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The Effect of Various Organo-Phosphorous Compounds on the Thermal Degredation of Cellulose

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THE EFFECT OF VARIOUS ORGANO-PHOSPHOROUS COMPOUNDS

ON THE THERMAL DEGRADATION OF CELLULOSE

BY

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MASTER OF SCIENCE THESIS

OF

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ABSTRACT

The thermal decomposition products of cellulose treated with various organo-phosphorous compounds were investigated.

The function of a flame-retardant in cellulose is to favor the production of carbon and water rather than flammable tarry products which are formed in the thermal degradation of untreated cellulose. Furthermore, if the oxidation of the charred residue is directed toward the production of carbon monoxide rather than carbon dioxide, it is believed that the heat produced in this reaction would not be sufficient to sustain an afterglow when the flame has been removed.

A comparison was made between the amounts of char and tar produced and the efficiency of the retardants used. A correlation between the carbon monoxide-carbon dioxide ratio and the afterglow exhibited by treated cotton was made.

The results obtained support the theory that flame-resistant cellulose produces less flammable tars and more carbon monoxide than untreated cellulose. However, no significant differentiation as to the relative effectiveness of the various compounds investigated was possible.

It is suggested that further studies be completed on the various types of compounds exhibiting fire-retardancy to provide a more general theory of fire-resistant cellulose.

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I. INTRODUCTION

During the past few years considerable progress has been made in the development of methods for reducing the flammability of textile fabrics, particularly cotton fabrics. The increased interest in this problem was caused by the use of many incendiary type weapons in modern warfare. The need for efficient methods for producing flame-resistant military fabrics became all too apparent and several military projects were established to investigate this problem.

The first project was established in the Department of Chemical Engineering at Columbia University in 1942, under the sponsorship of the National Research Council Committee on Quartermaster Problems (1). The objectives of this project were:
(1) Improvement of existing flame-resistant treatments for cotton for temporary use; (2) investigation of the fundamental principles of flame retardancy, which included the study of the mechanisms by which flame-retardant chemicals function to decrease the combustibility of textile fabrics; and (3) search for more efficient flame-retardant agents and improved methods to provide a more satisfactory treatment of fabrics for military use.

As was the case with many developments and projects made necessary by war, the problem of producing flame-resistant fabrics for civilian use was of immediate interest to the consuming public. This is evidenced by

recent publicity regarding "torch sweaters" and other sportswear of high flammability. Several states have already adopted restrictive legislation regarding this hazardous situation, and have imposed rigid regulations on the manufacture and sale of such fabrics.

Many associated problems arise from the application of a flame-retardant to textile fabrics. Requirements other than the flame-retardant properties must be met. The treated fabric must not be injurious to the skin and must retain the qualities it possessed before treatment. The tensile strength must be maintained and care must be used not to cause stiffening. Many fire-retardants reduce the tear resistance of the fabric and have a detrimental effect on the dye. The clothing fabric must remain comfortable to the wearer, insofar as moisture, heat, and ventilation are concerned.

The injury caused the wearer of clothing which becomes ignited results from the thermal transfer of the heat evolved to the body. The heat produced by the thermal degradation of textiles of a cellulosic nature comes from a series of complicated reactions and may be summarized as follows (2):

(1) Flaming Source $\longrightarrow$ $\triangle H_1$

(2) Cellulose $\longrightarrow$ Decomposition Products + $\triangle H_2$

(3) Volatile Decomposition Products + $O_2 \longrightarrow CO_2 + H_2O + \triangle H_3$

(4) Solid Decomposition Products + $O_2 \longrightarrow CO + CO_2 + \triangle H_4$

The oxidation of the solid decomposition products is the process which is believed to propagate an afterglow when the flame has been removed. In this investigation the flame-resistance and effect on the afterglow of various organo-phosphorous compounds on cellulose was studied.

II. REVIEW OF LITERATURE

The exact mechanisms of the reactions involved in the degradation of cellulose are not yet fully understood because of their complex nature. It has been substantiated, however, that the thermal degradation of cellulose occurs in three steps (3). The primary reaction involves the initial decomposition at flame temperatures resulting in the formation of a charred residue composed mainly of carbon, a highly flammable tarry distillate, and a volatile fraction composed of water and gases. The second step is a rapid reaction which involves the cracking and flaming of the tarry distillate. A phenomenon known as afterglow is the final reaction. This reaction is a much slower decomposition which causes the oxidation of the charred residue resulting in an exothermic reaction which propagates a glow after the flame has been removed.

The charred residue is composed of carbonaceous material having much the same structure as the original cellulose and the decomposition products of the added flame retardant. The tarry constituents contain hydroxyl, methylene, methyl, carbonyl, ethylene and ester groupings as determined by their infrared absorption spectra. These products are in agreement with the theoretical considerations regarding the probable course of the disintegration of the cellulose molecule (4a). Little (5) found that the tars were practically insoluble in water, slightly soluble in isopropanol, and very soluble in acetone. The carbon and

hydrogen content appears to vary slightly depending on the chemical retardant added before combustion. The aldehyde content is affected in the same manner. Tars from cellulose treated with different retardants showed no appreciable differences in the rate of flaming. The function of an effective retardant would therefore not produce a pronounced change in the composition of the tar but rather reduce the amount of tar produced.

The volatile fraction consists of gases including carbon dioxide, carbon monoxide and some methane, and an aqueous distillate. The aqueous liquor contains aldehydes, ketones, furfural and pyroligeneous substances (6).

