a substantial amount of the retardant is being lost from the char zone, and the effectiveness of the flame retardant treatment would be severely diminished.

2. Aqueous Fraction. After the solid fraction was removed from the condensed pyrolyzate material by filtration, a dark brown aqueous

filtrate was obtained. The filtrate was extracted several times with methylene chloride and reduced to a dark syrupy residue by evaporation of the water. This residue amounted to approximately 15% of the total condensed pyrolyzate material. Based on TLC, infrared, and NMR data, this fraction was composed mainly of fragments from the degradation of cellulose, although both phosphorus and nitrogen were detected.

The water soluble fraction was chromatographed on a preparative scale (silica gel/n-propanol, $\text{NH}_4\text{OH}, \text{H}_2\text{O}/6:2:1$), and the main component was isolated. This material resisted additional efforts at purification and could not be induced to crystallize. However, spectroscopic evidence (Fig. 1 & 3) suggested that it might be levoglucosan (1).



To verify the identity of this substance an authentic specimen of levoglucosan was prepared.⁸ A 10-g sample of Whatman purified cellulose powder was pyrolyzed at 350°C and 1 mm. The crude condensate was dissolved in methanol, evaporated to a dark brown syrup, and then redissolved in acetone. Light brown crystals were obtained from the acetone solution and two additional recrystallizations gave colorless

8. F. Shafizadeh, R. H. Furneaux, T. T. Stevenson, and T. G. Cochran, *Carbohydrate Research*, 1978, 67, 433.

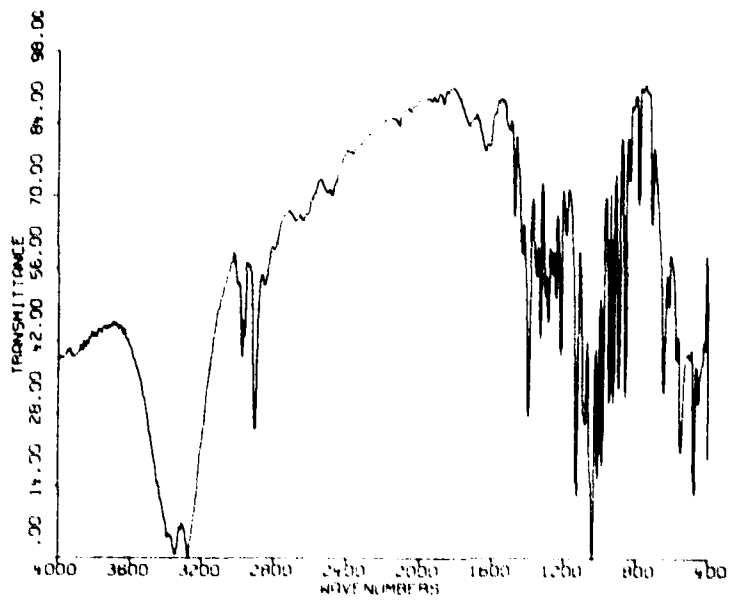


Fig. 1. Infrared Spectrum of Isolated Levoglucosan (KBr Pellet)

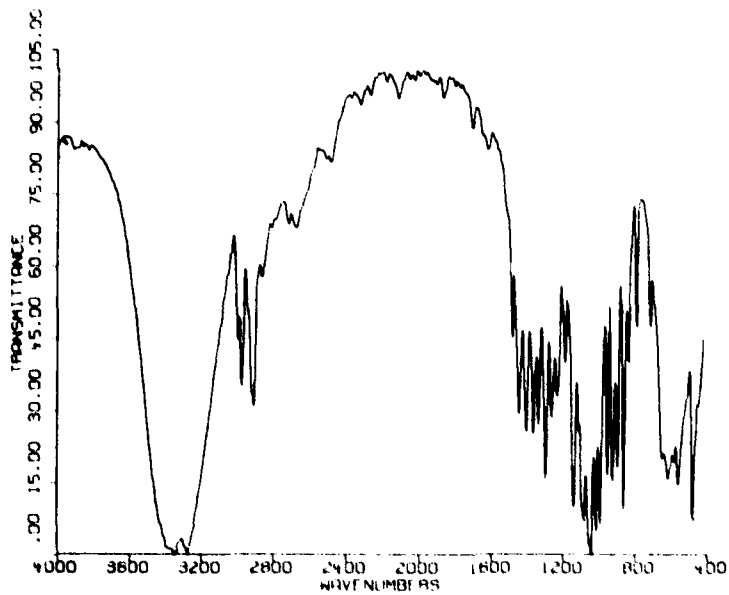


Fig. 2. Infrared Spectrum of Authentic Levoglucosan (KBr Pellet)

