

R58-39

RECENT WORK ON THE MECHANISM OF THE THERMAL DEGRADATION OF CELLULOSE* —A Review of Work Sponsored by the QMC—

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FOREWORD

DUE to the need for textile fabrics, which offer improved protection against flame and thermal hazards, the QMC has sponsored various research projects on the thermal degradation of cellulosic materials. The results of this research led to the development of several additive-type flame-retardant treatments and finally to actual modifications of the cellulose molecule itself. This report will attempt to summarize the steps leading to these developments and to point out the future course of work to be followed.

DISCUSSION

BACKGROUND—In the past fifteen years considerable effort has been expended in an effort to determine the mechanism of the thermal degradation of cellulose, cellulose derivatives, and of cellulose treated with flame-retardant compounds. Most of this research was conducted under the sponsorship of the U S Government by such agencies as the Quartermaster Corps, Navy, Department of Agriculture, Chemical Corps, and the Air Force. As a basis for this work, data were available on some of the products of the destructive distillation of cellulose. This very early work was not continued because of the complexity of the products and the variance in these products produced by different conditions of thermal degradation. Instead, the investigators were mainly concerned with determining major differences between the mechanism of the degradation of untreated cellulose and that of cellulose treated with various flame and glow retardants.

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Recent research work on the mechanism of the thermal degradation of cellulose is reviewed with emphasis on the practical application of this information. A theory was postulated in which levoglucosan was the important intermediate in the thermal degradation of cellulose responsible for the flaming reaction. Studies of the products of the pyrolysis and combustion of cellulosic materials added credence to the theory. Modified cellulose materials were then prepared which, in accordance with the theoretical predictions, showed significant glow and flame resistance. The studies leading up to this development and the future course of work are reviewed in the light of current requirements for protection against flame and thermal hazards.

EARLY PYROLYSIS WORK

In the investigations conducted at Columbia University during World War II, it was found that flame-retardant-treated fabrics produced much smaller percentages of tars than that characteristic of untreated fabric. An inverse correlation was possible, although not absolute, between the amount of tar liberated from a fabric flame-retardant combination and the relative effectiveness of the retardant in slowing down or inhibiting completely the flaming reaction (1). These results allowed one to screen flame retardants to some extent on the basis of their char/tar ratios.

A second difference in the degradation of treated and untreated fabrics was noted in the gas phase. Those treatments which furnished glow-retardancy to the fabric also produced a much different CO/CO₂ ratio in the gas phase. Even 1% of an effective glow retardant reduces the CO₂ evolution from 2.5 to 0.8 grams per gram of char when samples so treated are pyrolyzed at 550°C (1). Parks and coworkers at the University of Rhode Island found that effective glow retardants markedly

altered the CO/CO₂ ratio in the gaseous products of decomposition as shown in Table I.

TABLE I

Treatment	% CO ₂	% CO	Ratio CO/CO ₂
Blank-untreated fabric	12.1	1.3	.11
Sodium tetraphosphate	4.0	16.0	4.0

Sodium tetraphosphate inhibits afterglow when applied to fabric. This apparent correlation between the CO/CO₂ ratio and the glowing phenomenon can be explained thermodynamically by the use of the heats of formation of carbon monoxide and carbon dioxide.

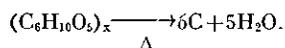
	Heat Evolved
$C + O_2 \longrightarrow CO_2$	94.4 Kcal
$C + \frac{1}{2} O_2 \longrightarrow CO$	26.4 Kcal

It appears that the heat liberated from the incomplete combustion of carbon to carbon monoxide favored by good glow retardants is not sufficient to sustain the glowing reaction.

