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THE FIRE RETARDANCE EFFECTIVENESS OF HIGH MOLECULAR WEIGHT, HIGH OXYGEN CONTAINING INORGANIC ADDITIVES IN CELLULOSIC AND SYNTHETIC MATERIALS

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Cedar shakes treated with either phosphotungstic acid or its insoluble ammonium salt required 65 seconds of exposure to a Fisher burner for ignition, whereas 4 seconds of exposure caused ignition in untreated shakes. Moreover, the treated specimens ceased flaming after they were removed from the Fisher flame and the untreated shakes continued to burn even when they were removed from the ignition source.

More extensive evaluation of the efficiency of these treatments and of our technique is needed to substantiate our present findings. For example, the procedure used to incorporate the phosphotungstic acid and its salt into nylon and polyester must be modified before the optimal loading and efficiency of the retardant can be achieved.

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ammonium phosphotungstate						
flaming ignition						
decomposition products						
char						
isothermal pyrolysis of cotton						
kinetics of decomposition						

Comparison of the results of isothermal pyrolysis of cotton with those of α-cellulose suggests that there might be differences in the kinetics of decomposition of the two materials. The differences will have to be resolved by additional experimentation, namely, comparison of the rate of monomer loss and the rate of change in the degree of polymerization of the two materials using at least three different temperatures higher than 276°C.

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Comparison of the results of isothermal pyrolysis of cotton with those of α-cellulose suggests that there might be differences in the kinetics of decomposition of the two materials. The differences will have to be resolved by additional experimentation, namely, comparison of the rate of monomer loss and the rate of change in the degree of

polymerization of the two materials using at least three different temperatures higher than 276° C.

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SUMMARY

In a nuclear explosion, roughly one-third of the energy is released in a short time as thermal radiation. The resulting exposure levels are high enough to ignite fabrics and other light-weight materials inside buildings even at distances from the explosion that, under favorable conditions, extend well beyond the range of severe blast damage. Some of these primary ignitions will survive the blast effects to result in destructive fires and, under some circumstances, might lead to development of mass fires that could destroy whole sections of a city that were not significantly damaged by the other initial effects of the detonation. The development of effective countermeasures to these fires rests on our knowledge of the processes that govern the decomposition of the materials found in the target areas.

Although much effort has been expended in attempting to elucidate the mechanisms and rates of decomposition of natural and synthetic polymers, our knowledge of those processes is still incomplete, particularly of the synthetics. The existing flame retardant treatments have certain shortcomings in that their durability is limited and their effect on appearance of the materials is considerable.

The present study has sought to determine whether high-molecular-weight, inorganic additives, particularly those with high oxygen content, are generally effective and potentially practical flame retardants in synthetic as well as natural polymers. The compounds investigated were first applied in their water-soluble forms and then precipitated interstitially within the various materials. The effectiveness of the insoluble retardants was compared to the effectiveness of their water-soluble counterparts. The additives were applied to α-cellulose, cotton, rayon, wood, polyester, and nylon.

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Cellulosic materials treated with phosphotungstic and phosphomolybdic acid in their near optimal range of concentration do not sustain flaming ignition after the samples are exposed to an irradiance of 6.2 cal cm^{-2} sec^{-1} from a CO_2 laser for 6.3 seconds. Materials containing interstitially precipitated ammonium phosphotungstate display the same behavior as their acid-treated counterparts and their char yields increase in identical amounts regardless of whether the retardant is applied in the form of the acid or salt.

The degradation products from the acid or salt-treated cellulosics were analyzed with the gas chromatograph/mass spectrometer combination instrument and compared with the degradation products of cellulose containing an acidic salt of low molecular weight. Results show that all three treatments render the following five dominant gc peaks: 11 (water), 14 (pyruvaldehyde + acetol), 18 (acetic acid), 19 (furfural), and 31-a (the furanose derivative). A typical chromatogram of the degradation products of untreated material consists of at least 59 compounds with only water as the dominant peak.

Results of preliminary evaluation of the retardance efficiency of phosphotungstic acid and its salt in cedar shakes are encouraging. Untreated samples ignited in 4 seconds when held in a Fisher burner; a sample treated to a depth of only 0.5 mm with either salt or the acid ignited after 14 seconds and a specimen with a 2.0-mm retardant layer flamed only after 65 seconds of exposure. The treated samples quit flaming when they were removed from the burner whereas the untreated shakes continued to burn when removed from the flames. A preliminary cost estimate indicates that the method has economic as well as technical feasibility.

More extensive tests to evaluate the efficiency of the treatments developed to date will be performed in the future to further substantiate our present findings. The experimental procedure used to apply such retardants as the phosphotungstic acid and its salt to nylon and polyester materials must be modified before the optimal loading and efficiency of the retardant are achieved.

Comparison of the results of isothermal pyrolysis of cotton with those of α-cellulose suggests that there might be differences in the kinetics of decomposition of the two materials. At 276°C in a nitrogen environment, the cotton cloth does not show the initial rapid weight loss previously observed for α-cellulose. The constant rate of weight loss for the cotton continues until about 70% of the material has volatilized as contrasted with α-cellulose where the linearity discontinues after approximately 46% of the material has decomposed. After the constant rate of weight loss discontinues, the residual weight for both samples begins to decay exponentially toward a constant value of about 17%. These findings will be supplmented by additional pyrolysis experiments, comparison of the rate of monomer loss and the rate of change in the degree of polymerization of the two materials using at least three different temperatures higher than 276°C.

ADMINISTRATIVE INFORMATION

The purpose of this task order is to continue the research conducted under Work Unit 2561H of Contract DAHC20-70-C-0219 at Stanford Research Institute since the closing of the Naval Radiological Laboratory in 1969. The subject matter covered in this annual report represents a portion of the overall objective of the subject task order that reads as follows:

> Objective To exploit the advantages of the use of analytical and reduced-scale modeling principles applicable to fires in urban structures as a practical means of evaluating and predicting the dynamic behavior of mass fires resulting from nuclear attack. To develop an improved understanding of the relevant fundamental aspects of fire, and thereby acquire the needed data base for civil defense applications, to ensure coordination of the efforts of OCD contractors in the performance of mass-fire-related research.

Based on this task order, a work plan dated 1 August 1971 was prepared containing a list of milestones and an anticipated schedule for their completion. This work plan was approved by the technical representatives of the Office of Civil Defense.

With the publication and distribution of this report, all contractual requirements have been satisfied. In every respect, the objectives of the contracted work, as further detailed in the approved work plan, have been successfully accomplished and completed on schedule.

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I INTRODUCTION

The development of effective countermeasures to the fires that are expected to follow a nuclear attack hinges on our knowledge of the processes that govern the decomposition of the materials found in the target, the dependence of the processes on the chemical makeup of the material, and on the nature of the environment itself.

Cellulosic-fuel materials constitute the principal portion of combustible materials that feed urban fires, although synthetic polymers are increasingly replacing the cellulosic materials. Our past studies focused on the pyrolysis process of cellulose and the effect of fire retardants on it. The results of this effort led to the development of a quantitative model that provides general guidance in prescribing optimal retardance treatment.[1] Last year's work[2] shows that cellulose treated with low concentrations of phosphotungstic acid (chosen by following the model's guidelines to seek compounds of high molecular weight having a large proportion of oxygen atoms per molecule) produced remarkably large yields of char indicating that such compounds might be effective flame retardants. It is now important to confirm this expectation and to ascertain its applicability to noncellulosic polymers, and then to seek nonleachable forms of such compounds and to compare their effectiveness with that of their soluble counterpart as a demonstration of the practical potential of this approach to flame retardancy.

Specifically, the objective of this year's work was to determine whether high-molecular-weight inorganic additives, particularly those with high oxygen content, are generally effective and potentially practical flame retardants.

The following approach was used to accomplish the above objective:

(1) Examine the literature for existing information on thermal degradation of some of the most widely distributed urban materials i.g., rayon, polyester, nylon, cotton, and wood. This effort indicates where research is most needed and establishes a rationale for choosing the most effective experimental approach to provide an understanding of the mechanisms of degradation of these materials.

(2) Prepare cellulose specimens containing concentrations of phosphotungstic acid and phosphomolybdic acid in the near optimal range and evaluate their retardant effectiveness in terms of char production, flammability, and composition of degradation products.

(3) Investigate insoluble forms of phosphotungstate-type compounds and evaluate retardant effectiveness of candidate additives in cellulose.

(4) Ascertain the applicability of the oxygen-rich, high-molecular-weight additives to other polymeric fuels commonly found in urban enclosures and evaluate retardant effectiveness.

(5) Initiate a study into the isothermal pyrolysis of selected synthetic polymers (e.g., nylon and rayon), seeking ultimately to describe, as was previously done for cellulose, the kinetics of weight and monomer loss, the mechanisms of char and volatile production, and the chemical composition of the volatile products as it varies with rate of heating, temperature, and the presence of catalytic additives.

This report describes these experimental procedures and measurements, and the conclusions drawn from them.

II LITERATURE SEARCH

The literature search focused on isothermal pyrolysis of cellulosic and synthetic materials, kinetics and gas chromatographic/mass spectrometric analysis of the degradation products, and temperature dependence of the molecular weight distribution of these materials. We were also interested in studies concerning thermal gravimetric analysis and differential thermal analysis of the above polymers. The standard literature search agencies were used (Defense Documentation Center and the National Aeronautics and Space Administration) as well as the following sources: Chemical Abstracts, Chemical Properties Information Agency, Chemical Titles, and the current combustion journals.

The results of our literature search (a comprehensive bibliography is included at the end of this report) show that much information has been generated concerning the thermal degradation process of untreated and flame-retardant treated cellulose and cellulose-related materials, such as rayon, cotton, and wood. However, not much data exist on the chemical processes governing thermal decomposition of nylon and polyesters. It appears that techniques used in the flame-proofing of cellulose paper can be applied also to rayon, cotton,and wood. However, the usual retardants for cellulosics, such as halogen compounds, inorganic and organic phosphates, do not function efficiently in flame-retarding nylon or nylon blends. A number of references show that only one method, namely, fabric finishing or after-treatment, has been proposed for conferring flame resistance to nylon or nylon blends. Many of these finishes utilized thiourea or formaldehyde condensates. Such finishes do not launder very satisfactorily, however.

Some of the efforts to flame-proof polyester fabric or fibers consisted of coating the fabrics with PVC, polychloroprene-chlorosulfonated polyethylene, PVC plastisol containing Sb_2O_3 and sulfide; blending the fibers with cellulose fibers treated with solution of condensed phosphoric acid and a quarternary ammonium hydroxide or amine and baking; embedding the fibers by layers in sodium silicate; or treating the fibers with alcohols or polyether polyols at elevated temperature in the presence of nonvolatile mineral acid. The durability of the flame-retardant properties conferred by these chemicals is limited and the effect on appearance is considerable.

It seems that more information pertaining to the mechanism of pyrolysis of nylon and polyester fabrics in terms of kinetics, monomer loss, weight loss, and distribution of pyrolysis products is needed for development of better flame retardants for these fabrics. A satisfactory solution may rest in incorporating the appropriate retardant in the molten nylon or polyester as it is being spun.

III EXPERIMENTAL PROCEDURES

A. Application of Phosphotungstic and Phosphomolybdic Acids to α-Cellulose

White α-cellulose sheets (0.030 in. thick)were cut into 2- x 6-in. specimens and saturated with 5, 10, 15, and 20% by weight aqueous solutions of phosphotungstic and phosphomolybdic acids. Approximately 5.0 ml of the aqueous solution was placed in a 2- x 6-in. shallow glass dish and each specimen was allowed to soak up the solution by capillary action. This procedure rendered a reasonably even distribution of the retardant throughout the sample and the volume of solution was sufficient for complete saturation of the cellulose. After air drying to constant weight, the samples retained from 1.2×10^{-5} to 1.1×10^{-4} mol/g of cellulose. The efficiency of the retardant was evaluated in the following tests:

1. Char Determination

A 1.5-cm square was cut from each specimen representing a particular add-on concentration. Each sample was sandwiched between two index cards and wrapped with aluminum foil to minimize air oxidation. The index cards protected the samples from possible detrimental effects of direct contact with the aluminum foil. Each treated sample and a control untreated sample were pyrolyzed in a muffle oven at 600°C for 12.0 min. and reweighed.

2. Flammability and Ignition Tests

The 2- x 6-in. samples were placed in an adjustable holder and subjected to 3 flammability tests; the vertical, horizontal, and a 45° angle test. Four samples, 2 treated and 2 untreated, were used in each of the above tests. In each pair one was ignited with a Fisher burner at the top and the other at the bottom. Results were recorded in terms of rate of flame spread over the length of the sample.

Next, treated and untreated specimens, 2- x 6-in. size, were exposed to an irradiance of 3.2 cal cm^{-2} sec^{-1} supplied by a tungsten-iodine lamp bank. Results were recorded in terms of ignition time and presence or absence of a char layer.

An additional ignition test that consisted of irradiating the untreated and treated cellulose samples with 6.2 cal cm^{-2} sec^{-1} from a CO_2 laser was used to evaluate retardant efficiency more extensively.