Heuser (7) reported that Ramsay and Chorley found the various phases in the thermal decomposition of cellulose take place in distinct steps. Water is produced at $200^{\circ}C.$, depending on the rate the temperature is increased. Above $200^{\circ}C.$, the tars begin to appear and the evolution of gases is initiated. At about $270^{\circ}C.$, the reaction becomes violent and no more decomposition products are formed. At this temperature the reaction becomes exothermal and it is believed that this is where the secondary and tertiary reactions take place. Further increase in the temperature causes a distillation of some of the products already formed and at $470^{\circ}C.$ the reaction ceases. Coppick (4b) found that the exothermic reaction accompanying the rapid formation of decomposition products does not occur in the absence of air. During pyrolysis, this reaction takes place isothermally. This

would indicate that at least part of the decomposition is caused by oxidative degradation.

Coppick (8) stated that the mechanism whereby a flame retardant becomes effective must be classified in one of three possibilities. The first is the retardation of the thermal decomposition of the cellulose, because without decomposition no flammable vapors can be produced. This retardation may be brought about by inhibition of the decomposition reaction by the addition of a negative catalyst or by the removal of an already present positive catalyst. The changes in the thermal conductivity properties of cellulose should also merit consideration as well as physical insulation of the fiber by a protective coating of the retardant.

The second possibility is the direction of the carbonaceous decomposition reaction products toward non-volative products. This reaction would mean that all of the carbon would be directed toward the elemental state without passing through any intermediate flammable stages.

$$(C_6H_{10}O_5)x \longrightarrow x6C + x5H_2O$$

The final possibility is that if volatile carbonaceous products must be produced, direction toward a highly oxidized, non-flammable type would be preferred. This reaction would require the addition of an oxidizing agent to take the place of the oxygen normally supplied by the air.

$$(C_6H_{10}O)x + x6O_2 \longrightarrow x6CO_2 + x5H_2O$$
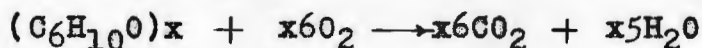
The many flame-resistant compounds and treatments available for textile fabrics may be classified on the basis of the chemical nature of the active ingredients, the mechanism by which they are believed to function, the permanence of the flame-resistant characteristics in terms of resistance to wet- and dry-cleaning operations, or the method of attachment to the fiber (9). Most of the retardants employed have been grouped according to these standards.

The compounds most generally regarded as flame retardants are inorganic salts which appear to function by the formation of a foam which serves as a blanket between the fabric and the flame. This group is composed of low-melting salts which form a foam with the decomposition products. Examples of this group are borax, aluminum sulfate, mixtures of borax and boric acid with and without added ammonium phosphates, borax and diammonium phosphate, and sodium phosphate-boric acid mixtures (9).

A less effective group of flame-retardants are water soluble inorganic acids and salts capable of liberating acids upon heating. Although these compounds are not as efficient as the previous group in preventing afterflaming, they are nevertheless more effective in preventing afterglow. Representatives of this group are sulfuric, sulfamic, boric, phosphoric, hydrochloric, hydrobromic, molybdic, and tungstic acids, their ammonium salts, and salts of organic bases such as urea, ethylenediamine, and the alkyl and alkylol amines (9).

The efficiency of these compounds results from their ability to furnish an acid or acid anhydride at the time of incipient flaming.

The organo-phosphorous compounds used in this investigation are believed to release phosphoric acid at flaming temperatures, and also catalyze the degradation of cellulose toward less flammable products. It has been shown that with the flame-resistant and glow-resistant fabrics of the phosphated type, the rate and temperature increase and the maximum temperature attained under the fabric compares favorably with similar data for asbestos paper or glass-asbestos fabric of similar thickness (3b). This thermal protection is directly attributed to the insulation provided by a combustion-resistant carbonaceous layer.

III. THE INVESTIGATION

A. OBJECT

The object of this investigation was to study the effects of various organo-phosphorous compounds on the thermal degradation of cellulose. The apparatus and experiments were designed to provide the following information:

1. The amount of charred residue and flammable tars produced from the combustion and pyrolysis of cellulose treated with various organo-phosphorous compounds.

2. A correlation between the products of the thermal degradation of cellulose and the effect on fire-retardancy of the added organo-phosphorous compounds.

3. The ratio of carbon monoxide to carbon dioxide produced in the oxidation of the charred residue from the pyrolysis of treated cellulose.

4. A correlation between the carbon monoxide-carbon dioxide ratio and the effect that the organo-phosphorous compounds have on the glow-resistance of cellulose.

5. Investigation of the possibility of one or more of these compounds directing the decomposition of cellulose toward the production of less flammable tars and a greater ratio of carbon monoxide to carbon dioxide.

6.   Investigation of what effect catalytic amounts of
     these retardants have on the fire-retardancy of
     cellulose and comparison of this effect with a
     larger add-on.

B. THEORETICAL DISCUSSION

A satisfactory mechanism for the thermal degradation of cellulose has not been substantiated, but it is known that the function of the flame-retardant is to favor the production of carbon and water rather than the decomposition to flammable tarry products which are favored in the degradation of untreated cellulose.

The tars produced from treated cellulose vary only slightly in composition with the tars from untreated cellulose. They appear to be of the same composition and are fairly similar in flammability. Therefore, the main effect of a retardant is not to alter the composition or the flammability of the tar, but to reduce the yield.

