Durable Flame-Retardant Finished Cotton Fabrics Characterized by Thermal Degradation Behaviors

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ABSTRACT: After a series of investigations on the durable flame-retardant finishes, it was thought to be important to study these durable flame-retardant finished materials from the thermal analytical standpoint. Accordingly, cotton fabric was finished with *N*-methylol dialkyl phosphonopropionamide (Pyrovatex C) by thermofixation and tetrakis (hydroxymethyl) phosphonium sulfate (THPS) precondensate by ammonia cure (Proban), as well as with THPS monomer by heat cure under various conditions, and subjected to the thermogravimetry (TG) to observe thermal degradation behaviors and obtain apparent activation energy (E_a). TG curves of Proban-finished samples showed the largest shift to lower temperatures with a steep slope; thermofixed THPS-finished sample gave a smaller shift with similar steep slope, whereas Pyrovatex-finished samples exhibited a similar shift but with a gradual slope. E_a versus residual ratio curves led us to conclude that C—N bond-rich Proban polymer requires the highest E_a and decomposes with considerable rapidity, whereas ethylene-bond-rich Pyrovatex-finished samples with melamine crosslinking decompose gradually with the lowest E_a. As for the relationship between flame retardance and E_a distribution in the process of thermal degradation, typical differences among the above three kinds of finished samples were found, which are compared and discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 975–987, 1999

Key words: durable flame-retardant finish; thermogravimetric curve; distribution of activation energy in the process of thermal degradation; limiting oxygen index; self-extinguishability

INTRODUCTION

The flame-retardant finish is highly required for the textile fibers for the security of the human life since they are extremely flammable.

Accordingly, we have performed successive studies on flame-retardant finishes and related investigations of cellulosic and polyester fibers, as well as of cotton–polyester blended fibers, from both fundamental and practical standpoints.

Since more attention has been paid to durable flame-retardant finishes because of the practical importance, we have studied on the finishing conditions to obtain the best flame retardance and favorable physical properties for the end uses from the practical viewpoints. But it was thought to still be important to investigate durable flame-retardant finished samples from the aspect of thermal degradation.

The studies on durable flame-retardant finishes have been attempted worldwide so far.[1–8]

But, as for studies on the thermal analysis of durable flame-retardant samples involving the activation energy of the thermal degradation reaction, little information has been available up to the present.

Therefore, we have extended our previous investigations on the three kinds of durable flame-retardant finishes[9–11] over the thermogravimetric (TG) analysis to observe the thermal degradation behaviors as well as to obtain activation energies for the thermal degradation reaction. The samples used for the investigation were the most flammable cellulosic (cotton, in this case) fabric treated with the most famous durable flame retardants worldwide, N-methylol dialkyl phosphonopropionamide (Pyrovatex CP), tetrakis (hydroxymethyl) phosphonium sulfate (THPS) in the forms of monomer, and a condensate with urea (THPS precondensate) with or without additives. The samples treated with Pyrovatex CP and THPS monomer were thermally fixed, and those treated with THPS precondensate were cured with ammonia (PROBAN finish). Comparing these three types practically, little difference was found in the flame retardances among them, but as to another important property, tensile strength, the thermofixed samples showed reduction by approximately 10% (THPS monomer) and 20% (Pyrovatex CP). As far as the tensile strength is concerned, it seems that PROBAN finish is the most recommendable durable flame-retardant finish. However, heating is much simpler and easier than applying such a hazardous gas, ammonia, under the pressure with a large-scale installation. Simplicity or facility is an important factor for the process of preparation for any product. Moreover, dyestuffs that can be used for these three types of finishes are limited in different ways because of different effects of the finishing conditions.[12,13] Thus, there is little to choose among the three. Accordingly, we adopted all these samples to observe the thermal degradation behaviors by the thermogravimetry. The thermal degradation onset point, flash point, and maximum degradation rate point were obtained from each TG curve to observe relative positions of these three temperatures.