3. Analysis of Thermal Degradation Products

The pyrolysis products (molecular weight $<$ 150) were analyzed with a combination gas-chromatograph (gc)/mass spectrometer (ms). Beckman GC-4 analytical gas chromatograph was linked with a Bendix gc/ms interface system to a modified time-of-flight mass spectrometer.

The treated cellulose sheets were rolled into cylinders and burned in air. The degradation products formed at about 400°C by this process were collected by placing one end of the cellulose cylinder in a liquid nitrogen-cooled centrifuge tube and igniting the other. This method allows the volatile products to flow down the center of the cylinder and condense out on the bottom of the centrifuge tube. Aliquots of 10 μl were injected with a syringe onto a 10-ft by 0.25-in.-o.d. stainless steel column packed with 10% by weight of Carbowax-20M on Chromosorb-T 40-60 mesh. This column was used to analyze compounds with molecular weight < 150. Products with molecular weight >150 need temperatures higher than the upper temperature limit at which the Carbowax 30-M is thermally stable. For effective analysis of the heavier substituents of the tar, other analytical means such as silylation or thin layer chromatography should be employed. The column was ballistically temperature-programmed from 90 to 220°C in 45 min at approximately

3°C/min. During the run, the helium flow rate was 60 ml/min. the thermoconductivity detector oven was maintained at 225°C, and both the injection port and the interface system were held at 220°C.

B. Interstitial Precipitation of Ammonium Phosphotungstate in α-Cellulose

Since the object of this portion of the program was to determine whether it is feasible to precipitate the high molecular weight acids interstitially in the various materials without sacrificing their retardance, only the most readily formed salt of the phosphotungstic acid was investigated. The 2- x 6-in. cellulose samples were first treated with various concentrations of the acid as described in Section A of this report. To achieve reasonably even distribution of the precipitated salt throughout the cellulose, the partially dried sample was placed in a premeasured amount of 0.5N NH_4OH in a shallow dish and the sample was allowed to soak up the solution. The salt formed as soon as the NH_4OH came in contact with the acid. It was important that the amount of NH_4OH not exceed the mol equivalent of the acid, since ammonium phosphotungstate is soluble in a basic medium and therefore could be leached out of the sample during treatment and subsequent exposure to moisture. The samples were then dried to a constant weight and subjected to the same tests as their acid counterparts. The salt add-on value ranged from 1×10^{-5} to 1×10^{-4} mol/g of sample.

C. Application of Phosphotungstic Acid and Ammonium Phosphotungstate to Other Cellulosic and Synthetic Materials

Most of the feasibility studies to determine whether or not the acid and its salt can be successfully applied to cotton and the synthetics were carried out on unwashed materials. However, after obtaining an unusually high yield of the final char from the untreated unwashed cotton, a comparative run on the washed and untreated and treated cotton was made to see whether a filler present in the cotton might contribute to the high char yield and possibly influence the rates of weight loss. A piece of cotton cloth was first boiled in alconox for 30 min., rinsed in water, and then boiled again in distilled water to assure that there was no trace of the detergent left in the material. The washed swatches were then air dried to a constant weight, cut into 2- x 6-in. samples and subjected to phosphotungstic acid and the ammonium phosphotungstate treatments. The technique employed was that already described for the α-cellulose paper.

The retardant efficiency in the four swatches was tested in terms of increased char yield, vertical flame test, and pyrolysis products. The approach used was that already described for the α-cellulose samples.

D. Application of Phosphotungstic Acid and Ammonium Phosphotungstate to Cedar Shakes

Since the rate of diffusion of the aqueous solution through wooden roofing materials is appreciably slower than through the cellulose paper or cloth, it was first necessary to determine the depth of penetration required for the retardant to become minimally effective. Therefore, in these preliminary tests, only one concentration of the solution was used and the length of soaking on each side of the 3/4-in. thick, 2- x 6-in. samples varied from 10 sec to 5 min.

Only a simple flammability test was performed on the treated shakes to determine whether or not the retardant can be effectively applied to wood. The samples were held in the hottest portion of the Fisher flame and the duration of time necessary for the shakes to ignite was recorded and compared to the ignition time for the untreated samples. In addition, whether or not the samples continued to flame after they were removed from the burner, was also noted and recorded.

E. Isothermal Pyrolysis of Cotton Cloth

The isothermal pyrolysis chamber (a nitrogen-fluidized sand bed) used in the kinetics studies has been described in an earlier publication.[3]

The cotton cloth used in this experiment was first boiled in the alconox solution for 30 min., washed in distilled water, and then boiled again in distilled water and air dried to free it of the filler used by the manufacturer. The cloth was then cut into 2.0-cm squares and placed in tared weighing bottles. The samples were evacuated for 30 mins., dried to a constant weight in nitrogen in the presence of phosphorous pentoxide, and each sample was transferred in its covered weighing bottle to the loading chamber and then inserted into the reaction chamber. The oxygen content in the loading chamber was kept below 10% by displacing most of the air in the chamber with liquid nitrogen boil-off. This was done to prevent adsorption of oxygen on the surface of the samples during the transfer process.

Immediately following their transfer, the samples were pyrolyzed at 276°C. At least three other temperatures will be used at a later time to determine the temperature dependence of the kinetics of decomposition of cotton as well as the synthetics. The results of the pyrolysis were recorded in terms of weight loss and compared with the previously obtained data for cellulose.

IV RESULTS AND DISCUSSION

A. Evaluation of Flame-Retardant Effectiveness of Phosphotungstic and Phosphomolybdic Acids in α-Cellulose

1. Char Determination

Results of our earlier study of thermal decomposition of retardant-treated cellulose show that one of the actions of the retardants is to increase the amount of char yield and that char production increases initially in direct proportion to the concentration, but rapidly approaches a limit--which for the retardants studied is about 10^{-4} mols of additive per gram of cellulose. At this point, nearly two-thirds of the potential char increase has been obtained, and further addition of the retardant provides decreasingly small returns in added char.

The effects of the retardants studied on char production are portrayed in Figure 1 along with those of $MgSO_4$ and H_3PO_4. It appears that the higher molecular weight compounds, particularly those with high oxygen content, produce larger char yields at a lower concentrations than their lower molecular weight counterparts, as predicted by the Parker-Lipska model. It also seems that the concentration leading to the optimum char production for the phosphomolybdic acid and phosphotungstic acid treated samples is between 5×10^{-5} and 1×10^{-4} mol/g of cellulose instead of 1×10^{-4} and 5×10^{-4} mol/g of cellulose for the lower molecular weight retardants. At this point the cause of these differences is not clear, nor whether the high oxygen content in the phosphotungstic and phosphomolybdic acids is the principal contributing factor to the higher char values. Since the char residues were not subjected to elemental analysis, it is not known whether the substantial char increase might be due, at least in part, to the large residual

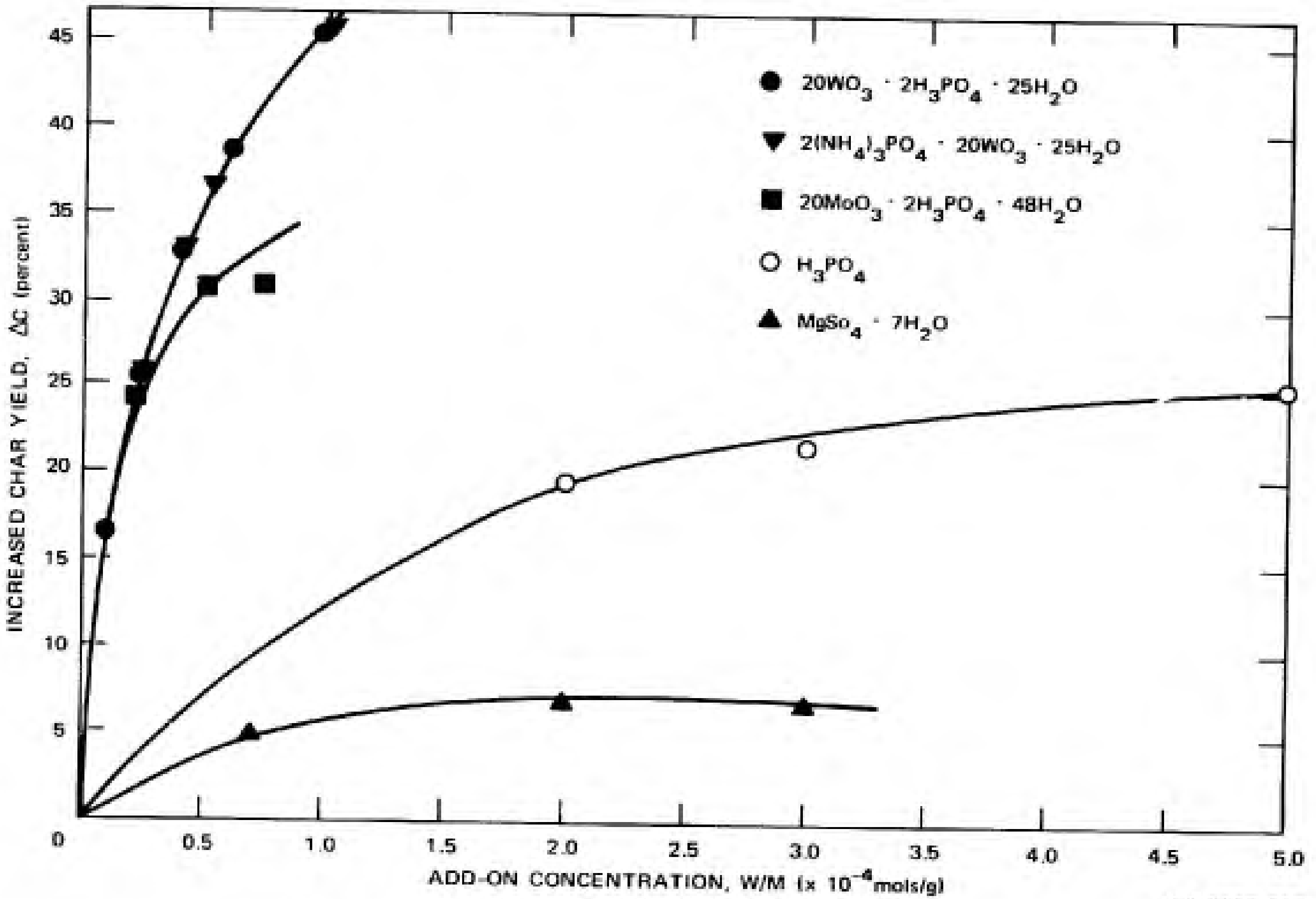

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FIGURE 1 THE EFFECT OF CONCENTRATION OF ADDITIVES ON CHAR YIELDS IN α-CELLULOSE weights of the oxides of the metals remaining in the solid residue. However, if we assume that most of the $20WO_3 \cdot P_2O_5 \cdot 28H_2O$ and $20MoO_3 \cdot 2H_3PO_4 \cdot 48H_2O$ convert to WO_3 and MoO_3 respectively, on heating to 600°C, we can estimate that the amount of the oxides left in the char residue might vary from about 20% of the increased char for samples having 5% add-on weight of either acid to over half of the residual char for samples with over 20% add-on weights. Thus it appears that char yields pass through peak values. To substantiate these estimates, it will be important to determine the amounts of the minerals in the char experimentally and compare the corrected increases in char with the values obtained with previously used retardants.

2. Flammability and Ignition Tests

Results of the tests on cellulose containing phosphotungstic acid and phosphomolybdic acids are summarized in Table 1. The 45° angle flammability test, as well as the vertical flammability test, show that optimal effectiveness of the retardant is achieved around 1×10^{-4} mol of the retardant/g of cellulose. However, the phosphotungstic acid and phosphomolybdic acids, even at concentrations as low as 3.2×10^{-5} mol/g of cellulose will prevent sustained flaming when positioned horizontally or at a 45°-angle and lit with a Fisher burner.

Thirty-second exposure of samples containing 5.0×10^{-5} mol of phosphotungstic acid or 6.0×10^{-5} mol of phosphomolybdic acid/g of cellulose to an irradiance of 3.2 cal cm^{-2} sec^{-1} from a tungsten-iodine lamp bank results in formation of a char layer, and, as in the 45°-angle test, samples treated with the phosphomolybdic acid continue to glow after the lamp is turned off, but neither flames.