Gases from treated and untreated cellulose show no appreciable change in composition and the production of carbon dioxide does not vary. These results indicate that gases have no relation to the flammability of cellulose. This conclusion must not be confused with the relation of gases to afterglow.

An analysis of the resultant char showed that it is composed of 85 to 90 per cent carbon, small amounts of oxygen, hydrogen and ash constituted the remainder. The relative efficiencies of the various flame-retarding compounds are fairly closely related to their ability to convert the cellulose at flame temperatures to large yields of this non-volatile carbonaceous material. When 10 to 15 per cent of the effective retardants are added to

cotton, the carbon residue is increased from 10 to 40 per cent of the original cellulose. Further addition of the retardant has little if any effect on the amount of the char produced (3c).

Cellulosic materials have a tendency to exhibit a glow type of combustion after the flame has been extinguished. This afterglow is an exothermic reaction and is often more injurious than flaming itself. It is an important phase in the study of the thermal degradation of cellulose. The afterglow is caused by the oxidation of the resultant carbonaceous char. The propagation of the glow is believed to be caused by the high exothermicity of the reaction. The direction of this oxidation toward a less exothermic reaction would result in a decrease in afterglow.

The principal gases produced in the oxidation of carbon are carbon dioxide and carbon monoxide. The production of the former is a much more exothermic reaction. If the oxidation is promoted in the direction of carbon monoxide formation rather than of carbon dioxide, the heat of the reaction is reduced from 94.4 to 26.4 kilocalories per mole (4c):

$$C + O_2 \longrightarrow CO_2 \quad \Delta H = 94.4 \text{ kc.}$$
$$C + \tfrac{1}{2}O_2 \longrightarrow CO \quad \Delta H = 26.4 \text{ kc.}$$
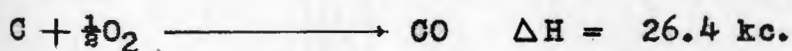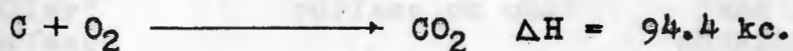
These data indicate that the first reaction is the one that sustains the glow and the second is of insufficient

exothermicity to propagate afterglow after the flame has been removed.

The phosphoric acid released from the organo-phosphorous compounds at flaming temperatures is believed responsible for the decreased exothermic production of carbon monoxide. The mechanism favoring this reaction may involve changes in energy barriers (heats of activation) for the two reactions or it may proceed by the following reactions (4c):

$$2H_3PO_4 + 5C \longrightarrow 2P + 5CO + 3H_2O$$
$$4P + 5O_2 \longrightarrow 2P_2O_5$$
$$P_2O_5 + 5C \longrightarrow 2P + 5CO$$

It is also possible that the phosphate may be absorbed on the active centers of the carbon resulting in a decrease in activity. The surface sorption may be similar chemically to the graphitic acid type, such as graphitic bisulfate or fluoride. The following diagrams illustrate such a reaction (4d):

cellulose "micellar" surface

normal active rurface on char

"inactivated" surface due to a phosphate retardant
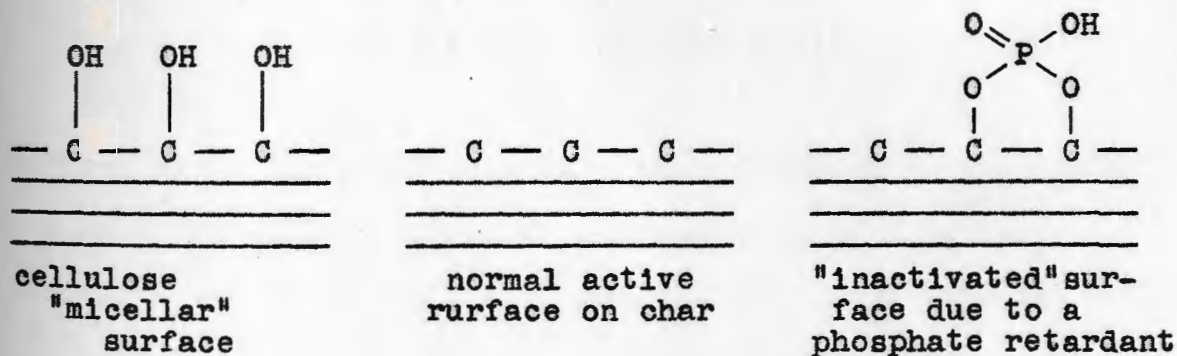
The method used for studying the products of the combustion of cellulose is similar to the procedure used by Coppick (4e).

16.

It was found that the temperature attained by burning a fabric is approximately 500°C. and complete combustion of a sample required less than 15 minutes. A rate of 100 cc. of air per minute was sufficient for complete oxidation. The combustion reactions in this investigation were performed at a temperature of 500°C. Each sample was allowed to burn 15 minutes. In order to insure complete combustion, an air flow of 180 cc. per minute was maintained.

The pyrolysis procedure used was similar to that described by Coppick (4f) with a modified pyrolysis tube. The experimental conditions were 500°C., 20 mm. of mercury and 15 minutes pyrolysis time.