DEVELOPMENT OF FLAME RETARDANTS — Many inorganic materials were investigated for their flame-retardant properties as determined by these two criteria and by their actual performance. The problem was then one of producing a permanent treatment incorporating the constituents producing these desirable effects of flame retardance and glow resistance. One method of accomplishing this objective was to incorporate the better inorganic agents in a binder which could be applied to the cloth. A second method involved attachment of the flame-retardant groups to the cellulose molecule itself. This method usually resulted in excessive degradation to the fabric. The third most successful method involved the application of phosphorus

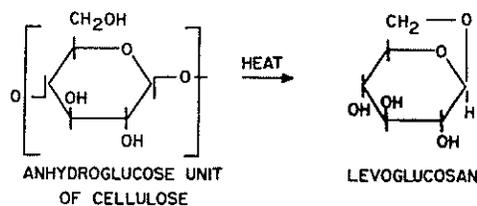
polymers to the cloth. As these polymers were organic they possessed the disadvantage of producing more tars than their inorganic analogs. To combat this deficiency, bromine was introduced so that, if the production of tars was not limited sufficiently, at least these tars would be rendered less combustible. Flame retardants such as brominated polymerized triallyl phosphate and triallyl phosphate — bromoform emulsion polymer were developed on this basis. In addition, other phosphorus polymers were developed, which, apparently, did not require bromine, such as Phoresin III and THPC. These developments and the development of other related flame retardants have been discussed in detail in papers by McQuade of the Quartermaster Corps (14, 15).

SOUTHERN REGIONAL RESEARCH LABORATORY THEORY — Reid, Schuyten, and Weaver at the Southern Regional Research Laboratory were dissatisfied with the theoretical aspects and explanations of flame retardancy. Although flame retardants were known to decrease tar formation, there was no one chemical theory to account for this fact. For this reason the group at Southern Regional Research Laboratory postulated a theory of dehydration and accelerated gas production (11). The first portion of this theory is based on the knowledge that the most favorable degradation path would be dehydration to water and carbon as illustrated by the following equation:



The strong Lewis acids necessary for dehydration by a carbonium ion mechanism would be formed by the flame retardant at the temperature of burning cellulose. There is evidence for this portion of the theory in that many effective flame retardants liberate Lewis acids and/or dehydration catalysts at flaming temperatures. A list of agents used as Friedel Crafts catalysts (usually Lewis acids) includes many compounds effective as flame retardants. For example, phosphoric acid, zinc chloride, titanium tetrachloride, titanium trichloride, and aluminum bromide have been used as Friedel Crafts catalysts. Many of these same agents entered into flame retardants used at one time or another. Zinc chloride and phosphoric acid may be used directly as flame retardants. As further evidence of this theory, Esteve and coworkers at the University of Rhode Island found that water was formed in greater amounts from

STEP 1 - FORMATION OF LEVOGLUCOSAN



STEP 2 - DEGRADATION OF LEVOGLUCOSAN

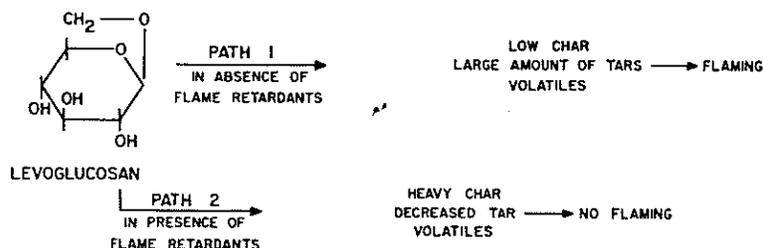


Figure 1
Levoglucosan theory

the pyrolysis of cloth samples treated with an effective fire retardant than in the case of cloth which was untreated or treated with an ineffective flame retardant (16). Table II illustrates this point.