E_a was determined by Ozawa's method,[14] and E_a distribution, not overall, was observed in the process of thermal degradation. E_a values at these three points were obtained to observe E_a change with the rise of temperature in each case.

Furthermore, we paid attention to the residual amount remaining after the thermal treatment.

Since the self-extinguishability is one of the important factors to evaluate quenching ability, which will act after the onset of combustion, and the residual amount of char can be a measure for the self-extinguishability, we attempted to evaluate the flame retardance also from the residual ratio shown by each TG curve after the termination of heating at FP or at 600°C.

Thus, this article reports on the thermal degradation behaviors of cotton fabric treated with the representative durable flame retardants under various conditions and reveals the results of comparison between flame-retardant samples and flammable samples, as well as among the types of finishing.

EXPERIMENTAL

Materials

Fabric

The fabric used for this investigation was 100% cotton plain woven fabric (100 g/m^2) with a yarn count of 20 tex in warp and 16 tex in weft. Fabric count was 141/5 cm in ends and 135/5 cm in picks.

Treating Reagents

Flame Retardants. N-methylol dialkyl phosphonopropionamide (Pyrovatex CP) was offered by Ciba Geigy Co. (Switzerland). Tetrakis hydroxymethyl phosphonium sulfate (THPS) monomer was a product of Nihonkayaku Co. THPS precondensate with urea was offered by Albright and Wilson Co. (United Kingdom).

Additives for Each Flame Retardant. Hexamethylol melamine (M6) (offered by Mitsuitohatsu Kagaku Co.), orthophosphoric acid, urea, and ammonium chloride (products of Wako Chem. Co.) were used with Pyrovatex CP for thermofixed Pyrovatex finish. Sodium acetate and polyoxyethylene nonylphenyl ether were used with THPS precondensate for Proban finish (THPS with ammonia cure = Proban finish). Trimethylol melamine (M3), aminomethyl propanol (catalyst P, offered by Mitsuitohatsu Co.), triethanol amine (TEA, pH adjuster, a product of Wako Chem. Co.) were used for thermofixed THPS monomer.

Methods

Flame-Retardant Finishes

Finishing with Pyrovatex CP. This finish was carried out on the basis of process and results already reported by Nakanishi and Aoki.[9]

The following five kinds of treating baths were prepared.

1. 32% (v/v%) of Pyrovatex CP solution alone (Py 1).
2. A solution consisting of 32% of Pyrovatex CP and 8% of hexamethylol melamine (M6) (Py 2).
3. A solution consisting of 32% of Pyrovatex CP and 2% of orthophosphoric acid (Py 3).
4. A solution consisting of 32% of Pyrovatex CP, 8% of M6, and 2% of orthophosphoric acid (Py 4).
5. A solution containing 32% of Pyrovatex CP, 8% of M6, 2% of orthophosphoric acid, 1% of urea, and 0.5% ammonium chloride (Py 5).

The cotton fabric was immersed in the above each solution separately, padded after 40 min, and treated in the same solution, again adjusting pick-up to 90%. Each sample was preliminarily air-dried, followed by a thermal treatment for 4.5 min at 160°C. This fabric was soaped with 0.2% of sodium carbonate to remove formaldehyde formed in the process of the thermal treatment.

Finishing with THPS–Urea Precondensate by Ammonia Cure (Proban Finish). This finish was performed according to the method established by Nakanishi and Ohkouchi before.[10] The cotton fabric was treated under the following five conditions.

1. The fabric was immersed in 40% (v/v%) of THPS precondensate solution for 10 min, padded to 90% pick-up, and air-dried until the water content reached down to 25% (Pb 1). This water content should be strictly controlled for the following ammonia cure.
2. The fabric treated as described above was treated further by the ammonia cure, as mentioned below (Pb 2).

The treated fabric was placed in a desiccator and aspirated to a negative pressure (40 mm Hg), to which NH_3 gas was introduced for 5–10 s. Nakanishi and Ohkouchi[10] have found that such a condition as negative pressure is indispensable for NH_3 introduction to get strong penetration of NH_3 gas into the fiber structure to allow sufficient contact between NH_3 and THPS precondensate permeated into the amorphous region of cotton cellulose.