C. APPARATUS AND MATERIALS

1. Absorbent cotton, U.S.P. sterile, was used in all experiments. Cotton is approximately 91 per cent cellulose.

2. The following retardants were investigated:

   Modified Triallyl Phosphate

   Brominated Triallyl Phosphite

   Brominated Modified Triallyl Phosphate

   Brominated bis-Allyl, n-Butyl Phosphate

   Brominated Aniline Triallyl Phosphite

3. The combustion apparatus as shown in Figure 1. consisted of pyrex glass tubing, seven-eighths by eight inches, constricted to approximately three-eights of an inch one third of the distance from the end to hold the cotton sample. This combustion tube was connected to a trap which was immersed in a salt-ice bath. Air was drawn through the system by a water aspirator. The rate of flow was measured with a dibutyl phthalate flow meter.

4. The pyrolysis apparatus as shown in Figure 2. consisted of a pyrex glass tube, three-fourths by six inches, which was connected to a trap immersed in a salt-ice bath. The system was evacuated by a water aspirator. The pressure was regulated and measured with a standard mercury closed manometer.

5. The oxidation apparatus as shown in Figure 3. consisted of a three inch quartz boat enclosed in a seven-eighths

by fourteen inch length of pyrex glass tubing. Dry, $CO-$ and CO_2- free air was passed through the oxidation chamber. The rate of flow was regulated by a dibutyl phthalate flow meter.

6. The electric furnace used in all experiments was composed of a one by eight inch length of quartz tubing around which was wound No. 18 Chromel-A resistance wire. This heater was covered with approximately one inch of asbestos.

7. An Electric Pyrometer was used to regulate the temperature.

8. A Standard Orsat Gas Analysis apparatus was used for the analysis of the gases in the oxidation procedure.

19.
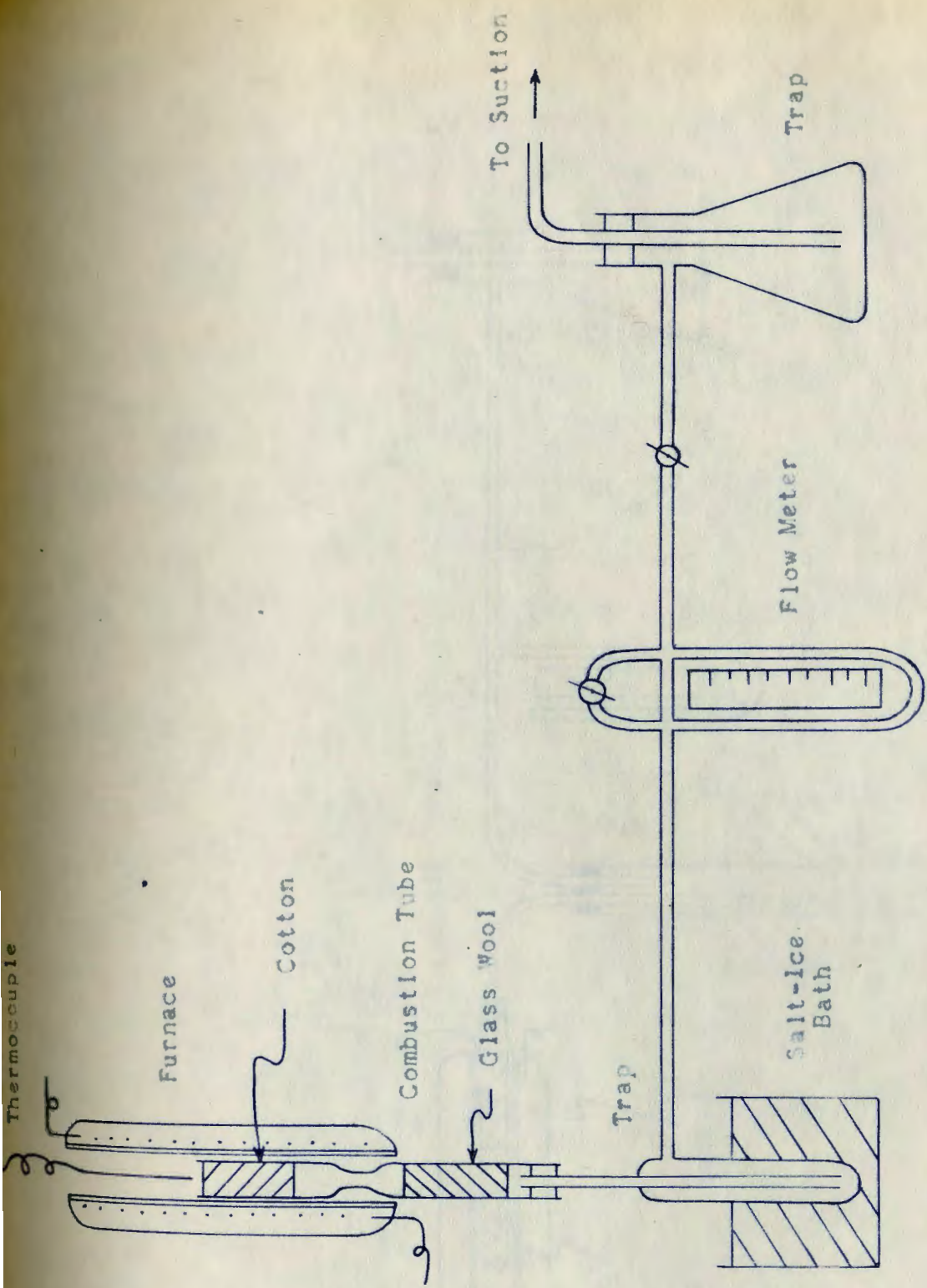
FIGURE 1. COMBUSTION APPARATUS
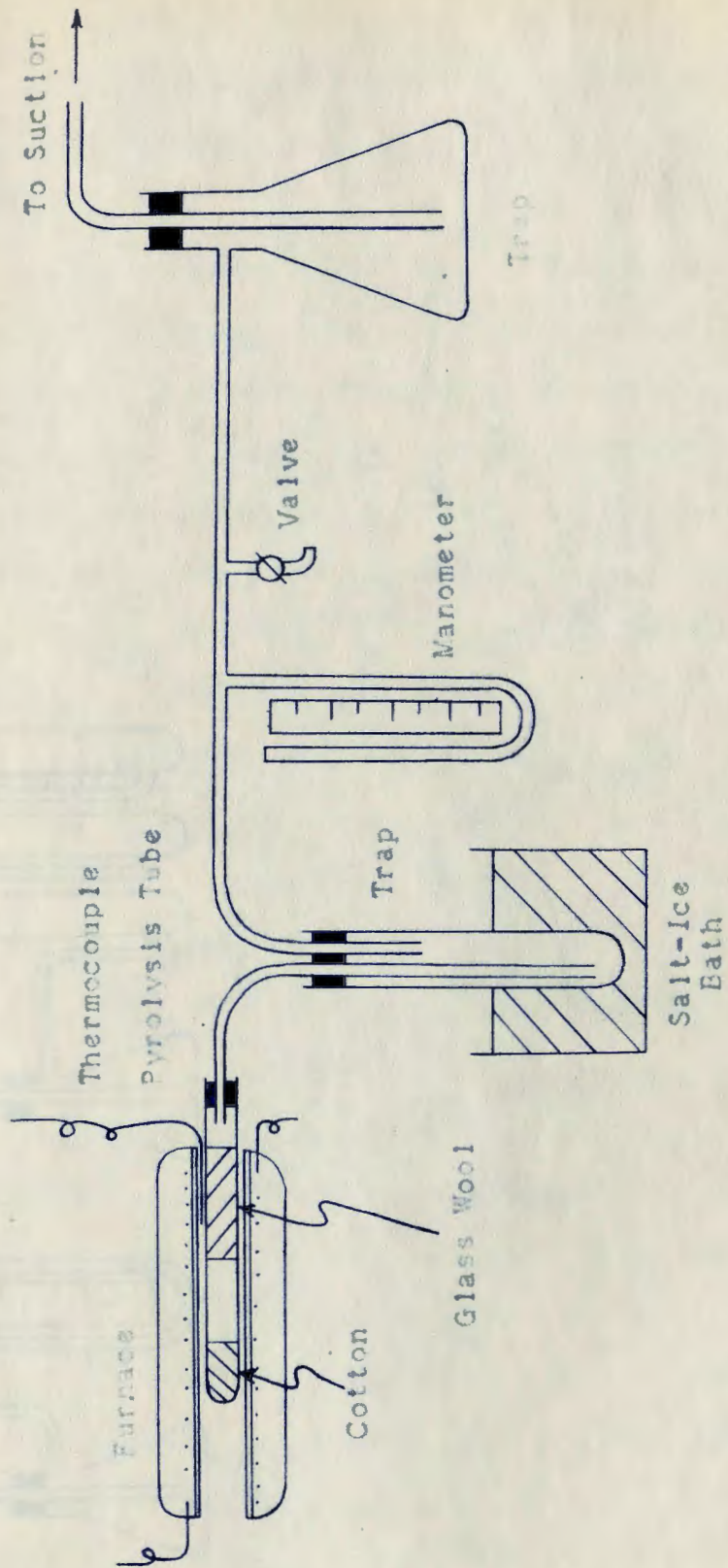
FIGURE 2. PYROLYSIS APPARATUS

