

Phosphorylation of Cellulose: Effect of the Reactivity of the Starting Polymer on the Properties of the Phosphorylated Product

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Synopsis

When cellulose is phosphorylated with phosphorus oxychloride, the reactivity of the cellulose, as well as reaction time and temperature, influences the relative amounts of phosphorylated and chlorinated product formed. The swelling ability of the phosphorylated product is affected by the pretreatment received by the cellulose (i.e., prior to phosphorylation) to change its reactivity. The thermal decomposition process of phosphorylated cellulose, as indicated by differential thermal analysis, is affected also by the pretreatment received by the cellulose.

INTRODUCTION

Numerous studies have been conducted to obtain an understanding of the effect of the supramolecular structure of cellulose on its reactivity.^{1,2} Less attention has been paid to the effect of the reactivity of cellulose on the chemical and physical properties of products formed by chemical reaction. However, this aspect could be of importance if the chemical or physical properties of the product were to be enhanced by increasing the level of reactivity of the starting material. There is evidence that the location of the reaction sites is affected by the reactivity of the starting cellulose when acetic anhydride reacts with cellulose.³ It may be speculated, for example, that a more uniform penetration of a flame retardant into the cotton fiber structure may be obtained by increasing the reactivity of the cellulose and may result in a change of the thermal properties of the fiber.

In this study, we examined the effect of increasing the reactivity of the starting cellulose on the reaction between cellulose and phosphorus oxychloride. In addition, we investigated the effect of the reactivity of the starting cellulose on the swelling ability and thermal properties of the phosphorylated products.

EXPERIMENTAL

Materials

"Cut skein" samples⁴ of commercially kiered cotton yarn (80/2's filling twist) were used as starting material. All chemicals were of analytical reagent grade.

Methods of Treatment

Treatment with Sodium Hydroxide (Mercerization). The cut skein (5 g) was immersed in 7*N* sodium hydroxide solution (5 g per 250 ml solution) in a stoppered ground-glass bottle for 30 min at 21°C. The alkali was then filtered off, and the sample was washed in several changes of distilled water before it was steeped in 10% acetic acid for 15 min at room temperature. The cotton was rewashed in distilled water, with the water being changed periodically until it was free of acid. Samples which were to be retained in the never-dried state were kept in water. The remaining samples were dried overnight in an oven at 55°C and then conditioned in the laboratory.

Phosphorylation. Procedures were based on those of Reid and Mazzeno.⁵ The cut skein (5 g) was washed in 125 ml pyridine. With air-dry samples, the washing was repeated three times; with samples wet with water, the washing was repeated four times. The sample was placed in a stoppered ground-glass bottle and the final portion of pyridine was adjusted to 200 ml by weighing. Then the predetermined volume of phosphorus oxychloride was added and the mixture was shaken well and kept at the preselected temperature in a thermostatically regulated water bath. Periodic shaking of the bottle followed, and the reaction was allowed to continue for the predetermined length of time. The reaction mixture was decanted, the sample was then washed with pyridine followed by distilled water and 1% hydrochloric acid solution. Finally, the sample was washed with distilled water until the water was free of acid. The sample was dried by exposure to the atmosphere at room temperature.

Preparation of Chlorodeoxycellulose. Never-dried mercerized cut skein cotton yarn (5 g) was prepared as described above, except that 5% hydrochloric acid solution was used instead of acetic acid in the washing treatments. The never-dried sample was washed several times, first with 95% ethanol and then with benzene. Chlorination was achieved using a procedure essentially similar to that described by Vigo and Welch,⁶ except that distilled water was used and the products were not dried with acetone.

Characterization of Product

Chemical Analyses. Phosphorus, nitrogen, and chlorine determinations were made at the Microchemistry Analytical Laboratory of the University of California at Berkeley.

Alkali Sorption Capacity (ASC). The procedure has been described previously.⁷ For this measurement, alkali-swollen samples were centrifuged at 760 g and ASC (%) was calculated from the formula

$$\text{ASC (\%)} = \frac{W_1 - W_2}{W_2} \times 100$$

in which W_1 is the weight of the specimen immediately after centrifugation and W_2 is the original weight of the specimen.