3. The sample thus treated was treated further by oxidation with 10% of H_2O_2 for 10 min at 60°C, followed by soaping with a solution containing 0.2% of sodium carbonate and 0.08% of a nonionic surfactant for 10 min at 60°C to remove formaldehyde formed in the finishing process (Pb 3).
4. The fabric was treated with 40% of THPS precondensate containing 2.6% of sodium acetate and 0.2% of the above-mentioned nonionic surfactant and predried to adjust the water content of sample to 25%, to which NH_3 gas was introduced for the ammonia cure, as mentioned above (Pb 4).
5. Sample Pb 4 was treated further by oxidation and soaping, as described above (Pb 5).

Finishing with THPS Monomer by Heat Cure. The cotton fabric was finished according to the method reported by Nakanishi and Ohkouch before.[11]

Cotton fabric was treated with the following 4 kinds of solutions by a 2 dip–2 nip method, adjusting its pick-up to 90%.

1. A solution containing 32% (v/v%) of THPS and 5% TEA to adjust pH at around 7 ± 0.2 (Ts 1).
2. A solution containing 32% of THPS, 5% of TEA, and 1% of urea as a nitrogen donor (Ts 2).
3. A solution consisting of 32% of THPS, 5% of TEA, 12% of M3, and 1% of Catalyst P (Ts 3).
4. A solution consisting of 32% of THPS, 5% of TEA, 1% of urea, 12% of M3, and 1% of Catalyst P (Ts 4).

These treated samples were heated for 20 min at 140°C, followed by oxidation and soaping to minimize contents of formaldehyde and any excess of reagents by the same procedure described above.

Evaluation of Flame Retardance

The flame retardance of each above-mentioned sample was determined by the burning test method for polymer materials regulated by the limiting oxygen index (LOI) method of Japanese Industry Standard (JIS) K7201-1976. A LOI-type burning tester NO1 (Suga Tester Manufacturing Co. Ltd.) was used to determine the volumes of O_2 and N_2 required for ignition and the onset of

Figure 1 An illustration to show how to determine TDOP, FP, and MDRP.

burning. LOI values were calculated by the following equation.

$$\text{LOI (\%)} = \frac{[O_2]}{[O_2] + [N_2]} \times 100$$

Thermal Analysis

Thermogravimetric (TG) curves and differential thermogravimetric (DTG) curves were obtained at a heating rate of 10°C/min in air using a Shimadzu thermal analysis equipment DT-TGA-40.

The maximum degradation rate point (abbreviated to MDRP) was determined for each sample as a temperature at which each DTG curve showed a peak (B) as illustrated in Figure 1.

The thermal degradation onset point (abbreviated to TDOP) was determined as a temperature where an extrapolated line from the initial stage of each TG curve intersects with a line from the (B) point tangent to a curve just above (B), as illustrated in Figure 1.

The flash point (FP) was estimated as a temperature where a baseline started to rise abruptly, as also shown in Figure 1. Shimadzu FPC-30 was used for this purpose.

Every sample to be used for the thermal analysis was cut into powdery fine particles to minimize any effect of air diffusion.

Evaluation for Self-Extinguishability

It was thought that residual amounts of char remaining after ignition could be a measure for burning. the evaluation of flammability or extinguishability since combustible samples would almost burn completely when ignited, whereas flame-retardant samples probably quench by themselves after ignition. Therefore, heating was stopped during the TG analysis at FP of each sample determined as mentioned above, and the ratio of residual amount was obtained from each TG curve at the points of FP and 600°C.

Determination of E_a

E_a was determined according to Ozawa's method[14] for each sample by using the following equation finally derived assuming that the kinetic equation of thermal degradation is represented by the following the Arrhenius equation:

$$-\log \beta_1 - \frac{0.4567E}{RT_1} = -\log 102_2$$

$$-\frac{0.4567E}{RT_2} = \cdots$$

where β is the heating rate, E is the activation energy, R is the gas constant, and T is the absolute temperature. TG curves were obtained at heating rates of 5, 10, 15, and 20°C/min. Temperatures at various residual weight ratios on these TG curves were read, and reciprocal absolute temperatures were plotted against the logarithmic heating rates. E_a was calculated from the slope of each line at each weight value for each sample.

