

DTA and TGA Studies of Flame-Resistant Fabrics

R. M. PERKINS, G. L. DRAKE, JR., and W. A. REEVES,
*Southern Regional Research Laboratory, Southern Utilization Research and
Development Division, Agricultural Research Service, U. S. Department of
Agriculture, New Orleans, Louisiana*

Synopsis

Preliminary thermal studies were made of cotton fabrics which had been made flame resistant by chemical modification or by blending with a flame-resistant modified acrylic fiber. DTA and TGA thermograms were made in both nitrogen and oxygen atmospheres. Differences were found in the thermograms of the untreated controls, depending upon amount of purification. Fabrics treated with the flame-retardant formulations had lower decomposition temperatures and higher percent residue. Decomposition in oxygen was more complete and proceeded at a lower temperature. Infrared spectra of selected samples, which had been partially or completely charred, were examined. These data are related to theories about the degradation of flame-resistant cotton fabrics.

Thermal degradation of cellulose has been studied extensively to better understand the mechanisms, products, and kinetics of degradation as a means of modifying the cellulose to render it more resistant to heat and flame. Investigators at the National Bureau of Standards, Textile Research Institute, Quartermaster Research and Development Center, Shirley Institute, and others have collected and analyzed the products of degradation. In the present study a differential thermal analyzer and a thermogravimetric analyzer have been used to follow the path of thermal degradation of flame-resistant textiles. The role of the flame retardant is to alter the course of decomposition so that a lower percent of flammable volatiles is produced and a correspondingly larger char is formed. Ideally, the treatment should cause the decomposition of cellulose on heating to yield only carbon and water vapor.

Reid et al. postulated that an effective flame retardant was, or was capable of forming just below the burning temperature of cellulose, a Lewis acid, which acted as a catalyst and changed both the course and speed of the reaction. They showed that decomposition of cellulose was accelerated and that gas production was decreased by effective flame-retardant formulations.^{1,2} In a mechanism proposed by a group at the University of Rhode Island,^{3,4} which was elucidated and supported by the work of Schwenker and others at the Textile Research Institute,⁵⁻⁷ Madorsky and co-workers at the National Bureau of Standards,^{8,9} and others, it is pos-

tulated that pyrolysis follows the same, nonoxidative mechanism in all situations, and that the decomposition occurs simultaneously with scissions of the C—O bonds at random along the chain, some scissions yielding monomer units which rearrange to form levoglucosan, others causing breakdown of part of the chain yielding low molecular weight products and a carbonaceous residue.

Within the last few years, commercial instruments have become available for studying the thermal behavior of materials as they undergo chemical and physical changes during heating.¹⁰ The differential thermal analyzer, DTA,¹¹ is one such instrument and involves the continuous comparison of temperatures in a reference material and a sample as they are both heated at a uniform rate. Ideally, the reference material is so selected that its heat capacity and other thermal characteristics are approximately the same as the sample material and that it does not undergo any physical or chemical transformation in the temperature range being used in the study. The direction of the deviation indicates whether this change is exothermic or endothermic. This is a suitable instrument for measuring the thermal changes of untreated cotton in different environments, (nitrogen, oxygen) and then comparing these results with those obtained from cotton treated with various flame-retardant formulations.

Another instrument, the thermogravimetric analyzer, TGA, measures the weight of the sample as it is heated at a uniform rate. Thus examination of the DTA and TGA thermograms show whether a loss of weight accompanies an endothermic or exothermic change. It should be remembered, however, that the thermograms show net change only; two or more competing reactions may occur simultaneously, but only the net result will appear on the thermogram. For example, pyrolysis is a complex reaction, during which various reactions, both endothermic bond rupture, volatilization, etc., and exothermic bond formation can happen simultaneously. Therefore, the DTA thermogram shows only the net effect. However, the thermogram is unique for a particular total reaction and is, therefore, useful in the identification and characterization of materials. The TGA assists in the interpretation of the results.

The objectives of this study were to examine the thermal behaviors of cottons made flame resistant by treatments with various flame-retardant formulations and of cotton blended with a synthetic flame-retardant fiber and to compare the thermal behavior of these flame-retardant fabrics with those of untreated controls. DTA and TGA thermograms of the samples were made in atmospheres of both nitrogen and oxygen. Chars of certain selected samples were also investigated by infrared absorption technique.

EXPERIMENTAL

The instruments used for thermal analyses were the DuPont 900 differential thermal analyzer and the DuPont 950 thermogravimetric analyzer. Both instruments are small, compact, and easy to operate. The DTA has been described by Chiu¹² and the TGA by Sarasohn and Tabeling.¹³

Briefly, the DTA consists of the cell assembly, temperature programmer, amplifier, and recorder. The thermogram is recorded on a $8\frac{1}{2} \times 11$ in. preprinted paper, where the temperature difference between the sample and a reference material (glass beads) forms the *Y* axis and the sample temperature is the *X* axis.

A heating rate of 15°C./min. was used for both TGA and DTA in our study. Occasionally DTA samples were heated at 30°C./min. or 45°C./min. to produce a larger ΔT and a sharper peak; however, peak temperatures are higher at the faster heating rates. This effect of heating rate was shown by Schwenker on a synthetic fiber.¹⁴ Most of the samples were examined from room temperature to about 475°C. Before heating, the bell jar in which the cell assembly is housed, was evacuated to about 20 in. of mercury. During heating a steady stream of either nitrogen or oxygen flowed into the bell jar at a rate of 2 standard ft.³/hr. The gas came in contact with the sample by diffusion, and in the DTA experiments this gas diffusion technique was used, except where stated otherwise. The samples were prepared for use in the instruments by grinding in a Wiley mill to pass through a 20-mesh screen. The sample materials were placed in a 4-mm. capillary tube to a height of about 3–4 mm. and weighed approximately 8 mg. The Alumel–Chromel thermocouple was inserted into the sample; another thermocouple was placed in a 4-mm. tube containing the glass beads reference material (loaded to approximately the same height); and a third thermocouple was inserted into a 1.5-mm. capillary tube, also containing glass beads. This third thermocouple was placed close to the 0.25×1 in., 30-w. cartridge heater which controls the temperature programming.

The TGA is a semimicrothermogravimetric analyzer designed as a modular attachment to the DTA and in this way uses the same basic electronic circuitry, switching devices, *X–Y* plotter, and temperature controller-programmer. The sample was placed in a cylindrical sample boat which was open at both ends and which was suspended directly from one end of a quartz beam. The beam was placed directly into a horizontal furnace. The thermocouple was placed about 1 mm. under the sample boat. Either nitrogen or oxygen flowed through the furnace tube at a rate of about 2 standard ft.³/hr. Heating was at a rate of 15°C./min. from room temperature to 500°C. and occasionally to higher temperatures. The ground samples were easily loaded into the sample boat by use of tweezers. For decomposition in nitrogen, 10 mg. samples were used. Not more than about 10 mg. of the ground sample could be conveniently inserted into the weighing boat. When decomposition occurred in oxygen, the results were off-scale for some samples; therefore, the sample size was reduced to 5 mg. (An alternate choice was to change the temperature scale.) The instrument was so set that per cent weight was read directly.

The differential scanning calorimeter was a Perkin-Elmer DSC-1. Samples of accurately weighed ground materials were heated, again with glass beads as a reference.

The infrared curves were made with a Perkin-Elmer spectrophotometer, Model 137B Infracord, which measured the per cent transmittance over a range from 2.5 to 15 μ (4000–667 cm.⁻¹). A KBr disk technique was used.¹⁵ Most of the samples analyzed were cotton materials, both treated and untreated. However, one synthetic fiber was examined. A modified acrylic, Verel, was selected because of its inability to support combustion. Cotton-Verel blends were also examined.

Three untreated cotton controls were examined: an 80 × 80 print cloth in the greige stage and after bleaching, and a cotton of unknown history which had been used to blend with Verel.

Flame-resistant cotton samples were: bleached print cloth treated with 10% and 20% solutions of A(MA)PO [bis(1-aziridinyldimethylamido-phosphine oxide), of APO [tris(1-aziridinyldimethylamido-phosphine oxide)], and of APN [2,2,4,4,6,6-hexa(1-aziridinyldimethylamido-phosphine oxide)-1,3,5-triazine];¹⁶ bleached print cloth treated with APO solutions of solids contents of 1–20%; gray dyed plain twill treated with THPC [tetrakis(hydroxymethyl)phosphonium chloride] plus MM [methylolmelamine], APO, or the THPC-urea precondensate chemically fixed with NH₃;¹⁷ a cotton flannelette treated with the allyl diester of phosphonitrilic chloride (PNE), the bromoform adduct of the allyl ester (PNE-CHBr₃)¹⁸ and the PNE-CHBr₃ with THPC;¹⁹ an O.D. sateen treated with the adduct of bromoform and triallyl phosphate (BAP)²⁰ and BAP plus THPC;²¹ a khaki-dyed twill treated with a brominated poly-TAP (triallyl phosphate); and aminized print cloth²² treated with THPC, bromendic anhydride, or chlorendic anhydride.