Five-second irradiation of the treated samples with 6.2 cal cm^{-2} sec^{-1} from the CO_2 laser results in flaming ignition. The flames rapidly extinguish after the samples are removed from the laser beam,

Table 1

RESPONSE OF CELLULOSE, COTTON, RAYON, NYLON, AND POLYESTER TO FLAMMABILITY AND IGNITION TESTS

Description of Test and Sample	Retardant and Concentration			Ignition with Fisher Burner		Time to Ignition (sec)	Sample Response to Flammability and Ignition Tests
	Phosphotungstic Acid (mols/g)	Ammonium Phosphotungstate (mols/g)	Phosphomolybdic Acid (mols/g)	Top	Bottom		
I. Flammability tests - ignitor removed from sample after 5 seconds							
A. 45° ramp test							
1. α-Cellulose - untreated				✓	✓		Continuous flaming over length of sample
2. α-Cellulose	1.19×10^{-5}			✓	✓		Flame goes out after 8 sec; top ignition - char front crosses 6 in. in 302, bottom ignition in 280 sec
3. α-Cellulose	2.52×10^{-5}			✓	✓		Does not flame
4. α-Cellulose	3.66×10^{-5}			✓	✓		Does not flame
5. α-Cellulose	5.14×10^{-5}			✓	✓		Does not flame
6. α-Cellulose	1.09×10^{-4}			✓	✓		Does not flame
7. α-Cellulose		2.20×10^{-5}		✓	✓		Flame goes out after 10 sec when ignited from top; [illegible]er 15 sec when ignited from bottom
8. α-Cellulose		2.45×10^{-5}		✓	✓		Flame goes out after 8 sec when ignited from top; after 13 sec when ignited from bottom
9. α-Cellulose		3.45×10^{-5}		✓	✓		Flame goes out after 5 sec when ignited from top; after 10 sec when ignited from bottom
10. α-Cellulose		5.45×10^{-5}		✓	✓		Does not flame
11. α-Cellulose		1.15×10^{-4}		✓	✓		Does not flame
12. α-Cellulose			3.20×10^{-5}	✓	✓		Char front glows; top ignition-char front crosses 6 in. in 1848 sec, bottom ignition in 1800 sec.
13. α-Cellulose			4.63×10^{-5}	✓	✓		Char front glows; top ignition-char front crosses 6 in. in 1735 sec, bottom ignition in 1700 sec
14. α-Cellulose			6.85×10^{-5}	✓	✓		Char front glows; top ignition-char front crosses 6 in. in 1736 sec, bottom ignition in 1710 sec
B. Horizontal test							
1. α-Cellulose - untreated				✓	✓		Continuous flaming over length of sample
2. α-Cellulose	1.20×10^{-5}			✓	✓		Flame goes out after 3 sec; top ignition-char front crosses 6 in. in 350 sec, bottom ignition, in 330 sec
3. α-Cellulose	2.45×10^{-5}			✓	✓		Does not flame
4. α-Cellulose	3.60×10^{-5}			✓	✓		Does not flame
5. α-Cellulose	5.0×10^{-5}			✓	✓		Does not flame
6. α-Cellulose	1.1×10^{-5}			✓	✓		Does not flame
7. α-Cellulose		2.00×10^{-5}		✓	✓		Flame goes out after 8 sec when ignited from top and after 10 sec when ignited from bottom
8. α-Cellulose		2.55×10^{-5}		✓	✓		Flame goes out after 3 sec when ignited from top and after 7 sec when ignited from bottom
9. α-Cellulose		3.20×10^{-5}		✓	✓		Does not flame
10. α-Cellulose		5.7×10^{-5}		✓	✓		Does not flame
11. α-Cellulose		1.0×10^{-4}		✓	✓		Does not flame
12. α-Cellulose			3.18×10^{-5}	✓	✓		Does not flame; char glows
13. α-Cellulose			4.6×10^{-5}	✓	✓		Does not flame; char glows
14. α-Cellulose			7.0×10^{-5}	✓	✓		Does not flame; char glows

Table 1 (Continued)

Description of Test and Sample	Retardant and Concentration			Ignition with Fisher Burner		Time to Ignition (sec)	Sample Response to Flammability and Ignition Tests
	Phosphotungstic Acid (mols/g)	Ammonium Phosphotungstate (mols/g)	Phosphomolybdic Acid (mols/g)	Top	Bottom		
I. (Continued)							
C. Vertical test							
1. α-Cellulose - untreated				✓	✓		Continuous flaming over length of sample
2. α-Cellulose	1.15×10^{-5}			✓	✓		Flame goes out after 15 sec; top ignition-char front crosses 6 in. in 280, bottom ignition in 240 sec
3. α-Cellulose	2.45×10^{-5}			✓	✓		Flame goes out after 10 sec; top ignition-char front crosses 6 in. in 320, bottom ignition in 280 sec
4. α-Cellulose	3.50×10^{-5}			✓	✓		Flame goes out after 8 sec; top ignition-char front crosses 6 in. in 400, bottom ignition in 340 sec
5. α-Cellulose	5.00×10^{-5}			✓	✓		Flame goes out after 6 sec; top ignition-char front crosses 6 in. in 560, bottom ignition in 400 sec
6. α-Cellulose	1.1×10^{-4}			✓	✓		Does not flame
7. α-Cellulose		2.10×10^{-5}		✓	✓		Flame goes out after 16 sec; top ignition-char front crosses 6 in. in 275, bottom ignition in 245 sec
8. α-Cellulose		2.70×10^{-5}		✓	✓		Flame goes out after 12 sec; top ignition-char front crosses 6 in. in 315, bottom ignition in 280 sec
9. α-Cellulose		3.10×10^{-5}		✓	✓		Flame goes out after 7 sec; top ignition-char front crosses 6 in. in 400, bottom ignition in 355
10. α-Cellulose		5.7×10^{-5}		✓	✓		Flame goes out after 6 sec; top ignition-char front crosses 6 in. in 585, bottom ignition in 415 sec
11. α-Cellulose		1.0×10^{-4}		✓	✓		Does not flame
12. α-Cellulose			3.4×10^{-5}	✓	✓		Char front glows; top ignition-char front crosses 6 in. in 1542 sec, bottom ignition in 1315 sec
13. α-Cellulose			4.5×10^{-5}	✓	✓		Char front glows; top ignition-char front crosses 6 in. in 1432 sec, bottom ignition in 1210 sec
14. α-Cellulose			7.1×10^{-5}	✓	✓		Char front glows; top ignition-char front crosses 6 in. in 1430 sec, bottom ignition in 1209
15. Cotton - untreated							Continuous flaming over length of sample leaving white ash
16. Cotton	4.37×10^{-5}				✓		Flames go out after 6 sec; char front crosses 6 in. in 240 sec
17. Cotton	9.42×10^{-5}				✓		Flames go out after 4 sec; char front crosses 6 in. in 270 sec
18. Cotton	1.2×10^{-5}						Smolders
		4.3×10^{-5}			✓		Flames go out after 5 sec; char front crosses 6 in. in 235 sec
		9.3×10^{-5}			✓		Flames go out after 3 sec; char front crosses 6 in. in 280 sec
		1.1×10^{-5}			✓		Smolders
19. Rayon - untreated					✓		Continuous flaming over length of sample
20. Rayon	2.37×10^{-5}				✓		Flames go out after 15 sec; leaving char layer behind
21. Rayon	4.30×10^{-5}				✓		Flames go out after 10 sec; leaving char layer behind
22. Rayon	1.10×10^{-4}				✓		Flames go out after 1 sec; leaving char layer behind
23. Rayon		2.3×10^{-5}			✓		Flames go out after 14 sec; leaving char layer behind
24. Rayon		4.34×10^{-5}			✓		Flames go out after 9 sec; leaving char layer behind
25. Rayon		1.28×10^{-4}			✓		Flames go out after 1 sec; leaving char layer behind
26. Polyester - untreated					✓		Burns with luminous flame, leaves droplets of burning melt as flame front advances
27. Polyester	5.1×10^{-5}				✓		Burns with less luminous flame than untreated sample
28. Polyester		4.5×10^{-5}			✓		Burns with less luminous flame than untreated sample
29. Nylon - untreated					✓		Burns with luminous flame, leaves droplets of burning melt as flame front advances

Table 1 (Concluded)

Description of Test and Sample	Retardant and Concentration			Ignition with Fisher Burner		Time to Ignition (sec)	Sample Response to Flammability and Ignition Tests
	Phosphotungstic Acid (mols/g)	Ammonium Phosphotungstate (mols/g)	Phosphomolybdic Acid (mols/g)	Top	Bottom		
I. (Concluded)							
C. (Concluded)							
30. Nylon	5.1×10^{-5}				√		Burns with less luminous flame than untreated sample
31. Nylon		5.0×10^{-5}			√		Burns with less luminous flame than untreated sample
D. Tungsten - iodine lamp 3.2 cal cm^{-2} sec^{-1}							
1. α-Cellulose - untreated						4	Leaves no char
2. α-Cellulose	1.18×10^{-5}					29	Forms char layer after 12 sec; discontinues flaming after lamp is turned off
3. α-Cellulose	2.53×10^{-5}					30	Forms char layer after 10 sec
4. α-Cellulose	3.95×10^{-5}					29	Forms char layer after 7 sec
5. α-Cellulose	5.04×10^{-5}						Does not flame, forms char layer after 10 sec
6. α-Cellulose			1.08×10^{-5}			28	Forms char layer after 13 sec, discontinuous flaming after lamp is turned off; char glows
7. α-Cellulose			2.45×10^{-5}			30	Forms char layer after 9 sec
8. α-Cellulose			4.00×10^{-5}			29	Forms char layer after 7 sec
9. α-Cellulose			6.10×10^{-5}				Does not flame, forms char layer after 9 sec; the char glows
E. CO_2 Laser - 6.2 cal cm^{-2} sec^{-1}							
1. α-Cellulose - untreated						1.3	Continued flaming after removal from laser
2. α-Cellulose	1.26×10^{-5}					1.3	Stopped flaming after removal from laser
3. α-Cellulose	2.60×10^{-5}					1.5	Stopped flaming after removal from laser
4. α-Cellulose	3.96×10^{-5}					4.8	Stopped flaming after removal from laser
5. α-Cellulose	4.97×10^{-5}					6.3	Stopped flaming after removal from laser
6. α-Cellulose		1.20×10^{-5}				1.4	Stopped flaming after removal from laser
7. α-Cellulose		2.5×10^{-5}				1.5	Stopped flaming after removal from laser
8. α-Cellulose		3.9×10^{-5}				4.8	Stopped flaming after removal from laser
9. α-Cellulose		4.7×10^{-5}				5.7	Stopped flaming after removal from laser
10. α-Cellulose			2.35×10^{-5}			4.9	Stopped flaming after removal from laser, char glows
11. α-Cellulose			3.74×10^{-5}			6.0	Stopped flaming after removal from laser, char glows
12. α-Cellulose			4.89×10^{-5}			6.0	Stopped flaming after removal from laser, char glows
13. α-Cellulose			7.61×10^{-5}			6.3	Stopped flaming after removal from laser, char glows

however. This sequence occurs when the add-on value is as little as 3.7×10^{-5} mol of either the phosphotungstic or phosphomolybdic acid/g of cellulose.

3. Analysis of Thermal Degradation Products.

The effect of the additives on the degradation products is shown on Figure 2. The gas chromatographic analysis includes only compounds with molecular weight less than 150. For comparison chromatograms of the degradation products from untreated cellulose and $(NH_4)_2SO_4$-treated samples are also included. A typical chromatogram of the degradation products of untreated cellulose consists of at least 59 compounds. The products formed from cellulose containing either 5×10^{-5} mol phosphotungstic acid or 7.0×10^{-5} mol of phosphomolybdic acid per gram of cellulose resemble the degradation products of samples treated with the 1.76×10^{-4} mol $(NH_4)_2SO_4$ per gram of cellulose. All three treatments render the following five dominant gc peaks: 11 (water), 14 (pyruvaldehyde + acetol), 18 (acetic acid), 19 (furfural), and 31a (the furanose derivative). However, the chromatogram showing the degradation products of cellulose treated with phosphomolybdic acid depicts higher concentrations of peak numbers 24, 26, 28, 29, and 33. It is interesting to note that both the phosphotungstic acid and phosphomolybdic acid treatments produce smaller amounts of 31a (the furanose derivative) than the $(NH_4)_2SO_4$ treatment. This difference, however, might be due to the concentration effect rather than to the retardant effect.