Thermal Analyses. Samples were ground in a Wiley mill to pass a 20-mesh screen. Differential thermal analysis (DTA) was run on a Deltatherm III thermal analyzer under nitrogen at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Effect of Reactivity of Cellulose on Reaction with Phosphorus
Oxychloride

It is clearly evident that the reaction between phosphorus oxychloride and cellulose at 60°C was affected by the pretreatment given the cellulose prior to phosphorylation to change its reactivity (Figs. 1 and 2). Reaction conditions in the set of experiments recorded in these graphs were: temperature, 60°C; molar ratio POCl_3 :cellulose hydroxyl group, 4:1; and molar ratio POCl_3 :pyridine, 1:6.67. The phosphorus and chlorine contents were highest, for a given reaction time, for cellulose which had been mercerized and then retained in a water-swollen state (never-dried mercerized cellulose) until the water was displaced with pyridine by solvent exchange prior to the addition of phosphorus oxychloride. It was lowest for cellulose which had been mercerized and dried (dried mercerized cellulose) before swelling with pyridine and then adding of phosphorus oxychloride. Cellulose which had not been given a pretreatment (non-mercerized cellulose) had an intermediate reactivity.

The phosphorus uptake is due to phosphorylation while the chlorine uptake is probably due to chlorodeoxycellulose formation. It should be noted that, as observed by Reid and Mazzeno,⁵ a small amount of nitrogen, due to tenaciously retained pyridine, was found. The amount was small (normally $\text{N} < 1\%$) and

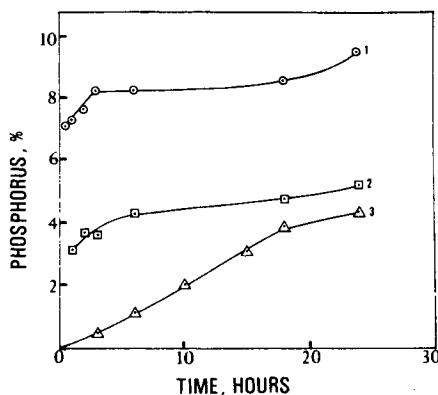


Fig. 1. Effect of pretreatment of cellulose on phosphorus uptake: (1) never-dried mercerized cellulose; (2) starting nonmercerized cellulose; (3) dried mercerized cellulose.

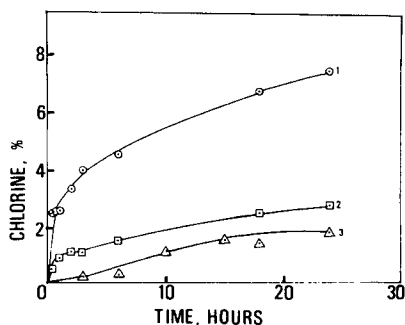


Fig. 2. Effect of pretreatment of cellulose on chlorine uptake: (1) never-dried mercerized cellulose; (2) starting nonmercerized cellulose; (3) dried mercerized cellulose.

is ignored since it does not influence the properties to be discussed. Never-dried mercerized cellulose is highly swollen and is a "water cellulose"⁸ which is highly accessible to chemical reagents. When water is displaced by pyridine by solvent exchange, the cellulose product remains highly accessible to phosphorus oxychloride on subsequent reaction with this reagent. When mercerized cellulose is dried, its structure collapses. Pyridine can only penetrate noncrystalline portions of dried mercerized cellulose, and thus the product is less accessible to phosphorus oxychloride. Consequently, never-dried mercerized cellulose is more reactive than dried mercerized cellulose. The nonmercerized cellulose has an intermediate reactivity. Its structure after immersion in pyridine is more accessible to phosphorus oxychloride than is dried mercerized cellulose but not as accessible as never-dried mercerized cellulose.