DISCUSSION AND RESULTS

Untreated Controls

The application of DTA for the characterization and investigation of the thermal degradation of synthetic textile fibers and of modified cotton fibers has been used by Schwenker and co-workers at the Textile Research Institute.²³ He has noted that at high temperature DTA curves in an oxidizing atmosphere often result in poorly defined curves due to many overlapping reactions and has analyzed most of his samples in nitrogen. In our work, we have also used nitrogen for simplicity, but in addition we have examined the degradation in oxygen. For bleached print cloth heated in nitrogen, the major endotherm had a peak temperature of 363–365°C. Examination of the TGA curve indicates onset of this cellulose depolymerization at about 300°C. These results are in close agreement with Schwenker, although in his system the reference temperature was recorded rather than the sample temperature. His reference was calcined alumina; his heating rates were slower; and his sample size was larger. Feldman at the QM R&D Center examined some flame-retardant-treated samples. His DTA curve on untreated cotton had a shape similar to our bleached print cloth; his peak temperatures were higher due to a heating rate that was twice as fast as ours.²⁴

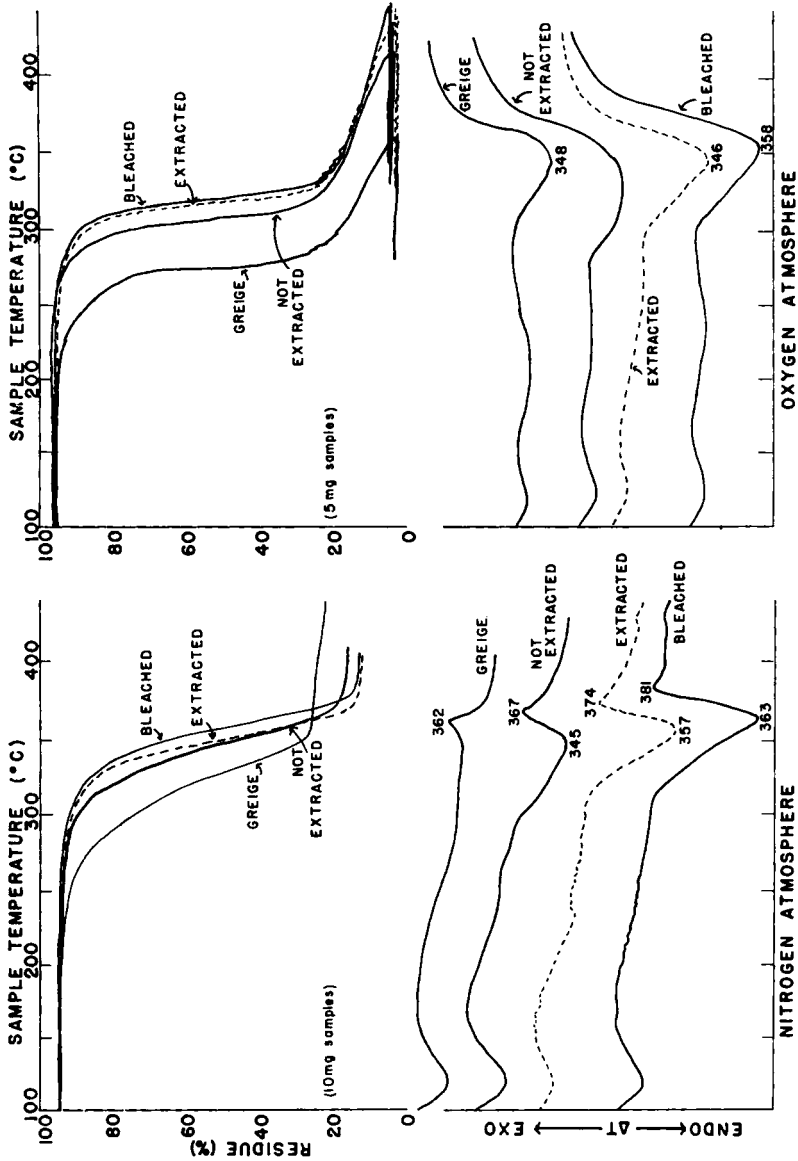


Fig. 1. TGA and DTA (gas diffusion, GD) thermograms of untreated cotton controls in nitrogen and in oxygen atmospheres. Heating rate = 15°C./min.

The DTA thermogram of a greige print cloth showed a small exotherm with a peak at 362°C. Because the thermograms for these two samples (greige and bleached print cloth) differed, they were examined with a Perkin-Elmer DSC-1 differential scanning calorimeter and the results were similar: a large endotherm for the purified fabric and a small exotherm for the greige. Degradation as measured by the TGA occurred at a lower temperature for the greige fabric, and the per cent residue was larger. Coppick et al.²⁵ observed the thermal behavior of untreated cellulosic fabric in air and in nitrogen. They concluded that in nitrogen there was a slight exothermic reaction, with some indications that it might be endothermic; in any case, ΔH could be considered negligible.

The cotton of unknown origin that had been used to blend with Verel gave a rather small, broad endotherm peaking at about 345°C. After the sample had been refluxed with chloroform for 4 hr., the endotherm became sharper and peaked at 357°C. In greige cotton, the noncellulosic materials, that is the waxes, pectins, protein, ash, etc., are only about 6% of the total; yet these apparently have a significant influence on the DTA thermogram and can alter the overall shape of the curve.

DTA and TGA curves of the untreated samples in nitrogen and in oxygen are shown in Figure 1.

The major weight loss of untreated cotton in oxygen occurs at a lower temperature than in nitrogen. In oxygen, when the purified sample reached about 325°C., or the nonpurified 280°C., there was a sudden microexplosion as the gases ignited. The temperature advanced roughly a hundred degrees, rapidly cooled, and then proceeded at the programmed rate. Large amounts of gas were given off. It has been reported that these gases can ignite at temperatures above 320°C. when the cellulose decomposes into a carbonaceous char and volatile materials.²⁵

Studies at the QM R&D Command showed the temperature in air at which volatiles first form is 276°C. That report was on cotton cloth, wear-resistant sateen, 8.5 oz., OD-7.²⁶

Since the DTA thermogram did not show a sharp exotherm at these explosion temperatures, it was concluded that only a limited amount of oxygen was being diffused into the sample. With the use of a visual attachment for the DTA,²⁷ it was seen that the sample did not ignite in the 4-mm. tube. A flow accessory was next used with the DTA to increase contact between the sample and the gas. The gas was pre-heated and blown directly into the sample and the reference. Some difficulty was encountered; the glass beads were easily blown out of the 4-mm. reference tube. The DTA thermogram in nitrogen under these dynamic gas flow conditions was similar to the one using the gas diffusion technique, except that the endotherm was somewhat smaller. When oxygen was used, the reaction was exothermic, ignition occurred, and the resultant temperature change was beyond the limits of the recorder. Therefore, it must be remembered when DTA and TGA thermograms of a particular sample are compared that the DTA curves were drawn using the gas diffusion technique, whereas,

with the TGA measurements, the gas was in more intimate contact with the sample.

THPC Polymers

One of the earliest durable flame retardants for clothing was based on tetrakis(hydroxymethyl)phosphonium chloride (THPC). In 1953 Reeves and Guthrie found that THPC and an amino resin, such as trimethylol-melamine, could be applied to cotton fabric by a pad-dry-cure technique.²⁸ Later THPC and urea were made into a prepolymer and applied to fabric. The prepolymer was further insolubilized with ammonia. These processes produced better fabric handle. Later tris(1-aziridinyl)phosphine oxide, APO, was mixed in equimolecular proportions with THPC and applied to cotton. About 12% add-on based on the weight of the fabric gave good results, probably due to increased phosphorous content.

DTA and TGA curves of these three treated fabrics in a nitrogen and in an oxygen atmosphere are shown in Figure 2. These fabrics have phosphorus contents of 1.5% for the APO-THPC fabric, 1.7% for the THPC-urea-NH₃ fabric, and 1.2% for the THPC-MM fabric. The three DTA curves in nitrogen are similarly shaped, each having two sharp exothermic peaks. The APO-THPC peaks appear at the lowest temperature, 257 and 295°C.; the THPC-MM, at the highest, 305 and 335°C. Examination of the TGA curves also show the major weight loss at a lower temperature for the APO-THPC sample and a higher per cent residue. The loss of weight begins at 240°C., and at 290°C. about 45% of the sample has volatilized. The sample continues to slowly decompose. Comparison of the DTA and TGA curves for the APO-THPC sample shows that the first exotherm begins also at about 230-240°C. At 257°C. the exotherm is interrupted, a low is reached at 285°C., the second exothermic peak is at 295°C. The first exothermic reaction occurs simultaneously with the major loss of weight; the second exothermic reaction is possibly due to bond formation and in the oxygen atmosphere to oxidation of the charred residue.²⁹ Further degradation of the residue, which would be an endothermic process, is apparently overshadowed by the exothermic reactions.

The double peak pattern in nitrogen is typical for these three flame-retardant resins; all three lower the decomposition temperature of the sample and increase the residue. Approximately 40% residue remained at 450°C.