A. Trap
B. Flow Meter
C. NaOH
D. $CaCl_2$
E. Drierite
F. Ascarite
G. Electric Furnace
H. Pyrex Tube
I. Boat
J. To Orsat Gas Analyzer
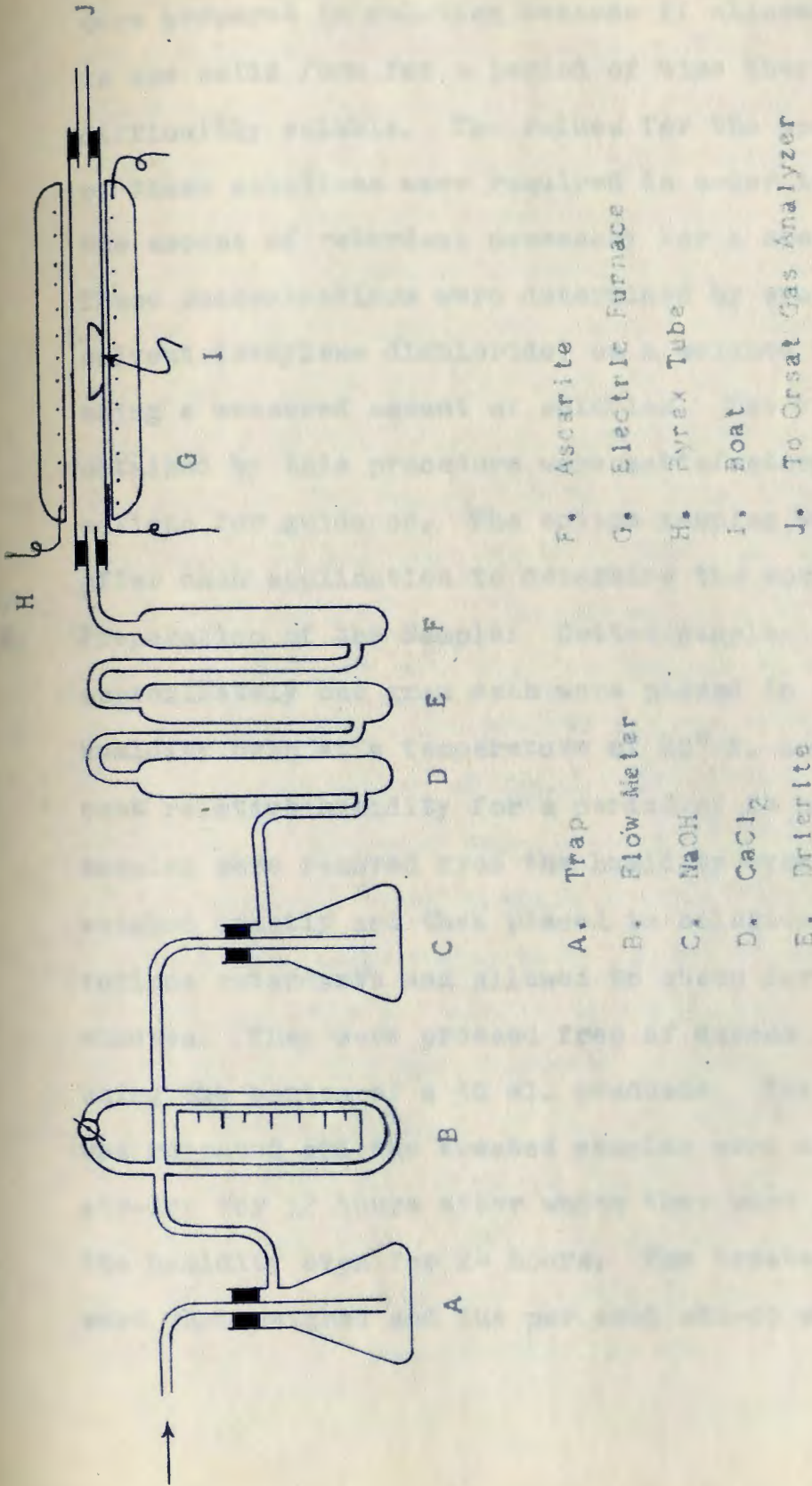
FIGURE 3. OXIDATION APPARATUS