The reactivity of the cellulose as well as reaction time influences the relative amounts of phosphorylated and chlorinated product formed (cf. Figs. 1 and 2). For example, phosphorus content of the never-dried mercerized cotton increased only from about 7.2 to 9.5% as the time of reaction was extended from 30 min to 24 hr. However chlorine content increased roughly threefold from 2.5 to 7.4% by this extension of reaction time. For nonmercerized cellulose, chlorine content also increased relatively faster than phosphorus content as the reaction time was increased. However, for the least reactive material, i.e., dried mercerized cellulose, the ratio of the uptakes of phosphorus and chlorine appeared to remain roughly constant at about 2 as the time of reaction was increased. Increasing the reactivity of the cellulose affects the formation of chlorinated cellulose even more than the formation of phosphorylated cellulose. After 24 hr, for the reaction conditions used, percent phosphorus for never-dried mercerized cellulose, nonmercerized cellulose, and dried mercerized cellulose was 9.5, 5.2, and 4.3, respectively, while percent chlorine was 7.4, 2.7, and 1.8, respectively.

The temperature also influenced the relative amounts of phosphorylated and chlorinated products formed by the reaction between POCl_3 and never-dried mercerized cellulose. Phosphorus content increased only a small amount as the reaction temperature was raised from 25 to 60°C for a given reaction time (Table I). However, the chlorine content increased markedly indicating that the formation of chlorinated cellulose was affected strongly by reaction temperature.

TABLE I
Effect of Temperature on Phosphorylation of Never-Dried Mercerized Cellulose^a

Reaction time, hr	P, %	Cl, %
Reaction Temperature 25°C		
6	8.09	2.08
18	8.28	2.41
24	8.55	3.06
Reaction Temperature 60°C		
6	8.28	4.47
18	8.58	6.62
24	9.48	7.37

^a Molar ratio POCl_3 :cellulose hydroxyl group, 4:1, molar ratio POCl_3 :pyridine, 1:6.67.

ASC Results

It can be inferred from ASC determinations (Fig. 3) that the physical properties of phosphorylated cellulose are affected by the level of reactivity of the starting cellulose. ASC is a measure of the swelling of cellulosic fibers in 15% NaOH. The alkali concentration is sufficiently high that intra- as well as intercrystalline swelling occurs. For a phosphorylated material of given phosphorus content, ASC decreased in the following cellulose pretreatment order: no treatment (nonmercerized) > never-dried mercerized > dried mercerized. The differences in swelling ability of the phosphorylated products probably depend on the amount of disubstituted phosphate ester in the fiber which is present as intercellulose crosslinks and on whether the cellulose is mercerized. The work of Reid and co-workers⁹ indicates that a fraction of the combined phosphorus in cellulose phosphorylated with POCl_3 /pyridine can be accounted for as a disubstituted phosphate ester. For example, intercellulose crosslinking may not be favored in never-dried mercerized cellulose where the cellulose is highly swollen and thus polymer molecules are far apart. Collapse of the cellulose fiber structure occurs if it is dried after mercerization. Thus, when dried mercerized cellulose is phosphorylated there is a greater possibility of intercellulose crosslinking since the polymer chains are likely to be closer together than in never-dried mercerized cellulose. Differences in swelling ability after phosphorylation between never-dried mercerized cellulose and nonmercerized cellulose may be due in part to changes in supramolecular structure of the cellulose caused by mercerization. ASC for the cotton cellulose used in this study decreased from 204 to 185% when mercerized. We assume that the swelling of the phosphorylated cellulose is little affected by chlorination. For example, ASC for chlorodeoxycellulose of 6.1% chlorine content is 208%. The ASC for this product calculated in terms of weight of cellulose is 215%. The ASC of phosphorylated never-dried mercerized cellulose of 8.6% phosphorus and 6.6% chlorine is 113%. If the ASC is calculated on the basis of chlorinated cellulose or of cellulose, it is 145 and 152%, respectively.

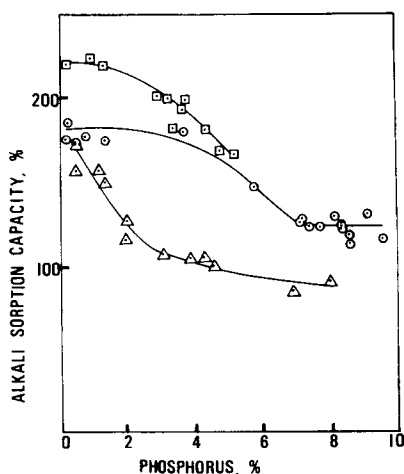


Fig. 3. Relation between alkali sorption capacity and phosphorus content for different celluloses: (—□—) starting nonmercerized cellulose; (—○—) never-dried mercerized cellulose; (—△—) dried mercerized cellulose.