It is apparent from the TGA curves that the decomposition temperature of the textiles actually covers a range. One could arbitrarily take the midpoint along that portion of the curve showing the major weight loss for comparing samples; however, the total range is important since it determines the slope of the curve. For example, two samples could have a decomposition midtemperature at 275°C.; yet, if the initial temperature was 250°C. in one and only 225°C. in the other, one would offer more heat resistance than the other. Perhaps, then the initial temperature at which there is an indication of a change taking place is more important. Fuoss

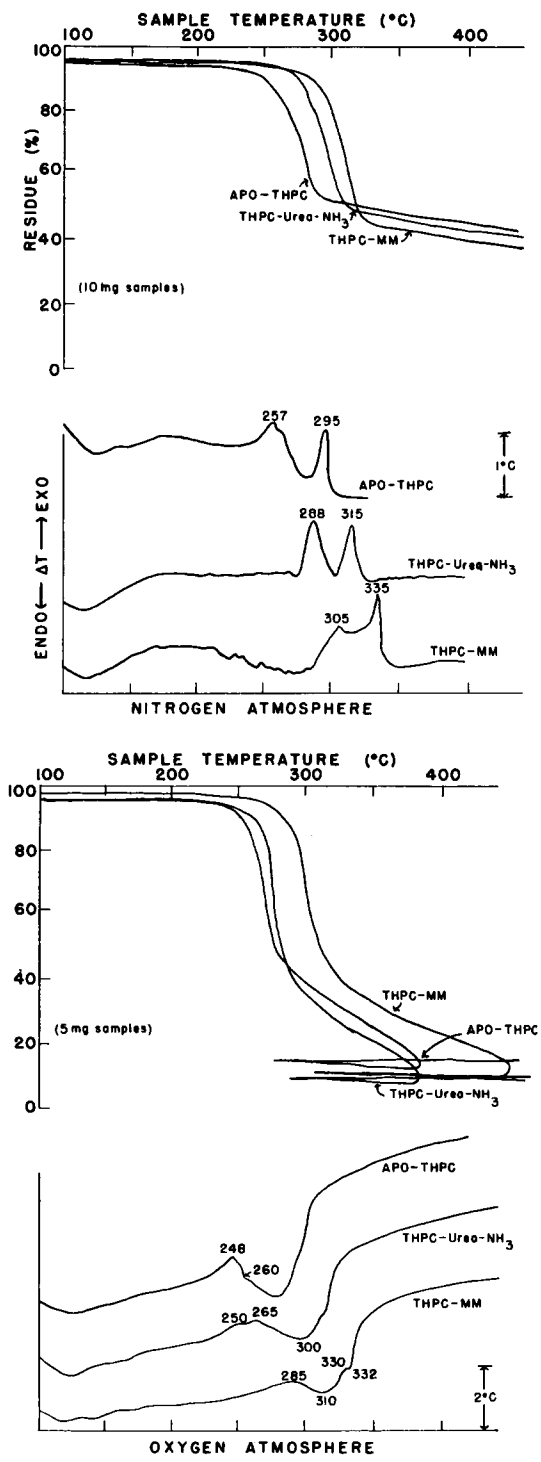


Fig. 2. TGA and DTA (GD) thermograms of THPC resin-treated cotton fabrics in nitrogen and in oxygen atmospheres. Heating rate = 15°C./min.

et al. used TGA data to calculate activation energies.³⁰ The method involves the location of the inflection point and the slope of the curve at that point from the TGA, followed by a simple calculation. Reich³¹ proposed a procedure for the estimation of activation energy without using the thermogram slopes. Both methods, however, require a prior knowledge of the reaction order. Although these methods apparently cannot be used for our decomposition studies, the importance of the mid-point, or inflection point temperature, and the slope of the line does appear quite significant. In another study, Witnauer and Wisnewski³² found that the shrinkage temperature of leather determined by a conventional method was between the onset temperature and the peak temperature recorded on a DTA thermogram.

The TGA curves in oxygen for the THPC-resin-treated fabrics were similar to the controls, in that there was a temperature at which micro-explosion and rapid heating occurred. This was always at a lower temperature than for the untreated control. The residue from the oxidized samples was lower than of those heated in nitrogen. It should be noted, however, that heating to higher temperatures in nitrogen prolongs the decomposition until about 1000°C., when the residue has approached that which remained after oxidation. Madorsky has studied the pyrolysis of cellulose in a vacuum and observed that the chars obtained at the carbonization end points at 280°C. contained volatile material. Upon further heating to 1000°C., the weight of the char was reduced roughly one-half, that is, from 20% to 10%.⁹

APO-Treated Fabrics

A series of print cloth samples had been treated with solutions of APO without THPC. APO imparts flame resistance and produces a high degree of wrinkle resistance. Table I records the sample weight increase due to

TABLE I
Some Properties of APO-Treated Cotton Fabrics

| APO in fabric treating solution, % | Fabric wt. gain due to APO polymer, % | N in fabric, % | Temp. at 60% residue, °C. | Residue at 400°C., % | Match test, degrees ^a |
|------------------------------------|---------------------------------------|----------------|---------------------------|----------------------|----------------------------------|
| 0 | 0 | 0 | 350 | 13 | 0 |
| 1 | Neg. | 0.1 | 333 | 17 | 0 |
| 3 | 0.9 | 0.4 | 308 | 27 | 0 |
| 5 | 2.3 | 0.7 | 300 | 36 | 60 |
| 10 | 6.4 | 1.5 | 291 | 42 | 75 |
| 15 | 9.2 | 2.3 | 290 | 47 | 135 |
| 20 | 15.9 | 3.1 | 286 | 48 | 135 |

^a Angle at which 1-cm. strip fails to support combustion when held at the angle indicated and ignited at the end with a match.³³

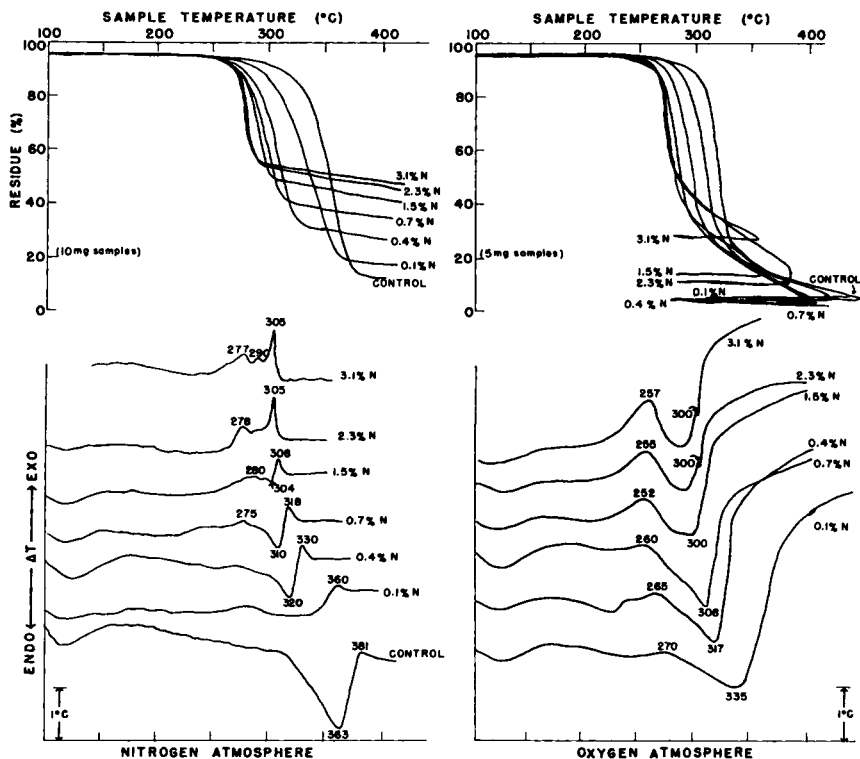


Fig. 3. TGA and DTA (GD) thermograms of APO-treated cotton fabrics in nitrogen and in oxygen atmospheres. Heating rate = 15°C./min.

treatment, the combined nitrogen in the fabric, the temperature at which 60% residue remains while heating in an atmosphere of nitrogen, the residue at 400°C., and the results of the match test.

There is a gradual lowering of the temperature at 60% residue from 350°C. for the control to 286°C. for the sample having 3.1% nitrogen. At 400°C., the residue increased from 13% for the control to 47% for the sample having 2.3% nitrogen and 48% for the sample having 3.1% nitrogen. Only these two (2.3 and 3.1% nitrogen) had a 135°C. match test and would be expected to pass the standard vertical flame test.

The DTA and TGA curves for the samples recorded in Table I in nitrogen and oxygen from 225 to 400°C. are shown in Figure 3.