B. Evaluation of Flame-Retardant Effectiveness of Ammonium Phosphotungstate in α-Cellulose

1. Char Determination

Figure 1 shows that the effect of ammonium phosphotungstate on the increase of char yield (ΔC) from α-cellulose is similar to that

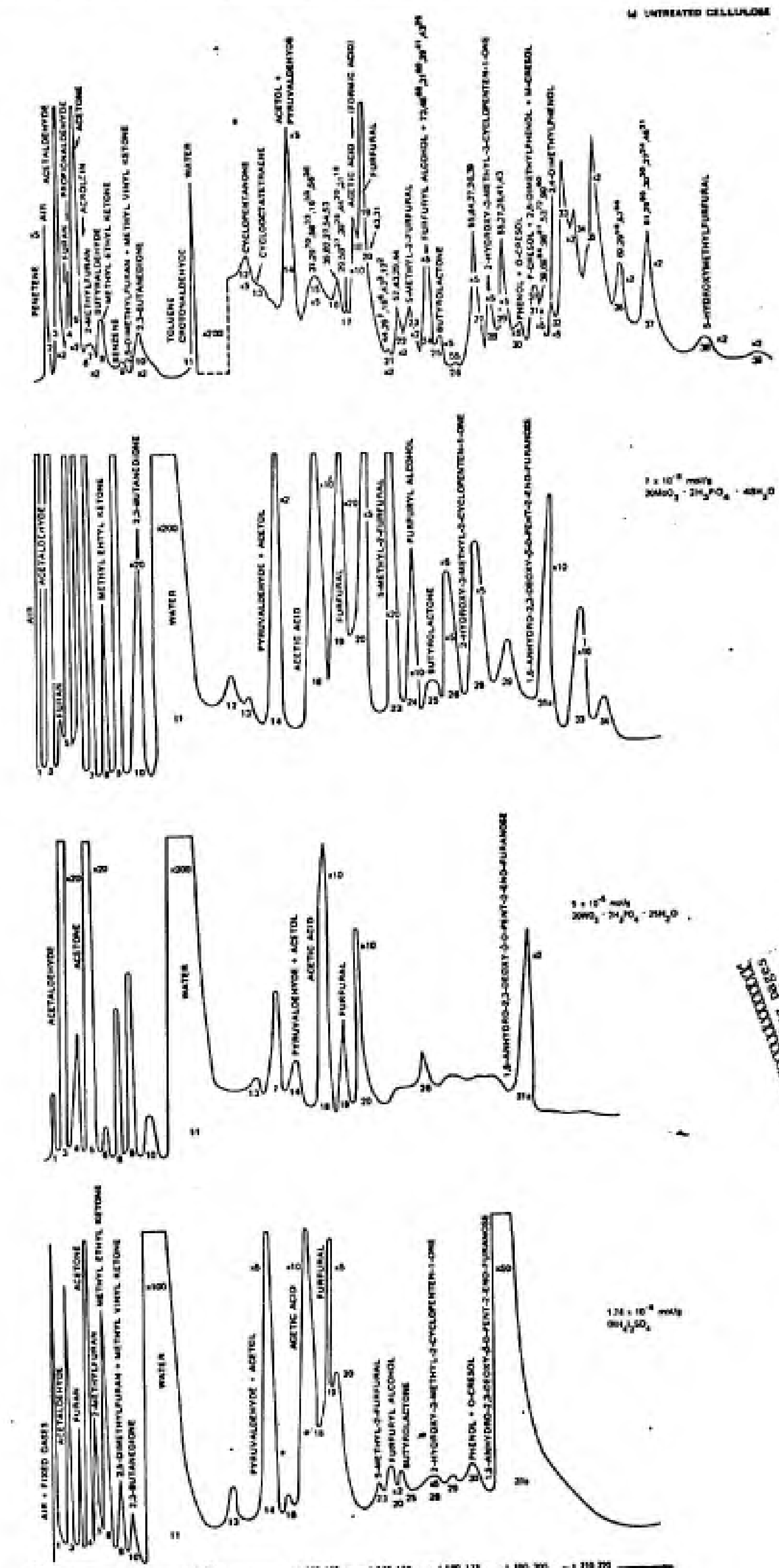

FIGURE 2 GAS CHROMATOGRAMS OF THE VOLATILE PRODUCTS FROM THE PYROLYSIS OF UNTREATED CELLULOSE AND CELLULOSE CONTAINING PHOSPHOMOLYBDIC ACID, PHOSPHOTUNGSTIC ACID, AND AMMONIUM SULFATE

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18.2

18.1

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See the following pages
for greater detail.
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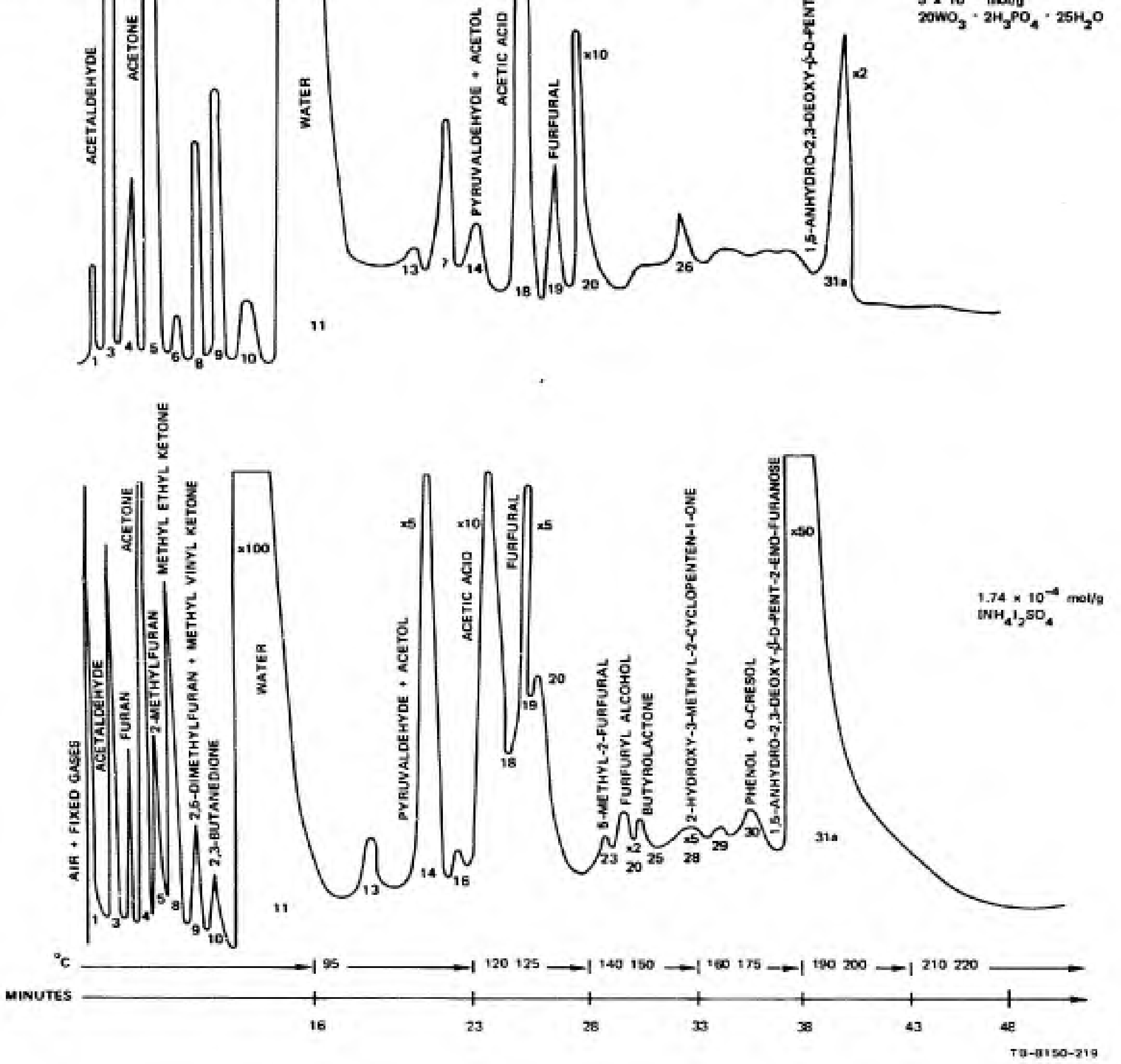
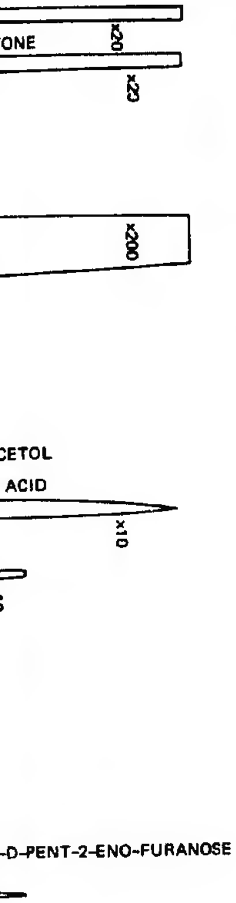
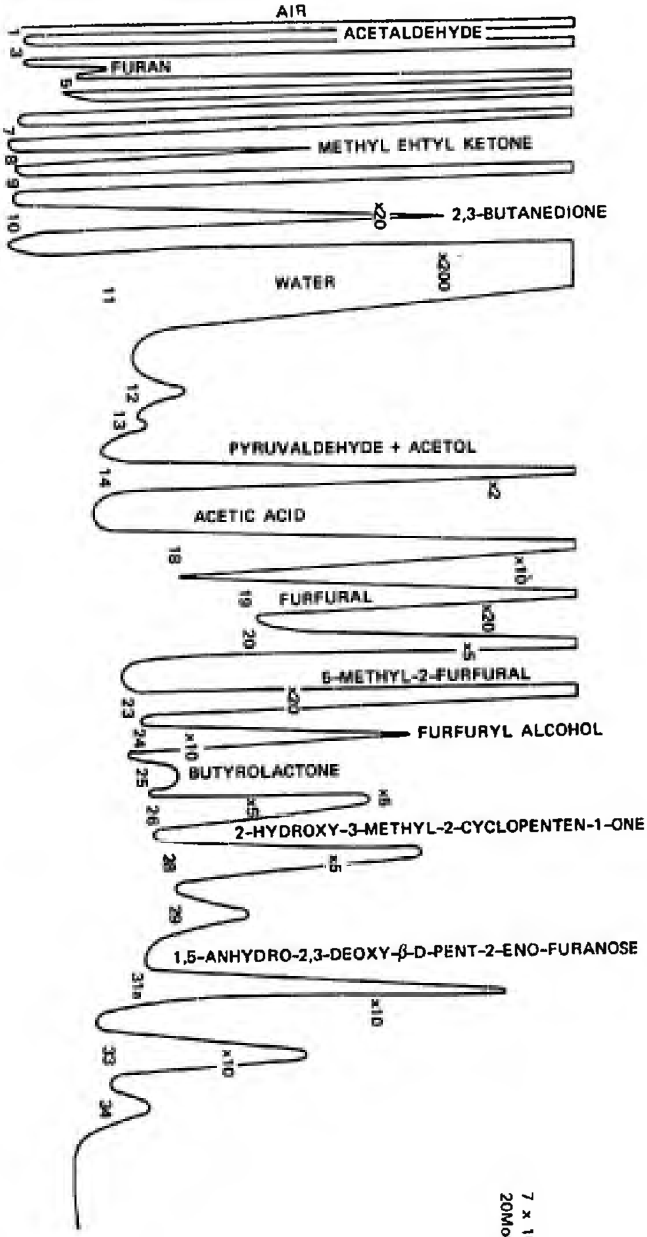


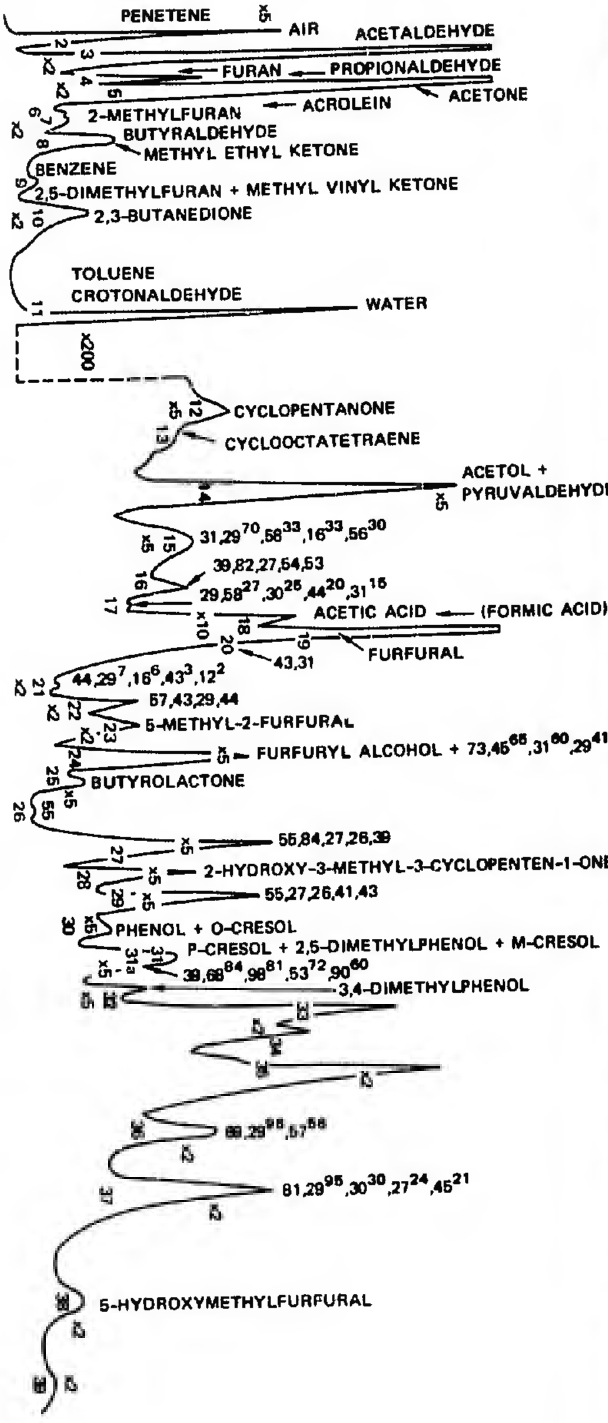
FIGURE 2 GAS CHROMATOGRAMS OF THE VOLATILE PRODUCTS FROM THE PYROLYSIS OF UNTREATED CELLULOSE AND CELLULOSE CONTAINING PHOSPHOMOLYBDIC ACID, PHOSPHOTUNGSTIC ACID, AND AMMONIUM SULFATE



5 x 10^{-5} mol/g
$20WO_3 \cdot 2H_3PO_4 \cdot 25H_2O$



7 x 10^{-5} mol/g
$20MoO_3 \cdot 2H_3PO_4 \cdot 48H_2O$



18.2

19

of phosphotungstic acid. The ΔC values at the various concentrations are the same as that from the cellulose containing phosphotungstic acid, and the optimum char production for both the acid and the salt-treated samples occurs at approximately the same concentration of the retardant.