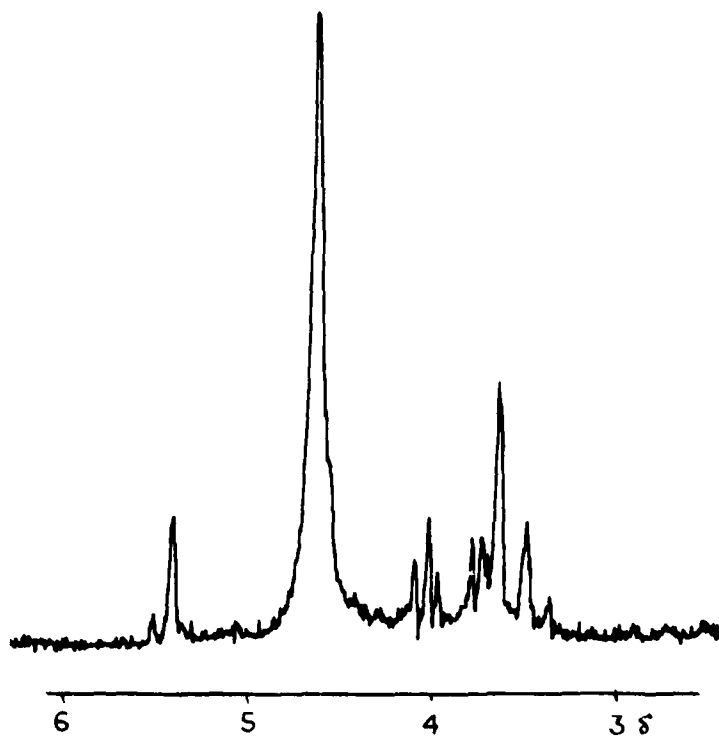


Fig. 3: NMR Spectrum of Isolated Levoglucosan (Solvent: D₂O Ref: TMS)



Fig. 4: NMR Spectrum of Authentic Levoglucosan (Solvent: D₂O Ref: TMS)

crystals of levoglucosan with mp 180-181°C. The infrared spectrum of this sample (Fig. 2) was similar to the spectrum of the material isolated by chromatography. The NMR spectrum (Fig. 4) of this authentic sample also essentially matches the spectrum of the isolated material (Fig. 3). It is noteworthy that levoglucosan which is the main pyrolysis product from the thermal degradation of untreated cellulose is also present in relatively large amounts in the pyrolyzates from this particular flame retardant treated cellulose. A very limited amount of levoglucosan would be expected to form in the presence of an effective flame retardant of this type.

3. Organic Extractable Fraction. The methylene chloride extracts from the aqueous fraction were dried over anhydrous magnesium sulfate and distilled at 40-45°C. This distillate, in addition to methylene chloride, contained small amounts of various volatile products, observed as minor peaks in the gas chromatogram. An approximate correspondence of retention times for several of these minor peaks was found for known compounds such as: acetaldehyde, propionaldehyde, acetone, and possibly acrolein. Similar compounds have been postulated in the pyrolytic decomposition of other cotton materials⁹ and an extensive characterization of the distillate was not undertaken.

A dark viscous liquid amounting to about 28% of the total volatile pyrolysis residue remained after the distillation. This material was shown to be a complex mixture by both HPLC and GC

