

## Pyrolysis and Combustion of Cellulose. I. Effects of Triphenyl Phosphate in the Presence of Nitrogenous Bases

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### Synopsis

The ability of selected phosphorus-containing compounds and nitrogen-containing compounds to act as flame retardants for cotton cellulose was investigated using flame tests, thermal gravimetric analysis (TGA), and differential thermal analysis (DTA). The effectiveness of the organophosphorus compounds was found to correlate with the changes which they induced in the pyrolytic degradation of the cellulose as indicated by DTA. Many of the samples containing nitrogen were found to exhibit DTA curves having pronounced exotherms. The presence of nitrogen-containing compounds in conjunction with the organophosphorus systems enhanced their ability to retard flame propagation but did not produce significant changes in the pyrolytic endotherm as observed by DTA. More conclusive evidence for a chemically based phosphorus-nitrogen synergism was obtained by the use of TGA. These data can be interpreted in terms of the phosphorus-nitrogen synergistic effects and flame retardance mechanisms which have been proposed in the literature.

### INTRODUCTION

Because of the dangers inherent in the use of flammable cellulosic textiles, man has been interested in the development of fabrics exhibiting reduced combustibility for several centuries. Many natural fibers, such as cotton, are intrinsically flammable; thus the emphasis on reducing combustibility has centered around the chemical modification of textile materials. As early as 1640, clay and plaster of paris were applied to theater canvas as flame retardants. By 1740, the flame-retardant properties of alum had been discovered and put to use. However, it was in 1786, with the discovery of the flame-retardant properties of ammonium phosphate, that the foundation for most of the currently used flame-retardant systems was laid. Since that time, the majority of the work in the area of flame retardants for cellulosic materials has been centered around the use of phosphorus-containing compounds.

The types of phosphorus compounds originally used as flame retardants were predominantly water-soluble inorganic salts. These were easily

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applicable to the fabrics in aqueous systems but suffered from the very obvious disadvantage of being nondurable toward laundering. In order to obviate this problem, considerable effort has been expended in recent years toward the development of durable treatments. This work has been quite successful, and a number of permanent-type flame retardants are now available for cellulose. Unfortunately, none of these treatments is completely satisfactory. The treating agents are frequently quite expensive, and effective treatments require the addition of large amounts of these materials. The necessity for high add-ons also often results in poor physical and aesthetic properties in the finished fabrics.

It is generally conceded that the phosphorus-containing polymer formers most frequently used in commercial treatments exert their flame-retarding influence by thermally decomposing to some species, perhaps Lewis acids or other dehydrating agents. These species are then capable of altering the pyrolysis of the cellulose in such a way that a lesser amount of flammable gaseous material is produced. The decomposition reactions of cellulose, and a few treated celluloses, have been studied by a number of workers and are the subject of several recent reviews.<sup>1,2</sup> In spite of the progress which has been made in understanding the thermal degradation of the cellulose substrate and its relation to the flaming phenomenon, little is known about the decomposition of flame-retardant additives, the nature of the active species, or the mechanisms whereby these active species alter the mode of decomposition of the cellulose. A program of research is therefore underway at Clemson University to systematically investigate the basic mechanisms through which flame retardants exert their influence. It is hoped that the information derived from these studies might provide the basis for designing more effective and efficient flame-retardant treatments for cellulose fabrics, and thus accomplish the desired results at lower cost and lower add-ons.

It has long been known that organophosphorus flame retardants are generally more effective when used in conjunction with nitrogen-containing systems. Recently, Tesoro and co-workers<sup>3-5</sup> have attempted to put these generalizations on a more quantitative basis and have described the nitrogen-phosphorus interdependence as being synergistic. Unfortunately, these workers made no correlation with the structures of the nitrogen-containing moieties but treated all the structures as simply sources of nitrogen. Since an effect such as they described, if truly synergistic, would seem to offer great promise for the design and development of improved finishes, its nature and mechanism were selected for immediate study, and the results of this study are reported herein.

## EXPERIMENTAL

**Chemicals.** All chemicals and solvents were reagent-grade commercial samples, with the exception of diphenyl aminophosphate and triphenyl phosphate, which were prepared by the methods of Audrieth and Toy,<sup>6</sup> and

diphenyl hydrogen phosphate, which was prepared by the method of Freeman and Colver.<sup>7</sup>

**Fabric.** 80 × 80 bleached and mercerized 100% cotton print cloth was used.

**Fabric Treatment.** Each sample was immersed in a solution containing the requisite quantity of phosphorus and/or nitrogen-containing compounds necessary to attain a selected add-on of the respective element. The specimen was then mechanically squeezed using the nip rolls of a laboratory pad to ensure uniform penetration, and was subsequently air-dried. In cases where two different compounds were applied to the same fabric sample, either multicomponent solutions or successive treatments were used. Solvents for the successive treatment applications were selected so that each compound applied was soluble in only one of the solvents used. The compounds used to treat the fabric samples and their respective solvents were: phosphoric acid-water, diammonium phosphate-water, diphenyl hydrogen phosphate-acetone, diphenyl aminophosphate-acetone, triphenyl phosphate-acetone, urea-water, and guanidine carbonate-water.

To avoid using a trial-and-error approach, the following formula was used to prepare the treating solutions:

$$x = \frac{bz}{ay}$$

where  $a$  = pad pickup (grams of solution per gram of cotton),  $b$  = specific gravity of the solvent,  $x$  = grams of compound per total grams of solution,  $y$  = fractional weight of nitrogen or phosphorus in the compound, and  $z$  = desired nitrogen or phosphorus add-on.

After being dried, the fabric pickup was determined gravimetrically and per cent phosphorus and/or nitrogen content was then calculated from the molecular weights of the compounds.

**Rates of Combustion.** Rates of combustion were obtained through ignition of the fabric samples in an AATCC Flammability Tester. This device consists of a sample holder mounted at an angle of 45° with the horizontal in a ventilated cabinet. As specified by Standard Test Method AATCC 33-1962,<sup>8</sup> 2-in. by 6-in. fabric specimens were ignited with a butane microburner and the time required for the flame to burn a stop cord, or to extinguish itself, was recorded. Throughout testing, the burner flame was held in contact with the fabric specimens.

When obtaining the rate of combustion data, it was necessary to choose a point on the fabric where burning was determined to occur independently from that resulting from the burner. To determine this point, a piece of paper was placed in the sample holder and the flame was applied until the paper was charred but not ignited. This resulted in an imprint of the flame on the paper. The distance from the uppermost point of the imprint to the stop cord was measured to be 4.75 in. This distance served as the maximum distance the flame traveled in calculating rates of combustion. In numerous cases, the flame did not travel a sufficient distance up the fabric

to sever the stop cord. For these samples, the recorded time of burning represents the period from application of the butane flame until the independent fabric flame began to diminish. Five replications were obtained for each sample as suggested in the original test method; however, the samples were conditioned in the laboratory rather than in a forced-air oven. Rates of combustion were calculated as follows:

$$\text{rate of combustion} = \frac{\text{distance flame traveled (inches)}}{\text{time fabric burned (minutes)}}$$

Flameless combustion (afterglow) was not included in the combustion data.

**Differential Thermal Analysis (DTA).** The fabric specimens were pulverized in a Wiley Mill. All curves were obtained using a du Pont 900 Differential Thermal Analyzer equipped with 2-mm capillary tubes for both sample and reference. The reference material was glass in all cases. A constant heating rate of 20°C/min and a scale sensitivity of 0.5°C/in. were used.

**Thermogravimetric Analysis (TGA).** The samples were prepared in the same manner as for the DTA, except in cases where reactions were highly exothermic, thus making it advantageous to analyze the fabric forms. The measurements were made in a dynamic atmosphere of nitrogen using a du Pont 950 Thermogravimetric Analyzer with a constant heating rate of 5°C/min and a scale sensitivity of 2 mg/in.

## RESULTS AND DISCUSSION

Although thermal decomposition of cellulose is an extremely complex chemical process, the reaction products generally fall into three distinct categories: a series of permanent gases, primarily water and carbon dioxide; a solid carbonaceous char; and a rather ill-defined tar which decomposes further with the production of numerous flammable gases. The work of several investigators has shown that the primary constituent of this tar is 1,6-anhydroglucopyranose (levoglucosan),<sup>1,2</sup> and it is this decomposition to levoglucosan which is generally considered to be the key to the flammability problem. Most of the flame retardants in common use today are assumed to act by thermal decomposition to produce latent P<sub>2</sub>O<sub>5</sub> or some other agent capable of catalyzing the dehydration and decomposition of the cellulose to produce more of the nonflammable gases and solid carbonaceous char. In a simplified mechanism, this is accomplished by dehydration of the anhydroglucose units.