It is interesting to note that only 0.1% nitrogen in the fabric caused the DTA curve to shift from an endotherm to an exotherm at about 360–365°C. This peak gradually moves to a lower temperature, and two other peaks occur at still lower temperatures. These curves are not as clear as the APO-THPC curves. However, the TGA thermograms help to define the initial temperature change. The reproducibility of these is illustrated in Figure 4. The TGA curves in oxygen were much more difficult to repro-

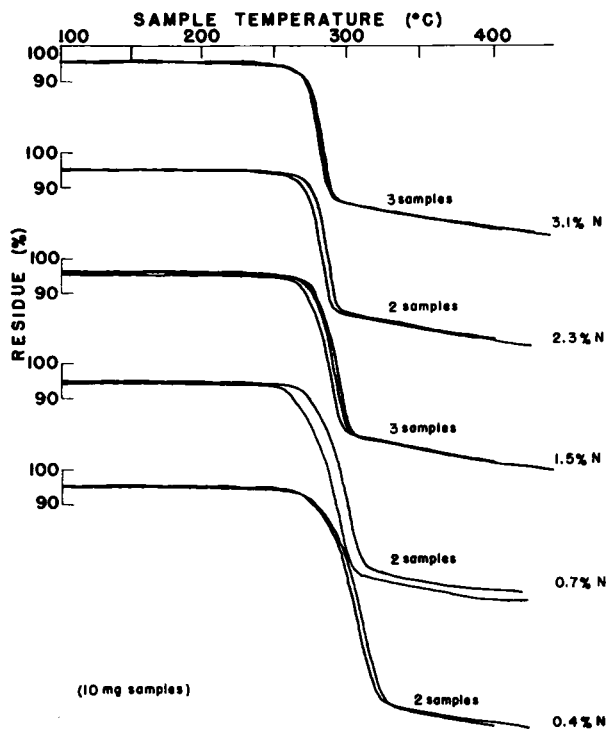


Fig. 4. TGA thermograms in nitrogen atmosphere of APO-treated fabrics. Heating rate = 15°C./min.

duce. During the "explosion," some of the sample possibly was blown out of the weighing pan, causing problems in duplication.

APO Compared to A(MA)PO and APN

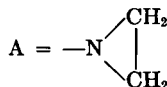
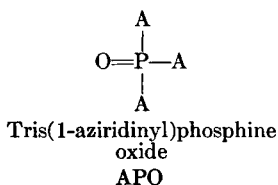
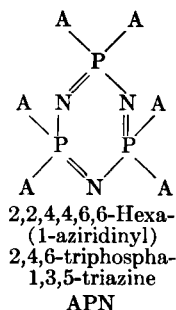
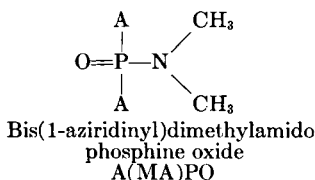
In an earlier study in our laboratory a difunctional compound closely related to APO had been prepared; it was bis(1-aziridinyl)dimethylamido-phosphine oxide, A(MA)PO. Structurally, it is similar to APO, since both

TABLE II
Some Properties of Cotton Fabrics Treated with APN, APO, and A(MA)PO

| Solution concentration and crosslinking agent | Add-on, % | N, % | WRA(W + F), degrees ^a |
|---|-----------|------|----------------------------------|
| 20% APN | 15.5 | 3.8 | 302 |
| 10% APN | 9.8 | 2.2 | 285 |
| 20% APO | 15.9 | 3.1 | 294 |
| 10% APO | 6.4 | 1.5 | 289 |
| 20% A(MA)PO | 13.6 | 2.4 | 241 |
| 10% A(MA)PO | 6.2 | 1.4 | 242 |

^a WRA(W + F) means wrinkle recovery angle in the warp and filling directions.

are phosphine oxides. A hexafunctional compound, 2,2,4,4,6,6-hexa-(1-aziridinyl)-2,4,6-triphospha-1,3,5-triazine, called APN, was also included in this particular work.



In Table II, some properties of fabrics treated with these compounds are shown.

Thermograms of these treated fabrics made in nitrogen and oxygen are shown in Figures 5 and 6.

The DTA thermograms show initial exothermic reactions, quite small for the A(MA)PO and large for the APN. The second exothermic reaction peaks between 300 and 310°C. There appears to be an endothermic reaction occurring between these two exothermic ones, probably due to bond rupture and volatilization. As the add-on of polymer increases, this endotherm is overshadowed by the first decomposition exotherm and the second bond reformation exotherm, until with the APO or APN samples having about 15½-16% add-on, it has virtually disappeared.

The TGA curve of APN in nitrogen shows advanced heating beginning at about 297°C. and going to 302°C., cooling back to 292°C., and then continuing at the programmed rate. The corresponding DTA thermogram shows an exothermic peak at 300°C. and a smaller one at 302°C. The ΔT between the peak and the lower reversal point is about 6°C.

Halogen-Containing Flame Retardants

Polymeric materials containing phosphorus and bromine have been studied as flame retardants for cotton. Fabrics finished with the allyl ester of phosphonitrilic chloride (PNE), the bromoform adduct polymer of allyl phosphonitrilate (PNE-CHBr₃), and this adduct polymer in combination with THPC (THPC-PNE-CHBr₃) have been investigated. These fabrics had weight increases of 29.0%, PNE; 35%, PNE-CHBr₃; and 28.2% of the THPC-PNE-CHBr₃.

The thermograms of fabrics treated with PNE and PNE- CHBr_3 are similar, both showing early decomposition at about 200°C . and an exothermic peak at 220°C . The addition of THPC improved the heat resistance of the material by about 50°C ., and the DTA curve resembled the other THPC-resin curves. Thermograms of the phosphonitrilates are shown in Figure 7. Of particular interest is the fact that the PNE and PNE- CHBr_3 TGA curves in oxygen do not show the advanced heating. This shows that the ignition point was not reached and the samples did not burn under these conditions.

Another system studied for flameproofing cotton was composed of an emulsion polymer of bromoform and triallyl phosphate (BAP). This also has been combined with THPC (THPC-BAP). Closely related to the BAP fabric (20% add-on) was cotton treated with a brominated polytriallyl phosphate, Br-poly-TAP (32% add-on). (The THPC-BAP fabric had a 22% add-on.) Examination of the thermograms of these three materials, shown in Figure 8, shows a small exothermic reaction beginning at about 215°C . immediately interrupted by at least two significant endothermic processes, as shown by the asymmetry of the peak and the shoulder at 225°C . followed by a peak at 240°C ., and a small exotherm at 257°C . for the BAP sample. The Br-poly-TAP sample has one large endotherm with a peak at 247°C . followed immediately by a small exotherm at 260°C . The THPC-BAP sample more nearly resembles the THPC-PNE- CHBr_3 samples with two small exotherms at 253 and 295°C . In oxygen, the TGA patterns again show that there was no flashing and ignition of the samples without THPC.

Cotton fabric can be made to react with 2-aminoethylsulfuric acid in the presence of sodium hydroxide to produce an aminized cotton. This chemically modified cotton was further reacted with THPC, bromendic anhydride, or chlorendic anhydride. In this way, the samples containing phosphorus could be compared with those having no phosphorus but containing nitrogen and bromine or chlorine.

Thermograms of these materials are shown in Figure 9. The two anhydrides have one large endotherm each at 215°C . for the bromendic anhydride and at 229°C . for the chlorendic anhydride. Surprisingly, the THPC-AM fabric also had only the one endotherm instead of the double peak pattern, which was typical of the THPC-resin samples. However, this sample had only about 0.6% phosphorus, and apparently at this low add-on the two exothermic reactions are extremely small. This curve could be compared with the APO curve of Figure 3, representing the sample treated with 5% APO. The nitrogen content was 0.7%, the corresponding phosphorus content would be about 0.5%; this curve shows two very small exothermic peaks separated by a large endotherm. In oxygen, only the bromendic anhydride-AM fabric resisted explosion and ignition. However, when the heating rate of the chlorendic anhydride-AM sample was reduced to $5^\circ\text{C}/\text{min}$., or when the sample size was reduced from 5 mg. to 2 mg., the sample did not explode. Furthermore, a 2-mg. sample of THPC-

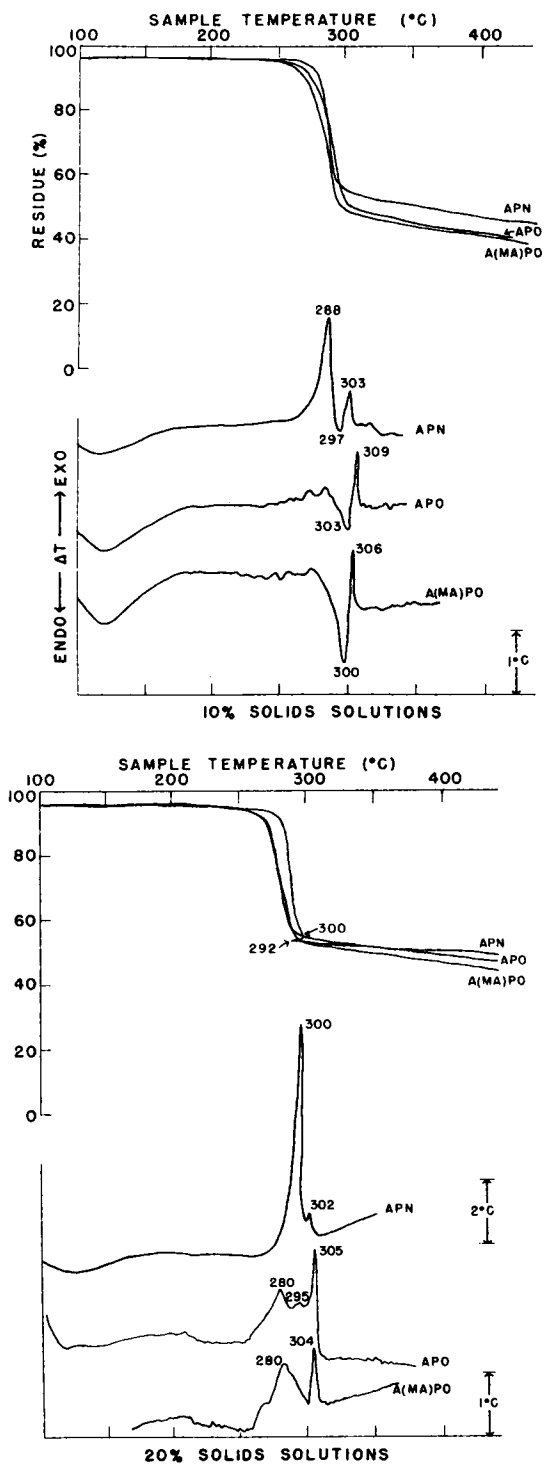


Fig. 5. TGA and DTA (GD) thermograms in nitrogen atmosphere of cotton fabrics treated with 10% and with 20% solutions of A(MA)PO, APO, or APN. Heating rate = 15°C./min.