9. J. B. Berkowitz-Mattuck and T. Noguchi, J. Appl. Poly Sci, 1963, 7, 709.

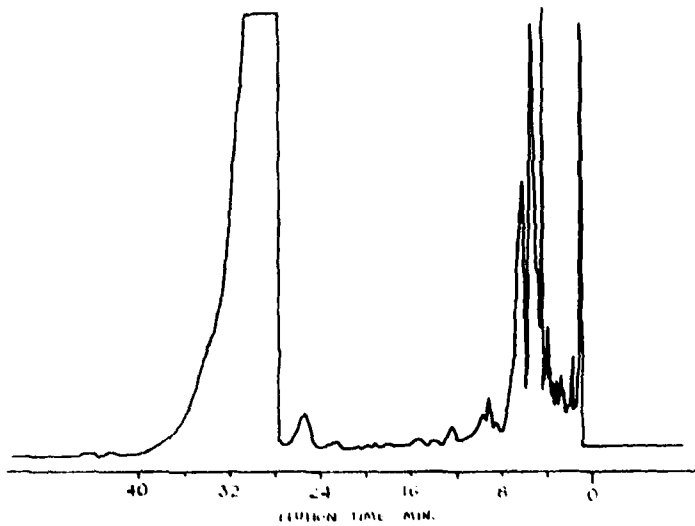


Fig. 51. 1972 Chromatogram of Collected Flycatcher

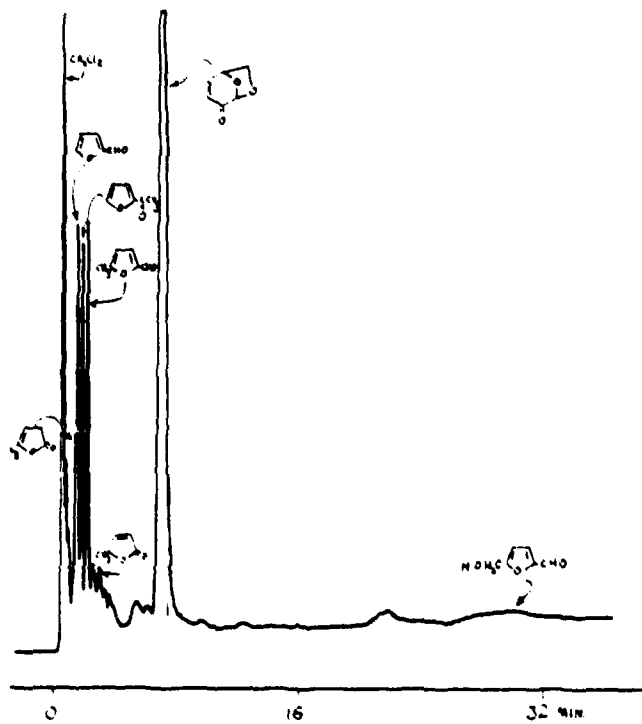


Fig. 52. Gas Chromatogram of Methylene Chloride Extracts

(Fig. 5 & 6 respectively) and was further fractionated by Kugelrohr distillation. Approximately one-third of the material was obtained as two separate distillation fractions, and the remainder was left as a dark brown tar. The lower boiling of these two fractions was colorless and gave negative tests for both phosphorus and nitrogen. The second fraction was collected as a yellow oil and gave a positive test for nitrogen only. Both phosphorus and nitrogen were detected in the tarry residue.

The first fraction was analyzed by GC-FTIR and the chromatogram (Fig. 7) shows several broad peaks which correspond to the main components of the mixture. Infrared scans were run on the peaks in the chromatogram labeled "A" through "E" and although many of the components were not completely resolved, preliminary conclusions about the structures present could be made. The first large peak in the chromatogram was identified as solvent, methylene chloride. A shoulder at "A" was scanned and the infrared spectrum (Fig. 8) indicates that this region of the chromatogram was heavily contaminated by the peak at "B". Peak "B" (Fig. 9) was tentatively identified as 2-furaldehyde (2). Peaks "C" and "D" were later found to be composed mainly of 2-furyl methyl ketone (3) and 5-methyl-2-furfural (4) respectively and their spectra (Figs. 10 & 11) conform to the structures assigned.

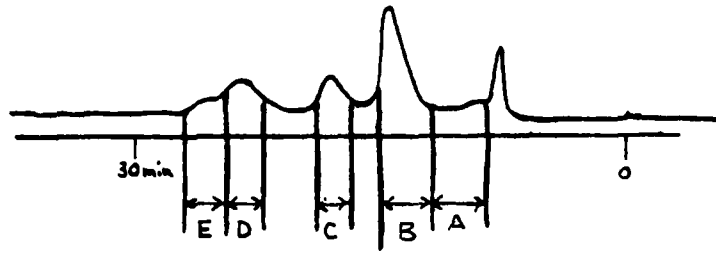
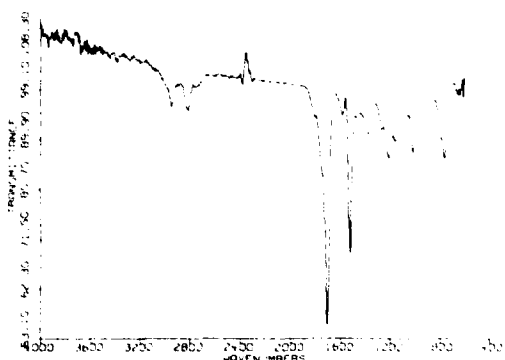
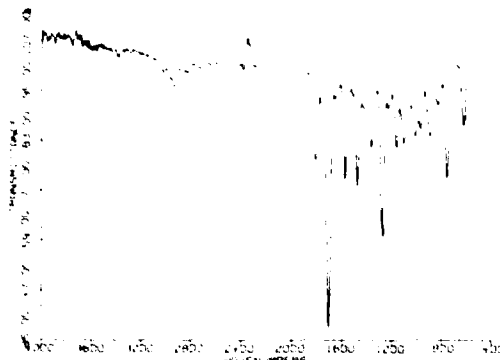
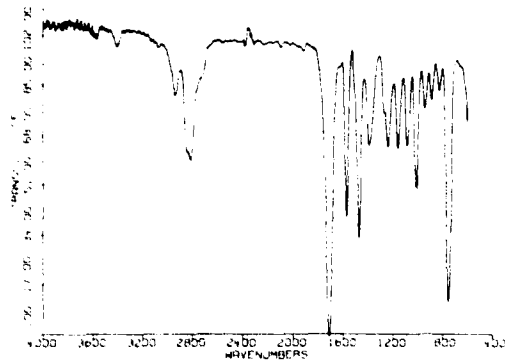
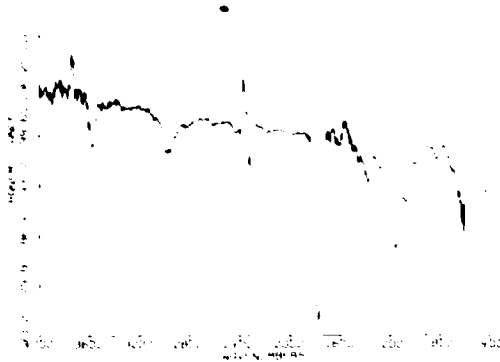


