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TEXTILE RESEARCH INSTITUTE
Princeton, New Jersey

THERMAL CHARACTERISTICS OF COATED
TEXTILE FABRICS

by

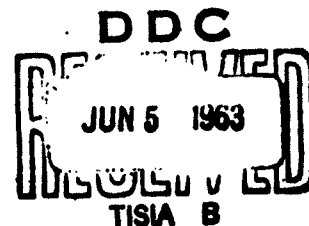
Robert F. Schwenker, Jr., Robert K. Zuccarello,
and Louis R. Beck, Jr.

Final Report

(Summary Report II)
Contract No. N140(138)67979B

to

U. S. Naval Supply Research and Development Facility
Brooklyn, New York



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Summary Report II
(Progress Reports Nos. 7 and 8)
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Robert F. Schwenker, Jr., Robert K. Zuccarello
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to

Clothing and Textile Division
U. S. Naval Supply Research and Development Facility
Brooklyn, New York

for the period
1 July 1960 to 1 September 1961

29 March 1963

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ABSTRACT

An apparatus for thermogravimetric analysis (TGA), built for the work of this contract, is described. The effects of elastomers as coatings on cotton and nylon fabrics have been studied by TGA. Fabric samples were double-coated with butyl rubber, Neoprene-W* and Hypalon-20*. TGA curves were obtained in air and in nitrogen for all samples to include those of the separate component materials. A good correlation was found between TGA data and previously obtained DTA data. The results indicated the cotton-butyl rubber and nylon-butyl rubber systems to have the greatest thermal stability whereas the Neoprene-coated fabrics were the least stable. The most pronounced chemical interaction occurred between Neoprene and the two textile substrates. Some chemical coating interaction was indicated for the butyl rubber-coated samples with the least interaction observed where Hypalon-20* was used as the coating. The chemical interaction mechanisms were indicated to be largely nonoxidative in character.

The thermal degradation of cotton, nylon, butyl rubber, and butyl rubber-coated cotton fabric was studied via gas chromatography. A pyrolysis technique for the thermal degradation of textile materials directly in the carrier gas stream of the gas chromatograph is described whereby degradation takes place in less than ten seconds and the products are analyzed immediately without precondensation. A minimum of thirty-seven different compounds was found from the thermal decomposition of cotton, twenty of which were identified. It was found that the major products were the same irrespective of the atmosphere in which cotton was decomposed. In the case of nylon a minimum of twenty-five products was found to be present. Data were also obtained from the thermal decomposition of butyl rubber and rubber-coated cotton.

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INTRODUCTION

The importance of coated textiles in various military applications led to the establishment of a broad study in 1956 at Textile Research Institute on the thermal characteristics of coated textile systems under a previous Navy contract [Contract No. N140(132)57442B]. The primary objective of the study was the investigation of the interactions between fabrics and compatible textile coatings at elevated temperatures in the range of 200° to 450°C. The first phase of the work, involved analysis by static thermogravimetry of the thermal stability as well as of the interactions of cotton, nylon, and Orlon* fabrics with the coating elastomers, butyl rubber, Neoprene W* and Hypalon*. The results suggested that coating fabrics with elastomers generally provided textile systems with improved thermal stability and that in air at elevated temperatures fabric-coating interactions did occur involving both physical and chemical effects. In subsequent work a new approach, differential thermal analysis (DTA) in controlled atmospheres, provided greater insight into the nature of the fabric-coating interactions [4].

This report constitutes the final report on the second contract in the study, Contract No. N140(138)67979B, and consists primarily of a detailed technical summary of the research of the last contract period, 1 July 1960 to 1 September 1961. The primary objectives, essentially the same as those of the first contract, were to carry out advanced investigations on the thermal behavior and the fabric-coating interactions of the systems previously studied. However, the scope of the program was also significantly broadened since it was concluded that in order to realize the long-range objective of the development of basic knowledge as to the character and mechanisms of the interaction of

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Powerful, thermoanalytical methods have been pioneered in new applications for textile research. It seems fair to say that the popular methods extant, during the term of this and the preceeding contract, for investigating the thermal behavior of textile materials were unduly cumbersome, time consuming, and limited in scope so that little definitive information on the thermal behavior of textiles existed. Therefore, new and improved methods for characterizing the thermal behavior of textile materials and for probing the complex reactions that occur at elevated temperatures were badly needed. The methods used in this work, each complementing the other in providing data unique and supplemental at the same time, are briefly described as follows.