Thermal Properties

The DTA curve of the mercerized cotton was typical of that obtained by pure cellulosic materials (Fig. 4, curve 1). The DTA curve of the nonmercerized cotton (i.e., native cellulose) showed a major endotherm at about 330°C also. This endotherm occurs as cellulose depolymerizes and forms a tarry mixture which then evaporates as transglycosylation reactions occur.¹⁰

In general, irrespective of the pretreatment received by the cellulose, essentially similar changes occurred in the DTA curves of the phosphorylated products as the phosphorus content increased (Figs. 5-7). At small phosphorus contents the major endotherm present in cellulose shifts below 300°C. As the phosphorus content increases, exotherms develop and become progressively stronger until a major exotherm occurs below 200°C.

At low phosphorus contents ($P < 2.0\%$), the major feature of the DTA curve of the samples is similar to that observed by Parks¹¹ for cellulose treated with small quantities of sulfuric acid, i.e., the cellulose decomposition endotherm becomes broader and shifts to lower temperatures. It is suggested that for our samples the initial reactions at about 200°C are dephosphorylation and dehydrohalogenation and that the released acids then catalyze the decomposition of the cellulose.

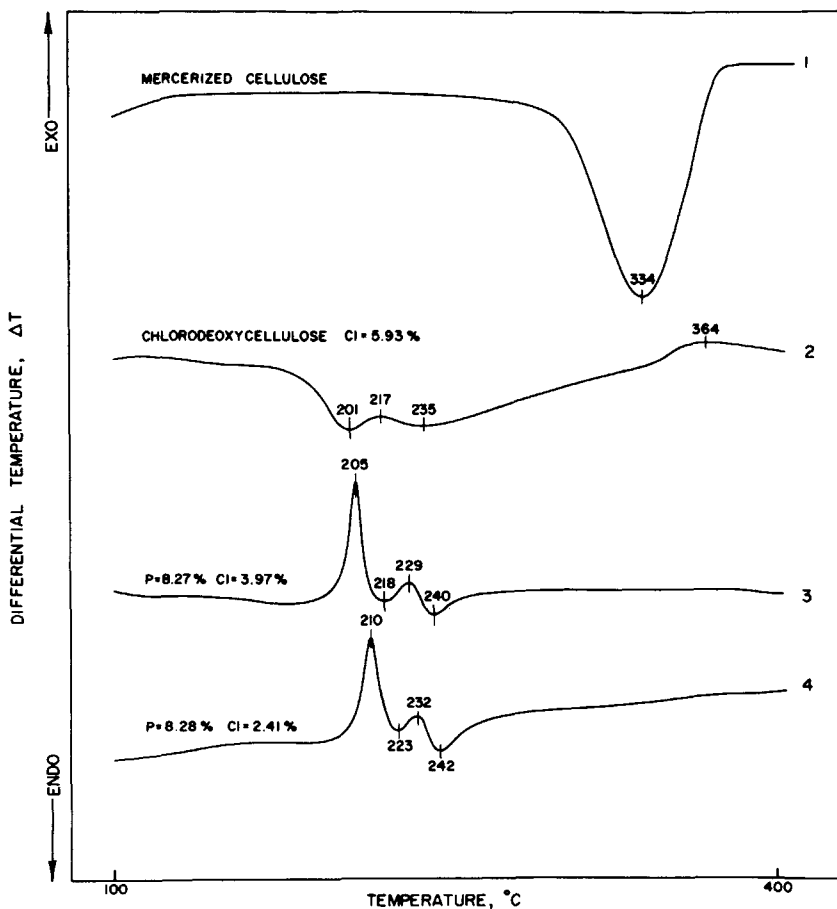


Fig. 4. DTA curves of various samples.