This type of acid-catalyzed dehydration and its flame-retardant properties are demonstrated by the impregnation of cotton cellulose fabric with phosphoric acid. Representative data for such treated fabrics (Table I) show that the fabric becomes self-extinguishing at concentrations of phosphorus somewhere above 1.5%. These data are in complete agreement with the known ability of phosphoric acid to act as a flame retardant at relatively low add-ons. Comparison of the data from Table I with the data

TABLE I  
Rates of Combustion of Treated Cotton Celluloses

Treating compounds	N, %	P, %	Distance flame traveled, in.	Rate of combustion, in./min
Untreated control			4.75	23.8
Phosphoric acid		1.1	4.75	8.9
		1.8	0.50	3.0
		2.7	0.30	2.5
		3.8	0.30	2.7
		5.2	0.25	negligible
Diammonium phosphate	0.9	1.1	4.75	9.5
	1.4	1.5	0.80	5.7
	2.1	2.4	0.60	4.6

shown in Figure 1 illustrates further the validity of this type of interpretation. The DTA curves of the phosphoric acid-treated cellulose samples show thermal decomposition occurring at a much lower temperature than the untreated control. As would be expected, the nadir of the endothermic peak, indicative of the thermal decomposition of the cellulose, is shifted to much lower temperatures in the treated samples. This is exactly what one would expect in the case of a catalyzed decomposition. The DTA curve of the sample containing 1.1% phosphorus supports the data given in Table I by showing a much lower temperature of decomposition.

This is also in agreement with the significantly decreased rate of combustion shown by the sample. Although rate of combustion and temperature of decomposition are not always related, it is usually observed that samples which decompose below 300°C produce less levoglucosan and thus lower the fuel available for flame propagation. This results in a decreased rate of combustion. Increasing the amount of phosphoric acid present in the fabric causes a somewhat smaller decrease in the rate of burning and the fabric becomes self-extinguishing. The DTA curves of the corresponding samples show shall shifts in the position of the endothermic nadir. These observations are in complete agreement with the previous findings of a variety of investigators.

Of perhaps greater significance is the observation that the endotherm for the treated celluloses appears to be actually two ill-defined endotherms. The larger nadir is generally associated with the endothermic dehydration and decomposition of the cellulose sample. Although it is extremely difficult to attempt an assignment of the chemical reaction responsible for the lower temperature endotherm using only thermal data, there is chemical evidence available<sup>9</sup> which provides the basis for assigning it to a phosphorylation reaction. The most probable phosphorylation site is the C-6 hydroxyl of the anhydroglucose units. If this should actually be the case, it could be of major significance in interpreting the mechanism of the flame-retardant action produced by the phosphoric acid. It has been previously shown by Schwenker and co-workers<sup>10</sup> that reactions blocking the

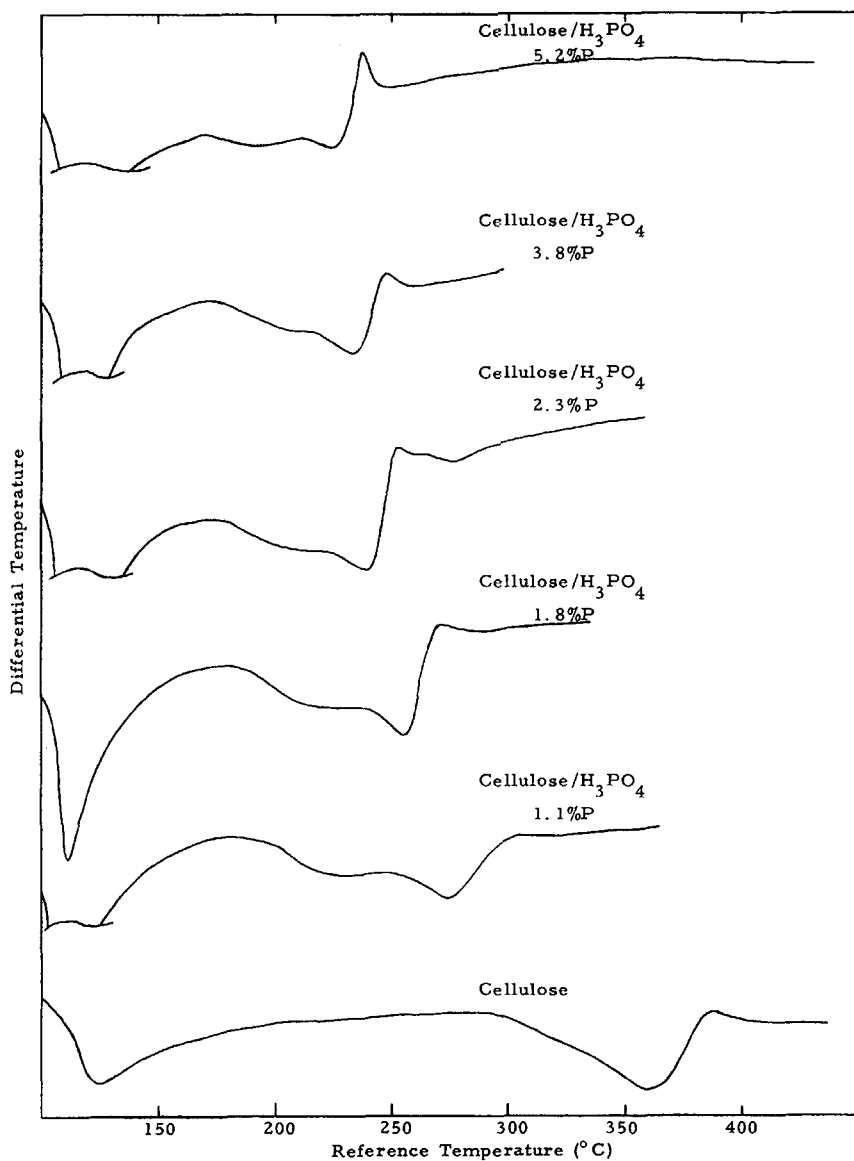


Figure 1.

C-6 hydroxyl tend to prevent the formation of levoglucosan and thus inhibit flaming.

Such interpretation of the results from the burning tests and DTA of the phosphoric acid-treated samples becomes even more attractive when compared to the following results obtained using diammonium phosphate treatments. As in the case of phosphoric acid, the diammonium phosphate is found to be a good flame retardant with add-ons approximating 1.5% phosphorus and more. The DTA curves of the corresponding samples

show two distinct endothermic peaks not associated with reactions of the pure diammonium phosphate. Since it is assumed that diammonium phosphate decomposes under these conditions to produce primarily ammonia and phosphoric acid, it is to be expected that the mode of reaction exhibited by diammonium phosphate-treated samples should be similar to that exhibited by those containing phosphoric acid. The DTA curves shown in Figure 2 indicate a sharp endothermic reaction whose temperature seems to