RESULTS AND DISCUSSION

Evaluation of Flame Retardance and Effects of Finishes

The flame retardance was evaluated by LOI value determined for each sample and listed in Table I. We have recognized that LOI can be a convenient measure for the evaluation of flame retardance since Nakanishi and Masuko[15] have already confirmed that LOI values correlate well with char lengths and char areas evidenced to be the measures for evaluating the flame retardance from a practical standpoint.

Samples with LOI values of 27–28% or higher are recognized to be flame-retardant, showing short char lengths or small char areas, which

Table I List of LOI, TDOP, MDRP, and E_a Values at These 3 Points and Residual Ratios Obtained After Heating Up to FP and 600°C. Samples are Cotton Fabric Untreated and Treated with Pyrovatex CP, THPS Monomer, and Precondensate Under Various Conditions

Symbol for Sample	Treating Conditions	LOI (%)	TDOP		FP		MDRP		Residue (%)	
			Temp (°C)	E_a (kJ/mL)	Temp (°C)	E_a (kJ/mL)	Temp (°C)	E_a (kJ/mL)	Up to FP	Up to 600°C
UT	untreated	18.9	350	174	353	178	374	190	12.0	0.2
Py1	Pyrovatex CP (Py)	20.4	328	30	335	48	354	112	40.0	6.0
Py2	Py + M6	22.2	302	30	320	100	321	110	41.0	7.0
Py3	Py + H₃PO₄	25.5	310	50	326	100	330	126	43.0	13.0
Py4	Py + M6 + H₃PO₄	29.5	312	100	328	143	333	186	51.0	20.0
Py5	Py + M6 + H₃PO₄ + urea + NH₄Cl	30.0	316	158	326	180	336	206	60.0	25.0
Pb1	THPS precondensate before NH₃ cure	26.5	213	160	270	210	245	205	43.0	17.0
Pb2	THPS precondensate after NH₃ cure	28.5	284	130	292	180	300	250	71.0	20.0
Pb3	Pb2 → oxidation → soaping	29.0	298	128	306	172	310	250	53.0	23.0
Pb4	THPS precond + NaOAC + nonionic surfactant after NH₃ cure	30.0	284	120	294	180	297	212	76.0	25.0
Pb5	Pb5 → oxidation → soaping	29.5	298	126	304	160	308	210	53.0	24.0
Ts1	THPS + TEA	20.0	314	246	327	230	337	228	40.0	7.0
Ts2	THPS + TEA + urea	24.4	314	248	328	260	336	263	42.0	10.0
Ts3	THPS + TEA + M3 + Catalyst P	29.0	312	120	320	148	329	168	50.0	20.0
Ts4	THPS + TEA + urea + M3 + Catalyst P	30.0	318	120	325	160	330	190	55.0	22.0

Pyrovatex CP : *N*-methylol dialkyl phosphonopropionamide. THPS : tetrakis hydroxymethyl phosphonium sulfate. TEA : triethanolamine. M3 : trimethylol melamine. M6 : hexamethylol melamine. Catalyst P : aminomethyl propanol.

proves that they could quench by themselves before long after ignition.

The effects of the treatment with the above flame retardants are as follows.

Finish with Pyrovatex

Among 5 kinds of conditions, the finish with Pyrovatex CP alone (Py 1) gave the lowest LOI not much different from that of untreated sample, which means that some additives are required. Resin and orthophosphoric acid did not give enough of an effect when added singly, but the samples treated with both resin and orthophosphoric acid in combination with Pyrovatex CP showed sufficient flame retardance, and further addition of urea and ammonium chloride elevated the LOI value. The above results will suggest that the resin and phosphoric acid showed a synergistic effect, and additional nitrogen and a halogen from urea and ammonium chloride enhanced the effect.

