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Thermal decomposition of cotton cellulose treated with selected salts [1]

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Abstract

Thermal decomposition of untreated and treated cotton fabric was performed in oxidative and inert atmospheres using TGA–FTIR. Cotton fabric samples treated with selected alkali, alkaline earth and other inorganic salts are compared and contrasted to untreated and acid-washed samples. Cations and anions were varied. Sample weight loss with temperature and decomposition products depend on the type of treatment. Cations of alkali metals impart a different decomposition route compared to alkaline earth or transition metal cations.

INTRODUCTION

Historically, cellulosic cotton fibers have played a major role in the manufacture of fabrics for furniture. Cotton and wool predominated for centuries before synthetic fibers were introduced, but cotton still plays a major role as a fiber source because it is less expensive, easily obtained and has good processing and wear capabilities. However, cellulosic cotton fibers can be sensitive to a heat source and undergo smoldering ignition, depending on the presence or absence of certain salts. Potassium salts are most frequently implicated [1,2]. Smoldering ignition of cotton and the effects of salts have been, and continues to be, of interest to researchers [1–7].

The decomposition of cotton fabric that has been scoured, bleached and mercerized is entirely different from the decomposition of the same cotton fabric which contains salts. An understanding of the decomposition and combustion mechanisms of cotton cellulose on heating and the effects of

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various salts on the processes can lead to developing fabric with new, improved smoldering characteristics.

This study examines the effects of selected alkali and alkaline earth salts on the decomposition of cotton. A TGA–FTIR technique was used because it provides weight loss/temperature relationships and allows evaluation of the gases evolved during pyrolysis or combustion. Kinetic parameters are also being investigated, and future work will include additional salts.

EXPERIMENTAL

The cotton fabric used in this study was selected because it is simple in weave, consistent in characteristics, and made in large quantities. The as-received, nearly 100% cellulosic, 7.5 oz yd^{-2} (254.3 g m^{-2}) cotton fabric had been scoured, bleached and mercerized in a commercial process. Analysis for cations, using a Fisons direct current plasma (DCP) showed potassium to be absent. Sodium, magnesium and calcium ions were low: 170, 214 and 380 ppm, respectively. All traces of cations could be removed by soaking the fabric in a 1% HCl bath for four hours and rinsing in deionized water.

Subsequent TGA–FTIR analysis of the as-received fabric, with its low cation content, produced a similar decomposition pattern to the hydrochloric acid-washed fabric. Therefore, the as-received fabric was used for salt treatment. Six-inch by twleve-inch pieces (15 cm × 30 cm) were soaked in the various salt solutions, the excess solution was expressed with rubber rolls, and the cotton was air-dried in a conditioned laboratory. Each fabric was analyzed for the appropriate cation by DCP, and the salt level was calculated. The salts used and the analyzed levels determined in the fabric are listed in Table 1.

Thermal analysis was carried out on a Du Pont 951 TGA interfaced with

TABLE 1

Analysis of cotton samples for cation content

Salt	Cation concentration in ppm	Salt	Cation concentration in ppm
NaCl	1485	KBr	2644
KCl	2100	$NaC_2H_3O_2$	1419
$MgCl_2$	1033	$KC_2H_3O_2$	2303
$CaCl_2$	1566	$Mg(C_2H_3O_2)_2$	1820
KH_2PO_4	2124	$Ca(C_2H_3O_2)_2$	1990
K_2HPO_4	2440	$Ba(C_2H_3O_2)_2$	1900
$KHCO_3$	2736	$Zn(C_2H_3O_2)_2$	1890
K_2CO_3	2294		

a Bomen MB-100 FTIR. Decomposition gases passed directly to a heatable gas cell, constantly scanned by an IR beam. Inert atmosphere experiments used helium gas sweep at 864 ml min^{-1}; an oxidative atmosphere consisted of 24 ml min^{-1} oxygen and 864 ml min^{-1} helium. Three sequential heating ramps were used on each experiment: ambient to 250°C at 20°C min^{-1}, 250–400°C at 5°C min^{-1} and 400–600°C at 15°C min^{-1}. Samples to be tested were cut into 1 mm × 1 mm pieces and placed in a stainless steel basket, which was placed on the balance beam.

RESULTS AND DISCUSSION

The scoured, bleached and mercerized cotton fabric contains small quantities of sodium, calcium and magnesium which are readily removed by acid washing.