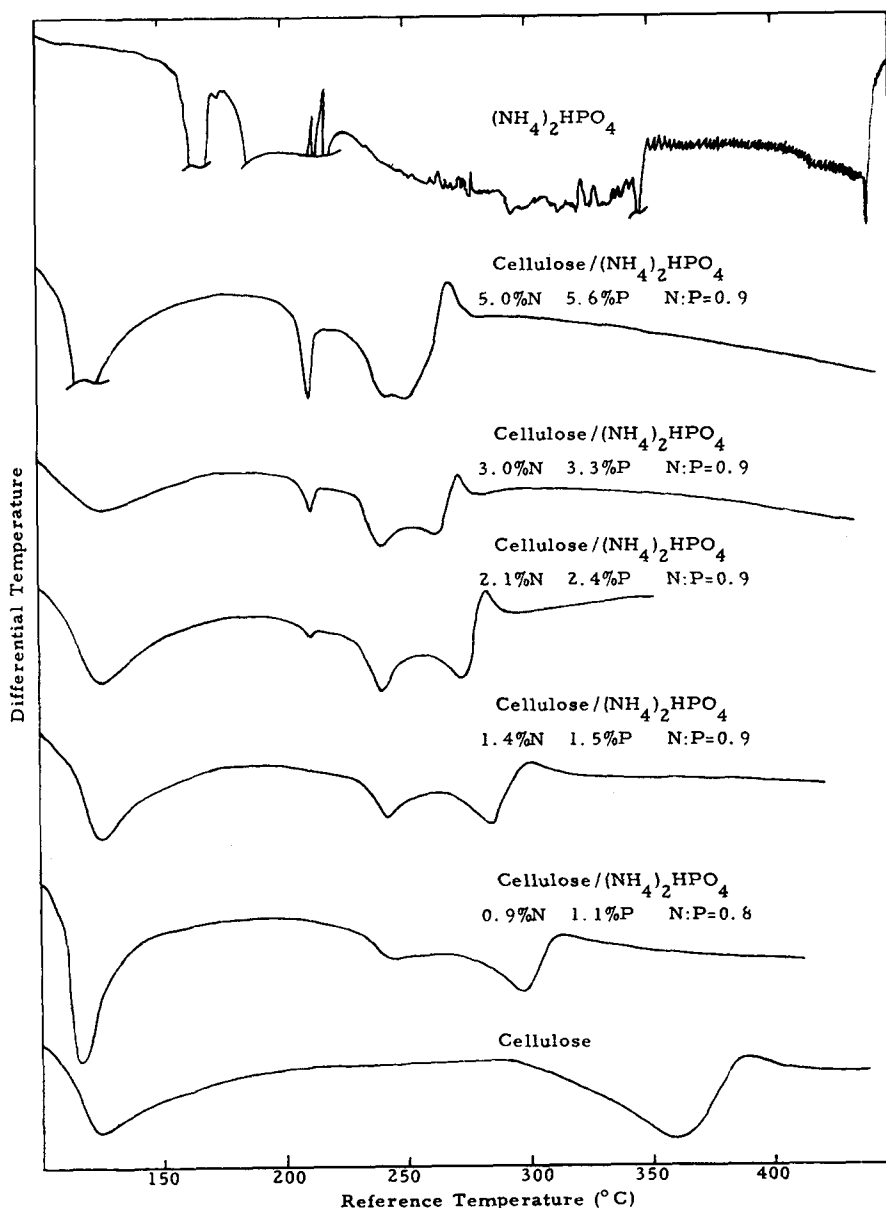


Figure 2.

vary with the amount of the treating material on the cellulose. The lower-temperature endotherm is apparently invariant as in the case of phosphoric acid. Again, a logical interpretation would seem to be in terms of a phosphorylation occurring at approximately 240°C. Phosphorylation is then followed by an acid-catalyzed dehydration and thermal decomposition occurring between 250° and 310°C, depending upon the amount of phosphorous compound present.

Further confirmation of this interpretation is gained from the thermogravimetric analysis (TGA) of the corresponding samples. The TGA curves for the diammonium phosphate samples show three significant areas of weight loss. The first, occurring below 150°C, is almost certainly the loss of occluded water from the fabric sample. The second decomposition occurs in the same region as the lower-temperature endotherm seen in the DTA curves, and also involves a small weight loss. This is exactly the type of behavior which would be expected by the loss of water during the phosphorylation process. The third weight loss is very pronounced, with the sample being almost completely decomposed. This would be expected in the dehydration and decomposition reactions.

In order to study these reactions more conveniently, a series of model compounds was synthesized and applied to the cotton fabric. In choosing these model compounds, two primary criteria were used. First, the compounds selected were all structurally related to phosphoric acid or diammonium phosphate in order that their behavior might be more easily correlated with the parent phosphoric acid. Second, compounds were selected which were not good flame retardants by themselves. This was necessary since small effects were being sought and these effects would be masked by the use of structures which were potent flame retardants. It was also for this reason that the modified 45° angle flame test was employed for the determination of the burning data. More stringent tests, such as the vertical flame test, would have completely obliterated small effects caused by the structural modifications.

Although triphenyl phosphate seemed to best satisfy these needs, it was necessary to first examine a related free acid and the corresponding aminophosphate with a direct P—N bond. These compounds provide a good basis for comparison and also supply some significant information of their own. Examination of Table II indicates that both diphenyl hydrogen phosphate and diphenyl aminophosphate are capable of acting as flame retardants. The difference in the relative effectiveness of the two is, however, quite striking. While both impart self-extinguishing characteristics to the fabric, the flame travels more than 1 in. up the sample treated with diphenyl hydrogen phosphate even when add-ons as high as 7.6% P were employed. On the other hand, the incorporation of 2.5% P in the form of diphenyl aminophosphate renders the sample almost totally incombustible under these test conditions.

Thus, if these are accurate models, one is drawn to the conclusion that compounds containing P—N bonds might be better flame retardants than



TABLE II  
Rates of Combustion of Treated Cotton Celluloses

Treating compounds	N, %	P, %	Distance flame traveled, in.	Rate of combustion, in./min
Untreated control			4.75	23.8
Diphenyl hydrogen phosphate		1.1	4.75	8.8
		2.2	1.51	7.2
		3.5	1.25	6.9
		5.2	1.35	6.1
		7.6	1.35	5.4
Diphenyl aminophosphate	1.1	2.5	1.05	negligible

the corresponding free acids. But such a result has rather limited practical significance since most P—N bond-containing structures are quite labile hydrolytically and thus currently find little use on fabrics. However, in view of the reports of phosphorus-nitrogen synergism in systems such as these, these data might be indicative of a mechanism to explain a synergistic effect based on the formation of a P—N bond during thermal degradation. A more complete study of the thermal behavior of these and related compounds is therefore necessary to determine whether this is actually the case.

An examination of Figure 3 shows that diphenyl hydrogen phosphate is capable of catalyzing the degradation of cotton cellulose in much the same manner as the parent phosphoric acid. Similarly, Figure 4 shows the catalytic effect of diphenyl aminophosphate as revealed by DTA. Surprisingly, the endothermic nadir, in the case of the amino compound, occurs at a slightly higher temperature than that of the corresponding acid. There also appears to be a significant exothermic reaction immediately preceding the decomposition of the diphenyl aminophosphate-treated sample. The presence of this exotherm is confirmed by the TGA curve, but the nature of the reaction involved is not understood at present.

Thus, it would seem that the DTA data do not agree with the results from the burning tests. In order to provide an explanation for this apparent disagreement, it is necessary to examine the TGA curves for the two treated samples shown in Figure 4. The onset of the thermal decompositions is found to occur at the same temperature with both treatments, indicating that the mode of degradation has been altered in essentially the same manner in both samples. In spite of the similarity in the onset temperatures, the curves for the two catalyzed decompositions seem to indicate that the diphenyl aminophosphate sample decomposes at a slower rate, as shown by the slopes in the 200–300°C region. Retardation of the decomposition reaction should further decrease the fuel supply for the flame and may therefore account for the enhanced flame-retarding ability of the diphenyl aminophosphate. Treatment with both diphenyl hydrogen phosphate and diphenyl aminophosphate increases the amount of solid residue caused by degradation, but with no significant differences in the