Finish with THPS Precondensate with Ammonia Cure (Pb)

Comparing the flame retardance before and after the ammonia cure, the LOI value is lower than 28% (in the case of Pb1) before the ammonia cure but becomes higher after curing, irrespective of with/without additives and the after-treatment.

Finish with THPS Monomer by Heat Cure (Ts)

Addition of a pH adjuster, TEA, and nitrogen donor, urea, failed to give the flame retardance, but further addition of resin and a catalyst showed an efficiency for flame retardance.

TG Curves of Treated Samples in Comparison with That of Untreated Sample

As shown in Figure 2, the TG curve of every treated sample showed a shift to a lower temperature, which was the same tendency already observed by other researchers with samples con-

THPS NH3 cure (PROBAN)

UT

Pb 4   Pb 5

Pb 2

Pb 3

Pb 1

Pb 1 : THPS precondensate alone
       before NH3 cure
Pb 2 : THPS precondensate alone
       after NH3 cure
Pb 3 : Pb 2 → oxidation and soaping
Pb 4 : THPS precondensate + NaOAC +
       nonionic surfactant
       after NH3 cure
Pb 5 : Pb 4 → oxidation and soaping

THPS HEAT cure

UT

Ts 2   Ts 4

Ts 3   Ts 1

Ts 1 : THPS monomer + TEA
Ts 2 : THPS monomer + TEA + urea   ⎤ after
Ts 3 : THPS monomer + TEA + M3 + Catalyst P ⎬ heat cure
Ts 4 : THPS monomer + TEA + urea + M3 +   ⎦
       Catalyst P

$\dfrac{W}{W_0} \times 100$ (%)

PYROVATEX

UT

Py 5   Py 1

Py 3   Py 2

Py 4

Py1 : Pyrovatex CP alone
Py2 : Pyrovatex CP + M6
Py3 : Pyrovatex CP + H3PO4   ⎤ after
Py4 : Pyrovatex CP + M6 + H3PO4   ⎬ heat cure
Py5 : Pyrovatex CP + M6 + H3PO4 + urea + NH4Cl ⎦

Temperature (°C)

taining nitrogen and phosphorus,[16–21] as well as with other flame-retardant elements. Proban finish gave the largest shift, and the Pyrovatex finish apparently gave the smallest shift.

In the case of Proban finish, the sample treated with THPS precondensate alone before ammonia cure exhibited an extremely large shift showing the onset of weight loss at around 165°C. After curing, TG curves shifted back to higher temperatures, starting weight loss at about 270–280°C. Not much difference was observed among TG curves of the cured samples. The above results can probably be explained as follows. THPS precondensate with urea, a comparatively decomposable THPS dimer with an amide bond, as shown in Figure 3, is easily decomposed at a much lower temperature, which gave a large effect on the TG curve of the sample treated with this dimer before curing. After the ammonia cure, THPS precondensate absorbed in the amorphous regions of fiber structure polymerizes to form a Proban polymer by the mechanism shown in Figure 3. It can be deduced that such a flame-retardant polymer is much less decomposable; moreover, char formation from cellulosic fiber by the dehydrating action of the heated polymer retarded the decomposition of the cured samples.

The thermogravimetric behaviors of samples finished with THPS monomer by thermal treatment (Ts1–Ts4) are similar to those of the samples obtained by Proban finish after the ammonia cure (Pb2, Pb3, Pb4, and Pb5), except that the shift of TG curves of Ts samples was less than that of Proban samples by approximately 20°C.

TG curves of Pyrovatex-finished samples showed a somewhat different behavior, curving and descending with a comparatively gentle slope from 290 to 370–390°C, whereas the slope of TG curves shown by the samples finished with Proban polymer and those finished with thermofixed THPS were steeper, descending from 300–310°C to 340–350°C. This means that Pyrovatex finish gives more gradual thermal degradation.