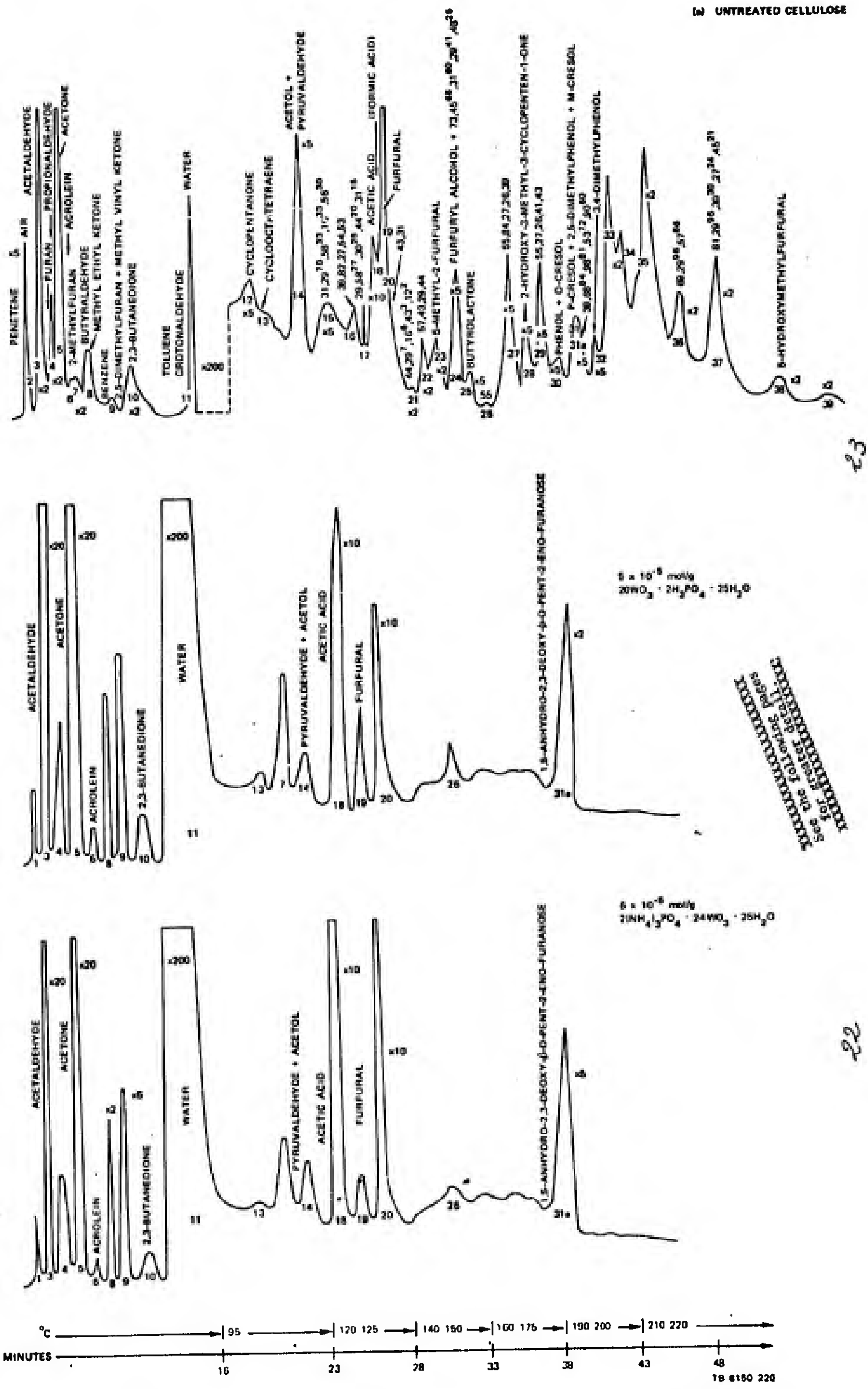
Although at this point the salt of the phosphomolybdic acid was not investigated as a potential flame retardant for either the cellulosic or the synthetic materials, there is no reason to believe that its behavior should differ from that of its acid counterpart.

2. Flammability and Ignition Tests

Results of the flammability tests of the ammonium phosphotungstate-treated cellulose are also shown in Table 1. Similar flammability behavior is observed in cellulose containing either the phosphotungstic acid or the sale of the acid precipitated interstitially. The most effective concentration of the salt to pass the vertical flame test was around 1.0×10^{-4} mol/g of cellulose. Exposure of cellulose containing 5.43×10^{-5} mol of ammonium phosphotungstate salt/g of cellulose to 6.2 cal cm^{-2} sec^{-1} from a CO_2 laser for 6.3 sec resulted in flaming ignition; however, the flames rapidly extinguished after the samples were removed from the laser beam. In contrast, untreated samples ignited after 2.3 sec and continued flaming after they were removed from the laser source.

3. Analysis of Thermal Degradation Products

Figure 3 compares chromatograms of the thermal degradation products of cellulose containing 5×10^{-5} mol phosphotungstic acid and 6×10^{-5} mol ammonium phosphotungstate per gram of cellulose. There are no substantial differences in the chromatograms for compounds with molecular weight less than 150. There are five dominant gc peaks: 11 (water), 14 (pyruvaldehyde and acetol), 18 (acetic acid), 19 (furfural), and 31a (the furanose derivative). To ascertain that the only difference between the two retardants centers on the durability of the treatment,



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for greater detail.
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FIGURE 3 GAS CHROMATOGRAMS OF THE VOLATILE PRODUCTS OF UNTREATED CELLULOSE AND CELLULOSE CONTAINING PHOSPHOTUNGSTIC ACID AND AMMONIUM PHOSPHOTUNGSTATE

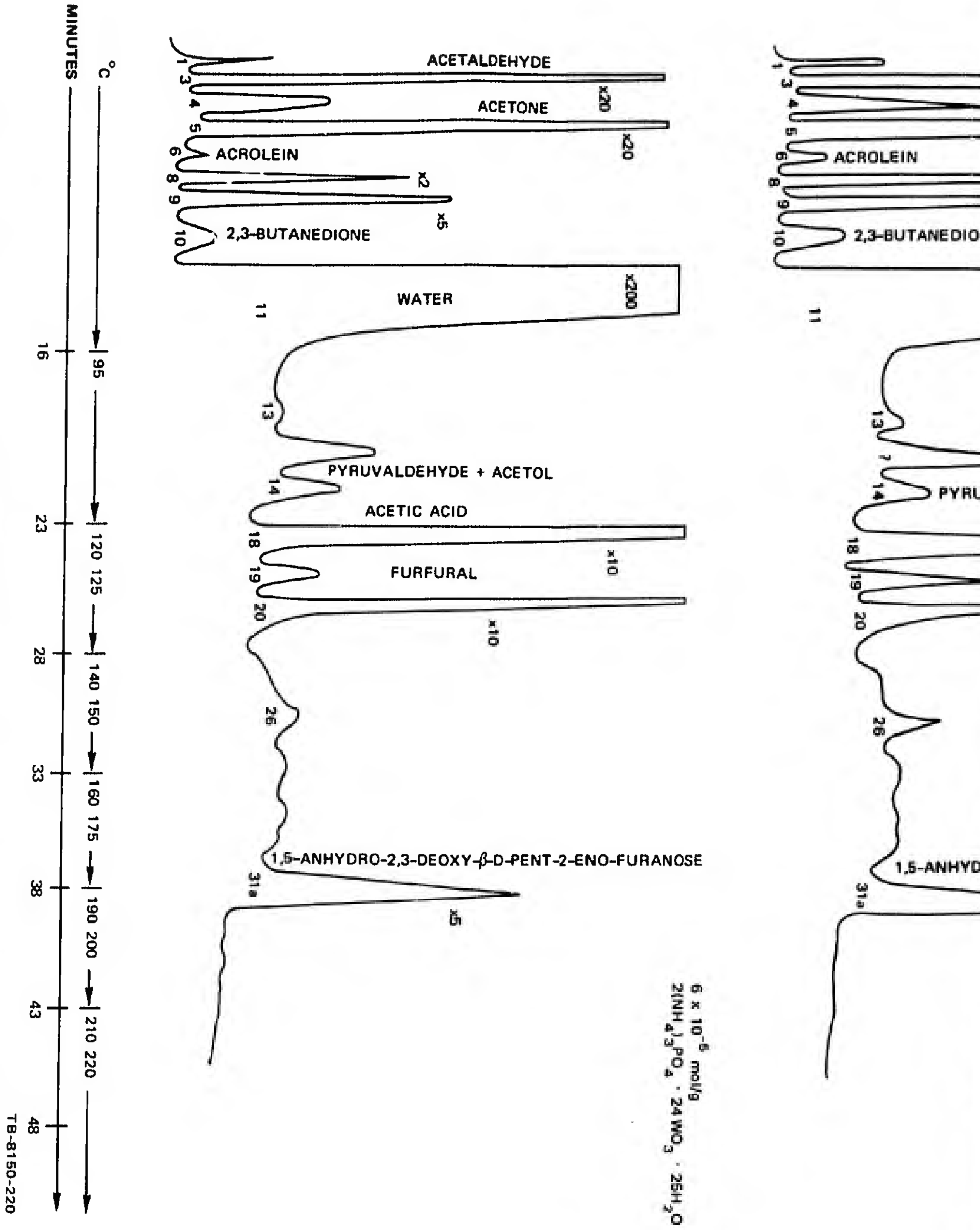
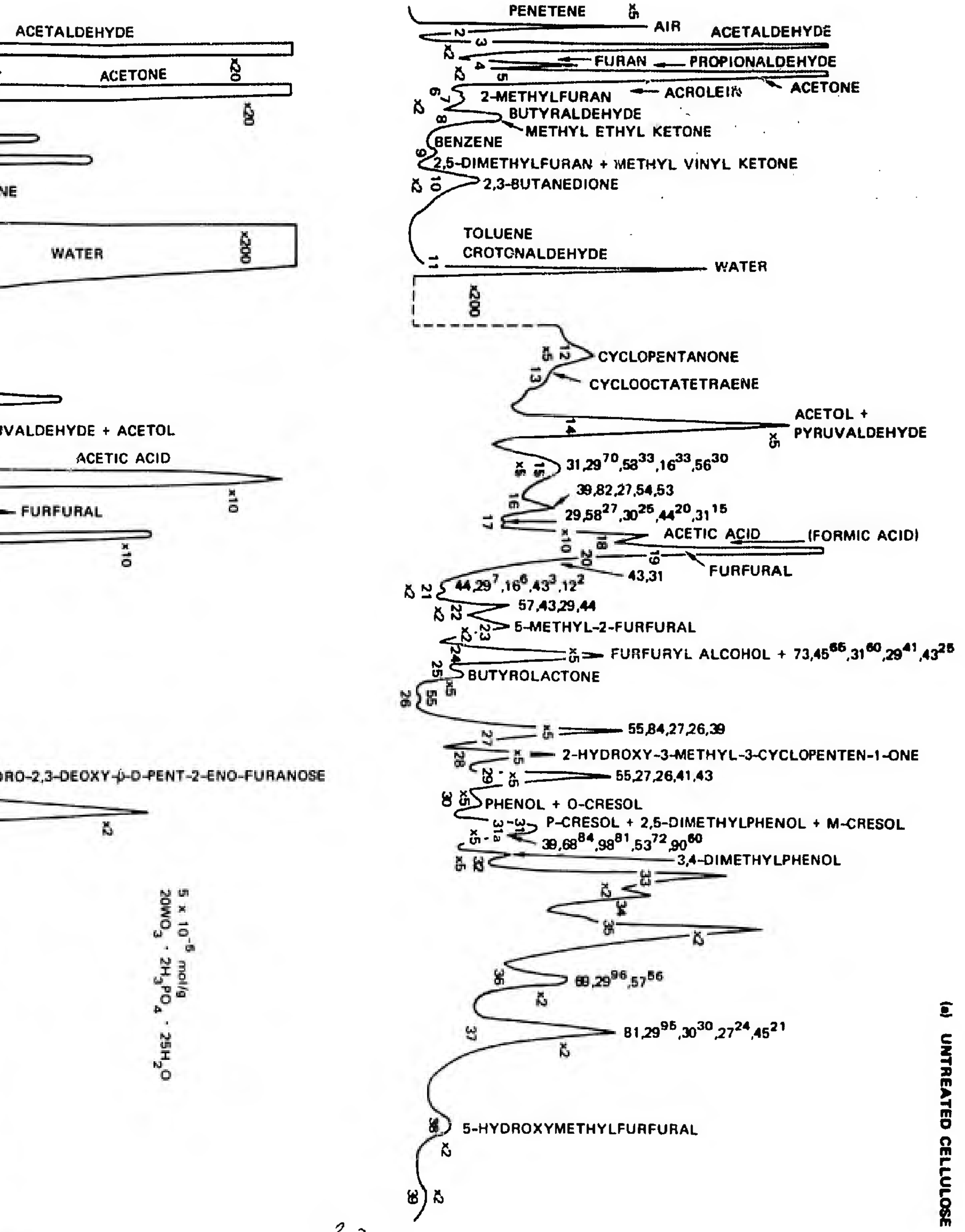