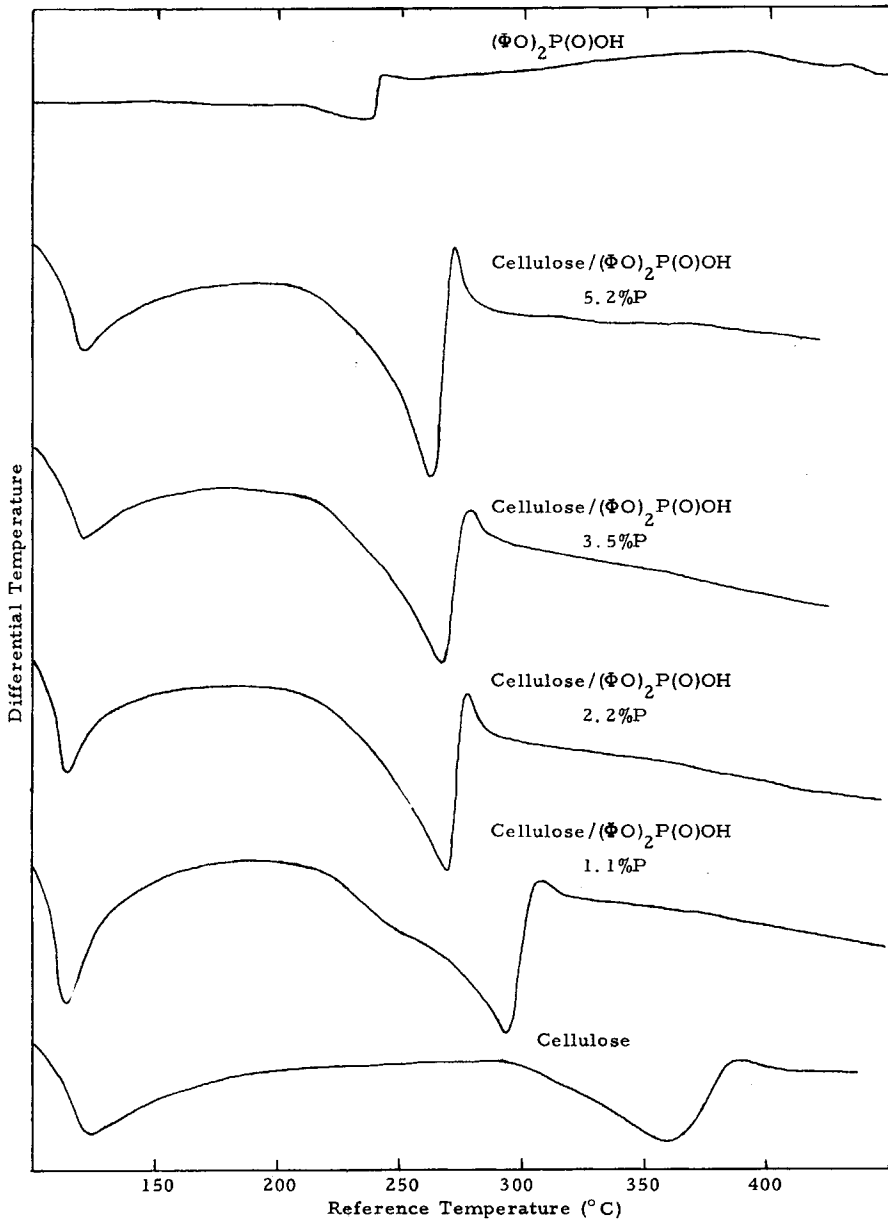


Figure 3.

amount of residue produced by the two treatments. This is somewhat surprising, since most of the better flame retardants are usually observed to produce considerably larger char fractions.

In an attempt to gain more insight into the nature of this phosphorus-nitrogen interaction, a series of cotton cellulose samples was treated with

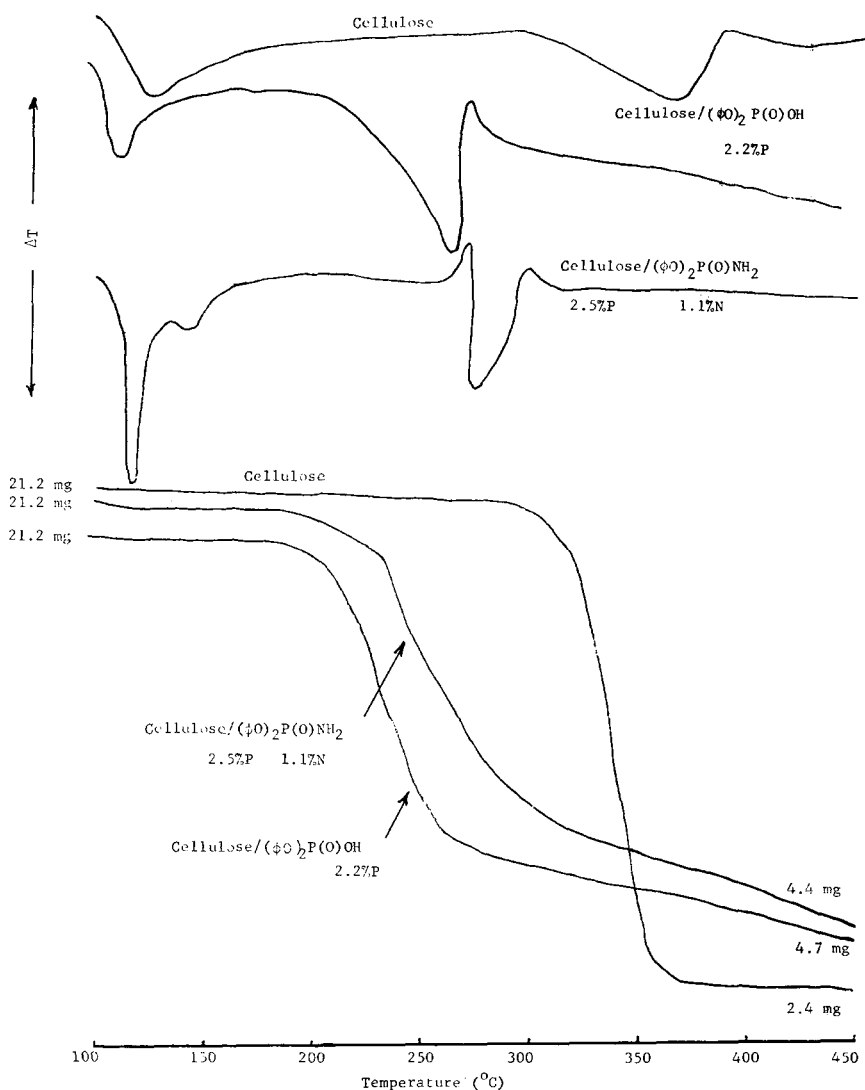


Figure 4.

triphenyl phosphate both by itself and in conjunction with selected nitrogen sources. Triphenyl phosphate exhibits some flame-retardant properties, but, as expected, it is much less effective than the free acid. Therefore, much larger add-ons are required to achieve self-extinguishing characteristics, as shown in Table III. This is in keeping with the theory that the free acid is capable of acting as a decomposition catalyst without structural modification. Triphenyl phosphate, on the other hand, must undergo degradation or some other type of reaction before it can exert any significant effect on the cellulose pyrolysis.

TABLE III  
Rates of Combustion of Treated Cotton Celluloses

Treating compounds	P, %	Distance flame traveled, in.	Rate of combustion, in./min
Untreated control		4.75	23.8
Triphenyl phosphate	1.1	4.75	18.3
	2.3	4.75	6.5
	3.4	4.23	5.6
	7.5	1.25	4.2

Further confirmation of this interpretation is gained from an examination of Figure 5. The DTA curves show that the degradation reactions for both the untreated and treated cellulose samples occur below the temperature where pure triphenyl phosphate decomposes. Thus, there should be little if any active phosphorus species present in any of the samples. As expected, the endothermic peak, usually associated with cellulose decomposition, occurs at essentially the same temperature in each of the curves. This behavior is confirmed by the TGA curves produced by these samples. However, there is a second endothermic reaction which occurs prior to the primary degradation reaction and is evident in both the DTA and TGA curves of all of the treated samples. As in the cases of phosphoric acid and diammonium phosphate, chemical evidence makes it logical to assign this peak to a phosphorylation reaction, in this instance a transesterification.<sup>9</sup> Since this should occur predominantly at C-6 of the anhydroglucose units, it could limit levoglucosan formation and thus account for the reduced flaming observed when higher concentrations are applied.

Because of the greater effectiveness of diphenyl aminophosphate as compared to diphenyl hydrogen phosphate, it was of interest to determine whether or not similar effect might be produced by impregnating the fabric with nitrogen-containing compounds along with the triphenyl phosphate. It was necessary, however, to first determine the effects on the pyrolysis of the cellulose of various nitrogen-containing compounds by themselves. Urea and guanidine carbonate were chosen as representatives of the commercially important classes of nitrogen sources commonly used in conjunction with phosphorus flame retardants. Since these compounds are basic, and since Mack and Donaldson<sup>11</sup> have previously shown that inorganic bases alter the mode of thermal degradation of cellulose to produce less tar and more solid residue, it was expected that these nitrogenous bases would produce a similar but less pronounced effect.