1. Differential Thermal Analysis (DTA)

In DTA thermally detectable transitions or reactions that occur as a substance is heated at constant rate through the temperature range of interest are determined by measuring the temperature differences that obtain between the sample and a thermostable reference material. The major and minor transitions or reactions that occur can be quickly determined for any desired temperature range. Some of the phenomena described by DTA curves include fusion reactions, second-order transitions, crystallization processes, dissociation and formation of covalent bonds and the thermal nature of each reaction. Prior to its application in this program no systematic study by DTA on textile materials had appeared in the scientific literature.

2. Dynamic Thermogravimetric Analysis (TGA)

TGA involves the determination on a continuous and quantitative basis, of the change in sample weights as a function of time and temperature. The sample is subjected to conditions of continually increasing temperature where the increase is linear with time as for DTA. The changes in weight

are automatically recorded to yield a stepped curve disclosing discrete reaction zones. This method should be distinguished from isothermal and/or static thermogravimetric analysis. TGA complements DTA in further classifying endothermic and exothermic DTA peaks and in providing quantitative data whereby rates of decomposition, orders of reaction, activation energies and thermal stabilities can be estimated. This method had not previously been used in studying the thermal behavior of textiles.

3. Gas Chromatography

In gas chromatography an inert gas, such as helium, functioning as a carrier for the mixtures requiring analysis is passed continuously through special chromatographic columns. Samples of products volatile in the operating temperature range of a column are introduced into the carrier gas stream to be swept onto the column. The column exerts a selective retardation as a result of the partition of the components between the carrier gas phase and the column itself such that the components of a mixture move at different rates and are thus separated. As components are detected a chart recording of the detector response shows each component as a peak. The separated components may be collected as pure compounds as they emerge from the column for final identification. Investigation of the thermal degradation products of textile materials by this means had not been previously reported in the literature.

EXPERIMENTAL

1. Samples

The following fabrics were used in the work:

- a. Cotton fabric - plain weave, 4 oz./sq. yd.
- b. Nylon 66 fabric - twill weave, 3.5 oz./sq. yd.

The elastomers used as coatings were as follows:

- a. Butyl rubber (Enjay Butyl 365, Enjay Company, Inc. Linden, N. J.) : an isobutylene-isoprene copolymer.
- b. Hypalon-20 (E.I. du Pont de Nemours & Co., Inc. Wilmington, Del.) : a chlorosulfonated polyethylene.
- c. Neoprene W. (E.I. du Pont de Nemours & Co., Inc. Wilmington, Del.) : a polychloroprene.

Coated fabric samples were prepared with a commercial-type knife edge spreader. The elastomers were applied to the fabrics from a benzene solution containing 20% solids and the samples dried followed by oven curing at 150°C. Double-coated samples, i.e., fabrics coated on both sides, consisting of 50% fabric and 50% elastomer were used for evaluation.

2. Apparatus

a. Thermogravimetric Analysis (TGA)

A thermobalance of the deflection type [2,3] was constructed for the program and is described in detail later in the report. The instrumentation provided automatic recording of weight loss and temperature data and controlled atmosphere operation.

b. Gas Chromatography

A commercial instrument, an F & M Model 500 Linear Programmed High Temperature Gas Chromatograph was used. The unit featured a hot wire filament detector and temperature programming to 500°C.

c. Differential Thermal Analysis (DTA)

This apparatus, built at these laboratories and in use since 1958, has been described in detail previously [4]. A metal sample holder fitted with Chromel-Alumel differential and straight temperature measuring thermocouples is heated in a standard combustion furnace. The holder and furnace assembly is instrumented to provide constant heating rates and automatic recording with atmosphere control by furnace gas-flooding and diffusion.