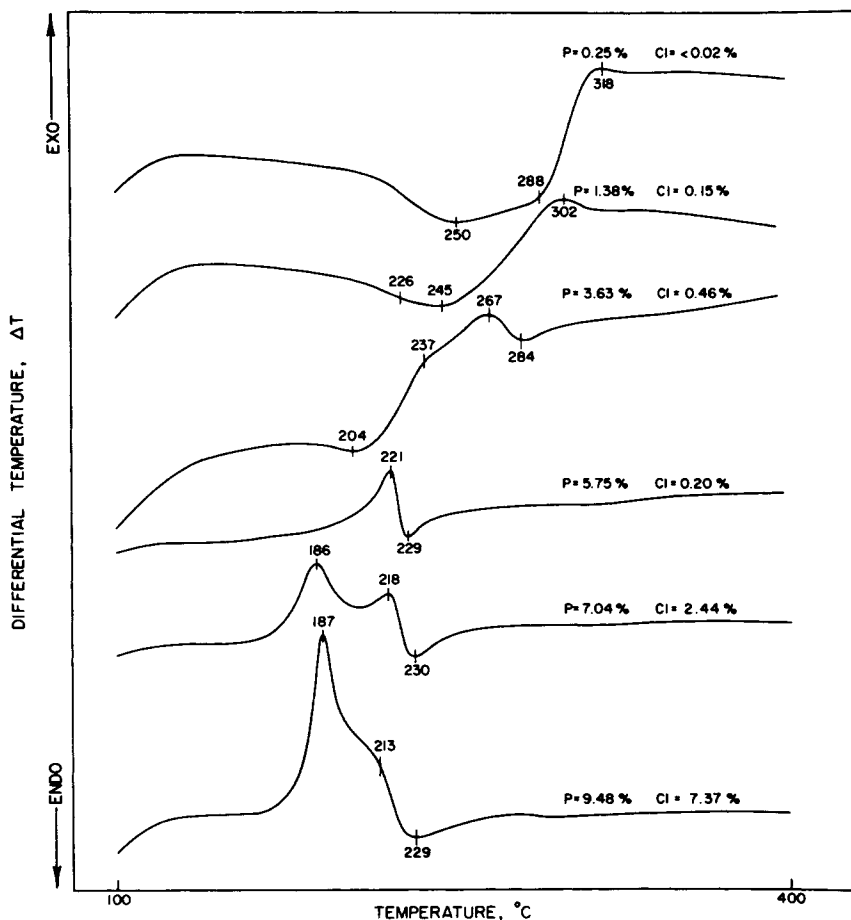


Fig. 5. DTA curves of phosphorylated samples. Cellulose pretreatment: mercerized and never dried.

At high phosphorus contents, we assume that the phosphate ester is the primary cause of the exothermic reactions which occur, as indicated by the DTA curves of the samples, for the following reasons. First, the DTA curve of chlorodeoxycellulose with chlorine content between 0.40 and 5.72% contains a shallow endotherm in the range of 190–360°C.¹⁰ The DTA curve of a chlorodeoxycellulose is presented in Figure 4, curve 2. Shafizadeh and co-workers¹⁰ have discussed the thermal degradation of chlorodeoxycellulose. They state that for partially substituted 6-chloro-6-deoxycellulose, the initial decomposition reactions begin with dehydrohalogenation at ~200°C, and the released hydrogen chloride then catalyzes a series of heterolytic reactions. Second, the DTA curve of the products remained the same (Fig. 4, curves 3 and 4) for phosphorylated samples which had received identical pretreatments and had similar phosphorus contents but differed in chlorine content. It should be noted that these two DTA curves were obtained on samples that had been soaked in dilute ammonium hydroxide after phosphorylation. The ammonium hydroxide treatment has the effect of shifting the position of exothermic peaks to slightly higher temperatures (<10°C). None of the other DTA curves presented in Figures 4