TABLE II
Water content of volatile products from the pyrolysis of cotton cloth at 400°C

Additive	Water in volatile products (%)	Flame-retardant properties
None-untreated	18	none
19% Brominated TAP	33	good to excellent
14% TAP-CHCl ₃ (chain transfer polymer)	30	good
7% Diallyl melamine	19	none

The second portion of this theory, accelerated gas production, is based on the relative rates of degradation of untreated and flame-retardant-treated fabric. Fabric treated with an effective flame retardant degrades at a much more rapid rate than untreated fabric and as a consequence the volatile products are liberated in more concentrated form. It is postulated that this high concentration of volatiles (flammable or nonflammable) inhibits the flaming reaction. This theory is credible because many authors have shown that inflammable gases are often not flammable when present in high enough concentrations, especially when halogen-containing molecules are also present (23, 24, 25). An additional factor is that the volatiles from flame-retardant-treated cellulose are given off at a lower temperature, which may be below the ignition point (30).

A REAPPRAISAL OF THE PROBLEM — Two or three years ago it was decided that the work on the development of flame retardants suffered from two deficiencies. The first was that flame retardants which possessed desirable properties in flame tests and under usual flame hazards possessed much less desirable properties under high-energy, very fast degradations. It was further found that these flame-retardant-treated fabrics, which possessed favorable char/tar ratios under long-time degradations, produced considerably more tars as the rate of degradation was increased. These tars, although of limited flammability, may have aided the transfer of considerable heat through a fabric system to the skin adding to the burn produced.

The second deficiency was that the mechanism work that had been conducted was no longer leading to newer-type fire retardants. Instead, selection was made empirically by testing various resinous phosphates for permanency and ease of application. It was thought that fundamental knowledge of the actual mechanisms involved in the pyrolysis and combustion of cellulose would be required in order to prepare better flame retardants. For both objectives the best approach would be to determine the amount and chemical nature of the products from the degradation of untreated and flame-retardant-treated cellulose.

Several contracts were obtained with educational and scientific installations to cover various approaches to these problems. The contractors included Textile Research Institute, University of Pennsylvania, University of Rhode Island, National Bureau

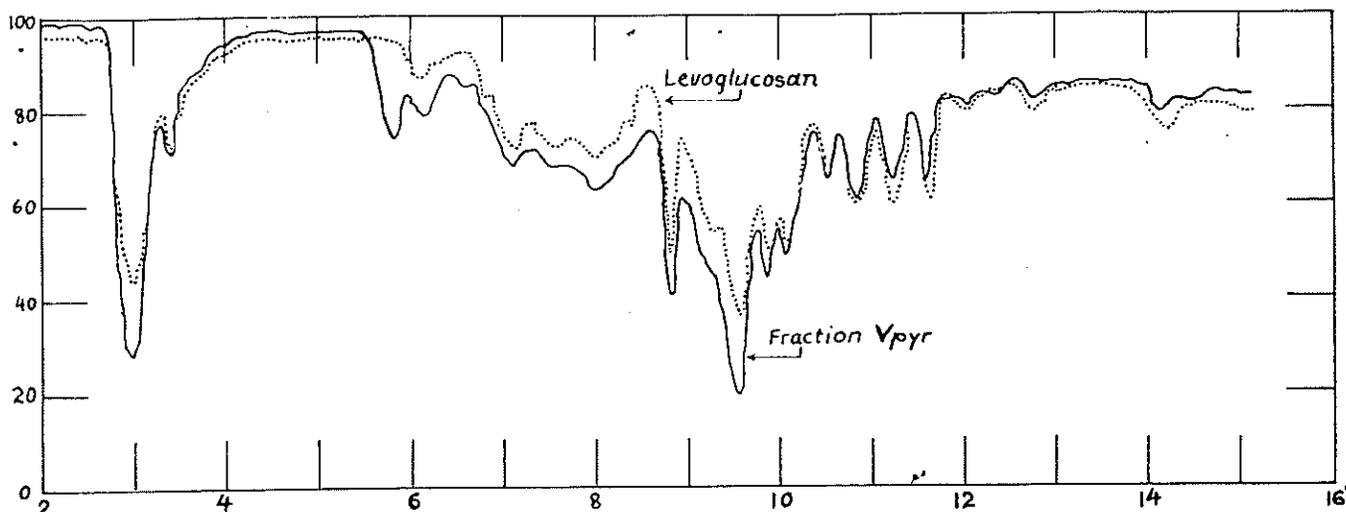


Figure 2
Infra-red spectra of tar fraction, V_{pyr} , and of levoglucosan

of Standards, and Southern Regional Research Laboratory. These approaches included studies under aerobic and anaerobic conditions, using fast and slow rates of degradation. The principal accomplishments of this contract work follow.