d. Pyrolysis

The pyrolysis equipment consists of a demountable combustion tube and train. The pyrolysis chamber is a thick-walled pyrex tube 10 inches long and approximately 1-1/8 inches inside diameter whose efflux end is connected by a ground glass joint to three traps placed in series and, in the operation of the apparatus, maintained at temperatures in the range of 0°C to -78°C. The pyrolysis chamber was heated by being placed in a furnace made in two halves with a hinged top for easy access (Hevi-Duty Electric Co., Milwaukee, Wisconsin). Temperature control is obtained with the Gardsman stepless program controller used with the DTA equipment (West Instrument Corp., Chicago, Illinois). A special sample holder and thermocouple arrangement for measuring sample and pyrolysis tube temperatures is fitted into the pyrolysis chamber.

3. Techniques and Procedures

Samples for DTA were handled as described previously [1,4] by fine-cutting the various materials into squares of 2 mm size with the total amount of sample generally in the range of 75 mg. to 150 mg. TGA samples were similarly prepared. Rates of heating were 5 to 10°C/min. for TGA and 10°C/min. for DTA. TGA and DTA runs were carried out in air and in purified nitrogen.

Approximately two gram samples were used in the pyrolysis experiments which were carried out at the temperatures indicated by the DTA curves. Pyrolysis behavior was observed and all products condensable at -78°C and above were collected in the cold traps and taken up in appropriate solvents. The conditions of pyrolysis were dynamic in that a flow of gas around and past the sample was maintained to remove decomposition products to the traps as they formed. The pyrolyses were carried out in air and in nitrogen atmosphere.

DYNAMIC THERMOGRAVIMETRIC ANALYSIS STUDIES

1. Instrumentation and Procedure

Using a design by Gordon and Campbell [2] a suitable thermobalance, shown schematically in Figure 1, was constructed and tested at Textile Research Institute.

The balance component is a spring deflection type involving suspension of the sample holder from a pair of matched, helical, metal springs. As changes in the weight of the sample occur, expansion or contraction of the springs is measured by a linear variable differential transformer. Weight changes are thus automatically recorded on an L & N Speedomax G recorder to give a plot of weight loss versus the temperature of the atmosphere surrounding the sample holder.

The spring assembly is suspended from the top of a glass column which also enclosed the sample holder. The lower end of the column, containing the sample holder, fits into the core of an electric furnace. The glass enclosure permits operation in vacuum or at any other desired pressure while the ambient atmosphere is controlled. The heating rate is controlled by an automatic temperature programmer. A Chromel-Alumel thermocouple of 28 gauge wire is positioned near the base of the sample holder to measure the temperature, which

is recorded separately on a time base recorder. A similar thermocouple positioned between the furnace wall and the furnace elements controls the rate of heating. The operational temperature range is from 25° to 700°C at heating rates of 1° to 15° per minute. Samples in the range of 25 to 200 milligrams can be conveniently handled. The sample holders used in this work were (1) No. 00000 Coors porcelain crucible and (2) a platinum crucible. All runs were made in either air or nitrogen at a flow rate of 3000 cc/min.

In Figure 2 the results of a typical test run to determine heating rate linearity are shown by a plot of time versus recorded temperatures. The resulting heating rate curve is shown to be linear from about 50° to 500°C (the end of the run). The nominal rate was 10°C/min. compared with an experimentally determined rate of 10.3°C/min. The rate fluctuation was less than 1° over the entire range.