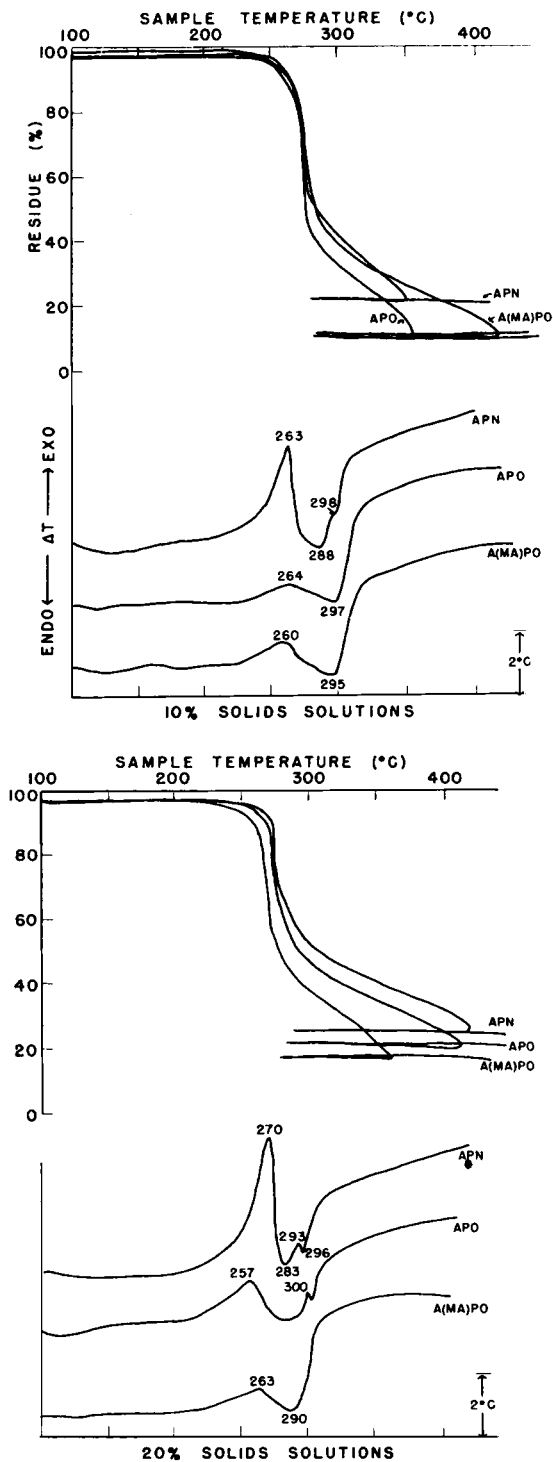


Fig. 6. TGA and DTA (GD) thermograms in oxygen atmosphere of cotton fabrics treated with 10% and with 20% solutions of A(MA)PO, APO, or APN. Heating rate = 15°C./min.

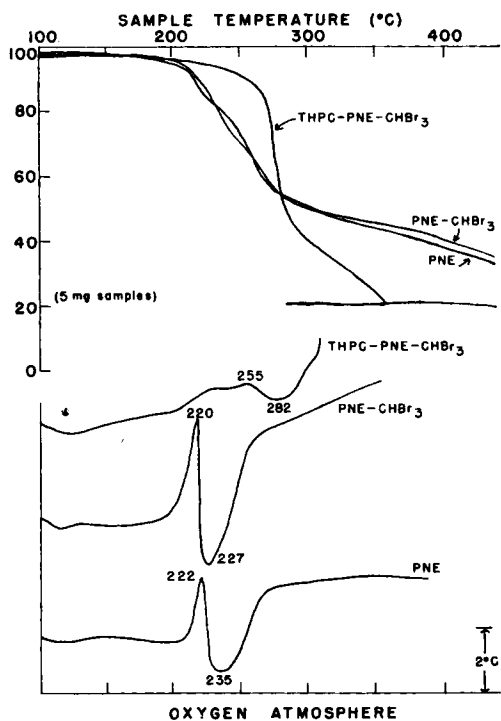
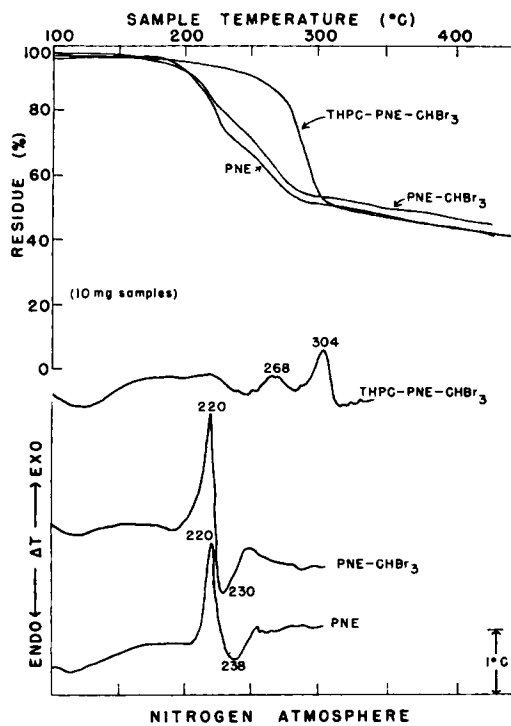


Fig. 7. TGA and DTA (GD) thermograms in nitrogen and in oxygen atmospheres of cotton fabrics treated with PNE, PNE-CHBr₃, or THPC-PNE-CHBr₃. Heating rate = 15°C./min.

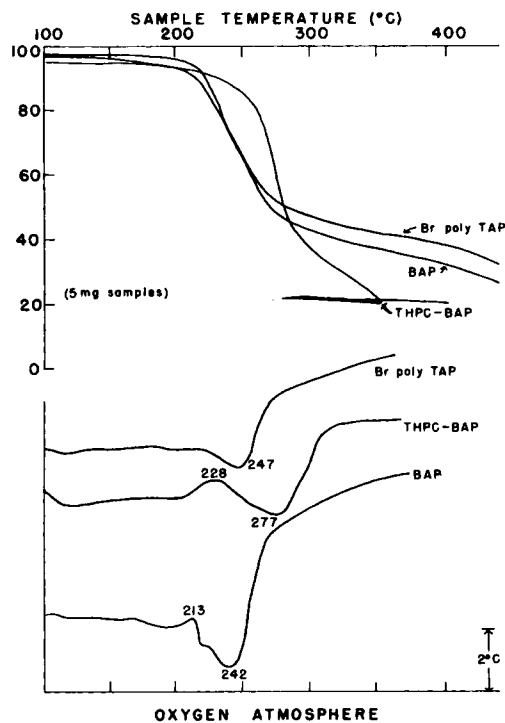
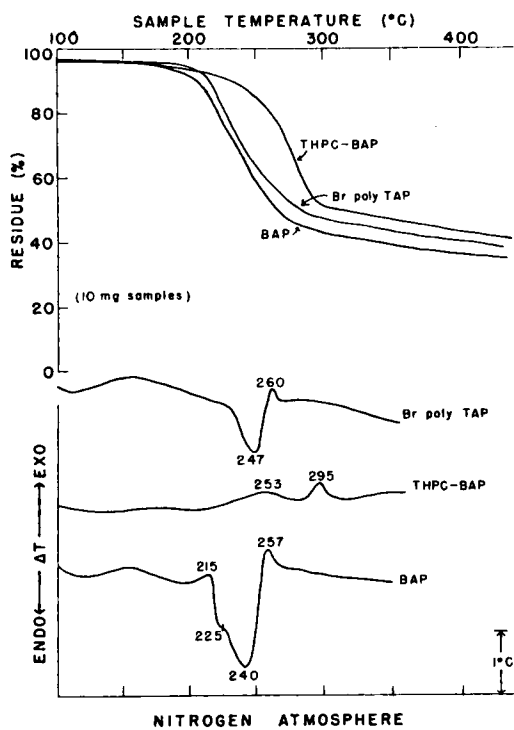


Fig. 8. TGA and DTA (GD) thermograms in nitrogen and in oxygen atmospheres of cotton fabrics treated with BAP, THPC-BAP, or Br-poly-TAP. Heating rate = 15°C./min.