Fig. 7: Gas Chromatogram of Kugelrohr Distillation Fraction for FT-IR Spectra



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DO NOT

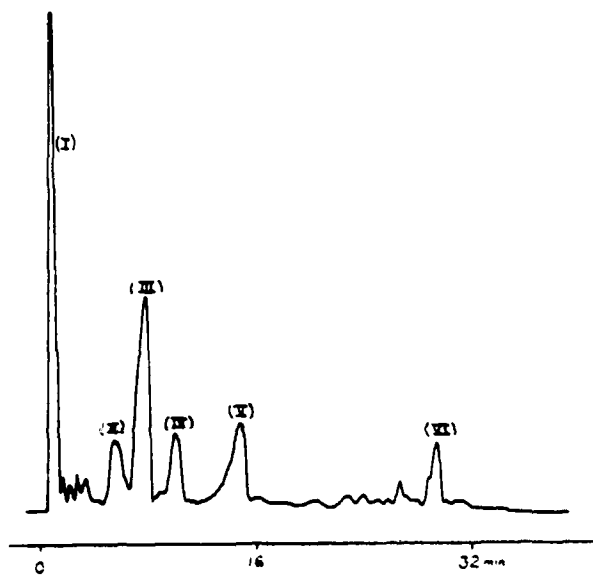
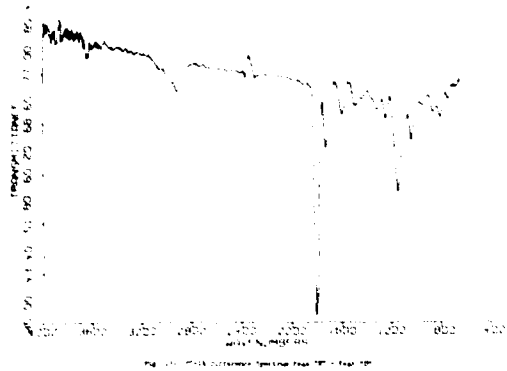
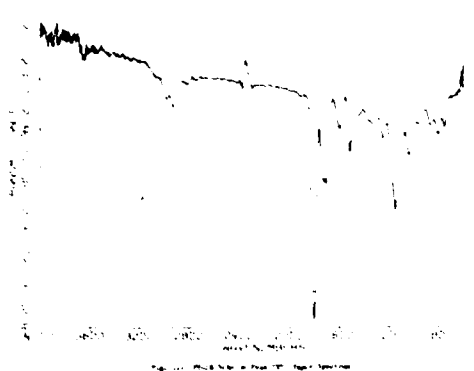
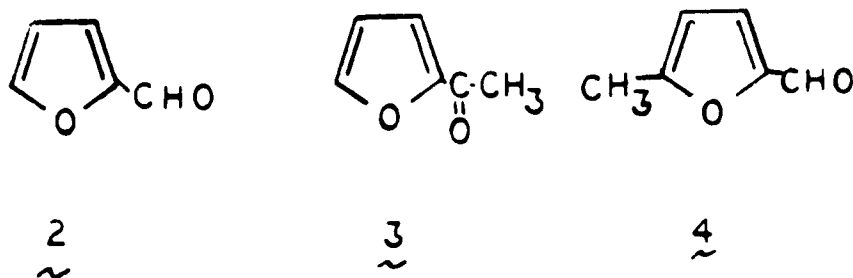


Fig. 1a: Gas Chromatogram of the Low Boiling Kugelrohr Fraction



According to its spectrum the peak collected at "E" (Fig. 12) appeared to be contaminated by the larger peak at "D". A difference spectrum (Fig. 13) was run in which the contaminating elements of the "D" spectrum were subtracted from the "E" spectrum by the instrument computer. Two carbonyl bands at 1810 and 1740 cm^{-1} in the difference spectrum (Fig. 13) suggest an acyclic anhydride.

The light yellow second fraction from the Kugelrohr distillation was also examined by GC-FTIR and a single main component was observed which was only partially resolved. The infrared spectrum of the trapped peak had a carbonyl absorption around 1700 cm^{-1} and additional major bands at 1100, 970, 890, and 830 cm^{-1} . This substance represented the largest single component present in the distillable pyrolyzates.

To augment the preliminary findings from the GC-FTIR results some of the main components from the two fractions were isolated by preparative GC and further characterized by their infrared and NMR spectra.