D. PROCEDURES

1. Preparation of the flame-retardant: The retardants were prepared in solution because if allowed to stand in the solid form for a period of time they become difficultly soluble. The values for the concentrations of these solutions were required in order to calculate the amount of retardant necessary for a specific add-on. These concentrations were determined by evaporating the solvent (ethylene dichloride) on a weighed watch glass using a measured amount of solution. The values obtained by this procedure were satisfactory approximations for guidance. The cotton samples were weighed after each application to determine the correct add-on.

2. Preparation of the Sample: Cotton samples of approximately one gram each were placed in a constant humidity oven at a temperature of 80° F. and 65 per cent relative humidity for a period of 24 hours. The samples were removed from the humidity oven and weighed exactly and then placed in solutions of the various retardants and allowed to steep for a few minutes. They were pressed free of excess retardant using the botton of a 50 ml. graduate. This procedure was repeated and the treated samples were allowed to air-dry for 12 hours after which they were replaced in the humidity oven for 24 hours. The treated samples were then weighed and the per cent add-on was calculated.

3. Combustion Method: Approximately one gram of pyrex glass wool was inserted in the longer end of the combustion tube and dried at 120°C. for 12 hours. After weighing the tube containing the glass wool, the treated cotton was placed in the upper end of the tube. The end of the tube containing the sample was inserted into the electric furnace and allowed to burn for 15 minutes at 500°C. with a flow of air at 180 cc. per minute. The combustion tube was removed and allowed to cool. The char was easily removed to a weighing bottle. The weighing bottle containing the char and the combustion tube, which now contained the flammable tars entrapped in the glass wool, were both dried at 120°C. for 12 hours. The weights of the char and the tars were then determined by weighing.

4. Pyrolysis Method: The treated cotton sample was placed in the bottom of the pyrolysis tube and the remainder of the tube was filled with glass wool, with a space of approximately one-half inch between the sample and the glass wool. This procedure was followed to hold the sample in place when the vacuum was applied. The tube was then connected to the system and evacuated to 20 mm. of mercury and inserted into the horizontal electric furnace, which was controlled at 500°C. After 15 minutes pyrolysis time, the tube was removed and allowed to cool. The char was removed by breaking the tube and was placed in a

weighing bottle and dried at 120°C. for 12 hours.
The weight of the char was then determined.

5.   Oxidation Method: The residual char from the
pyrolysis of the cotton sample was placed in a
quartz combustion boat in the oxidation chamber.
The chamber was heated to 500°C. with a continuous
flow of dry, CO- and CO_2- free air (180 cc. per
minute). After five minutes oxidation, 100 ml. of
resulting gas was collected directly in the Orsat
Gas Analysis apparatus. The gas sample was analyzed
for carbon-dioxide, oxygen and carbon monoxide using
potassium hydroxide, Oxsorbent, and ammoniacal
cuprous chloride respectively as absorbents. The
CO/CO_2 ratio was calculated.