BAP did not ignite, and a 10-mg. sample of BAP did explode. It appears that we may have selected a set of conditions for examining our samples that is just at the threshold for combustion. Since the C—Br bond is weaker than the C—Cl, it breaks at a lower temperature than the C—Cl, probably with a free-radical formation. This begins an earlier degradation of the cellulose and production of gases at a temperature below the ignition temperature. The stronger bonds of the samples treated with chlorendic anhydride, THPC, etc., break at higher temperatures, thus catalyzing the degradation and gas formation at a temperature where these will ignite.

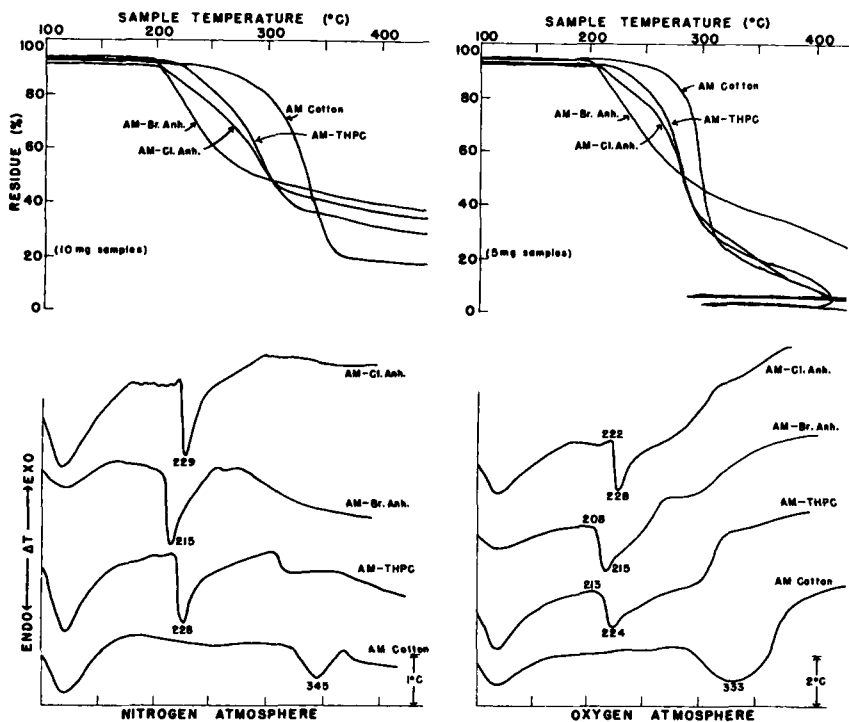


Fig. 9. TGA and DTA (GD) thermograms in nitrogen and in oxygen atmospheres of aminized cotton fabrics treated with THPC, bromendic anhydride, or chlorendic anhydride. Heating rate = 15°C./min.

Thus, we have the BAP, the Br-poly-TAP, the phosphonitrilates, and the bromendic anhydride-AM-treated samples slowly decomposing and not flaming, but this decomposition begins at an earlier stage, therefore reducing the heat resistance of the treated fabric. Translated into a practical application, garments made of these materials would need more careful ironing to prevent scorching: The cotton setting on a hand iron is about 260–290°C., the synthetic setting, about 180–230°C.

Differential scanning calorimeter curves were made on cottons treated with BAP, THPC-BAP, APO-THPC, and AM plus bromendic anhydride

or chlorendic anhydride. The curves were in close agreement with the DTA data.

Synthetic Fibers

Verel is an example of a modified acrylic having specialized end uses, as in fabrics where flame retardancy is desired, because of its inability to support combustion. The reported melting point of Verel is about 210°C. Thermograms of Verel showed an initial endotherm peaking at 210°C., followed by an exotherm with a peak at 230°C., which corresponds to the point of inflection weight loss of about 35%. The second major change begins at 375°C. in nitrogen; in oxygen the next change is at about 440°C., when ignition occurred and the material was nearly completely consumed. This material passed the standard vertical flame test. A blend of 35% cotton and 65% Verel also passed the test and had similar thermograms. When the proportion of cotton was increased to 50%, the fabric became a borderline example for the flame test. In nitrogen, the thermograms still resembled that of 100% Verel. These thermograms are shown in Figure 10. Schwenker²³ showed that a blend of 65% Dacron and 35% cotton

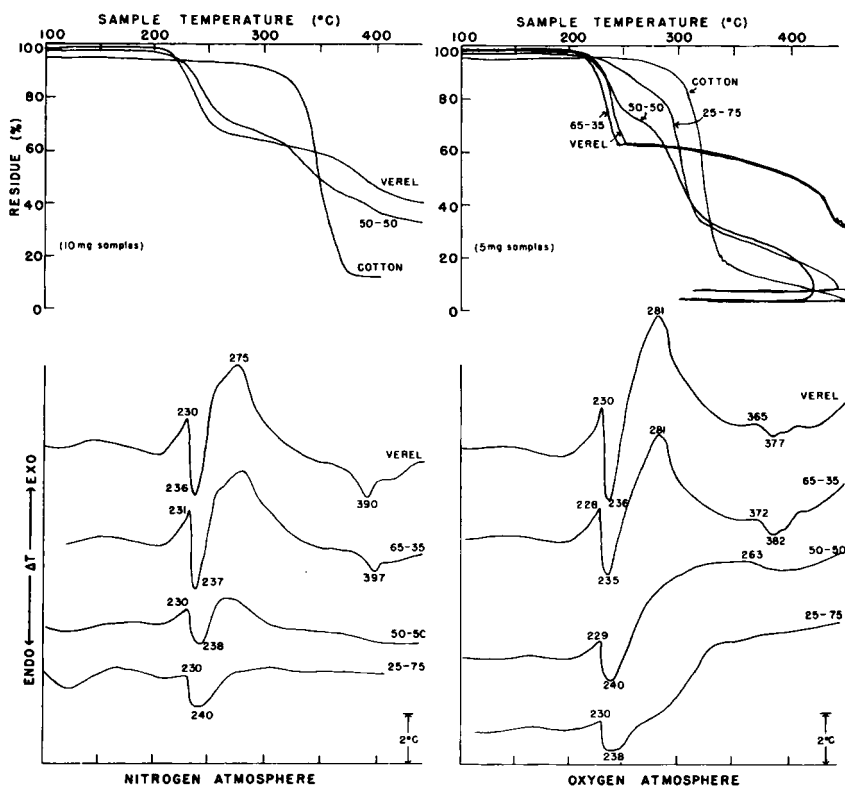


Fig. 10. TGA and DTA (GD) thermograms in nitrogen and in oxygen atmospheres of Verel and Verel-cotton blends. Heating rate = 15°C./min.

gave the characteristic DTA peaks of both the 100% cotton and 100% Dacron, and this was duplicated in our laboratory. However, with cotton-Verel blends, the cotton peak is not evident by our standard technique. This is possibly due to overshadowing by the Verel since the ΔT 's of Verel are very large. Although Verel decomposes at a higher temperature than cellulose, because of the low melting temperature and weight loss the fabric would become useless after exposure to temperatures above 210°C., due to stiffness and embrittlement. Some of the treated cottons remain unaffected for another 65–75°C. degrees.

Infrared Examination of Chars

The DTA thermograms draw a continuous picture of changes brought about by a steady increase in temperature. Work at the Shirley Institute showed a definite change in infrared curves of untreated cotton before and after charring. We were interested in the relationship between the DTA diagram and the initial char pattern, and the effect of the flame retardant on the temperature at which the char pattern appears.

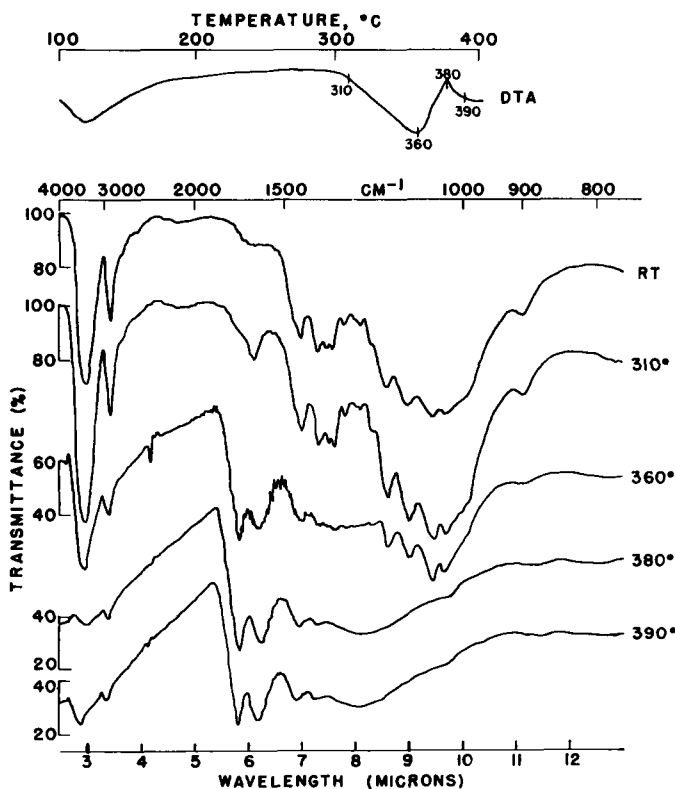


Fig. 11. Infrared spectra of bleached print cloth after heating in the DTA (GD) cell in nitrogen from room temperature to 310, 360, 380, and 390°C. The DTA thermogram appears above.