However, the low concentration of ions does not significantly interfere in the TGA–FTIR analysis: acid-washed and as-received samples produce similar oxidative-atmosphere decomposition patterns and nearly identical onset temperatures. This is shown by the TG curves in Fig. 1. A large weight loss step due to depolymerization begins at about 325°C. This is followed by a char residue oxidation step, for which derivative TG (DTG) shows a maximum at 509°C. The onset, depolymerization, and char oxidation temperatures for the fabric treatments are listed in Table 2. The

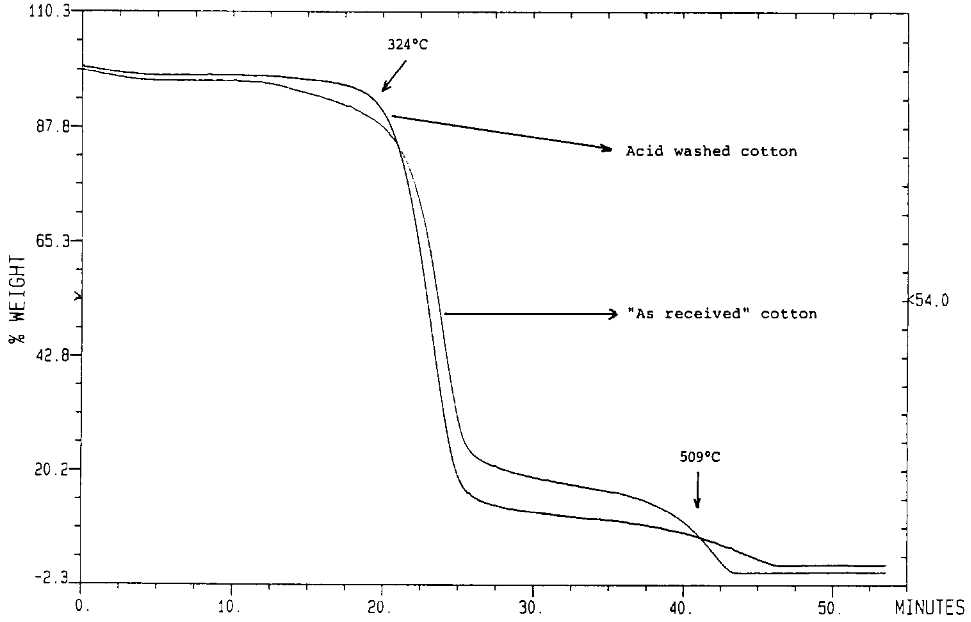

Fig. 1. Thermograph plots of acid washed and "as-received" cotton.

TABLE 2

Decomposition temperatures of cotton samples in an oxidative atmosphere

Cotton treatment	Onset temperature/°C [a]	DTG maxima/°C	
		Depolymerization [a]	Oxidation [b]
As-received	327	345	506 ± 6
Acid-washed	324	341	–
NaCl	298	334	432
KCl	304	338	442
KBr	307	333	466
$MgCl_2$	312	331	465
$CaCl_2$	316	336	445
KH_2PO_4	305	322	515 ± 3
K_2HPO_4	306	332	494
$KHCO_3$	287	341	464
K_2CO_3	293	341	472
$NaC_2H_3O_2$	291	338	445
$KC_2H_3O_2$	291	340	453
$Mg(C_2H_3O_2)_2$	325	346	446
$Ca(C_2H_3O_2)_2$	327	349	425
$Ba(C_2H_3O_2)_2$	325	346	432
$Zn(C_2H_3O_2)_2$	325	339	497 ± 6

[a] Onset and DTG maximum temperatures for depolymerization temperature readings are within 2°C or less.

[b] Temperatures for DTG maximum for oxidation are within 2°C or less, except where noted. The acid-washed sample gave a flat DTG for oxidation.

acid-washed sample has 9% residual char after depolymerization, compared to 15% for the as-received sample, and a very diffuse oxidative step (flat DTG, see Fig. 1).

Cotton fabrics treated with alkali metals ions, such as sodium and potassium, have lower onset temperatures and lower DTG maxima for depolymerization and char oxidation as compared to as-received and acid-washed fabrics. Alkaline-earth salts also lower the onset temperature and DTG maxima but not to the same magnitude as the alkali metal salts. Anions also play a role, as demonstrated in samples treated with alkaline-earth salts; for example, the magnesium and calcium salts with chloride anion produce lower onset temperature than the salts with acetate anion which does not affect the onset temperature (see Table 2). A transition metal such as zinc, as the acetate, does not appear to alter cellulosic decomposition: the TG pattern is similar to the acid-washed sample.