A series of samples was tested after being impregnated with various concentrations of urea and revealed a small decrease in burning rate (Table IV), but no significant increase in solid residue. The DTA curves exhibited by these samples (Fig. 6) were of little assistance in examining the reaction, because the superimposition of the base-catalyzed exotherm on the pyrolysis endotherm results in a rather structureless curve. Data provided by TGA,

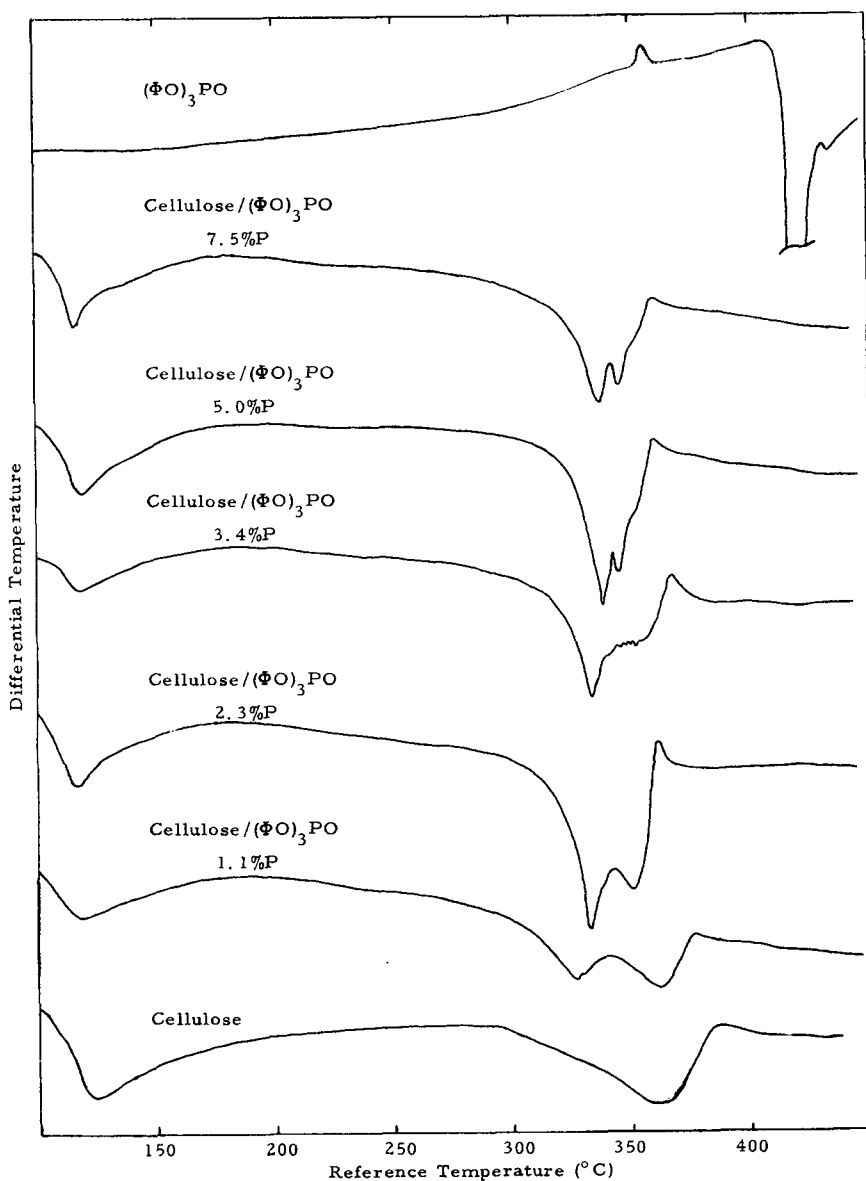


Figure 5.

shown in Figure 7, proved to be somewhat more enlightening. A small weight loss was found to occur above 160°C, which is in keeping with the known thermal decomposition of urea.

The major decomposition reaction is shown to begin at approximately the same temperature as with untreated cellulose and to proceed at essentially the same rate in both cases. Thus, it seems that such nitrogenous bases, unlike the strong inorganic bases used by Mack and Donaldson, do

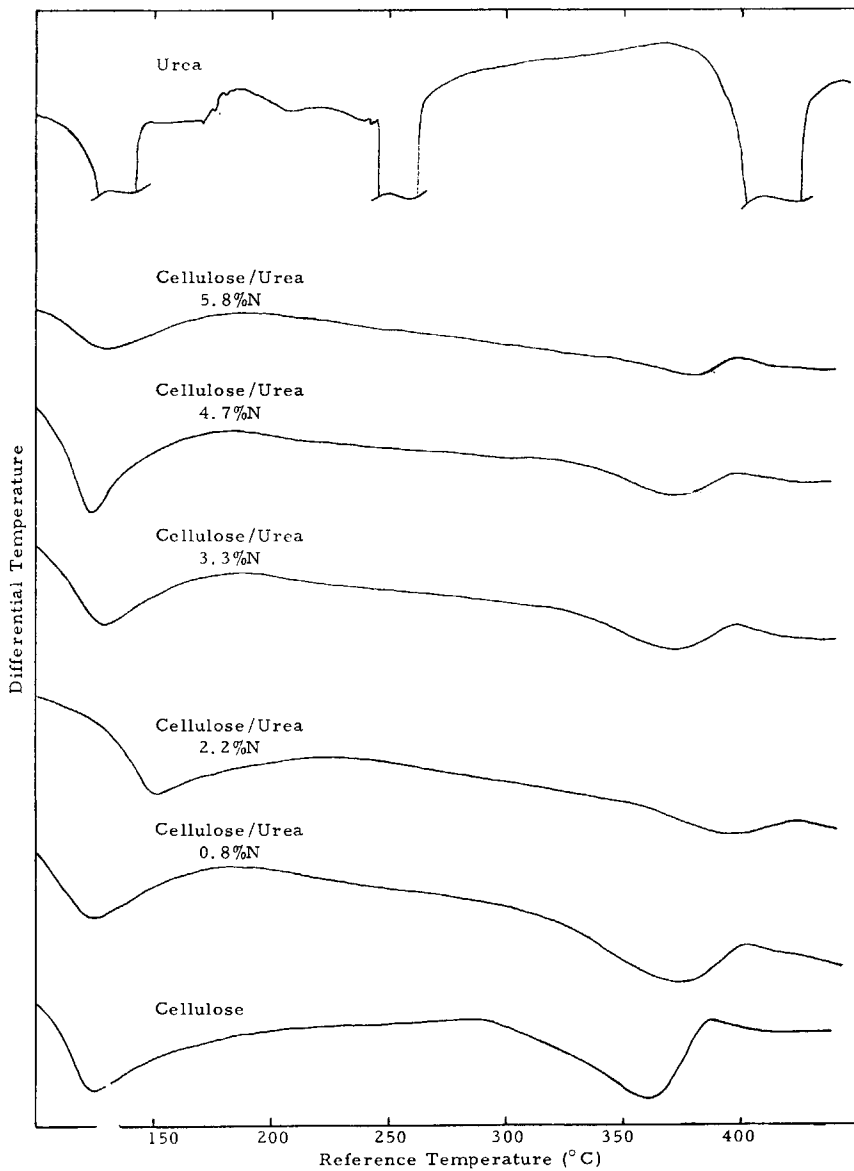


Figure 6.

not effectively catalyze the cellulose pyrolysis reaction. This is of some significance in view of the observation that urea is capable of changing the nature of the DTA curve in the 300–450°C region from strongly endothermic to mildly exothermic (Fig. 6). In order to explain this behavior, it seems necessary to invoke an effect on some reaction other than the pyrolysis.

TABLE IV  
Rates of Combustion of Treated Cotton Cellulose

Treating compounds	N, %	Distance flame traveled, in.	Rate of combustion, in./min
Untreated control		4.75	23.8
Urea	0.8	4.75	19.0
	2.2	4.75	17.0
	3.3	4.75	15.3
	4.7	4.75	11.9
	5.8	4.75	13.2
Guanidine carbonate	1.4	4.75	12.5
	2.2	4.75	8.6
	3.2	4.75	9.0
	4.8	4.75	6.2

Similar results were obtained with guanidine carbonate, a considerably more basic species than urea. Although this material was not effective in imparting self-extinguishing characteristics at the levels of application employed, it did significantly decrease the rate of combustion at the higher concentrations. The DTA curves exhibited by these samples are shown in