E. RESULTS

Table 1. **Char-Tar Ratio of Cellulose Treated with Catalytic Amounts of Flame-Retardants**

Compound	Char, %	Tar, %	Char/Tar
Blank	*	43.36	------
Modified Triallyl Phosphate	3.58	18.69	0.1904
Brominated Triallyl Phosphite	1.49	25.04	.0595
Brom. Modified Triallyl Phosphate	1.49	24.33	.0612
Brom. bis-Allyl, n-Butyl Phosphate	1.67	20.78	.0803
Brominated Aniline Triallyl Phosphite	1.35	24.67	.0548

Table 2. **Char-Tar Ratio of Cellulose Treated with 15-25% Add-on of Flame-Retardants**

Compound	Char, %	Tar, %	Char/Tar
Blank	*	43.36	------
Modified Triallyl Phosphate	15.93	19.51	0.8165
Brominated Triallyl Phosphite	11.52	18.41	.6257
Brom. Modified Triallyl Phosphate	9.55	16.16	.5909
Brom. bis-Allyl, n-Butyl Phosphate	11.91	16.32	.7297
Brominated Aniline Triallyl Phosphite	15.54	17.34	.8967

(*) Impossible to recover char.

Table 3. Char-Volatiles and CO-CO$_2$ Ratio of Cellulose
Treated with Catalytic Amounts
of Flame-Retardants

Compound	Char, %	Char/ Vols.	CO, %	CO$_2$, %	CO/CO$_2$
Blank	7.80	0.0850	7.8	8.2	0.947
Modified Triallyl Phosphate	16.62	.1993	15.4	4.6	3.348
Brominated Triallyl Phosphite	18.23	.2229	8.8	5.0	1.760
Brom. Modified Triallyl Phosphate	19.58	.2434	12.5	5.4	2.314
Brom. bis-Allyl, n-Butyl Phosphate	16.93	.2038	15.8	5.3	2.981
Brominated Aniline Triallyl Phosphite	16.62	.1993	15.8	5.4	2.926

Table 4. Char-Volatiles and CO-CO$_2$ Ratio of Cellulose
Treated with 10-20% Add-on of
Flame-Retardants

Compound	Char, %	Char/ Vols.	CO, %	CO$_2$, %	CO/CO$_2$
Blank	7.80	0.0850	7.8	8.2	0.947
Modified Triallyl Phosphate	33.45	.5026	7.9	6.0	1.316
Brominated Triallyl Phosphite	36.22	.5679	9.0	6.8	1.550
Brom. Modified Triallyl Phosphate	32.09	.4726	9.3	6.0	1.729
Brom. bis-Allyl, n-Butyl Phosphate	32.68	.4854	12.8	7.4	1.729
Brominated Aniline Triallyl Phosphite	36.11	.5636	12.4	7.4	1.610

IV. DISCUSSION OF RESULTS AND CONCLUSION

The combustion of cellulose treated with catalytic amounts (approximately one per cent) of the retardants used in this investigation gave no indication as to the relative effectiveness of the compounds. It was demonstrated that as a group these organo-phosphorous compounds exhibited promise as flame-retardants. The flammable tars produced by the treated samples were reduced by approximately one-half as compared to the untreated sample (Table 1).

The cotton samples treated with an increased add-on ranging from 10 to 20 per cent decreased the production of flammable tars by approximately 60 per cent (Table 2). The charred residues showed a marked increase in weight as compared to the chars from samples which were treated with catalytic amounts of retardant. This increase in weight is probably caused by the decomposition products of the added retardant and would not serve as a correct indication of the efficiency of the retardant. The relative effectiveness of the various retardants was not apparent.

According to the works of Esteve and Laible (10), the brominated tri-allyl phosphate was the outstanding flame-retardant in the group of compounds investigated. There was no evidence obtained substantiating this conclusion in the data obtained from the combustion experiments.

Oxidation of the char obtained from the pyrolysis of cellulose treated with catalytic amounts of retardants exhibited a marked increase in the production of carbon monoxide when compared with the char from the untreated sample (Table 3). A comparison of these data and the results of the afterglow tests (10) on fabric treated with similar add-ons showed no correlation. The treated fabric exhibited considerable afterglow, comparable to an untreated sample.

Similar results were obtained from samples treated with 10 to 20 per cent add-on (Table 4). There was no correlation with similarly treated fabrics which exhibited varying degrees of afterglow.

The char-volatiles ratio was no indication of effectiveness because of the added weight of the decomposition products of the retardant.

The results obtained from these experiments provide evidence supporting the theory that flame-resistant cellulose, when compared with untreated cellulose, produces less flammable tars and an increased amount of carbon monoxide. There was no significant differentiation possible as to relative effectiveness of the various compounds investigated. This lack of correlation suggests that these methods of evaluating the relative effectiveness of other fire-retardants are not conclusive.