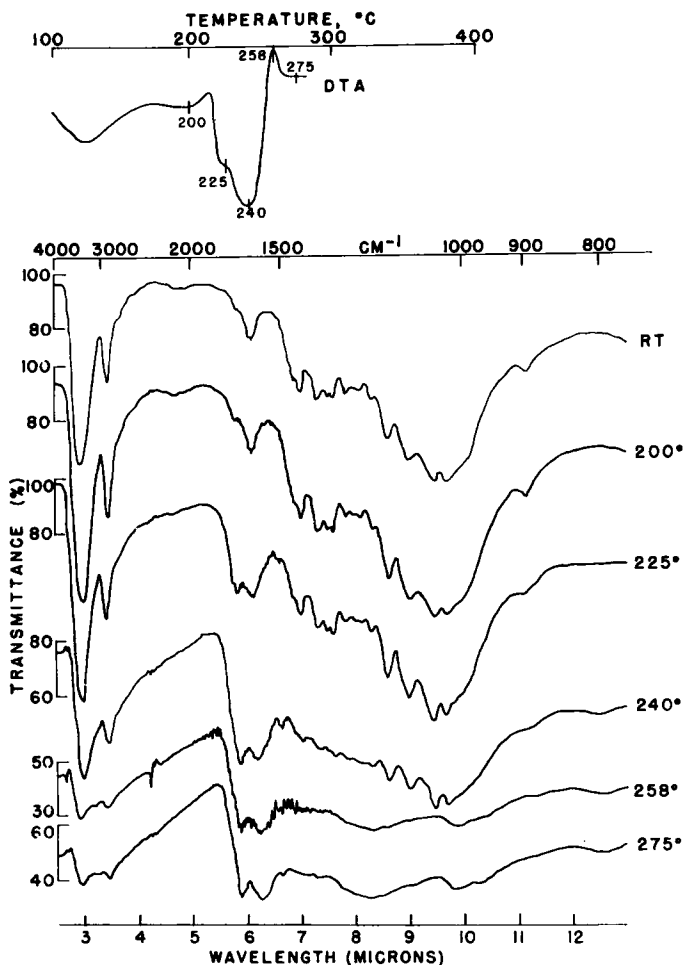


Fig. 12. Infrared spectra of BAP-treated cotton fabric after heating in the DTA (GD) cell in nitrogen from room temperature to 200, 225, 240, 258, and 275°C. The DTA thermogram appears above.

Samples of the untreated cotton were prepared for infrared absorption by heating in the DTA cell under nitrogen at the usual rate of 15°C./min. Heating was stopped at the desired temperature, as determined by selecting strategic points along the DTA curve, and rapidly cooled. These partially or completely charred specimens were then made into a KBr disk. The specimens examined had been heated to 310, 360, 380, and 390°C. in a nitrogen atmosphere. The char pattern began appearing in the 360°C. specimen. The O—H and C—H stretching frequencies at 3400 and 2900 cm^{-1} were decreasing, the cellulose maxima were disappearing, the crystalline band at 900 cm^{-1} had practically disappeared, and bands near 1720 cm^{-1} (carbonyl) and at 1620 cm^{-1} , possibly due to C=C, were forming.

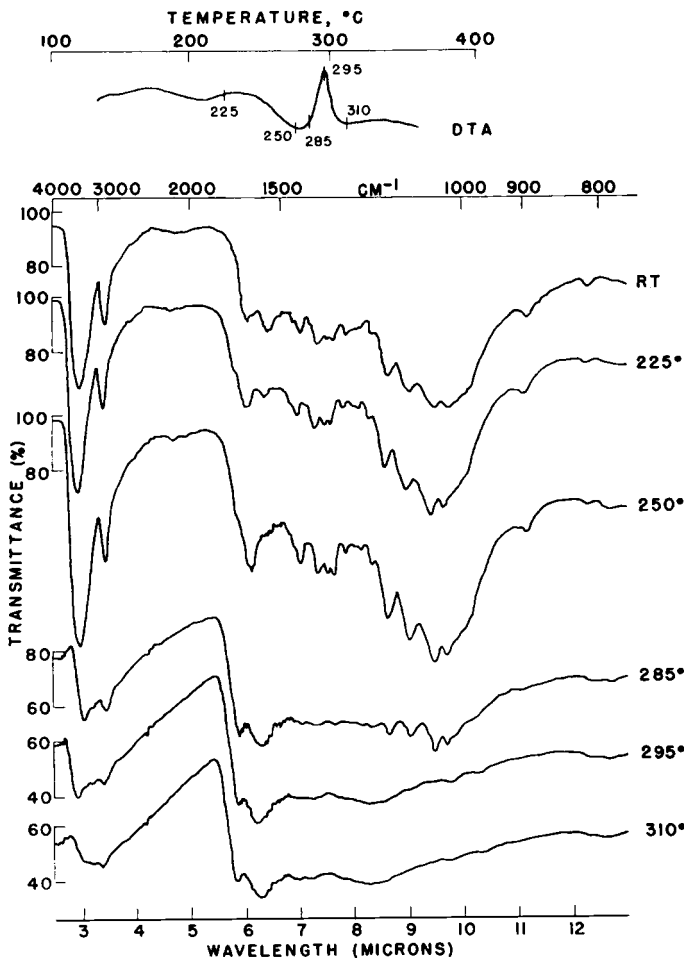


Fig. 13. Infrared spectra of THPC-BAP-treated cotton fabric after heating in a DTA (GD) cell in nitrogen from room temperature to 225, 250, 285, 295, and 310°C. The DTA thermogram appears above.

At 380°C. the typical char pattern was clear. From the TGA curve, it can be seen that at 380°C. decomposition was almost complete (see Fig. 11).

Specimens of BAP samples were selected for infrared examination after heating to 200, 225, 240, 258, and 275°C. The cellulosic structure was disappearing at 240°C. and disappeared at 258°C. The sample had only decomposed about 50% at 258°C. and had not yet shifted to the slower rate of decomposition. These curves are shown in Figure 12.

THPC-BAP specimens were prepared by heating to 225, 250, 285, 295, and 310°C. The char pattern was apparent at 285–295°C. which corresponds from the TGA curve to 50–60% residue. Again decomposition had not reached its slower rate (see Fig. 13).

Specimens of APO-THPC samples were prepared after heating to 225,

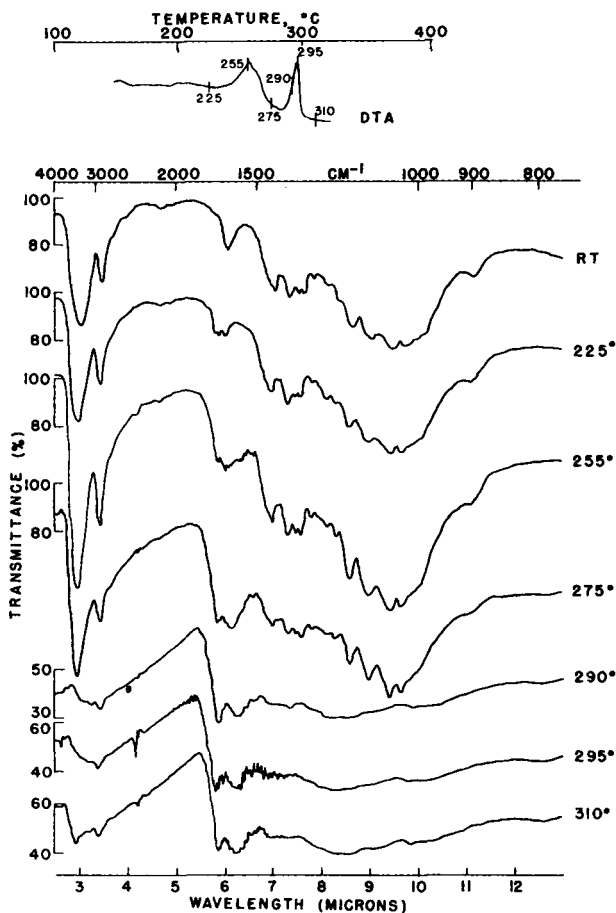


Fig. 14. Infrared spectra of APO-THPC-treated cotton fabrics after heating in a DTA (GD) cell in nitrogen from room temperature to 225, 255, 275, 290, 295, and 310°C. The DTA thermogram appears above.

255, 275, 290, 295, and 310°C. At 290°C. the char pattern appeared. This corresponded to 50% decomposition, and the point of inflection in the rate of decomposition (see Fig. 14).