The sample treated with KH_2PO_4 has a different TG weight loss curve

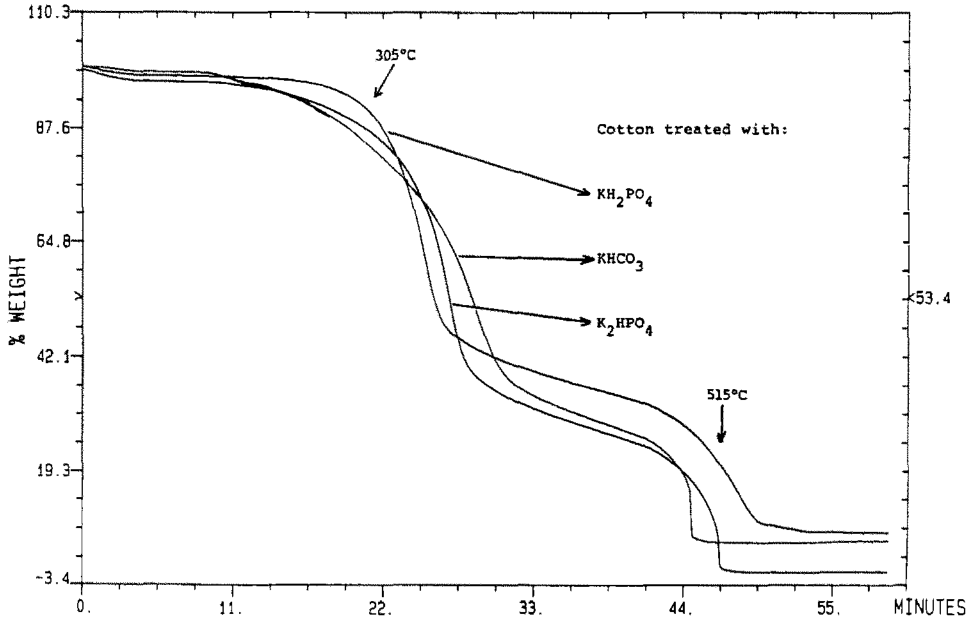

Fig. 2. Thermograph of treated cotton samples.

compared to other treated samples (see Fig. 2). There is about 32% char after the first decomposition step; most other treated samples have 15%–20% char. The DTG peak temperature for char oxidation of this sample is also higher than for all other samples. These results suggest that the monobasic phosphate anion is acting as a retardant and the potassium cation is acting as a promoter.

The FTIR spectra of evolved gases from the decomposition of selected samples are shown in Figs. 3 and 4. Carbon dioxide, carbon monoxide, formaldehyde, ethanol, methanol, and acetic acid are major products. Samples treated with alkali metals salts do not evolve ethanol or methanol but they do produce more carbon dioxide. This could be due to different decomposition routes. A peak at 1105 cm^{-1}, not yet completely characterized, appears at different times during the decomposition process depending on the salt used. Further investigations are being pursued.

Decomposition patterns of as-received, acid-washed, potassium bromide, calcium chloride and zinc acetate treated fabrics were also studied in an inert atmosphere. Onset and DTG maximum temperatures for depolymerization of these samples were higher by 10°C and 20°C, respectively, except for the acid-washed sample for which the increases were 5°C and 10°C, respectively. The pyrolysis gases were qualitatively similar upon decomposition in either atmosphere for this sample. FTIR spectra of the decomposition gases of as-received and KBr-treated fabrics in an inert atmosphere are shown in Fig. 5.

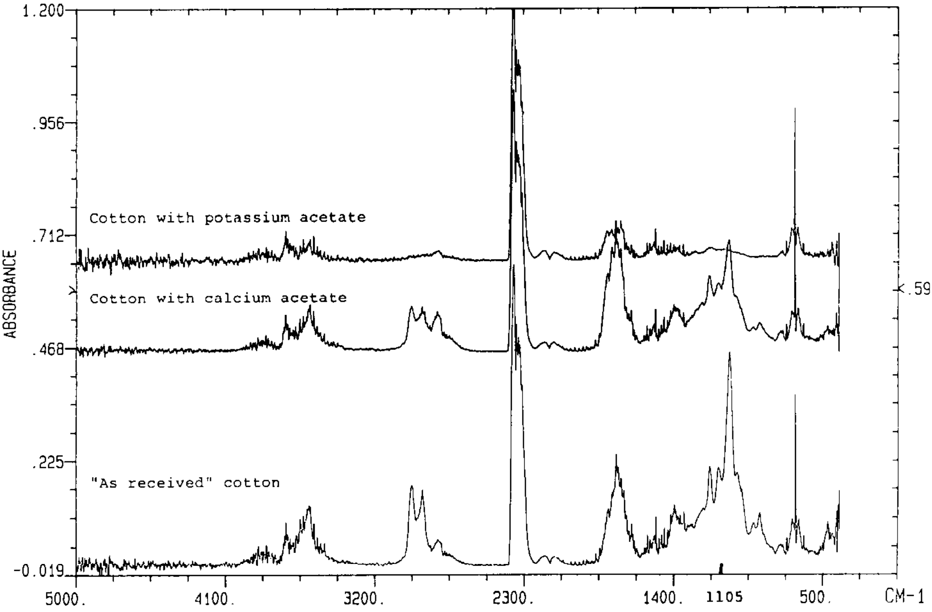

Fig. 3. FTIR spectra of gases evolved from cotton treated with potassium acetate, calcium acetate and "as received" cotton.