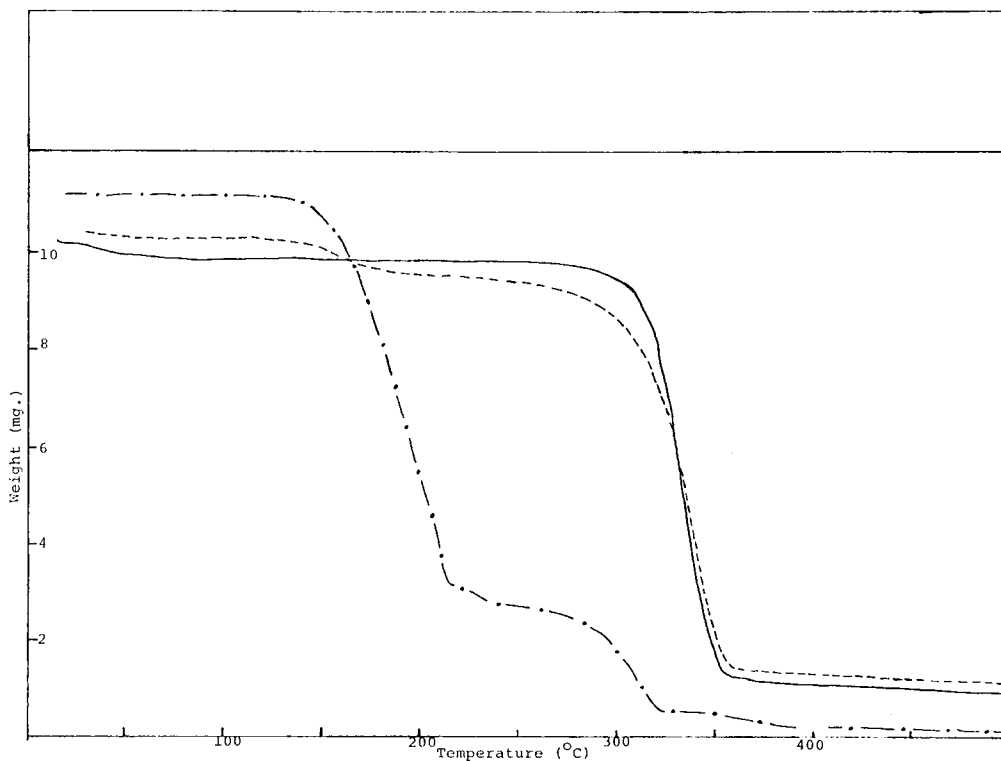


Fig. 7. — cellulose; — cellulose/urea, 5.8% N; - - - urea.

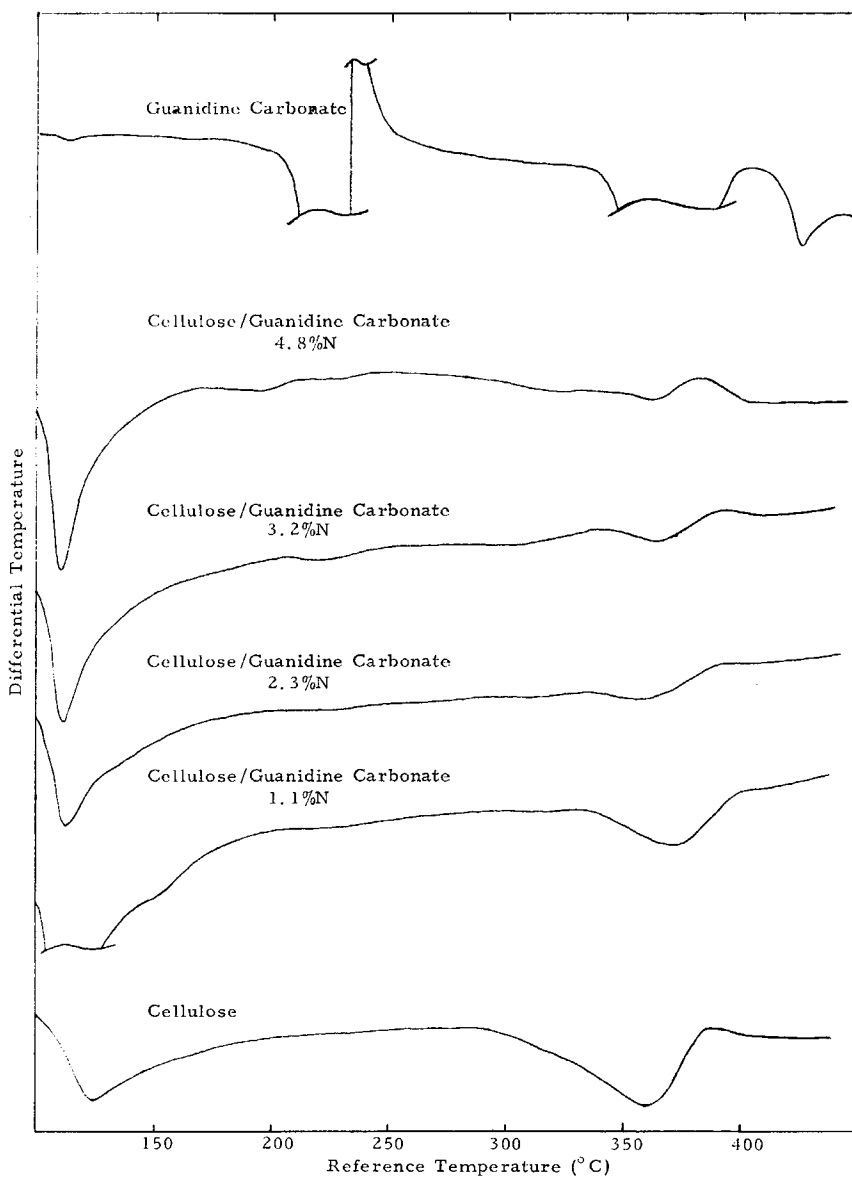


Figure 8.

Figure 8. As in the case of urea, the incorporation of guanidine carbonate into the sample induces an exothermic reaction which occurs in the same temperature range as the pyrolytic decomposition. Also, the TGA curves shown in Figure 9 are found to be analogous to those obtained using urea.

These results present a strong argument against the interpretations of data from flame tests on flame-retardant fabrics which require the direct intervention of urea or guanidine in the pyrolytic reaction of the cellulose.



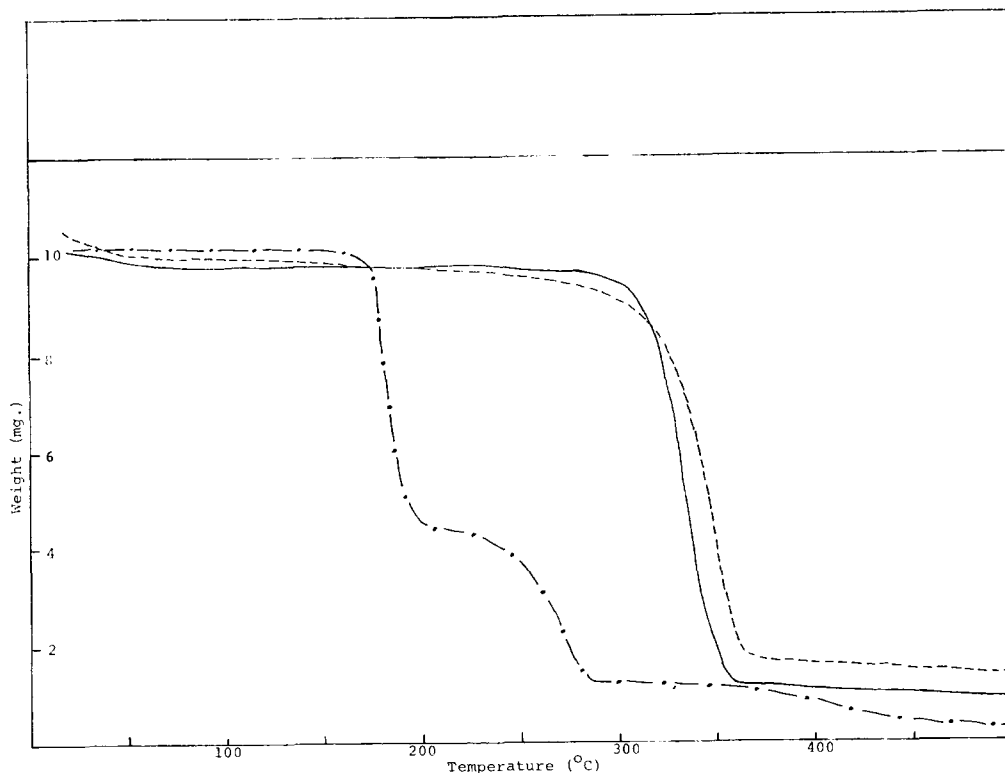


Fig. 9. — cellulose; --- cellulose/guanidine carbonate, 5.8% N; -·- guanidine carbonate.