EFFECT OF RATE OF DEGRADATION—The group at the University of Rhode Island found that the char/tar ratio characteristic of a given flame-retardant treatment was not a constant figure. As the rate of degradation was increased, the amount of tar produced also increased and the amount of char or residue remaining decreased (20). The results obtained from the degradation of three fire-retardant treatments are given in Table III.

TABLE III
Effect of rate of degradation upon char/tar formation

	Furnace block decomposition				Radiant energy (6 secs)	
	Slow 400° C		Fast 400° C		Char	Tar
Untreated	21%	46%	18%	50%	9%	44%
Brominated TAP	41%	18%	34%	38%	18%	40%
THPC	49%	17%	44%	20%	30%	28%
Phoresin III	51%	16%	45%	21%	27%	33%

The radiant energy decompositions were conducted using a tungsten lamp source capable of delivering 5.3 cal/cm²/sec and a flow of nitrogen equal to 2600 cc/min. The tars from the degradation of 25 replicate samples were combined in each run. Chars given are also the average of 25 samples (20). This information was considered to be a possible explanation for the previous field observation that flame retardants which proved to be satisfactory for thermal hazards of long duration were not completely satisfactory for protection against the

more modern thermal hazards of short duration.

The same treatments which were evaluated at the University of Rhode Island, using the tungsten lamp heat source, were also degraded at the Quartermaster Laboratories in Natick using the carbon arc. The brominated TAP treatment was found to give the lowest temperature rise under the conditions of testing. The amount of tar driven through the fabric to the backing or underlayer was also lower for this treatment (22). This work illustrates the importance of the heat transferred by the tarry distillate from the degradation of flame-retardant-treated cellulose on the thermal protection problem.

LEVOGLUCOSAN THEORY—Another important result of this contract work was the crystallization and partial confirmation of a theory of the thermal degradation of cellulose advanced by Esteve and his coworkers (2) at the University of Rhode Island based upon the general mechanism proposed by Tamaru (34). This theory was based on the importance of an intermediate and final product of the degradation of cellulose, levoglucosan, which was thought to be the principal source of the combustible products from the degradation of cellulose (2). This compound, 1,6-anhydro-B-D-glucopyranose, had previously been shown to be a pyrolysis product of pure cellulose as far back as 1918 by Pictet and Sarasin (3). Esteve and Gollis found that, in the presence of a flame retardant, authentic samples of levoglucosan were thermally degraded to a heavier char than when the levoglucosan was degraded alone (2). It was proposed by Pacsu and Schwenker of Textile Research Institute (8, 17) that, instead of using an additive treatment to catalyze the

TABLE IV
Degradation products of untreated cellulose

Fraction	Composition
V_{pyr}	tar
V_{15}	86% water, 12% formaldehyde, 1% methanol, 1% acetone
V_{10}	CO ₂
V_{100}	CO

degradation of levoglucosan to char, it might be advantageous to determine the possibility of chemically modifying the cellulose so as to inhibit the formation of this intermediate altogether. The so-called levoglucosan theory is shown diagrammatically in Figure 1.