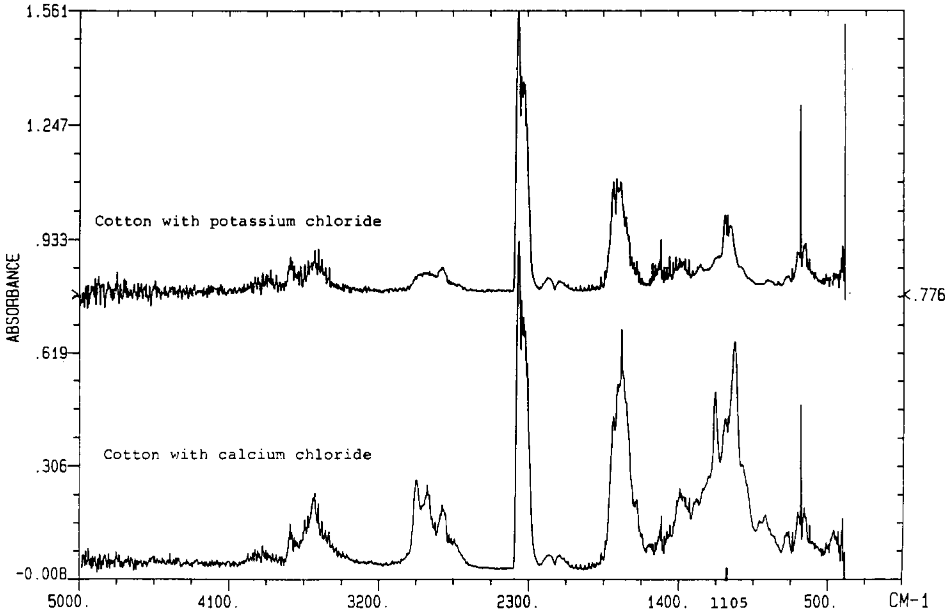

Fig. 4. FTIR spectra of gases evolved from cotton treated with potassium chloride and calcium chloride.

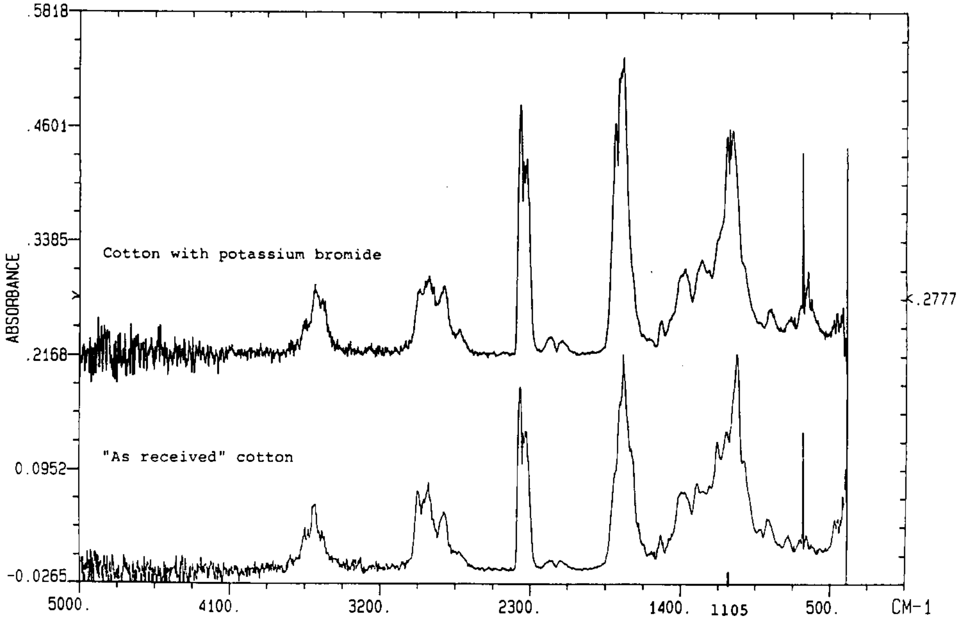

Fig. 5. FTIR spectra of gases evolved from cotton treated with potassium bromide and "as received" cotton, in an inert atmosphere.

CONCLUSIONS

Alkali metal ions such as potassium and sodium enhance pyrolysis and hence combustion of cotton fabrics. Alkaline-earth metal ions have less effect, with some associated anions playing a more significant role. Potassium dihydrogen phosphate acts as a retardant. Alkali metal cations act through a different, enhancing mechanism for decomposition than the alkaline-earth or transition metal cations.

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