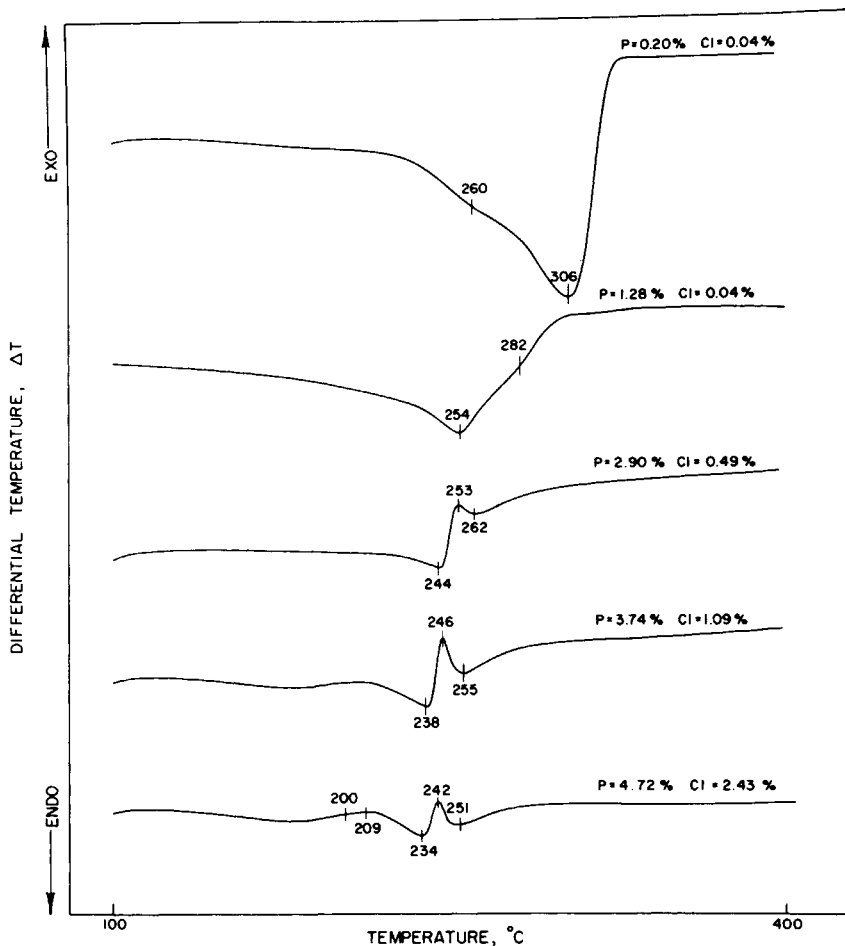


Fig. 6. DTA curves of phosphorylated samples. Cellulose not pretreated.

through 7 were obtained on products that had received this treatment. Thus, the temperature of the zenith of the exothermic peaks of curves 3 and 4 in Figure 4 should not be compared directly with those of other DTA curves presented.

The pretreatment, or activation of the cellulose, appears to affect the thermal degradation of the phosphorylated product. For example, the DTA curve (Fig. 5) of the product prepared from never-dried mercerized cellulose ($P = 1.38\%$) contains an exotherm at 302°C , whereas none can be seen in the DTA curve (Fig. 6) of the phosphorylated nonmercerized sample (1.28% P). At 3.74% P, a sharp exotherm occurs at 246°C on the phosphorylated nonmercerized sample (Fig. 6), whereas at about the same phosphorus content the phosphorylated never-dried mercerized sample has a broad exotherm peaking at 267°C (Fig. 5). When phosphorylated nonmercerized and phosphorylated dried mercerized samples in the range 2.9 – 4.7% phosphorus are compared (Figs. 6 and 7, respectively) it will be noted that the DTA curves of the dried mercerized samples contain an additional exotherm and the exotherms occur over a larger temperature range.