FIGURE 3 GAS CHROMATOGRAMS OF THE VOLATILE PRODUCTS OF UNTREATED CELLULOSE AND CELLULOSE CONTAINING PHOSPHOTUNGSTIC ACID AND AMMONIUM PHOSPHOTUNGSTATE

ACETALDEHYDE
ACETONE
x20
x20
NE
WATER
x200
VALDEHYDE + ACETOL
ACETIC ACID
x10
FURFURAL
x10
RO-2,3-DEOXY-β-D-PENT-2-ENO-FURANOSE
x2
5 x 10⁻⁵ mol/g
20WO3 · 2H3PO4 · 25H2O
PENETENE
x5
AIR
ACETALDEHYDE
FURAN
PROPIONALDEHYDE
ACETONE
2-METHYLFURAN
ACROLEIN
BUTYRALDEHYDE
METHYL ETHYL KETONE
BENZENE
2,5-DIMETHYLFURAN + METHYL VINYL KETONE
2,3-BUTANEDIONE
TOLUENE
CROTONALDEHYDE
WATER
x200
CYCLOPENTANONE
CYCLOOCTATETRAENE
ACETOL +
PYRUVALDEHYDE
x5
31,29⁷⁰,58³³,16³³,56³⁰
39,82,27,54,53
29,58²⁷,30²⁵,44²⁰,31¹⁵
ACETIC ACID
(FORMIC ACID)
x10
FURFURAL
43,31
44,29⁷,16⁶,43³,12²
57,43,29,44
5-METHYL-2-FURFURAL
FURFURYL ALCOHOL + 73,45⁶⁶,31⁶⁰,29⁴¹,43²⁵
BUTYROLACTONE
55,84,27,26,39
2-HYDROXY-3-METHYL-3-CYCLOPENTEN-1-ONE
55,27,26,41,43
PHENOL + O-CRESOL
P-CRESOL + 2,5-DIMETHYLPHENOL + M-CRESOL
39,68⁸⁴,98⁸¹,53⁷²,90⁶⁰
3,4-DIMETHYLPHENOL
69,29⁹⁶,57⁵⁶
81,29⁹⁵,30³⁰,27²⁴,45²¹
5-HYDROXYMETHYLFURFURAL
x2
x5
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 31a 32 33 34 35 36 37 38 39
(a) UNTREATED CELLULOSE

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a broader spectrum of the degradation products, ranging from the light gases (CO, CO_2, and hydrocarbons < 5 carbons) to levoglucosan and other carbohydrates, should be analyzed.

C. Evaluation of Retardant Effectiveness of Phosphotungstic Acid and Ammonium Phosphotungstate in Other Cellulosic and Synthetic Materials

Although the technique used in incorporating the acid and its salt in α-cellulose paper can be easily applied to cotton and rayon, a wetting agent should be included in the aqueous solution of the acid to facilitate the treatment of nylon and polyester. At present, single treatments of the nylon and rayon cloth with 20% aqueous solution of the acid results in an add-on weight of only 1.3×10^{-5} mol of retardant per gram of nylon. Similar data were collected for the polyester material. Three successive applications of the acid were needed to raise the add-on weight to about 5.1×10^{-5} mol of retardant per gram of either the nylon or the polyester.

Since the main objective of this portion of the program was to determine whether the high molecular weight compounds can successfully be applied to materials other than cellulose paper, the determinations evaluating the effectiveness of phosphotungstic acid and its salt centered primarily on samples containing close to the optimal add-on weight of the retardant.

1. Char Determination

The char values for the four untreated materials and those treated with the phosphotungstic acid and its salt are shown in Table 2. Unless otherwise specified, all samples were pyrolyzed at 600°C for 12 minutes. It is interesting to note that the filler present in the unwashed cotton increases almost by a factor of 2 the amount of char in the control sample as compared to the washed cotton control sample. Higher values of ΔC are shown by the treated washed sample than by the

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Table 2

THE EFFECT OF ADDITIVES ON CHAR YIELDS IN COTTON, RAYON, NYLON AND POLYESTER

Sample Description	Concentration of Phosphotungstic Acid (mols/g)	Concentration of Ammonium Phosphotungstate (mols/g)	Total Char (percent)	ΔC (percent)
Washed				
Cotton (control)	--	--	10%	--
Cotton	6.9×10^{-5}	--	61	50%
Cotton	--	5.9×10^{-5}	48	38
Cotton	--	5.0×10^{-5}	43	33
Unwashed				
Cotton (control)	--	--	17	--
Cotton	6.9×10^{-5}	--	51	34
Cotton	--	6.0×10^{-5}	46	29
Rayon (control)	--	--	23	
Rayon	1.1×10^{-4}	--	53	30
Rayon	--	1.05×10^{-5}	54	31
Polyester (control)	--	--	No char	
Polyester	--	4.85×10^{-5}	1.5	1.5
Polyester (control at 400°C)	--	--	41	--
Polyester (at 400°C)	--	4.85×10^{-5}	48	7
Nylon (control)	--	--	No char	No char
Nylon	--	4.3×10^{-5}	0.37	0.37
Nylon (control at 560)	--	--	89	--
Nylon (at 560)	--	4.35×10^{-5}	91	2

treated unwashed sample. This finding suggests that the filler might interfere with the char-forming process and, if a sample is treated before washing and used in kinetic studies of thermal degradation, erroneous results might be obtained.

The char yields of the unwashed rayon control sample were also high. However, since a washed counterpart was not run, the value cannot be attributed to the presence of a filler at this date.

The nylon and polyester control samples produced no char at 600°C and their treated counterparts showed very small amounts. When lower temperatures were tried, both the treated and untreated samples resulted in large quantities of char which in turn led to small ΔC values. These results suggest that the effect of the retardant on the decomposition of nylon and polyester might be different from that of cellulosic materials and might thus reinforce our literature findings that more study is needed on the Thermal degradation processes governing these materials, if successful retardants are to be developed for them.

2. Flammability Tests

The results of the flammability tests of the four cloths are included in Table 1.

The optimal effectiveness of the retardant on both cotton and rayon is achieved around 1.1×10^{-4} mol of the retardant per gram of either material. However, concentrations as low as 4.3×10^{-5} mol of the retardant/g of either fabric will prevent sustained flaming when a specimen is held vertically and lit with a Fisher flame. The untreated samples continued flaming when removed from the ignition source.

The polyester and nylon samples with a retardant load of 5.1×10^{-5} mol/g of material burned with a less luminous flame than the untreated samples when held vertically and lit with a Fisher burner and eventually ceased to flame after removal from the burner. The untreated samples burned with a luminous flame, leaving droplets of burning melt as the flame front advanced upward. A modification of the procedure for incorporation of the retardant in the synthetics is needed to achieve optimal effectiveness of the retardant.

3. Analysis of Thermal Degradation Products

The pyrolysis products (molecular weight <150) of cotton or rayon treated with the acid or salt are the same as those from cellulose treated with phosphotungstic acid or its salt. Figure 4 compares a chromatogram of the pyrolysis products of the acid-treated cellulose with chromatograms of the degradation products of the treated cotton and rayon.

The present method used in the gc analysis of thermal degradation products of untreated and treated nylon and the polyester cloths proved unsuccessful. Another attempt to analyze these products will be made in the future. The approach will employ a Curie point pyrolyzer and a hydrogen flame detector. In addition, a column packed with 10% dibutyl phosphate on Celite 545 will be used to analyze the nitrogen-containing compounds of thermally degraded nylon.

D. Evaluation of Retardant Effectiveness of Phosphotungstic Acid and Ammonium Phosphotungstate in Cedar Shakes

1. Flammability Tests

The results of the flammability tests of the treated shakes are summarized in Table 3. The Table also shows the depth of penetration the add-on weight per area, expressed as pounds of additive per square*

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* A "square" is a unit of roof coverage. It refers to the amount of shingles or other roofing material needed to cover a 10-by-10-ft. area. Since shingles and shakes are applied to a roof in an overlapping pattern, only about a third of each shingle or shake is exposed.