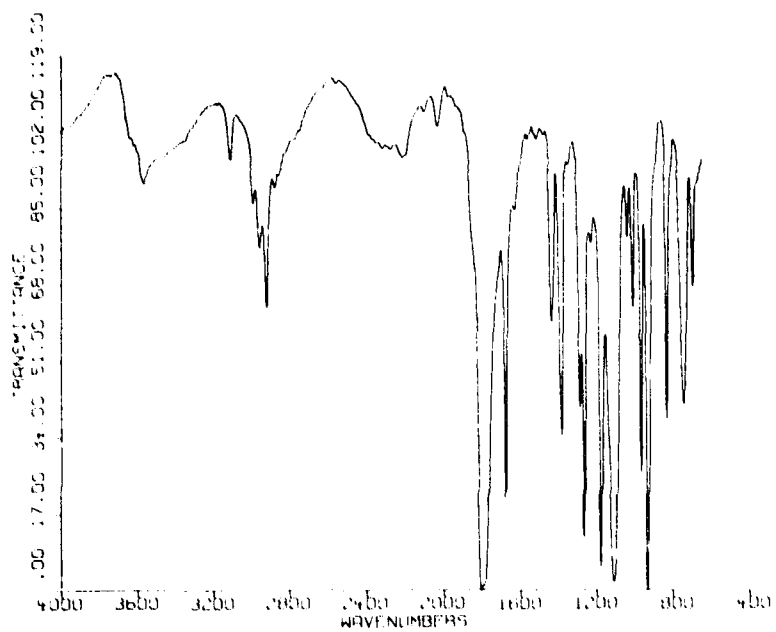


Fig. 15: Infrared spectrum of (-)-Angelicalactone (Neat, NaCl plates)

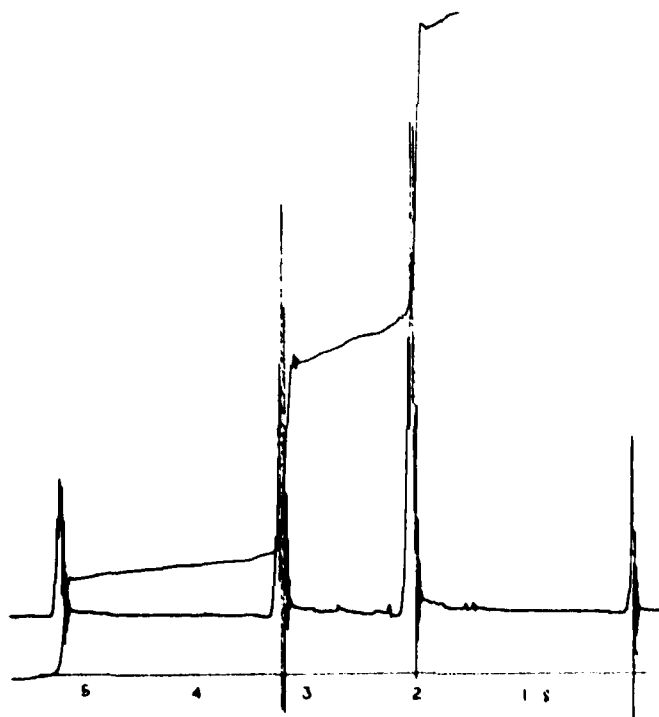


Fig. 16: NMR Spectrum of (-)-Angelicalactone (Solvent: CCl₄, Ref: TMS)

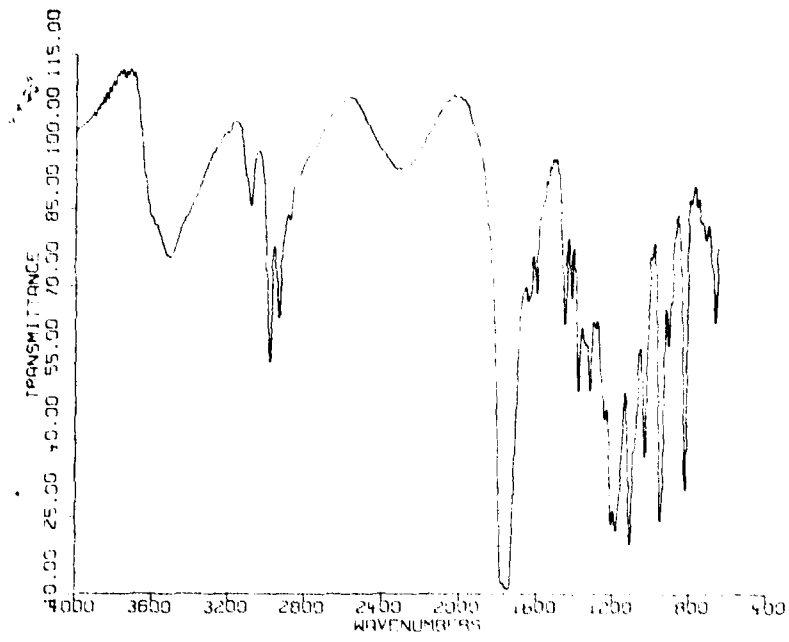


Fig. 17: Infrared Spectrum of (-)-Angelicalactone (Neat, NaCl plates)