TABLE V  
Rates of Combustion of Treated Cotton Celluloses

Treating compounds	N, %	P, %	Distance flame traveled, in.	Rate of combustion, in./min
Untreated control			4.75	23.8
Triphenyl phosphate-urea	1.9	1.0	4.75	5.9
	2.7	1.0	4.75	5.2
	3.8	1.0	4.75	4.9
	5.7	1.0	4.75	3.8
	10.2	1.0	0.60	1.2
Triphenyl phosphate- guanidine carbonate	1.6	0.9	4.75	5.6
	3.6	0.9	4.75	5.2
	4.3	0.9	4.75	4.8
	6.3	0.9	1.05	2.5
	17.2	0.9	0.45	1.7

However, in view of the combustion data indicating the greater flame-retardant ability of diphenyl aminophosphate as compared to diphenyl hydrogen phosphate, there is a need for a chemical explanation for the reports of phosphorus-nitrogen synergistic effects that have appeared in the litera-

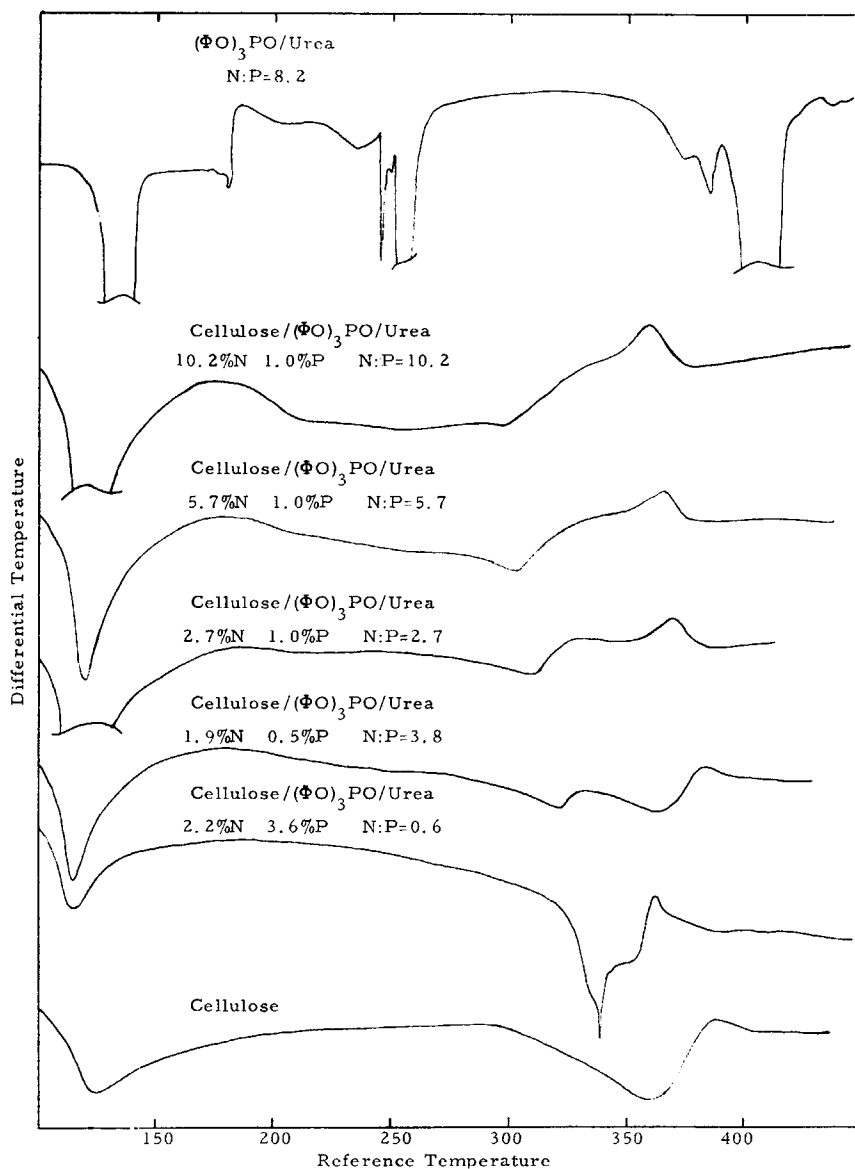


Figure 10.

ture.<sup>3,4</sup> One possibility would seem to lie in the interaction of the phosphorus- and nitrogen-containing systems to produce a more effective catalyst for the cellulose degradation. Alternatively, the effect of the nitrogenous bases could be due to a direct reaction with the products of the phosphorus-catalyzed cellulose decomposition.

In order to gain some insight into the nature of these effects as significant factors in flame-retardant action, a series of samples treated with triphenyl

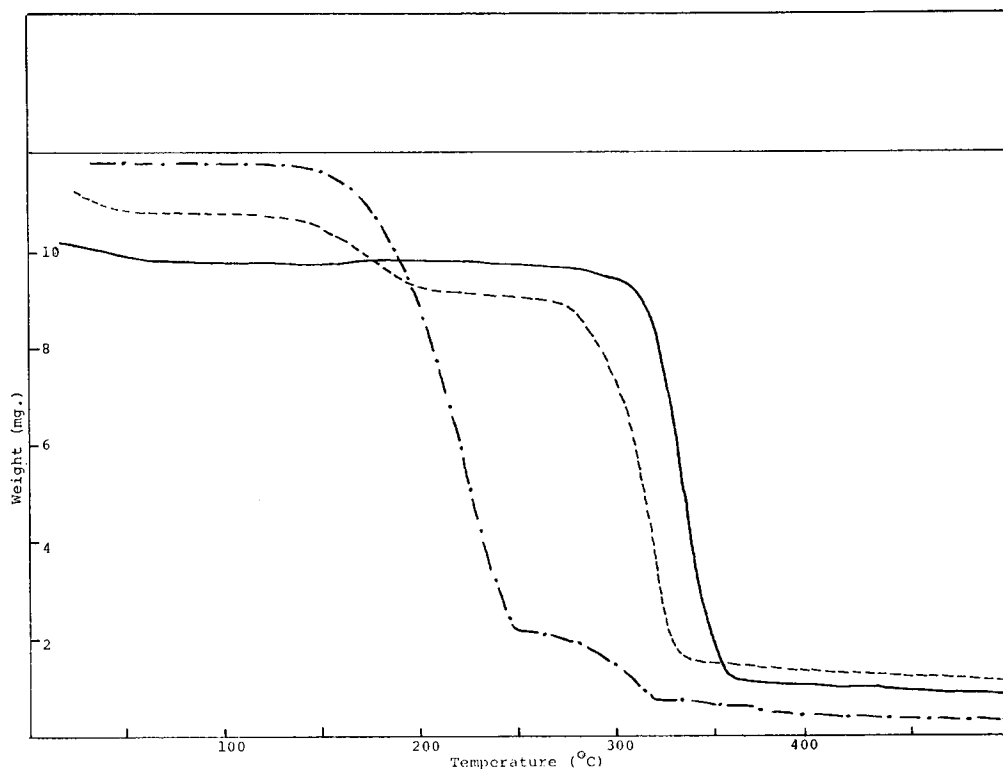


Fig. 11. — cellulose; --- cellulose/ $(\phi O)_3P(O)$ /urea, 1.0% P, 5.7% N; -·-·-  $(\phi O)_3P(O)$ /urea, 1:1.67.

phosphate in combination with urea and with guanidine carbonate was examined for flammability, mode of reaction, and residue formation. The phosphate alone was incapable of imparting self-extinguishing properties to the fabrics at the levels of add-on employed; however, addition of a sufficient quantity of either the urea or the guanidine carbonate resulted in the samples becoming self-extinguishing. The desired reduction in flammability was achieved with lower add-ons in the case of guanidine carbonate than in the case of urea.

The DTA curves obtained from the samples containing triphenyl phosphate and urea are shown in Figure 10. A comparison of the curve exhibited by the sample containing 3.6% P together with 2.2% N in the form of urea with that of a sample containing an equivalent amount of the triphenylphosphate alone (Fig. 5) shows no apparent differences. Similarly, the sample containing 0.5% P and 1.9% N shows the two peaks previously attributed to the transesterification and the uncatalyzed cellulose pyrolysis. Neither of these curves gives any indication of a chemical interaction between the phosphate and the urea. The possibility of observing such reactions at higher add-ons is precluded by the urea exotherm which ob-