Relationships Among TDOP, FP, and MDRP on TG Curves

The attention was further paid to the mutual relationship among the three temperatures at

Figure 3 Formation of THPS and its precondensate, and mechanisms for ammonia cure and oxidation of methylol groups with H_2O_2.

which the thermal degradation and piloted ignition start and thermal degradation rate reaches the maximum. These three points (TDOP, indi-

Figure 2 TG curves for cotton cellulose treated with three types of durable flame retardants under various conditions and TDOP, FP, and MDRP on these TG curves in comparison with those of untreated cotton cellulose.

Figure 4 Relationship between LOI values and TDOP, FP, or MDRP to compare these temperatures between samples with and without flame retardance as well as among Proban finish, thermofixed THPS monomer, and Pyrovatex finishes.

cated by ●, FP by □, and MDRP by ▲) are marked on the TG curve of each sample (Fig. 2). The order of the position of these three points on the TG curve is TDOP, FP, and MDRP, the same as that of the untreated sample, except for sample treated with THPS precondensate without ammonia cure (Pb 1), which showed much retard FP. Such a tendency is contrary to what was observed in the case of nondurable flame-retardant samples, which have shown that flammable samples are ignited soon after TDOP similar to the untreated sample, and flame-retardant samples are ignited after MDRP.[22] A characteristic difference from untreated sample observed with all the samples but Pb 1 without curing is that the interval between TDOP and FP is longer. This means prolonged ignition after the onset of thermal degradation. In addition, every MDRP locates at an upper position with a shorter interval from FP, which involves self-extinguishing at a lower temperature to leave more residual amount of char.

Particularly, Proban-finished samples with ammonia cure draw attention to that these three points fall in close positions to one another on each TG curve.

Relationship Between LOI and TDOP and FP and MDRP for Each Finished Sample

It is thought to be important to see if there is any difference between flame-retardant samples and flammable samples in TDOP, FP, and MDRP, as well as to mutually compare these three types of finished samples. Figure 4 shows plots of LOI values versus TDOP, FP, or MDRP for Proban-finished samples, thermofixed THPS, and monomer-finished or Pyrovatex-finished samples. The plots for flame-retardant samples with LOI values of ≥ 28% are indicated by solid marks, and those for the samples with LOI values of < 28% are indicated by open marks.

Figure 5 More comprehensible illustration for comparison of TDOP, FP, and MDRP between flame-retardant samples and flammable samples as well as among the three types of finishes.

The ammonia-cured Proban-finished samples with LOI values of > 28% occupied a temperature region higher than that of the samples with LOI values of < 28% without an ammonia cure. This is probably because the polymer formed by an ammonia cure required a higher temperature for the thermal decomposition than the dimer without curing.

On the other hand, little difference was shown in temperature ranges between flame-retardant samples with LOI values of > 28% and flammable samples with LOI values of < 28% in both cases of the thermofixed samples, which seems to be irreconcilable to the results observed with samples treated with nondurable inorganic flame retardants that flame-retardant samples with LOI values of 28% or higher showed lower temperature ranges than flammable samples with LOI values lower than 28%.[22] Such a difference is probably attributed to the difference in the retardation mechanisms between nondurable flame-retardant finished samples and durable flame-retardant finished samples.

Thus, as far as TDOP, FP, and MDRP in the process of thermal degradation are concerned, a little difference between samples with and without flame retardance in the case of samples finished with organic durable flame retardants after curing were found. Such a tendency is more clearly illustrated by plotting TDOP, FP, and MDRP for Proban, THPS monomer, and Pyrovatex-finished samples, respectively, as shown in Figure 5. Solid and open circles fall in almost the same temperature region in the cases of THPS monomer or Pyrovatex-finished samples with curing, whereas Proban-finished samples show that open marks for the sample without curing are located at lower positions than those of solid marks for the samples with curing. Therefore, these results led us to consider that the difference in the temperature region observed between solid and open marks is probably attributed not to with/without flame retardance but to with/without curing in the case of durable flame-retardant-finished samples.