EXPERIMENTAL WORK SUPPORTING THEORY—In order to investigate this theory outlined in Figure 1 and to practically apply the results to the preparation of fabric possessing flame and glow resistance, it was first necessary for the Textile Research Institute group to develop a satisfactory method of analysis for levoglucosan. Untreated cellulose was thermally degraded at temperatures from 350-370°C using an oxidizing atmosphere of 180-200 cc of air per minute. The products were collected at 0°C. Several products previously unreported were found, including formaldehyde, glyoxal, glycolic acid, lactic acid and either formic or acetic acid. The major products were water and levoglucosan. The levoglucosan was qualitatively determined using paper chromatography and comparing the R_f value* of the unknown with that of an authentic sample of levoglucosan. For quantitative determination, the levoglucosan was converted to D-glucose by hydrolysis with dilute sul-

*The R_f value =
Distance travelled by component
Distance travelled by solvent front

furic acid, isolated by paper chromatography, and finally determined by iodimetric titration. The average amount of levoglucosan obtained from the pyrolyzates was 12.5%. The presence of levoglucosan in the pyrolyzates was confirmed by studies which were conducted at the National Bureau of Standards at the same time. Untreated cellulose was pyrolyzed in a vacuum and the products separated into various fractions. These fractions were designated as volatile at the temperature of pyrolysis (V_{pyr}), volatile at 25° (V_{25}), volatile at -80°C (V_{-80}), and volatile at -190°C (V_{-190}). The approximate composition of these fractions is given in Table IV.

The tarry fraction, V_{pyr} , was shown to be principally levoglucosan by means of molecular-weight determination and infrared analysis. (Figure 2).

Oxidized cellulose was first pyrolyzed in air at Textile Research Institute. Oxidized cellulose is prepared from the oxidation of cellulose with nitrogen tetroxide, which results in the oxidation of the primary alcohol group at the No. 6 carbon of the anhydroglucose unit of cellulose to carboxyl. (Figure 3A). According to Pacsu and Schwenker (8, 17, 35), such a modification would be expected to block the formation of levoglucosan so that a different mechanism of degradation would become operative. Pyrolysis of oxidized cellulose in vacuum was subsequently studied at National Bureau of Standards. The results obtained from both groups confirmed the proposed effect of such modification. Pacsu and Schwenker at Textile Research Institute found that the percentage of levoglucosan in the pyrolyzate was decreased from 12% to 5% when 50% of the primary hydroxyl groups of the anhydroglucose units of cellulose were converted to carboxyl groups. Madorsky at National Bureau of Standards thermally degraded oxidized cellulose in a vacuum (Figure 3B), collected all the fractions, and found that the ratio of flammable products to those which would normally be considered unlikely to burn was greatly decreased. The chemical nature of the volatile products was determined with the help of the mass spectrometer. The results obtained with both untreated cellulose and oxidized cellulose are shown in Table V.

The comparison shows a ratio of $\frac{65}{11} = 2.0$ for untreated cellulose and .11 for oxidized cellulose (6). The exact ratios found are not strictly comparable due to differences in the extent of degradation but the lowered amount of flammable products from oxidized cellulose is unquestionable.

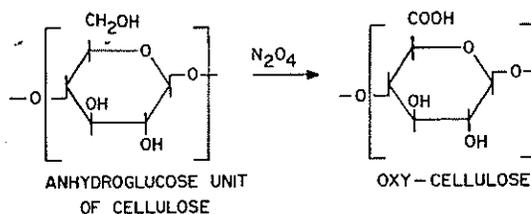


Figure 3A
Preparation of oxidized cellulose

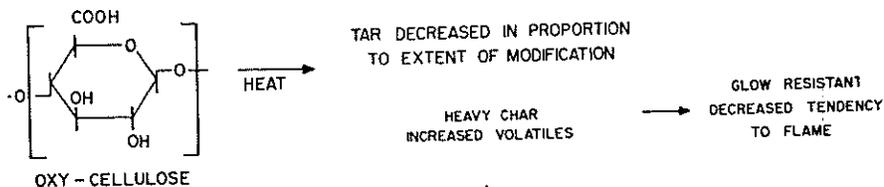


Figure 3B
Thermal degradation of oxidized cellulose

TABLE V
Comparison of degradation products from untreated cellulose with those from oxidized cellulose