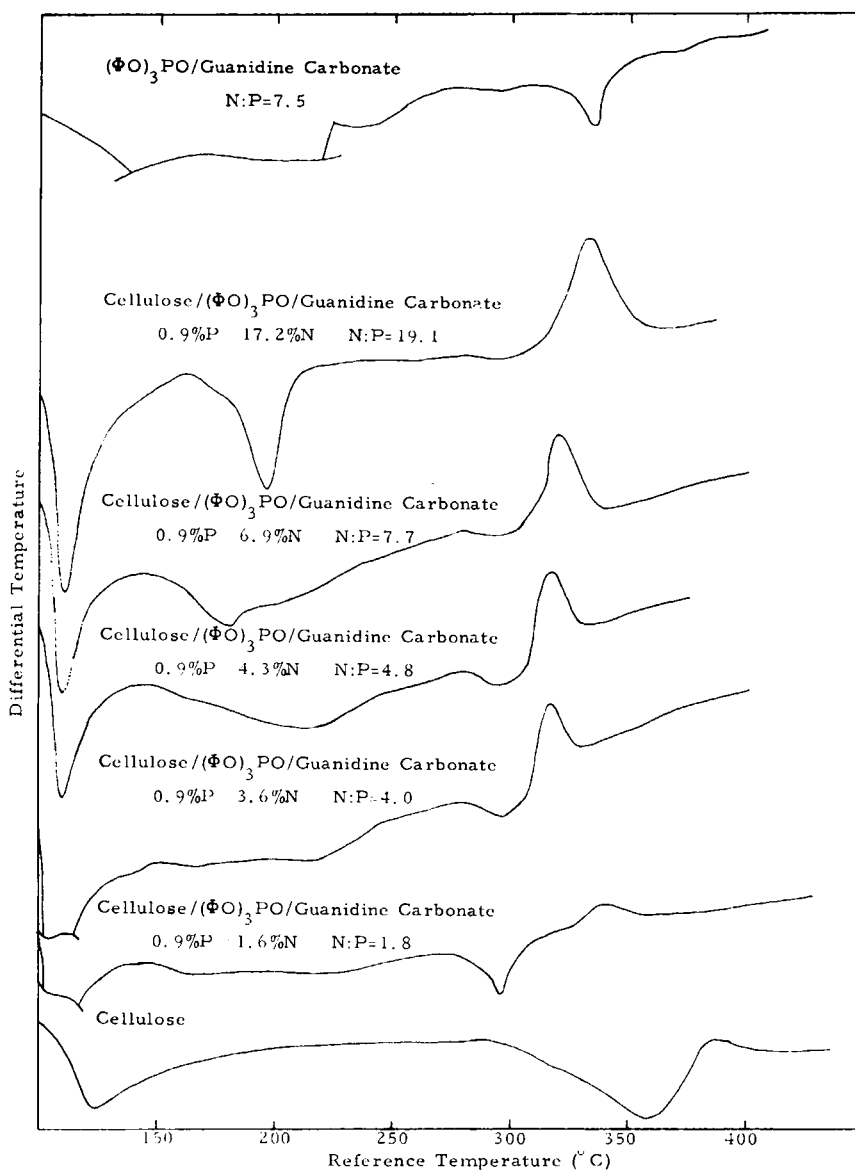


Figure 12.

literates the other effects in the 350–400°C region. Thus, the TGA is more useful in examining these higher add-on samples.

The thermogram from the triphenyl phosphate-urea-treated fabric (Fig. 11) indicates three areas of weight loss. The first onset temperature is the same as that observed in a sample treated with urea alone and is attributable to the urea decomposition. The second reaction is seen only as an inflection, but occurs at the same temperature as the first reaction in

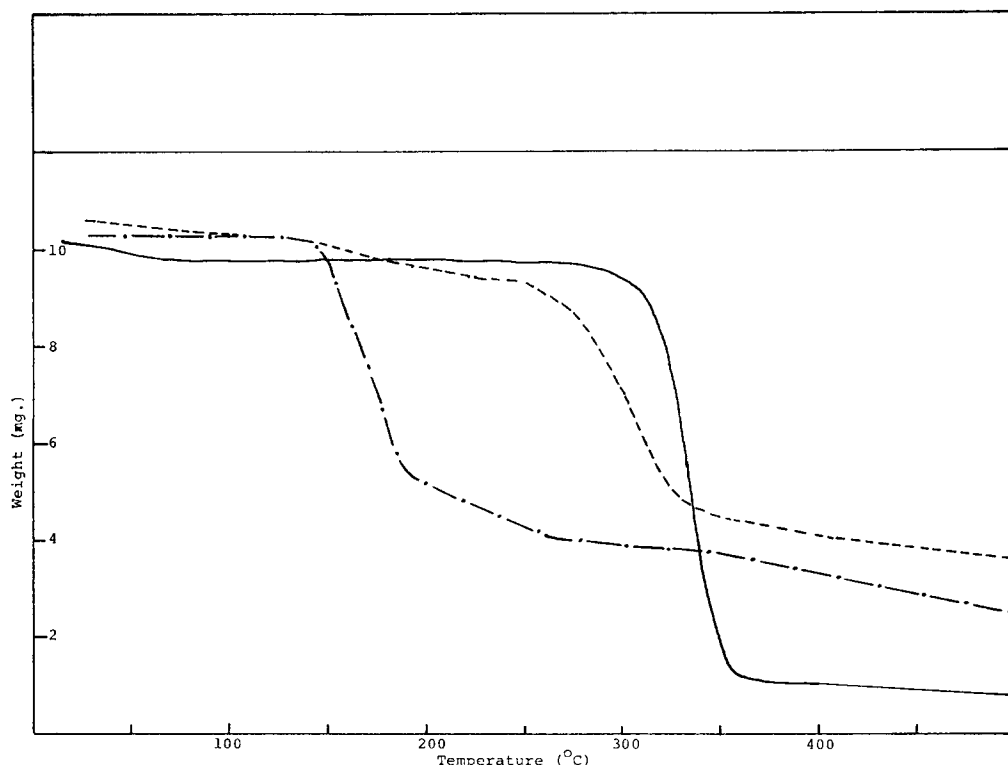


Fig. 13. — cellulose; --- cellulose/ $(\phi\text{O})_3\text{P}(\text{O})$ /guanidine carbonate, 0.9% P, 6.9% N; -·- cellulose/ $(\phi\text{O})_3\text{P}(\text{O})$ /N/P 7.5.

the thermogram of the sample treated with triphenyl phosphate alone. The third reaction is the large-scale decomposition whose rate of weight loss is essentially the same as those of the untreated cellulose and the cellulose with either of the two components alone. The onset temperature of this third stage appeared to be somewhat lower than when either of the reagents was applied alone. However, the magnitude of this difference was not sufficient to warrant any definite conclusions.

The results obtained using guanidine carbonate in conjunction with triphenyl phosphate were more definitive. The DTA curves for a series of these samples are shown in Figure 12. Again, the large exotherm observed above 300°C dominates the thermograms to such an extent that the cellulose decomposition reaction cannot be examined. There is, however, a noticeable endothermic reaction occurring in the vicinity of 300°C, as would be expected for the postulated transesterification reaction between cellulose and the triphenyl phosphate. As in the case of the urea treatments, the TGA curves, such as those shown in Figure 13, are considerably more revealing. The thermogram from the triphenyl phosphate-guanidine carbonate-treated sample shows the same general features as a composite of the two curves exhibited by cellulose with either of the reagents alone.

The first of the three areas of observable weight loss is assignable to the guanidine carbonate-melamine interconversion; the second has an onset temperature which is essentially the same as that seen in all of the triphenyl phosphate-treated fabrics and has been attributed to the transesterification reaction with the loss of phenol; the third and predominant weight loss occurred below 250°C, which was significantly lower than in any of the corresponding samples. This would seem to indicate a more effective catalysis of the cellulose degradation, probably through the formation of some intermediate product resulting from the interaction of the phosphorus and nitrogen compounds. Furthermore, the observation that the rate of weight loss in this was considerably slower and the residue formation greater may be indicative of the presence of an intermediate compound that is capable of altering the mode of decomposition of the cellulose. This would contribute further to the reduction of the fuel supply available to the flame.

Thus it would seem likely that the enhanced effectiveness of triphenyl phosphate as a flame retardant observed in the presence of nitrogenous bases is due, at least in part, to some thermally induced interaction between the compounds prior to the cellulose degradation. The exact nature of this interaction is the subject of continuing studies.

### SUMMARY AND CONCLUSIONS

The ability of selected phosphorus and nitrogen-containing compounds to act as flame retardants for cotton cellulose has been found to correlate with the structures of the compounds. Those systems which are intrinsically acidic or capable of forming free acids below 300°C are found to catalyze the thermal decomposition of cellulose and presumably reduce the flammable gas production to the point where the sample exhibits flame-retardant properties. In most cases, the active structure is probably a P—O—H function; but in the one case examined, a P—NH<sub>2</sub> group was found to be more effective than a P—OH group when all other structural features were held constant.

An examination of cotton fabrics treated with urea or guanidine carbonate showed that these bases are capable of changing the nature of the reaction energetics in the 300–450°C region from endothermic to exothermic. The degree of flame retardation obtained was greater with the stronger base guanidine; however, neither system showed a significant increase in char formation, as has been reported with stronger alkali metal bases.

Nitrogenous bases proved to enhance the flame-retardant properties of triphenyl phosphate. The nature of this enhancement is not fully understood but is suspected to be due, at least in part, to some thermally induced interaction between the compounds prior to degradation of the cellulose substrate.

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