According to Newkirk [5] TGA curve temperatures are usually higher than their DTA counterparts due to the standard practice of measuring temperature near the sample holder rather than in the sample holder. This situation was investigated in a series of dummy runs in different atmospheres wherein the temperatures inside the sample holder were measured as well as those conventionally measured outside the sample holder. The junction of a chromel-alumel thermocouple was positioned inside the sample holder so that the bead was adjacent to, but not in contact with, the crucible bottom and the temperature was measured by a manually controlled potentiometer. Standard temperature measurements were made simultaneously at the usual location outside the holder and near its base. The results in Table I show that the outside temperature is 6° to 9°C higher in the range 60° to 200°C and 3° to 5°C higher from 200° to 500°C. The temperature difference is most marked in the low range with a maximum around 170°C in

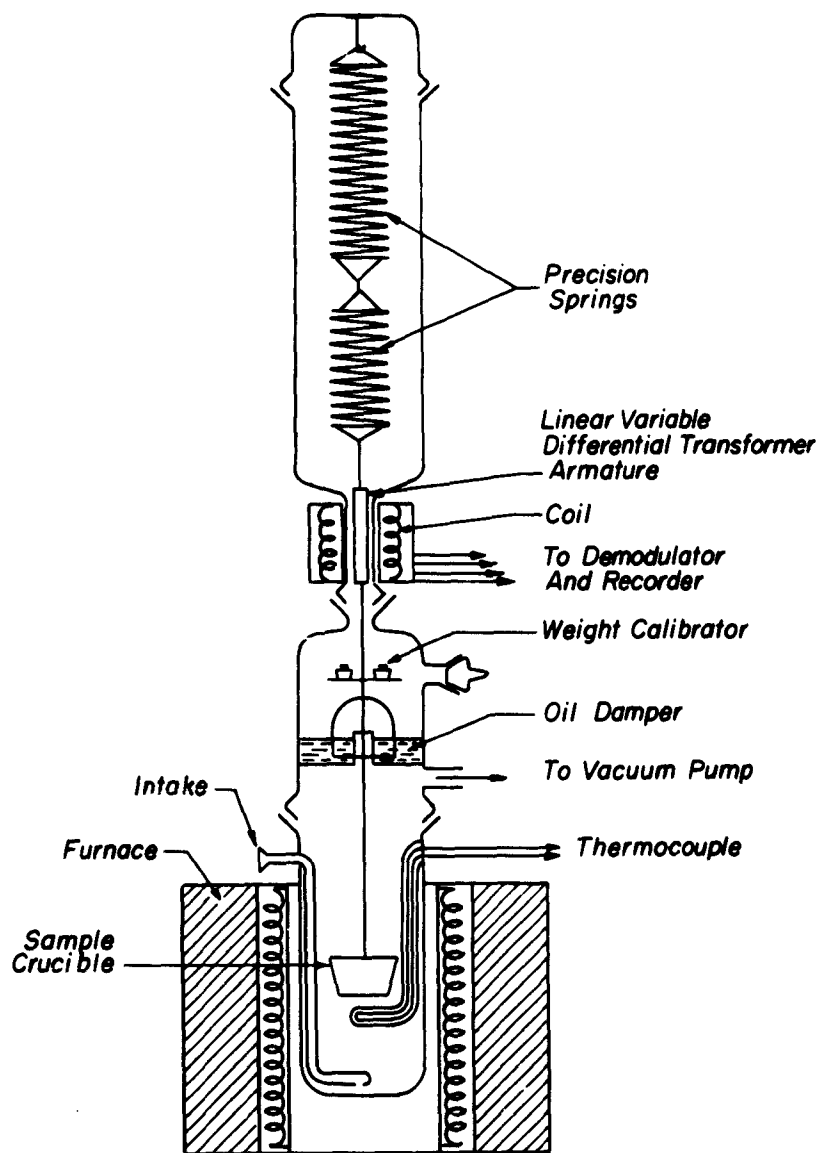


Figure 1. SCHEMATIC DIAGRAM OF TGA APPARATUS

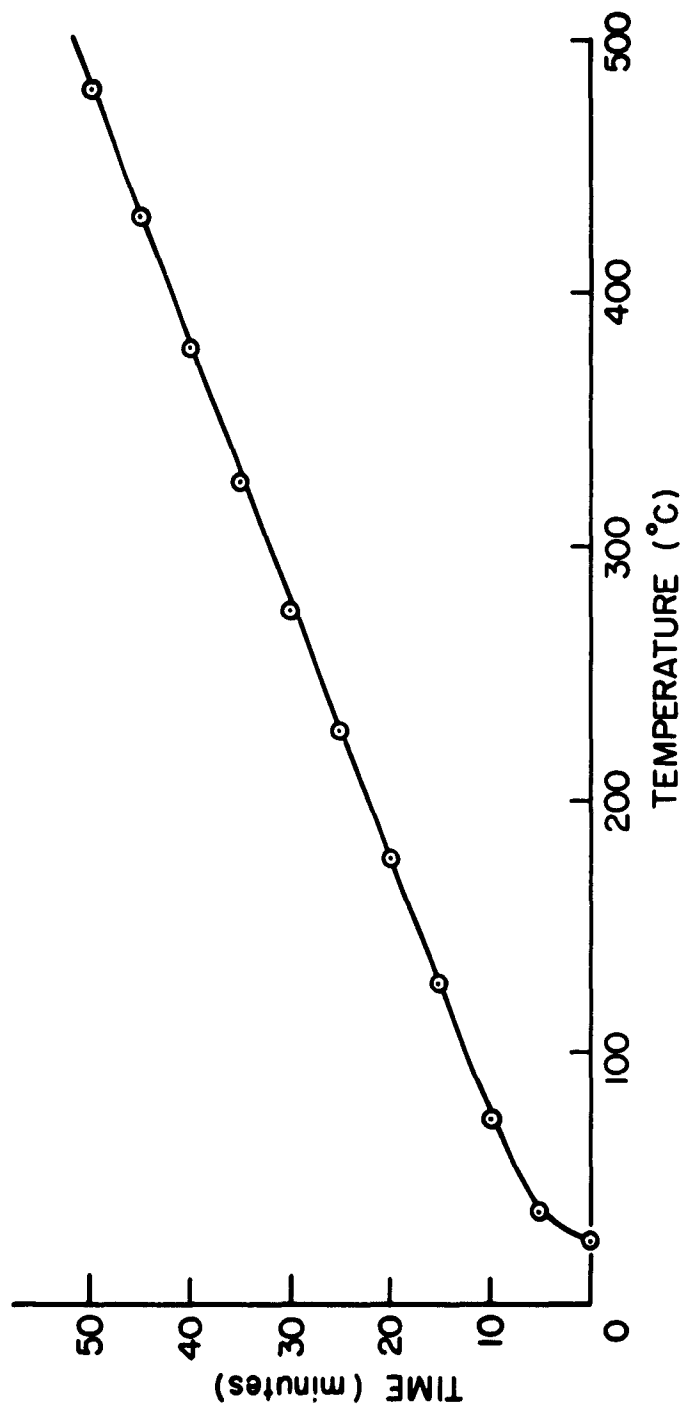