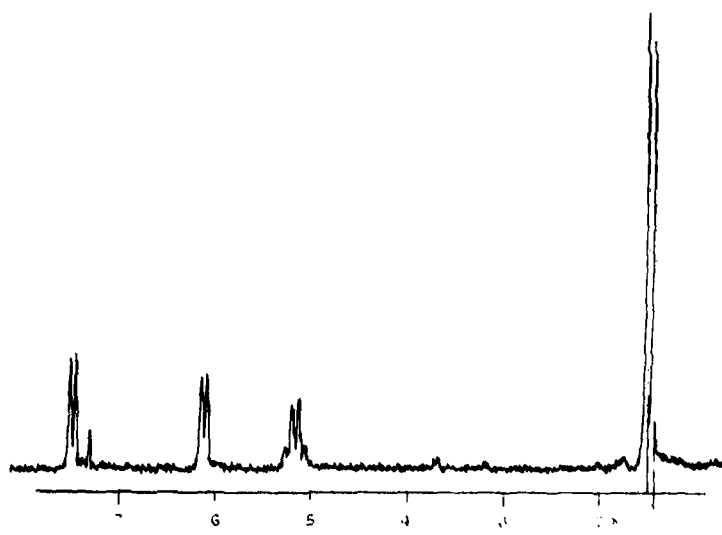
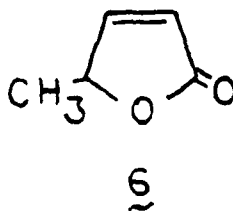
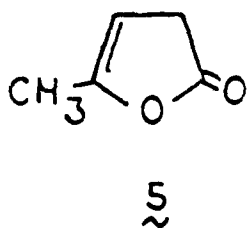


Fig. 18: NMR Spectrum of (-)-Angelicalactone (Solvent: CDCl₃, Ref: 98)

The chromatogram for the low boiling Kugelrohr fraction is presented in Fig. 14. This chromatogram was thermally programmed at 10°C/min to 160°C and held at this temperature for the remainder of the run. Numerous low boiling peaks are evident at the beginning of the chromatogram including a large solvent peak (I) (methylene chloride) which obscures several additional components. A partly resolved peak (II) was not collected but was found to have the same retention time as an authentic sample of α -angelicalactone (5). The infrared and NMR spectra are presented in Figs. 15 & 16 respectively. The α -form of this lactone 5 can undergo a thermal isomerization to a more stable β -isomer 6 and presumably this occurs to some extent during the fabric pyrolysis reaction.



A sample of 5 was converted to β -angelicalactone (6) in nearly quantitative yield by refluxing with a trace of triethylamine. The structure of 6 was confirmed by infrared and NMR (Figs. 17 & 18) and a peak (VI) in the chromatogram (Fig. 14) corresponded with the retention time of this known compound.

A large peak (III) was collected and its identity as 2-furaldehyde (2) was established on the basis of its infrared and NMR spectra. This

structural assignment was confirmed by comparison of the collected sample spectra with spectra of an authentic sample.

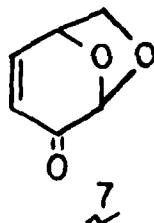
The next peak (IV) was collected and reinjected into the chromatograph. The collected material was found to be homogeneous in spite of a small shoulder at its leading edge. An infrared spectrum of this fraction indicated a carbonyl absorption at 1680 cm^{-1} . The NMR spectrum shows a multiplet at 7.52δ , a doublet at 7.15δ , an additional multiplet at 6.5δ and a strong three-proton singlet at 2.4δ . The spectroscopic data were all consistent with that expected for 2-furyl methyl ketone (3).

This compound has not been previously reported as a component in the pyrolyzates of similar phosphorous-based flame retardant cottons even though it may have been present and not isolated or identified. In studies on the controlled pyrolysis of anhydrous glucose, Walter and Fagerson¹⁰ found this ketone among the trapped volatile products. Therefore, it is not surprising that 3 would be found in the pyrolyzates of cotton, which can degrade thermally via transglycosylation to yield products similar to those of pyrolyzed glucose.

A final main component (V) was isolated and its infrared and NMR spectra established the structure of 5-methyl-2-furfuraldehyde (4). The structural assignment for this compound was confirmed by comparison of spectroscopic data with spectra of authentic material.

10. R. H. Walter and I. S. Fagerson, J. Food Sci. 1968, 33, 294.

The second fraction from the Kugelrohr distillation was almost entirely composed of a single component. This substance was purified by preparative GC and a light yellow oil was obtained. The compound was identified on the basis of its infrared and NMR spectra (Figs. 19 & 20). The infrared spectrum showed the presence of an alkene C-H at 3060cm^{-1} , and alkyl CH_2 group (2970 and 2900cm^{-1}), a conjugated carbonyl group (1720 and 1700cm^{-1}) and a C-O-C stretching band at 1110cm^{-1} . The NMR spectrum conformed to a published spectrum¹¹ of levoglucosenone (7).