	Flammable		Not	
	Tar	CO	Le:0	CO ₂
Untreated Cellulose	65%	2%	27%	6%
Oxidized Cellulose	6%	4%	51%	39%

OTHER APPROACHES — An entirely different approach to the problem of determining the mechanism of the thermal degradation of cellulose was taken by Krieger and Day under a contract held by the University of Pennsylvania. They directed this work toward dual goals of identifying the early products from the degradation of cellulose and of determining whether the nature of these products changed as the rate and temperature of degradation were altered. In other words, are the early products from the degradation more likely to be free radical in nature when the cellulose is decomposed very quickly, and ionic in nature when a result of slow thermal degradation? In this connection, the following approaches to the problem of the mechanism of the thermal degradation of cellulose were taken at the University of Pennsylvania (26, 27).

Attempts were made to decompose threads of untreated and flame-retardant-treated cotton fabric in a matter of seconds by means of a hot resistance wire (26). The early fragments, if free radical in nature, were to be trapped with the radioactive iodine which coated the inside walls of the glass apparatus. The pressure in the system was reduced sufficiently to ensure reaction between the free radical fragment and the iodine rather than any competing reaction. After reaction, a mixture of the alkyl halides suspected to be present was

added to the radioactive iodides to act as carriers, the excess iodine destroyed, and the mixture fractionally distilled. The activity of the various fractions was then determined as indicative of the amount of free radical fragments originally formed. From the resultant activity in the fractions, it appeared that vinyl, methyl and ethyl free radicals were among the early products of pyrolysis. However, it was later determined that the amount of thermal degradation was slight and that exchange reactions between the radioactive iodine and the alkyl halides accounted for most of the radioactivity. The first deficiency could have been surmounted by the use of a radiant heat source to accomplish rapid thermal degradation but the predominance of exchange reactions would have made it necessary to develop an entirely different method of trapping the radical fragments. Because of the preceding difficulties this portion of the project was dropped.

Gas chromatography was utilized as the second technique for determining early products from the degradation of cellulose. The cellulose was pyrolyzed at 450°C in an atmosphere of nitrogen, the products passed through a silica gel column at 140°C and detected by their heat of adsorption with an activated charcoal detector tube. The major product detected was water, which amounted to 75% of the water of constitution of the cotton decomposed (27). Dehydration would thus appear to be the major reaction under anaerobic pyrolysis conditions. However, the thermal degradation of flame-retardant-treated and untreated cellulose under oxidizing conditions corresponds to the usual situation encountered in the field and the value of the preceding work lies in the possible application of gas chromatography to the identification of volatile degradation products.