It appears then that all samples, treated and untreated, retain their cellulosic pattern until degradation is almost complete. These data suggest further experiments with samples kept for extended periods of time at a temperature below the charring temperature. Infrared absorption spectra of these specimens should be compared with those of samples only heated to the designated temperature and immediately cooled.

SUMMARY AND CONCLUSIONS

DTA and TGA measurements have been used to study the thermal degradation of some flame-resistant materials. The DTA curves are unique

for each material and define the temperature or temperature range at which various physical and chemical changes take place. The DTA curves reveal whether heat is absorbed or evolved during the change and are quite sensitive. Less than $1/2\%$ of a flame retardant, APO, in the cellulosic material was enough to completely alter the course of a reaction from an endotherm to an exotherm.

The TGA data have been useful in explaining the DTA results. An examination of the two types of thermograms more clearly defined the initial temperature at which a change took place. The presence of two exothermic peaks for some treated fabrics has been interpreted as the result of one exothermic change due to decomposition and is accompanied by the evolution of large volumes of gas; a second exotherm is attributed to bond formation. The TGA curves in nitrogen showed a slow continuous decomposition at high temperatures, whereas the DTA curves revealed nothing in that region.

Differences were found in the thermograms of the untreated controls. Purified, that is, scoured and bleached samples, gave a rather large, broad endotherm, whereas, greige print cloth decomposed in nitrogen with a small exothermic reaction. The TGA data showed a lower decomposition temperature for the greige fabric and a larger residue than for the bleached.

Fabrics treated with flame-resistant formulations had lower decomposition temperatures and higher percentages of residue. The halogen-containing resins had lower initial decomposition temperatures than the THPC resins.

Decomposition in oxygen was more complete and proceeded at a lower temperature. Under the conditions selected for our study, the bromine-containing materials (without THPC) did not cause ignition when heated in oxygen; all other samples, treated and control, did. This has been interpreted as due to the early liberation of the bromine free radical, which catalyzes the decomposition of cellulose, at a temperature below the ignition point of the liberated gases.

The DTA thermograms have been useful in selecting critical temperatures at which to examine the infrared spectra of the charred or partially charred materials. The cellulosic pattern remains until degradation is almost complete, i.e., about 15% residue for the untreated sample and 50% for the treated. In a similar manner, DTA curves could be used to select temperatures at which the gaseous materials could be collected and analyzed by chromatographic techniques.

It is not the policy of the Department to recommend the products of one company over those of any others engaged in the same business.

References

1. H. A. Schuyten, J. W. Weaver, and J. D. Reid, *Advan. Chem. Ser.*, **9**, 7 (1954).
2. H. A. Schuyten, J. W. Weaver, and J. D. Reid, *Ind. Eng. Chem.*, **47**, 1433 (1955).
3. M. H. Gollis and F. R. Fisher, Final Report, QM Contract DA 44-109-QM-1414, Univ. of Rhode Island (Feb. 1, 1953-June 3, 1955).

4. W. G. Parks, R. M. Esteve, M. H. Gollis, R. Guercia, and A. Petrarca, paper presented to Division of Cellulose Chem., 127th Meeting, American Chemical Society, Cincinnati, Ohio, April 1955.
5. R. F. Schwenker, Jr., and L. R. Beck, in *Fourth Cellulose Conference (J. Polymer Sci. C, 2)*, R. H. Marchessault, Ed., Interscience, New York, 1963, pp. 331-340.
6. R. F. Schwenker, Jr., and E. Pascu, *Ind. Eng. Chem., Chem. Eng. Data*, **2**, 83 (1957).
7. R. F. Schwenker, Jr., and E. Pascu, *Ind. Eng. Chem.*, **50**, 91 (1958).
8. S. L. Madorsky, *Thermal Degradation of Organic Polymers*, Interscience, New York, 1964, pp. 238-261.
9. S. L. Madorsky, V. E. Hart, and S. Straus, *J. Res. Natl. Bur. Std.*, **56**, 343 (1956).
10. W. W. Wendlandt, in *Thermal Methods of Analysis*, P. J. Elving and I. M. Kolthoff, Eds., Interscience, New York, 1964.
11. B. Ke, *Newer Methods of Polymer Characterization*, Interscience, New York, 1964, pp. 347-419.
12. J. Chiu, *Anal. Chem.*, **34**, 1841 (1962).
13. I. M. Sarasohn and R. W. Tabeling, paper presented at Pittsburgh Conference of Analytical Chemistry and Applied Spectroscopy, March 5, 1964.
14. R. F. Schwenker, Jr., and R. K. Zuccarello, in *Thermal Analysis of High Polymers, (J. Polymer Sci. C, 6)* B. Ke, Ed., Interscience, New York, 1964, pp. 1-16.
15. R. T. O'Connor, E. F. DuPré, and E. R. McCall, *Anal. Chem.*, **29**, 998 (1957).
16. R. M. Perkins, G. L. Drake, Jr., and L. H. Chance, *Am. Dyestuff Reprtr.*, **52**, 521 (1963).
17. R. M. Perkins, G. L. Drake, Jr., and W. A. Reeves, *Textile Ind.*, **130**, 125 (1966).
18. C. Hamalainen and J. D. Guthrie, *Textile Res. J.*, **26**, 141 (1956).
19. C. Hamalainen, W. A. Reeves, and J. D. Guthrie, *Textile Res. J.*, **26**, 145 (1956).
20. J. G. Frick, Jr., J. W. Weaver, and J. D. Reid, *Textile Res. J.*, **25**, 100 (1955).
21. J. D. Reid, J. G. Frick, Jr., and R. L. Arceneaux, *Textile Res. J.*, **26**, 137 (1956).
22. W. A. Reeves and J. D. Guthrie, *Textile Res. J.*, **23**, 522 (1953).
23. R. F. Schwenker, Jr., L. R. Beck, Jr., and R. K. Zuccarello, *Am. Dyestuff Reprtr.*, **53**, 817 (1964).
24. D. Feldman (QM R&D Command), Textile Functional Finishes Lab. Rept. No. 148 (March 2, 1955).
25. S. Coppick, J. M. Church, and R. W. Little, *Ind. Eng. Chem.*, **42**, 415 (1950).
26. T. D. Miles (QM R&D Command), Textile Functional Finishes Lab. Rept. No. 136 (April 5, 1954).
27. J. Chiu, *Anal. Chem.*, **35**, 933 (1963).
28. W. A. Reeves and J. D. Guthrie, U. S. Dept. Agric. and Ind. Chem. Mimeo Circ. Ser. AIC-364 (Nov. 2, 1953, rev. May 11, 1954).
29. J. M. Church, U. S. Quartermaster Corps, Textile Ser. Rept. 38, 308 (1952); released by Off. Tech. Serv. (U. S. Dept. Comm.) as PB-111007.
30. R. M. Fuoss, I. O. Salyer, and H. S. Wilson, *J. Polymer Sci. A*, **2**, 3147 (1964).
31. L. Reich, *J. Polymer Sci. B*, **3**, 231 (1965).
32. L. P. Witnauer and A. Wisniewski, *J. Am. Leather Chemists' Assoc.*, **59**, 598 (1964).
33. W. A. Reeves, O. J. McMillan, Jr., and J. D. Guthrie, *Textile Res. J.*, **23**, 527 (1953).

Résumé

Des études thermiques antérieures ont été effectuées sur des tissus de coton résistant à la flamme par modification chimique ou sur une fibre acrylique modifiée avec un agent résistant à la flamme. Des thermogrammes DTA et TGA ont été effectués dans une atmosphère d'azote et d'oxygène. Des différences ont été trouvées dans les thermogrammes des échantillons contrôle non-traités, suivant leur degré de purification. Les tissus traités avec des agents retardateurs de flamme ont des températures de décomposi-

tion plus basses et un résidu centésimal plus élevé. La décomposition dans l'oxygène était plus complète et se passait à température plus basse. Les spectres infra-rouges des échantillons qui ont été partiellement ou complètement carbonisés ont été examinés. Ces résultats sont liés aux théories concernant la dégradation de tissus à base de coton résistant à la flamme.

Zusammenfassung

Vorläufige thermische Untersuchungen an Baumwollgeweben, welche durch chemische Modifizierung oder durch Mischung mit flammenbeständig modifizierten Acrylfasern flammenbeständig gemacht worden waren, wurden ausgeführt. DTA- und TGA-Thermogramme wurden in Stickstoff- und Sauerstoffatmosphäre aufgenommen. In den Thermogrammen der unbehandelten Kontrollproben wurden in Abhängigkeit vom Reinheitsgrad unterschiede gefunden. Einer Entflammungsverzögerungsbehandlung unterzogene Gewebe besaßen niedrigere Zersetzungstemperaturen und einen höheren prozentuellen Rückstand. Die Zersetzung unter Sauerstoff war vollständiger und verlief bei einer niedrigeren Temperatur. Die Infrarotspektren ausgewählter partiell oder vollständig verkohlter Proben wurde untersucht. Die Ergebnisse werden an Hand der Theorien über den Abbau flammenbeständiger Baumwollgewebe diskutiert.

Received February 28, 1966

Prod. No. 1358