Levoglucosenone (7) results from a Lewis acid catalyzed dehydration of levoglucosan (1) and a mechanism for the formation of 7 from 1 has been proposed.¹¹ It is interesting to note that a variety of Lewis acids can transform 1 into 7 but in the absence of an acidic catalyst 7 is not produced.

One additional minor component in this fraction was tentatively identified as 5-(hydroxymethyl)-2-furaldehyde (8) since it had the same retention time on GC as an authentic sample.

11. Y. Halpern, R. Riffer and A. Broide, *J. Org. Chem.* 1973, 38, 204.

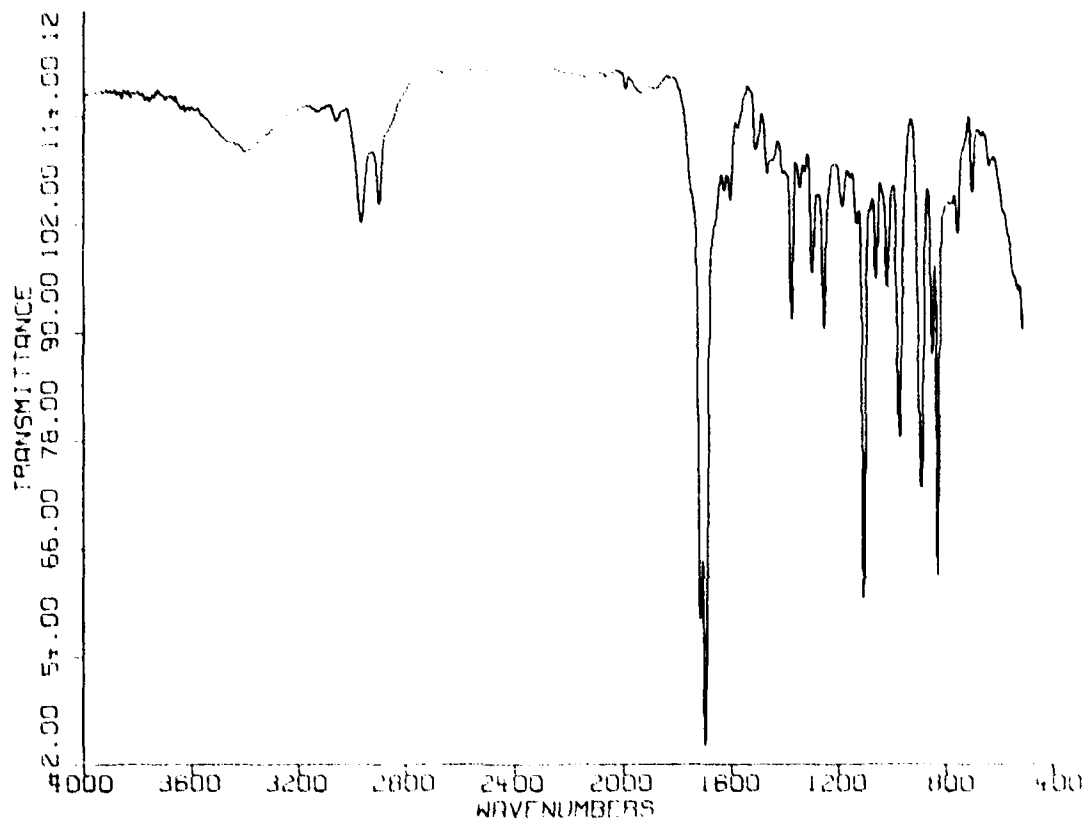


Fig. 19 Infrared Spectrum of Levoglucosenone (KBr Pellet)