Fig. 2. TGA Heating Rate Curve

nitrogen and 125°C in air. After the maximum the ΔT tends to decrease as temperature increases. Thus, it is apparent that the temperatures of TGA curves obtained on this instrumentation will be generally 5° to 10°C higher than the actual temperature at which a given event occurs and this situation is general for the TGA curves of most investigators.

Table I

Atmosphere Temperatures Inside and Outside the
Sample Holder During Normal TGA Operation

Time (min.)	Temperature (°C)			Heating Rate (°C/min.)	
	Inside	Outside	$\Delta T(^{\circ}\text{C})$	Inside	Outside
Atmosphere-Nitrogen at 3000 cc/min.					
0	25	25	0		
5	33	37	4	1.6	2.4
10	67	74	7	6.8	7.4
15	120	127	7	10.6	10.6
20	168	177	9	9.6	10.0
25	221	227	6	10.6	10.0
30	270	275	5	9.8	9.6
35	320	325	5	10.0	10.0
40	374	378	4	10.8	10.6
45	427	430	3	10.6	10.4
50	480	480	0	10.6	10.4
Atmosphere-Air at 3000 cc/min.					
0	23	25	2		
5	37	35	2	2.8	2.0
10	74	81	7	7.4	9.2
15	120	129	9	9.2	9.6
20	170	176	6	10.0	9.4
25	218	221	3	9.6	9.2
30	268	269	1	10.0	9.6
35	318	321	3	10.0	10.4
40	366	371	5	9.6	10.0
45	416	419	3	10.0	9.6
50	464	469	5	9.6	10.0