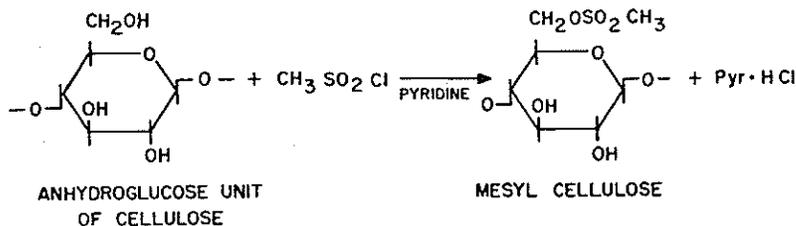


Figure 4A
Preparation of mesyl cellulose

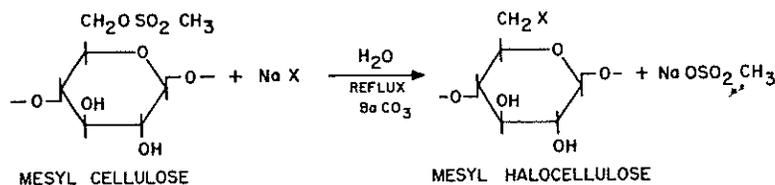


Figure 4B
Preparation of mesyl halocellulose

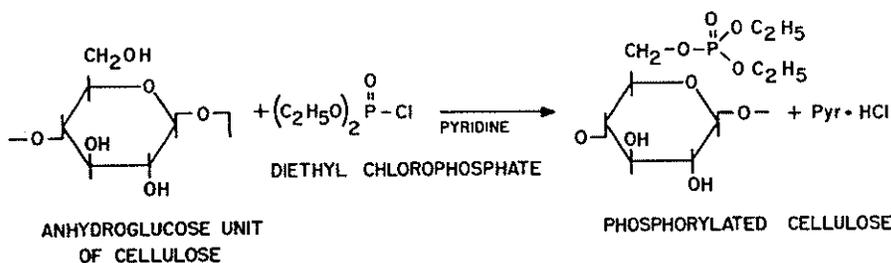


Figure 5A
Phosphorylation of cellulose

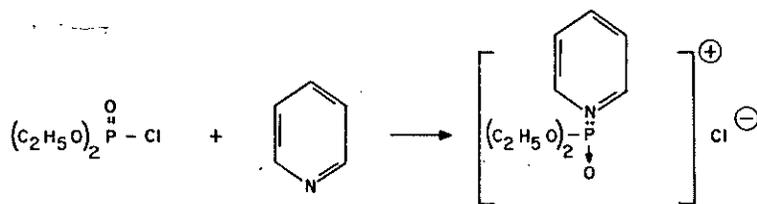


Figure 5B
Proposed mechanism—formation of pyridium complex

PRACTICAL MODIFICATIONS OF CELLULOSE—Historically, the chemical modification of cellulose fabrics to effect flame resistance had previously been conducted at Columbia University (31). Cotton was etherified with 2-aminoethyl sulfuric acid in alkaline solution and subsequently phosphorylated to provide flame and glow resistance with a relatively low-weight increase. The disadvantages of this and related modifications were loss in fabric tearing strength, excessive shrinkage, and susceptibility of the treated fabric to ion exchange (32, 33).

The results of the pyrolysis of untreated cellulose and of oxidized cellulose discussed in previous paragraphs have shown that the amount of levoglucosan formed is greatly decreased in the latter case. As levoglucosan is thought to be the major source of flammable products from the thermal degradation of cellulose, this finding was a clue to the prepara-

tion of modified cellulosic materials possessing flame-retardant properties. Due to its solubility in aqueous alkaline solutions, oxidized cellulose could only serve as a theoretical example of the type of modification desired and steps were taken to obtain more practical products. The Textile Research Institute was selected for this work because of the wide experience of personnel in the field of cellulose modifications. Pacsu and Schwenker of Textile Research Institute worked on several methods of cellulose modification and finally developed a method of reacting cotton cellulose cloth with methane sulfonyl chloride in pyridine to produce a mesyl cellulose. The reaction is shown in Figure 4A.

Modifications of this type had previously been conducted only with cotton linters or cellulose acetate materials (9). The mesyl cellulose was found to possess decreased flammability and improved glow resistance

without any apparent deleterious changes in the physical properties of the fabric (7).

The damping action of halogen on flaming is well-known and has been effectively used in commercial fire extinguishers. The effect of halogen with respect to the flaming of textile materials was studied by Church in 1943-1945 (1). A bromine-containing resin was later shown to be an effective flame-retardant finish (36). The halogen effect has also been discussed by Gottlieb in his consideration of theories of flame retarding involving additive finishes (4). Therefore, it was considered advisable to replace some of the mesyloxy groups with halogen atoms, such as bromine (8).