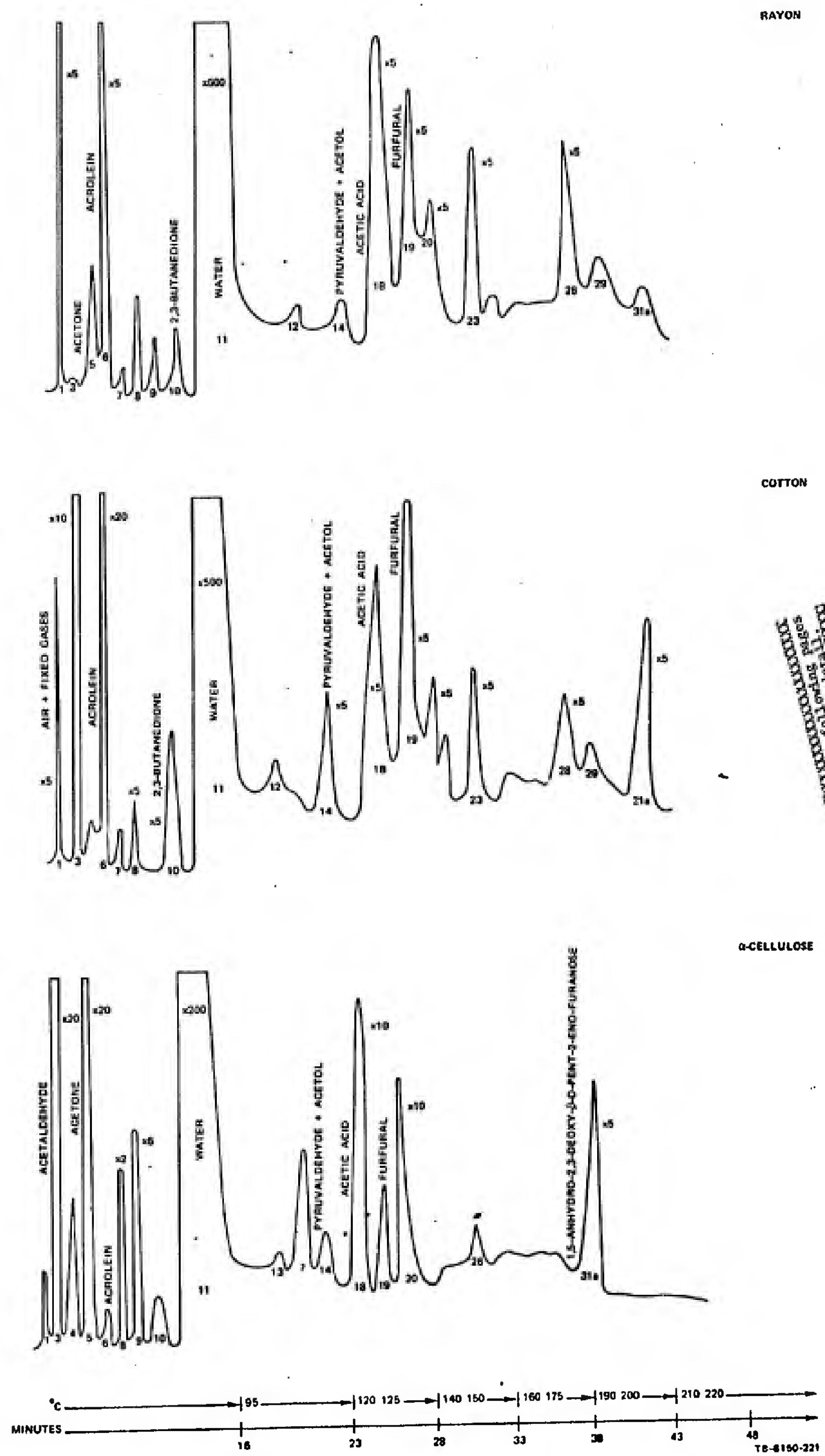

FIGURE 4 GAS CHROMATOGRAMS OF THE VOLATILE PRODUCTS OF PHOSPHOTUNGSTIC-ACID-TREATED RAYON, COTTON AND α-CELLULOSE

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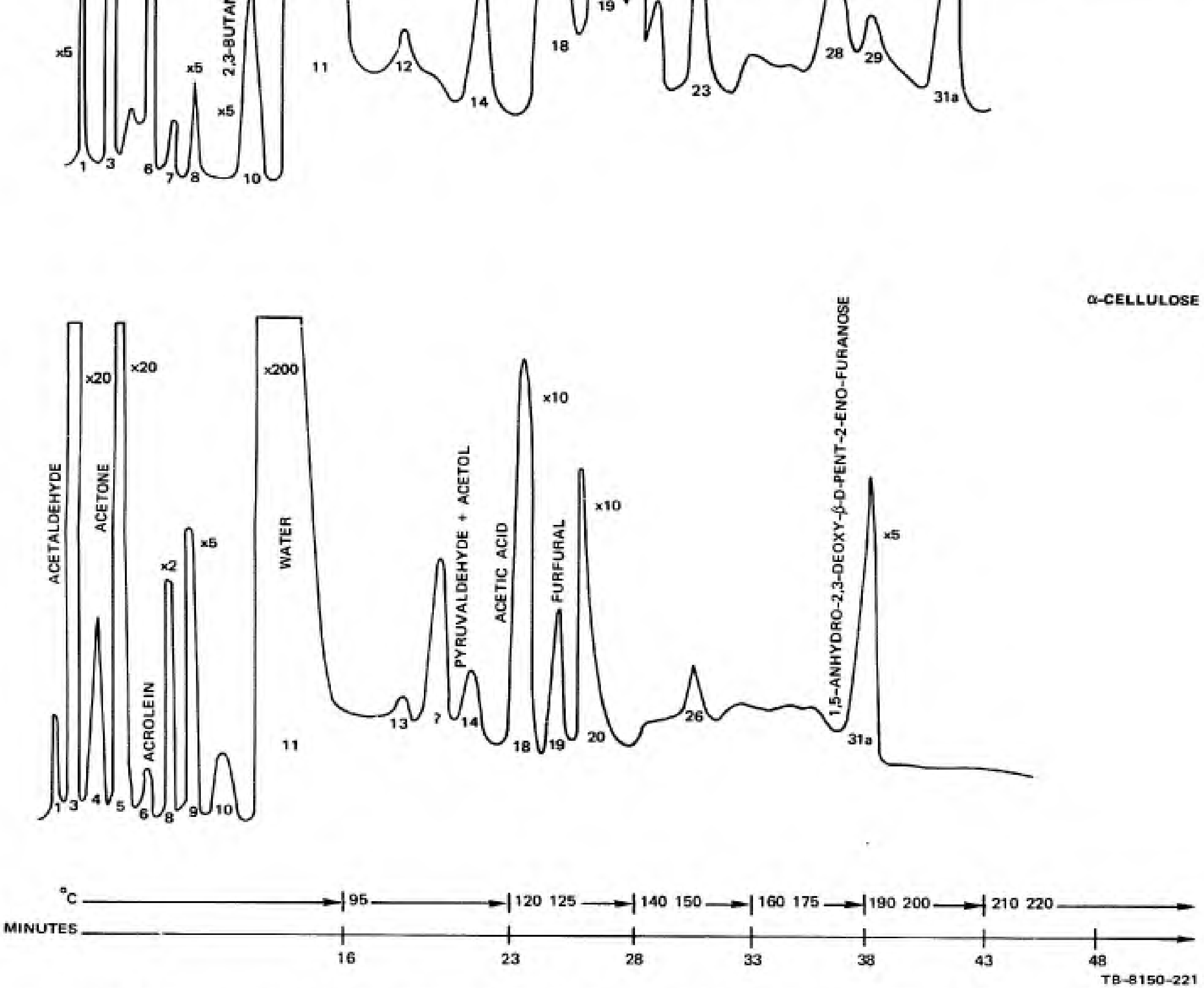
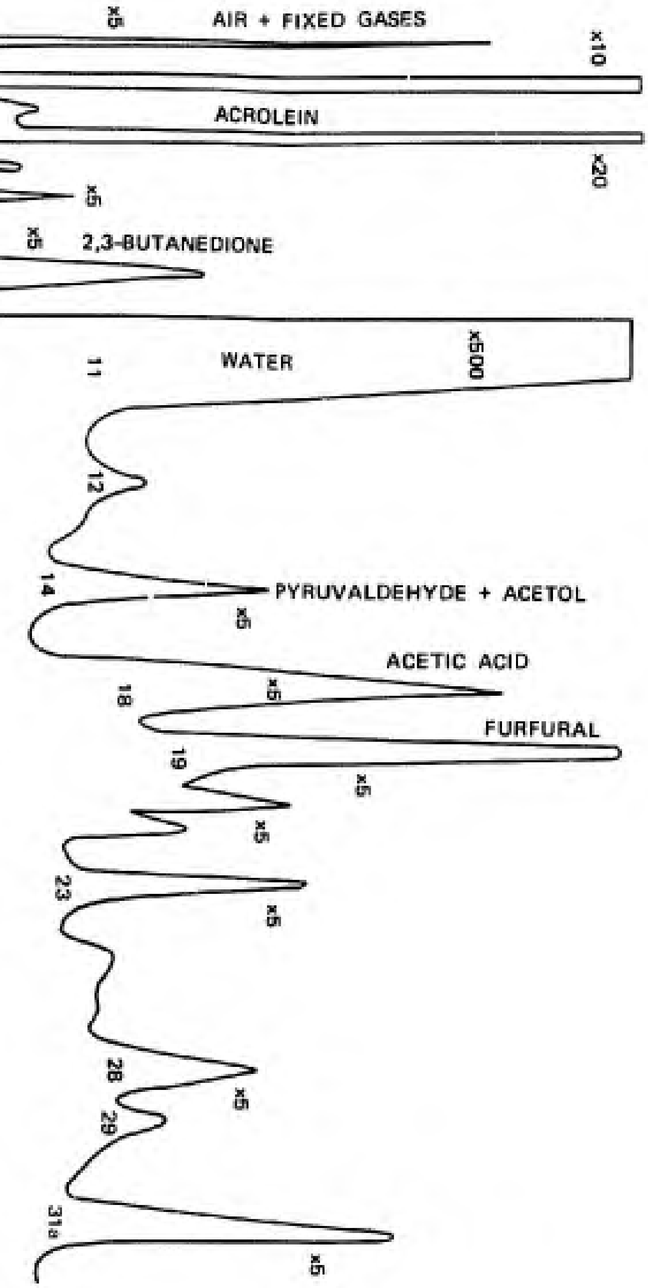
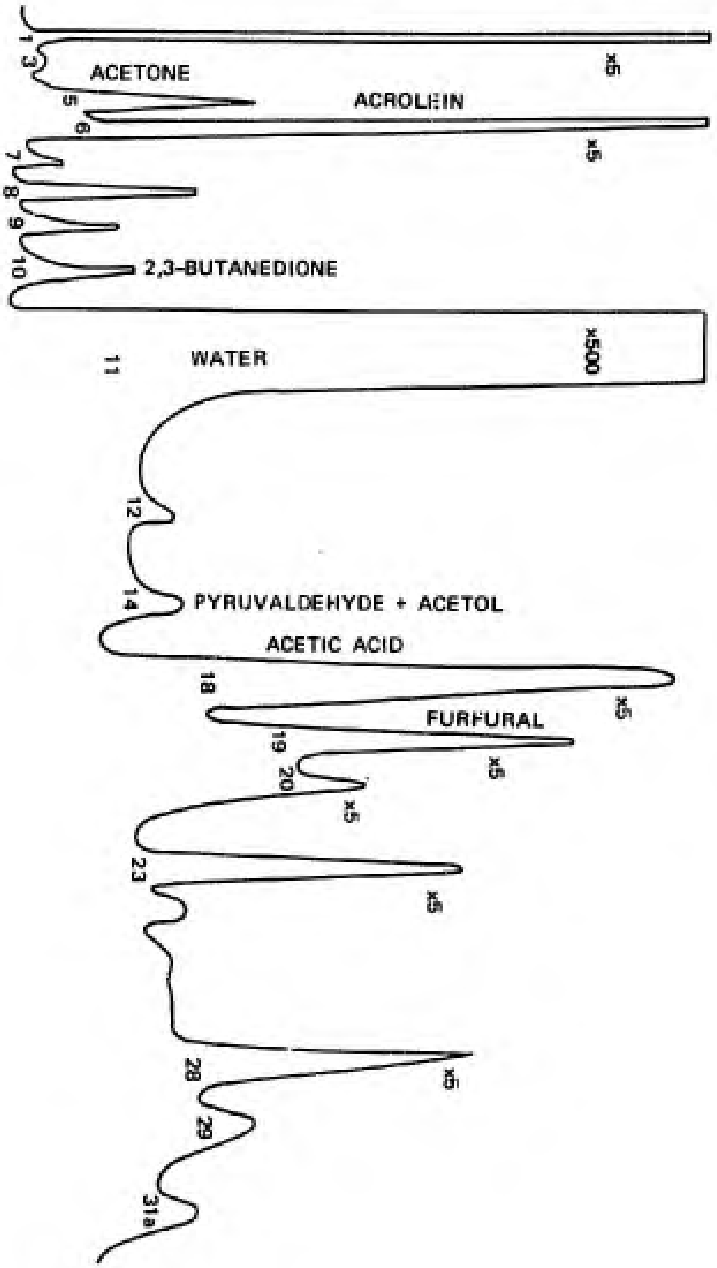


FIGURE 4 GAS CHROMATOGRAMS OF THE VOLATILE PRODUCTS OF PHOSPHOTUNGSTIC-ACID-TREATED RAYON, COTTON AND α-CELLULOSE



COTTON



RAYON

Table 3

EFFECT OF RETARDANTS ON IGNITION OF CEDAR SHAKES BY THE FISHER BURNER

Sample Description	Length of Soaking	Approximate Depth of Penetration (mx)	Add-on Weight (g)	Add-on Weight per Area (g/cm^2)	Add-on Weight per Area (lb/sq)	Concentration of Retardant in Layer (mols/g)	Time to Ignition (seconds)
Shakes containing phosphotungstic acid	10 sec	0.5	0.286	0.0061	3.99	2.18×10^{-5}	14 (flames go out after removal from ignitor)
	1 min	1.0	0.42	0.0089	5.83	1.59×10^{-5}	25 (flames go out after removal from ignitor)
	2 min	1.5	0.67	0.0142	9.30	1.68×10^{-5}	35 (flames go out after removal from ignitor)
	5 min	2.0	0.92	0.0196	12.84	1.74×10^{-5}	65 (flames go out after removal from ignitor)
Shakes containing ammonium phosphotungstate	10 sec	0.5	0.252	0.0054	3.53	1.92×10^{-5}	15 (flames go out after removal from ignitor)
	1 min	1.0	0.42	0.0089	5.83	1.58×10^{-5}	24 (flames go out after removal from ignitor)
	2 min	1.5	0.59	0.0125	8.18	1.47×10^{-5}	33 (flames go out after removal from ignitor)
	5 min	2.0	0.92	0.0196	12.84	1.73×10^{-5}	66 (flames go out after removal from ignitor)
Untreated shakes							4 (continued flaming)

of roofing (lb/sq), and the concentration of the retardant in the layer as functions of soaking time.

The ignition time for the untreated material was 4 seconds. For a sample with 0.5-mm retardant layer of either the salt or the acid, ignition required 14 seconds of exposure, while a 65-second exposure was required when a 2.0-mm protective layer of the acid or salt had previously been formed. The treated samples discontinued flaming when removed from the burner, and the untreated shakes continued to burn when removed from the flame.

Unfortunately, we did not have the time to try out the phospomolybdic acid and its salt on the shakes. However, there is a little a-priori reason to believe that their performance would fail to match that of the phosphotungstic acid and its salt.

2. Cost Analysis of Retardant Treatement of the Roofing Material

Having shown the basic technical feasibility of using phosphotungstic acid and its ammonium salt as fire retardants for several practical materials including red-cedar shakes, we felt it worthwhile to conduct a simple cost analysis to ascertain, in a preliminary way, whether this approach also has economic feasibility.

Figure 5 shows the add-on weight of phosphotungstic acid for unit area (lb/sq) versus the depth of penetration. The numbers shown are calculated using data derived from treatments involving both sides of the roofing material. Treatment of one side only will, therefore, decrease the add-on weight for a unit area by one half. Furthermore, no attempt has yet been made to ascertain the tradeoffs between solution concentration and length of soaking. While the estimated concentration of the phosphotungstic acid in the treated layer (approximately 2×10^{-5} mol per gram) is in the optimal range, based on studies with α-cellulose, lower concentrations at greater depths of penetration may prove superior for durability and fire endurance.