Figure 6 E_a versus residual ratio curves to demonstrate E_a distribution in the process of thermal degradation for samples treated with the three types of durable flame retardants.

E_a Distribution in the Process of Thermal Degradation

E_a for the thermal degradation is important as one of the kinetic parameters for the thermal degradation reaction. In this case, E_a distribution changing with the progress of thermal degradation was observed since the overall E_a value seems to be less significant. The residual ratios at various stage of thermal degradation were plotted against correspondent E_a values for all treated samples in comparison with those of unfinished sample, as shown in Figure 6. An obvious difference is found between Proban-finished samples and the other two thermofixed samples, that is, Proban-finished samples required higher E_a throughout the thermal degradation process, particularly the samples treated with THPS precondensate alone (Pb2 and Pb3) showed a steep rise in E_a curves after the ammonia cure, which implicates a rapid reaction of thermal decomposition requiring a high E_a within the initial short stage of thermal degradation reaction. In the case of Proban finish, the flame-retardation mechanism

is that Proban polymer is converted to phosphorus pentoxide by heat, which strongly dehydrates cotton fiber to convert it to carbon by changing itself to polyphosphoric acid. Once carbon is formed effectively with the simultaneous formation of polyphosphoric acid, the thermal reaction turns gradually, followed by leveling off, requiring 300 kJ/mol or higher E_a. But addition of a nonionic surfactant brought E_a down to that of the unfinished sample. This is supposedly due to the fact that since the nonionic surfactant is a strong penetrant, THPS precondensate permeated much more deeply into the fiber structure to get closer contact with fiber, which results in approaching the degradation of fiber itself, showing considerable access to the E_a curve of unfinished cotton fiber; whereas the sample without the ammonia cure exhibited a different behavior showing a peak. Since the THPS precondensate, dimer, is easily decomposable, the sample treated with this compound requires only a lower E_a for degradation before the ammonia cure; and at the completion of degradation of this dimer, it approaches the E_a curve of cotton fiber itself.

Figure 7 Relationship between LOI values and E_a showing a difference between samples with and without flame retardance and that among the three types of finishes.

In the case of samples treated with THPS monomer followed by thermofixation, samples with LOI values of < 28% containing TEA (Ts1 and Ts2) showed unusually high E_a values around 250 kJ/mol, even at the initial stage of the thermal degradation, and a little change in E_a throughout the degradation process, though higher E_a was required in the presence of urea, as shown by Ts2. On the other hand, samples with LOI values > 28% (Ts3, Ts4) gave normal E_a curves ascending in the initial stage and leveling off later. In this case, samples treated with THPS monomer and additives, TEA (pH adjuster), aminomethyl propanol (catalyst), and M3, resin for crosslinkage with cellulose by thermofixation, required fairly lower E_a compared with untreated cotton fiber throughout the degradation process, which means that addition of the catalyst probably facilitated the thermal degradation to reduce the E_a for decomposition. This can be one of merits of this flame-retardant finish. But further addition of urea to this mixture (Ts4) extremely raised E_a, as observed in the case of Ts2,

which suggests that the nitrogen donor, urea, decomposes separately, requiring extra E_a.

In contrast with the Proban finish, the Pyrovatex-finished sample gave E_a curves with gentle slopes, which implicates a gradual thermal reaction. Such a phenomenon is coincident with the tendency observed in the TG curves shown above. In addition, E_a curves showed a characteristic change with additives; that is, Pyrovatex CP alone or together with a resin required a lower E_a, especially in the case of a sample treated with Pyrovatex alone without flame retardance (Py 1) gave an extremely low E_a curve of only about 1/2 that of a flame-retardant sample (Py 5), and addition of M6 (Py 2) showed some rise by 26–27%. Another addition of phosphoric acid exhibited much more rise by 90% (Py3). LOI values of these samples are all below 28%. But addition of both resin and phosphoric acid (Py 4 and Py 5) gave the flame retardance showing LOI values > 28%, the E_a level of which is a little higher than that of unfinished sample showing the same level as that

Figure 8 E_a at TDOP, FP, and MDRP for comparison of the E_a region between samples with and without flame retardance showing a difference among the types of finishes.

of Py3 after leveling off. Addition of urea also showed a little higher curve in this case.