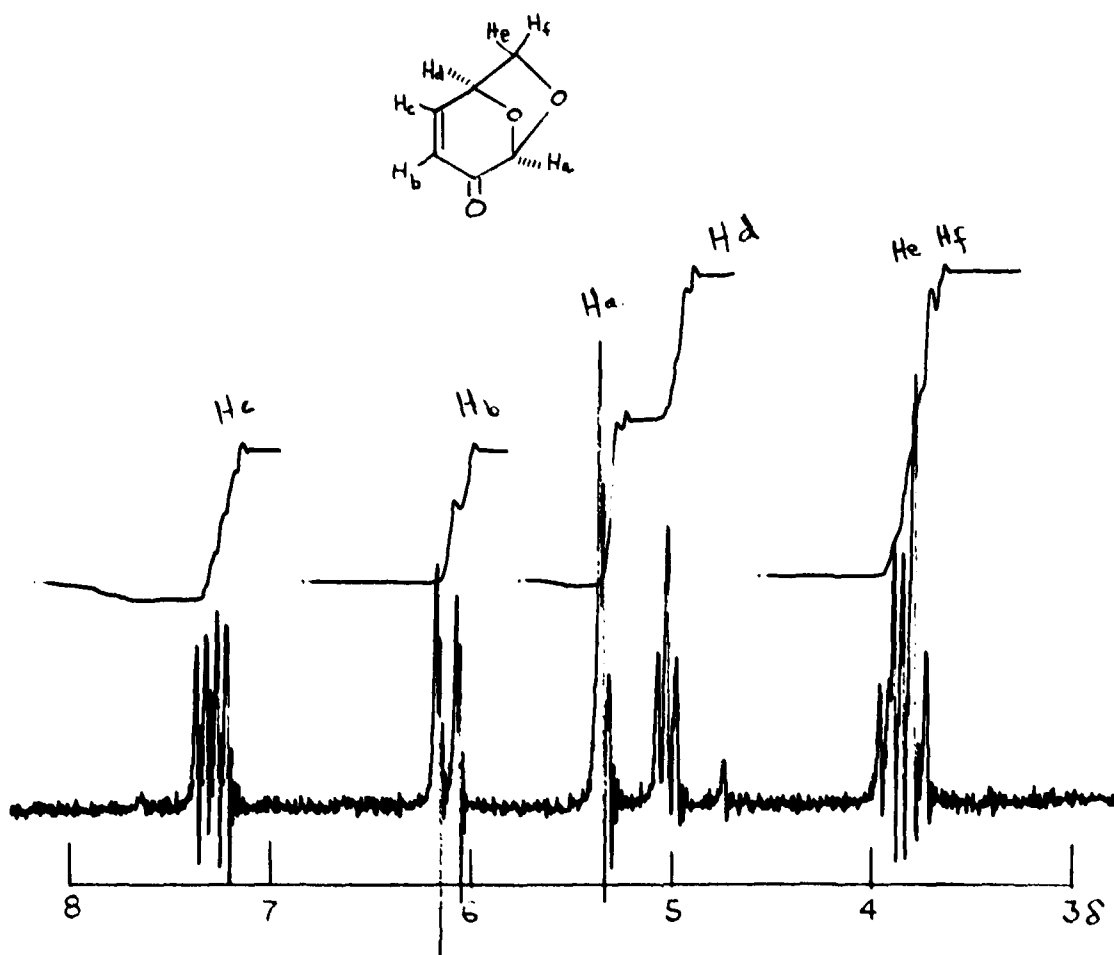
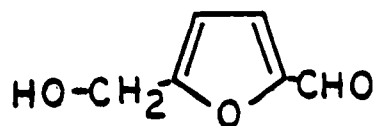


Fig. 20: NMR Spectrum of Levoglucosenone (Solvent: CDCl_3 Ref: TMS)



8

The small amount of this compound present, as shown by its chromatogram, may be due to further reaction to levulinic acid in the presence of phosphate products from the flame retardant.

CONCLUSION

A sample of cotton fabric treated with flame retardant based on the THPOH-ammonia cure process was thermally degraded under controlled laboratory conditions, and the pyrolysis products were examined. Nearly two-thirds of the weight of the fabric sample was lost as volatilized material, which was collected in a trap. Most of this material was collected as a brown solid, which could not be subsequently volatilized. On the basis of spectroscopic evidence and elemental analysis for phosphorus and nitrogen, the solid was presumed to be composed of fragments from the original flame retardant polymer. Also appreciable amounts of levoglucosan were found in the pyrolyzate. This material is normally found as a major product when untreated cellulose is pyrolyzed. In the presence of a flame retardant, very little levoglucosan is generally expected. These findings indicate that the flame retardant polymer may have been insufficiently crosslinked on the textile substrate and moderate loss of flame retardant polymer occurred during

the pyrolysis. A possible reason for this would be loss of formaldehyde from the fabric after treatment with the THPOH solution prior to cross-linking with ammonia. The premature loss of flame retardant polymer from the cotton fabric would be expected to severely diminish the efficiency of the flame retardant finish.

A cursory examination of the volatile products from the pyrolysis reaction was made, and several of the main components were isolated and structurally characterized. For many of these compounds this is the first time complete structural verification has been made by isolation of components from the pyrolyzate followed by infrared and NMR characterization. In previous work the components were often identified by correspondence of the gas chromatographic retention times with known compounds. One new pyrolyzate compound was identified, 2-furyl methyl ketone. This compound may have been present in the pyrolyzates from similar flame retardant cotton materials but not previously identified. In general the composition of the volatile portion of the collected pyrolyzates corresponded well with the reported pyrolysis products from cotton fabrics treated with similar flame retardants.

Several of the volatile pyrolysis products identified in this study are considered to be moderately toxic and generally can cause lachrimation, inflammation of mucous membranes, headache, and central nervous system disturbances. However, most of these products are also found in numerous other flame retarded cotton pyrolyzates, which have not, as yet, been shown to acutely toxic.

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