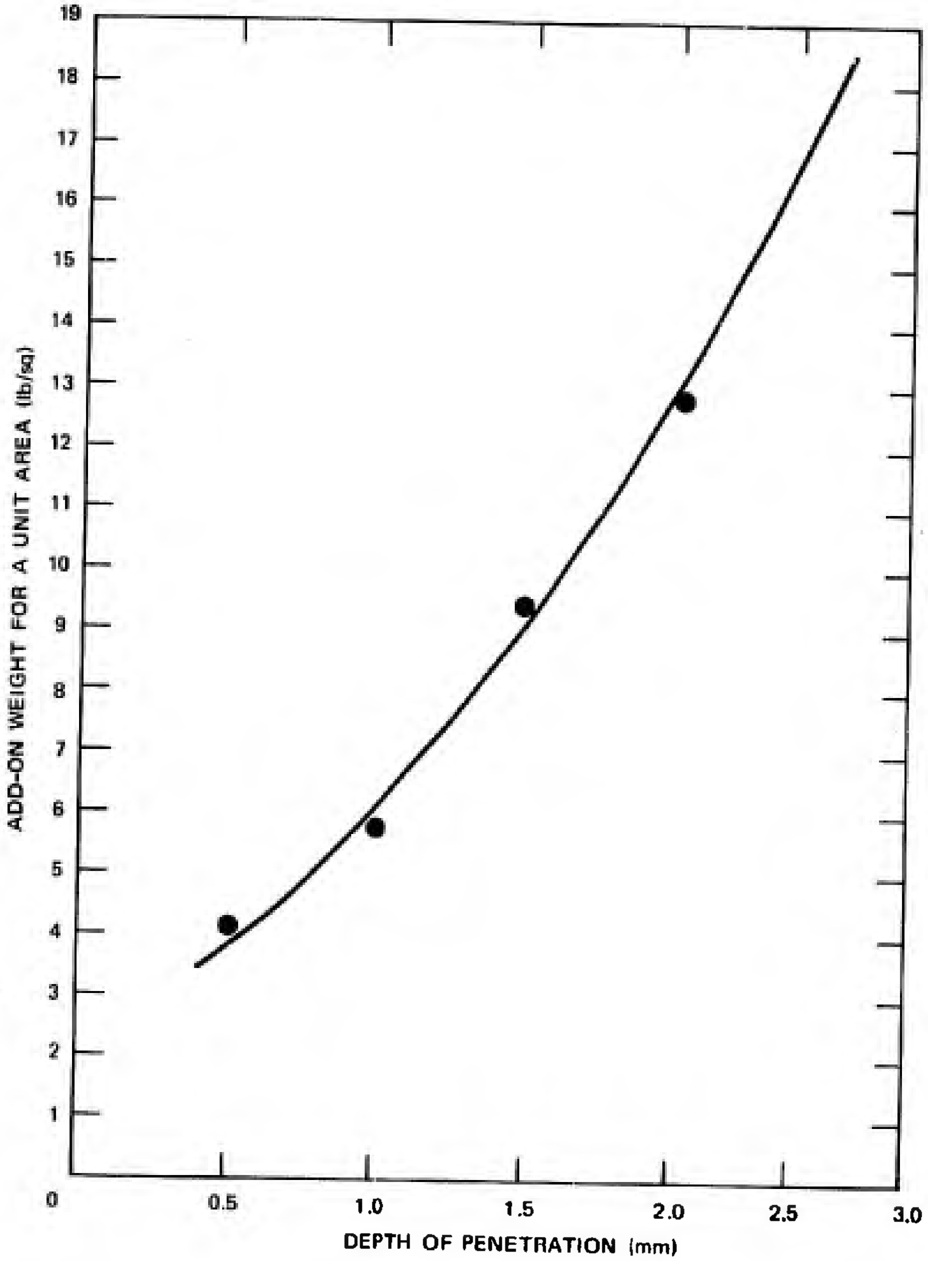


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FIGURE 5 COMPARISON OF THE ADD ON WEIGHT OF PHOSPHOTUNGSTIC ACID AS A FUNCTION OF DEPTH OF PENETRATION

Although it remains to be ascertained what practical levels of protection from fire spread can be obtained from this approach for any given value of add-on weight per unit area treated, it is reasonable to assume for the time being that the procedures will make use of weight add-ons of 4 to 5 lb/sq of pretreated shingles and shakes down to only a pound or two per square for spray treatment of already installed roofing, where only the exposed tab gets treated.

Both phosphomolybdic and phosphotungstic acids are expensive, but tungsten compounds are inherently dearer than the corresponding molybdenum compounds. Since we have little reason at present for favoring the tungsten compounds, let us turn our attention to the phosphomolybdates. Incidentally, we have found it much easier to get firm quotations on molybdenum compounds for large-scale applications than on tungsten.

Phosphomolybdic acid as it is commonly sold, in the crystalline form to be used as a catalyst, is a mixture of acids containing both Mo:P=9:1 and Mo:P=12:1; called 9-molybdenum and 12-molybdenum phosphoric acids, respectively. The cost of this material depends very much on the usage rates of a particular application. It is estimated that its price per pound drops from about \$10 to \$15 for applications of 1000 pounds-per-year to \$2 to \$2.50 for applications of 100,000 pounds-per-year and approaches \$1.50 for consumption rates in excess of, say, a million pounds a year.

There is a noteworthy difference between the characteristics of the 9-moly acid and the 12-moly acid that leads to further possible cost savings. The 12-moly acid, whose ammonium salt is appreciably more insoluable than its 9-moly counterpart--a fact that favors its weather durability--is formed in nearly quantitative yields when MoO_3 is refluxed with aqueous ortho-phosphoric acid. Bulk MoO_3 is available for about \$1.45 a pound. Phosphoric acid can be derived inexpensively by treating phosphate rock with sulphuric acid, but in a pure commercial grade it costs only about 8¢ per pound, which adds insignificantly to the final cost. The product of the refluxing is an aqueous solution of $24\ MoO_3 \cdot P_2O_5 \cdot nH_2O$ which, upon further dilution, is ready to use on the exterior wooden surfaces. Neutralization can be accomplished with commercial aqueous ammonia. A homeowner might use a dilute solution of ammonium sulfate (chemical fertilizer) to saturate the air-dried shingles, following spray treatment with the 12-moly acid, and then follow this with a solution of washing soda, or perhaps baking soda, to release the ammonia. At most the precipitation should add only pennies per square. Allowing for this and for the cost of heat needed to perform the refluxing process, the costs of the chemical should not exceed about $1.20 per pound. This translates to less than $2.50 per square in installed roofs and about $5.00 to $6.00 per square in new materials. If the average home requires 20 squares of roofing, the cost of materials ranges from about $50 to perhaps $120 or at most $150 per home--a very acceptable cost if the protection afforded can be shown to be good.

E. Comparison of Weight-Loss Rates of Cotton Cloth with α-Cellulose

Figure 6 compares the remaining weights of cotton cloth (0.008 in. thick) with α-cellulose (0.030 in. thick) as a function of time. The cotton cloth curve does not show the initial rapid weight loss exhibited by the α-cellulose weight loss curve. The linear portion of the weight loss curve of the cotton continues until about 70% of the sample has volatilized, as contrasted with the cellulose, where the linearity discontinues after approximately 46% of the material has decomposed. After the constant rate of degradation discontinues, the residual weight for both samples begins to decay exponentially toward a constant value of about 17%. Whether or not the differences in the weight loss curves are true indications of different processes of decomposition of the two materials will have to be resolved by further experimentation.

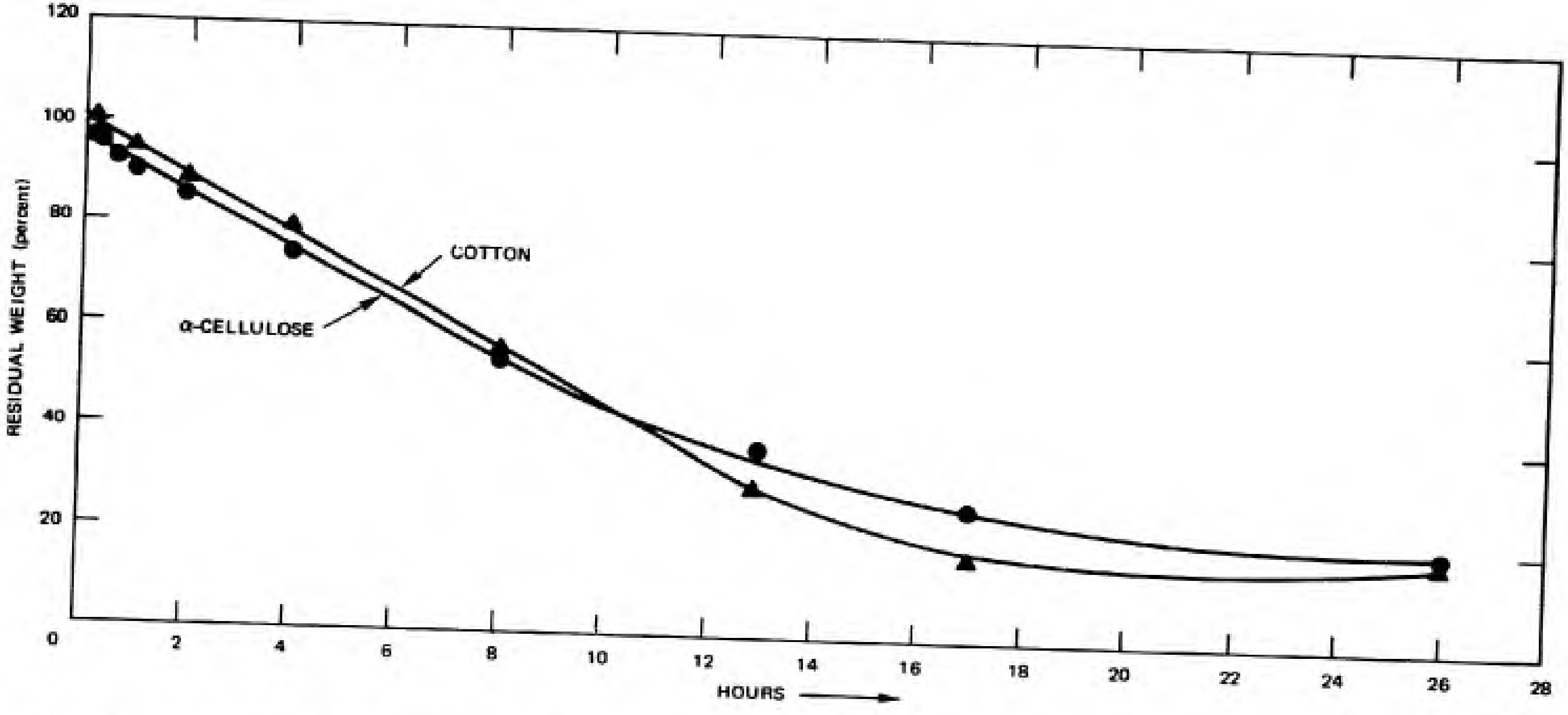

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FIGURE 6 COMPARISON OF KINETICS OF WEIGHT LOSS FOR COTTON AND α-CELLULOSE PYROLYZED IN NITROGEN AT 276°C

V CONCLUSIONS AND RECOMMENDATIONS

The conclusions of this study are as follows:

1. Much information is needed on the mechanism of decomposition of synthetic materials before effective flame retardants are developed for these materials. Future work should center on determining the kinetics of decomposition of the synthetics, on the distribution of their pyrolysis products as a function of temperature, and then on developing a technique for incorporating the appropriate retardant in the molten state of the synthetics as they are spun to yield a durable treatment.

2. The retardant effectiveness of phosphotungstic and phosphomolybdic acids in α-cellulose was validated by (1) the ignition resistance of the treated material to an irradiance of 6.2 cal cm^{-2} sec^{-1} from a CO_2 laser, (2) a pronounced change in the distribution of the pyrolysis products, and (3) pyrolytic production of large quantities of char. To determine how much of the large increase in char is due to the remaining oxides of the metals in the solid residue, the residual char should be ashed, the remaining minerals weighed, and the corrected increases in char yields compared to their values obtained with previously used retardants.

3. The effectiveness of the ammonium phosphotungstate as a flame retardant in α-cellulose was confirmed by results of the flame and ignition tests, char yields, and pyrolysis-product distributions of cellulose containing ammonium phosphotungstate and that with phosphotungstic acid. Although there is no reason to believe that the behavior of the ammonium phosphomolybdate treated sample should not be similar to its acid counterpart, experiments confirming this hypothesis

should be undertaken.

4. Results of the preliminary studies incorporating the phosphotungstic acid and its salt into cotton and rayon, as well as of evaluation of the efficiency of the retardant are encouraging. However, the procedure for applying these retardants to nylon and polyesters must be modified, before optimal loading and efficiency of the retardant will be achieved.

5. The fire protection afforded by the salts of phosphotungstic and phosphomolybdic acid in wooden roofing materials should be evaluated on a more extensive scale. It is desirable to find more effective ways to precipitate the salts interstitially; perhaps the partially dried, acid-treated shakes should be exposed to ammonia gas, or the samples should be treated with warm aqueous phosphotungstic acid solution to increase the depth of penetration; or the samples should be first treated with the phosphotungstic acid dissolved in a nonaqueous, but more wood-penetrating, medium and then exposed to ammonia gas. Once the optimal combination of concentration and depth of penetration is found, it will be necessary to test the weatherability of the treated shakes and their resistance to firebrands or thermal radiation from a nearby burning building, and to compare the results with those for treated unweathered shakes as well as shakes treated with standard known retardants both weathered and unweathered. The above experiments should be field tested where structural units, such as roof sections or full-scale buildings, can be employed in a more realistic manner.

Preliminary cost estimates for fireproofing exterior wooden surfaces are encouraging.

6. Comparison of the results of isothermal pyrolysis of cotton with those of α-cellulose suggests that there might be differences in the kinetics of decomposition of the two materials. These findings

should be supplemented by additional weight loss measurements of cotton, and comparison of the rate of monomer loss and the rate of change in the degree of polymerization of the two materials using at least three different temperatures higher than 276° C.

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