The reaction developed was a heterogeneous one, which consisted of refluxing mesyl cellulose with a 20% aqueous solution of the sodium salt of the desired halide (35) (Figure 4B). The halide introduced can be bromine, iodine, chlorine or fluorine. As has been found with additive-type flame retardants, the effectiveness of the halides in imparting flame resistance is in the order $\text{I} > \text{Br} > \text{Cl} > \text{F}$. Good flame resistance was found when light or heavy weight fabrics were modified with bromine or iodine,

Flame resistance is not the only factor involved in the thermal-protection problem. The phenomenon of afterglow can liberate a considerable amount of heat leading to the production of burns. For some applications the mesyl and halo mesyl cellulose materials mentioned might have insufficient resistance to glow. From experience with additive-type treatments, it is known that the application of materials containing boron or phosphorus to fabric prevents afterglow. For this reason a phosphorylation reaction was investigated, which was analogous to the mesylation modification. An organo-halophosphate, diethyl chlorophosphate, was reacted with cellulose in the presence of pyridine as shown in Figure 5. (35).

Realizing the lack of practicability in any large-scale production of modified fabric for which a contact time of three to four hours was necessary, the personnel at Textile Research Institute experimented with different methods of phosphorylation. Improvement in the reaction was obtained by phosphorylating the previously mesylated cellulose. Reaction times as low as five minutes were found to be satisfactory with a molar ratio of 3 moles of diethyl chlorophosphate to 1 mole of the anhydroglucose unit of cellulose. Afterglow was eliminated in samples containing as little as .5% chemically combined phosphorus. This small percentage of

phosphorus necessary to achieve glow resistance is in accord with the catalytic theory of glow resistance previously advanced (19).

A combination of the treatments of mesylation, phosphorylation and halogenation results in modified cellulosic fabrics which possess good glow and flame resistance. The fabric properties seem unimpaired and the flame retardant properties are theoretically permanent.

FUTURE WORK—The modified cellulosic materials discussed in the previous section have been prepared only in small samples and many problems must be solved before they can be practically utilized. These problems include: the preparation of suitable equipment for pilot plant manufacture, the cost of materials, the recovery of pyridine, the possible effect of such modifications on fabric properties such as dyeability, and the extension of the testing to include exposure to actual flame and thermal hazards.

Part of the value of this modification work lies in its possible extension to other fields. If cellulose can be successfully modified to impart flame and glow resistance, it may also be possible to modify the cellulose molecule so as to impart other desired properties, such as water resistance, mildew resistance, dimensional stability, etc.

Despite the successful application of the latest theory of flame retardancy, we are still a long way from either the perfect flame retardant or an irrefutable theory of flame and glow retardancy. Too little is known about the products of the thermal degradation of flame-retardant-treated cellulose, as investigators have concentrated their efforts on the study of the degradation of pure cellulose itself. Specifically three items require study as follows:

1) The first item involves the gaseous products of combustion. What part does the bromine play in preventing flaming—just a nonflammable diluent or a chain stopper? If the latter explanation is true, it should be possible to find cheaper chain stoppers (free radical inhibitors) which would be just as effective.

2) The second is related to the tarry products which were the subject of a large portion of this report. Although it is known that levoglucosan, water, acids and carbonyl compounds are formed from untreated cellulose, much less is known about the composition of the tars from flame-retardant-treated cellulose.

3) The last item requiring study is the black residue which results when a flame-retardant-treated fabric is thermally degraded. What are the

properties of this carbonaceous mass? Why does the presence of phosphorous or boron (in proper form) prevent the afterglow reaction? The explanation given in this paper was based on cause and effect while other more detailed explanations have been based at least partially on conjecture.

To fully exploit the thermal protection which flame-retardant-treated fabrics are capable of furnishing, it will be necessary to determine the heats of reaction involved. In this connection Feldman applied the technique of differential thermal analysis in an effort to determine which flame-retardant treatments tended to absorb rather than release heat when subjected to thermal stress (29). This work was not reported in the body of this report due to its preliminary nature. However, in the final analysis it would be necessary to determine not only the exothermicity of a particular fabric treatment, but also the distribution of the heat flow between that which adds to the thermal insult and that which is lost to the surroundings.

When the above knowledge becomes available, it is felt that considerable progress can be effected not only in the chemical development of flame-retardant treatments but also in improving their protective potential in the physical heat transfer system.

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