Relationship Between LOI and E_a Values at TDOP, FP, and MDRP

Finally, E_a values at TDOP, FP, and MDRP versus LOI values are shown in Figure 7 to see if another characteristic difference can be found between flame-retardant samples with LOI value > 28% and those with LOI values < 28%. The flame-retardant samples (closed marks) showed higher E_a values at all three temperatures than those of the flammable samples (open marks) with LOI values < 28% in the case of Pyrovatex finish, whereas THPS thermofixed samples showed just a contrary result; that is, the samples with LOI values < 28% required higher E_a. This result seems to reveal the fact that since the flame-retardant molecules are much more efficiently fixed to cotton fiber for higher flame retardance in the case of flame-retardant samples, the thermal degradation reaction of the flame-retardant sample is much in-

fluenced by cotton fiber itself, which results in changing the E_a to approach the E_a of the untreated sample. In the case of the Proban finish, the E_a values at TDOP and at FP are lower, and those at MDRP become higher after the ammonia cure when compared with those observed before curing, but plots locate in an E_a range the same as that of untreated sample, through scattering over a wider range. Such a tendency can also be expressed by another illustration, as shown in Figure 8, which shows E_a values at TDOP, FP, or MDRP observed for Proban, THPS monomer, and Pyrovatex-finished samples in comparison with those of the untreated sample. Solid marks indicate E_a values of samples with LOI values > 28%, and open marks indicate those of samples with LOI < 28%. The overall tendency is that in the cases of thermofixed THPS monomer and Pyrovatex-finished samples, E_a values of samples with LOI < 28% are considerably higher (THPS) or lower (Pyrovatex) than those of the untreated sample, but E_a values of flame-retardant samples with LOI > 28% get closer to those of untreated sample, as indicated by solid

marks. On the other hand, Proban-finished samples show such a different tendency that E_a values of all flame-retardant samples fall into the vicinity of those of untreated sample; for example, the locality of the E_a at FP for flame-retardant samples is almost the same as that of the untreated sample, though the E_a values of TDOP are lower and those of MDRP are higher than that of untreated sample.

Evaluation of Self-Extinguishability by Observing Residual Ratios

As described above, since the residual amount of char remaining after the thermal treatment can be a measure to evaluate self-extinguishability, residual ratios were obtained from TG curves after heating up to FP as well as to 600°C and are listed in Table I. It is obviously shown that residual ratios of all the samples are comparatively proportional to LOI values. Moreover, such a tendency is evidenced by comparing the end of TG curves shown in Figure 2, though these curves are terminated at 450°C in this figure.

CONCLUSION

TG curves of all treated samples shifted to a lower temperature than that of untreated cotton cellulose, Proban-treated samples showed the largest shift, and the other two thermofixed samples showed less shift; a steeper slope of TG curves was observed with samples treated with both the THPS oligomer and the monomer, and a more gradual slope with Pyrovatex-finished samples was observed. Such thermal degradation behaviors suggest that Pyrovatex-finished samples decompose comparatively slowly, and samples treated with two types of THPS-treated samples decompose more rapidly.

As to E_a versus residual ratios curves, Proban-finished samples are located in the highest region and Pyrovatex-treated samples are located at the lowest position. Comparing the slopes of these curves, Provatex-treated samples show the slowest curves, and the other two exhibit steeper curves. The above results suggest that the Pyrovatex polymer thermally decomposes gradually with comparatively lower E_a, whereas the THPS polymer decomposes more rapidly requiring higher E_a; specifically, the E_a for the thermal decomposition of ammonia-cured Proban polymer is the highest.

Residual ratios obtained after heating up to FP and 600°C are comparatively proportional to LOI values, which can be a measure for the self-extinguishability after ignition. A little difference is observed among the levels of self-extinguishability of the three kinds of finished samples.

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