It is suggested that studies be made as to the types of compounds exhibiting fire-retardancy. A theory that

should be expanded requires compounds that are capable
of hydrogen bonding. If these compounds were absorbed
by the cellulose fiber there is the possibility that
they might combine with the hydroxyl groups and direct
the degradation of cellulose toward larger, less volatile
fragments, e.i., the phosphoric acid released from the
organo-phosphorous compounds:

$$\begin{array}{c} O^- \quad O^{=}\text{-----}H\text{-}O\text{-} \\ H \\ \text{-}O \quad\quad P^+ \\ \quad\quad H\text{-}O \quad O^{=}\text{-----}H\text{-}O\text{-} \end{array}$$
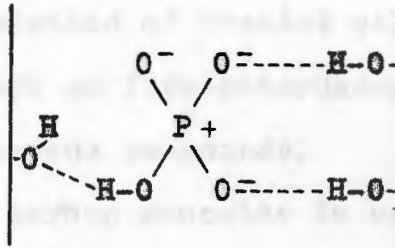
**Hydrogen Bonding Between
Phosphate and Cellulose Molecules**

V. SUMMARY

1. The charred residue and flammable tars produced from the combustion and pyrolysis of cellulose treated with various organo-phosphorous compounds were investigated.

2. The treated cellulose produced an increase in the amount of char and a lesser amount of flammable tars when compared with an untreated sample.

3. There was no correlation between the products of the thermal degradation of treated cellulose and the relative effect on fire-retardancy of the added organo-phosphorous compounds.

4. The ratio of carbon monoxide to carbon dioxide produced in the oxidation of the charred residue from the pyrolysis of treated cellulose was determined.

5. The treated cellulose produced an increase in the carbon monoxide-carbon dioxide ratio when compared with an untreated sample.

6. There was no correlation between the carbon monoxide-carbon dioxide ratio and afterglow of the treated samples.

7. There was no compound in the group of retardants investigated that was outstanding in directing the decomposition of cellulose toward the production of less flammable tars and a greater ratio of carbon monoxide to carbon dioxide.

8. When the retardants investigated were applied in catalytic amounts there was little effect observed on

the fire-retardancy of cellulose.

9. These methods, flammable tar formation and carbon
   monoxide-carbon dioxide ratio, for evaluating the
   relative effectiveness of fire-retardant for cellulose
   are not conclusive.

10. It is recommended that further studies be completed on
    the type of compounds imparting fire-retardant
    properties when applied to cellulose in order to
    develop a more general theory.

Table 1a.   Experimental Data Summarized in Table 1.

Compound	Add-on, %		Char, %		Tar, %	
	1x	2x	1x	2x	1x	2x
Blank	------	------	*	*	43.54	43.18
Modified Triallyl Phosphate	1.25	1.24	3.87	3.28	18.39	18.99
Brominated Triallyl Phosphite	1.11	1.12	1.09	1.09	23.39	24.09
Brom. Modified Triallyl Phosphate	1.02	1.01	1.64	1.34	23.83	24.63
Brom. bis-Allyl, n-Butyl Phosphate	1.35	1.36	1.51	1.03	29.83	30.63
Brominated Aniline Triallyl Phosphite	0.89	0.89	1.91	1.79	26.44	26.80

APPENDIXES

Table 2a.   Experimental Data Summarized in Table 2.

Compound	Add-on %		Char, %		Tar, %	
	1x	2x	1x	2x	1x	2x
Blank	------	------	*	*	43.54	43.18
Modified Triallyl Phosphate	23.65	23.73	15.74	16.12	79.84	19.18
Brominated Triallyl Phosphite	15.65	16.19	11.10	11.94	18.82	18.80
Brom. Modified Triallyl Phosphate	19.87	14.19	9.45	9.64	16.43	16.69
Brom. bis-Allyl, n-Butyl Phosphate	21.02	20.06	12.20	11.66	15.91	16.73
Brominated Aniline Triallyl Phosphite	17.02	16.33	15.95	15.13	18.91	17.97

(*) Impossible to recover char.

Table 1a.   Experimental Data Summarized in Table 1.

Compound	Add-on, %		Char, %		Tar, %	
	1.	2.	1.	2.	1.	2.
Blank	-----	-----	*	*	43.54	43.18
Modified Triallyl Phosphate	1.25	1.24	3.87	3.29	18.39	18.99
Brominated Triallyl Phosphite	1.11	1.12	1.09	1.89	25.39	24.69
Brom. Modified Triallyl Phosphate	1.02	1.01	1.64	1.34	23.83	24.83
Brom. bis-Allyl, n-Butyl Phosphate	1.35	1.36	1.51	1.83	20.83	20.63
Brominated Aniline Triallyl Phosphite	0.89	0.83	1.91	1.79	24.44	24.80

Table 2a.   Experimental Data Summarized in Table 2.

Compound	Add-on %		Char, %		Tar, %	
	1.	2.	1.	2.	1.	2.
Blank	-----	-----	*	*	43.54	43.18
Modified Triallyl Phosphate	23.65	23.73	15.74	16.12	19.84	19.18
Brominated Triallyl Phosphite	15.65	16.19	11.10	11.94	18.82	18.00
Brom. Modified Triallyl Phosphate	13.87	14.19	9.46	9.64	16.23	16.09
Brom. bis-Allyl, n-Butyl Phosphate	21.02	20.06	12.20	11.62	15.91	16.73
Brominated Aniline Triallyl Phosphite	17.01	16.35	15.95	15.13	16.91	17.77

(*) Impossible to recover char.

Table 3a.   **Retardant Used in the Gas Analyses**

Compound	Catalytic Amounts,%	10-20% Add-on
Modified Triallyl Phosphate	1.081	13.53
Brominated Triallyl Phosphite	1.723	18.68
Brom. Modified Triallyl Phosphate	0.929	13.09
Brom. bis-Allyl, n-Butyl, Phosphate	1.317	17.08
Brominated Aniline Triallyl Phosphite	1.421	11.29

VI. ACKNOWLEDGEMENTS

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