Differences observed between phosphorylated samples which have received

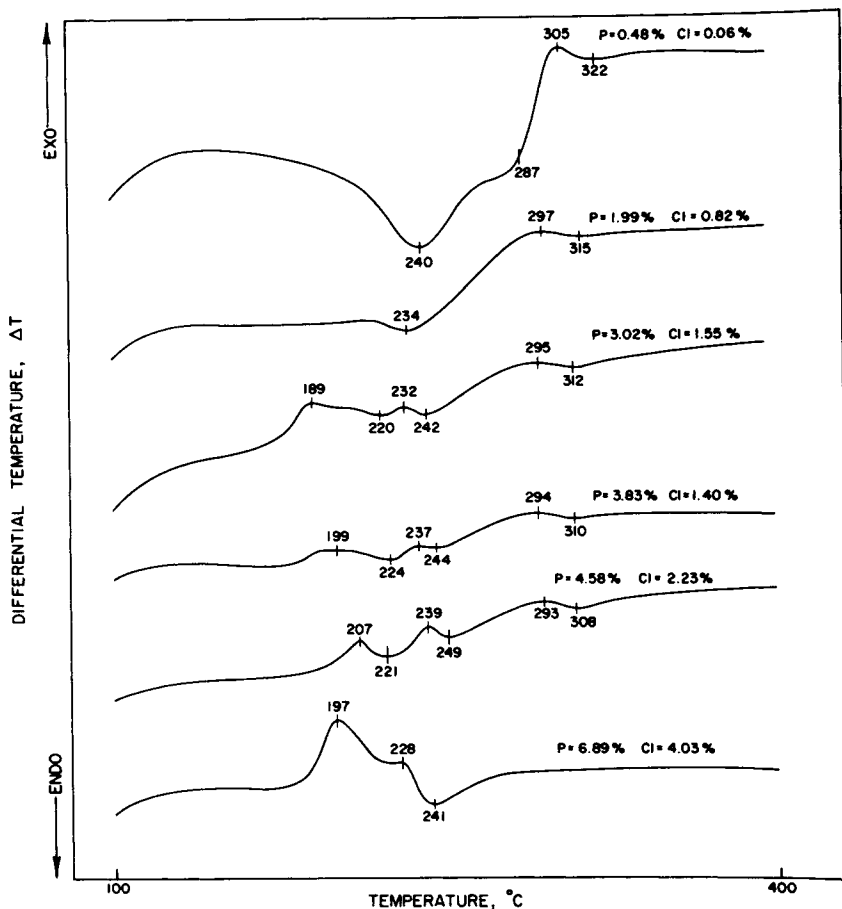


Fig. 7. DTA curves of phosphorylated samples. Cellulose pretreatment: mercerized and dried.

the dried mercerized or never-dried mercerized pretreatment appear to be related more to the intensity of the exotherms when specimens of 3.83% P (Fig. 7) and 3.63% P (Fig. 5) are compared. When the phosphorus content of the dried or never-dried mercerized samples is increased above 6.9%, the DTA curves become similar, resolving into two exotherms followed by an endotherm (Figs. 5 and 7, respectively).

We suggest that at higher phosphorus contents, thermal decomposition is controlled primarily by phosphorus compounds promoting dehydration and charring reactions. These phosphorus compounds are either the phosphate ester or are products formed by dephosphorylation. Factors related to the pretreatment of the cellulose that may have an effect on the thermal decomposition of phosphorylated samples include the following:

(1) It can be deduced from work reported earlier³ that for both the phosphorylated nonmercerized and dried mercerized samples, the distribution of phosphorus is not as uniform as that of the phosphorylated never-dried mercerized product. With the former samples the phosphorus is probably located more heavily at fiber peripheries. It is probable that the nonuniform distribution of phosphorus would be greater for the dried mercerized sample than the non-

mercerized sample. On thermal decomposition, it is conceivable that with phosphorylated dried mercerized or nonmercerized samples, following dephosphorylation, some of the released phosphorus compounds may volatilize and escape without reacting with the cellulose since the compounds produced will be close to fiber surfaces.

(2) Dephosphorylation of disubstituted phosphorus ester may occur at a different rate than monosubstituted ester. Also, disubstituted phosphorus ester may react with cellulose at a different rate than the monosubstituted ester. As already discussed, the fraction of disubstituted phosphorus ester appears to be greater in dried mercerized cotton than in the two other samples.

Differences, at high phosphorus contents, between the DTA curves of never-dried mercerized samples and nonmercerized samples, may be related to the first factor, while differences between the curves of dried mercerized samples and nonmercerized samples may be related to the second factor as well as the first factor, since the nonuniform distribution of phosphorus is probably greater for the dried mercerized sample.

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