2. General Results

The TGA behavior of several different fibers was examined in the course of testing the instrumentation and the curves obtained for cotton, nylon 66, and Orlon, both in air and in nitrogen are shown in Figure 3. Cotton fabric shows an early reaction, the loss of sorbed water, in both an oxidizing and an inert atmosphere, that is completed around 140°C. Then a slow decomposition starts at about 290°C in air and 310°C in nitrogen, becoming fast around 320°C, which is completed at 400°C in air and in nitrogen. This process appears to be essentially the same in both atmospheres and is believed to involve the thermal depolymerization of cellulose. In air a third reaction is indicated during which the carbonaceous residue is completely consumed. Nylon is indicated to have different initial decomposition temperatures in air (ca 300°C) and nitrogen (ca 370°C). However, the main reaction is essentially the same and is believed to involve thermal depolymerization of the polyamide.

In the case of Orlon, no major decomposition occurs until 300°C in air and 325°C in nitrogen, at which points a very fast but limited reaction occurs involving weight losses of 32.5% in air and 17.0% in nitrogen. In air, the Orlon curve shows four reaction zones: (1) 50° to 140°C; (2) 190° to 290°C; (3) 290° to 340°C; and (4) 340° to 500°C. It is noteworthy that in air even at 500°C over one-half the sample still remains. In nitrogen, four reactions are also indicated, but significant differences are evident in that the third zone begins around 310°C instead of 290°C, and the fourth zone starts at about 335°C. The third reaction (310° to 335°C) involves a weight loss of about one-half of that which appears to be the same reaction in air; the fourth reaction proceeds at a much faster rate than the corresponding one in air, and an appreciably greater loss of sample results in the nitrogen atmosphere. Orlon thus shows considerable stability in air compared with the other materials studied.

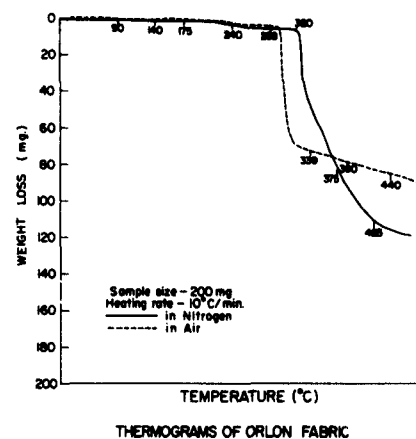
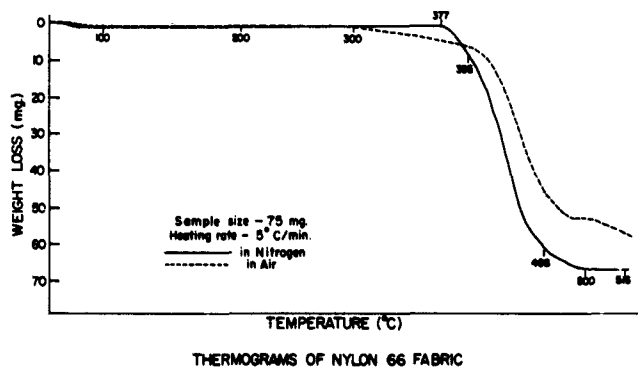
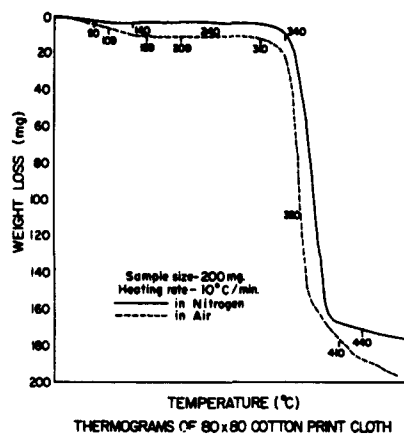
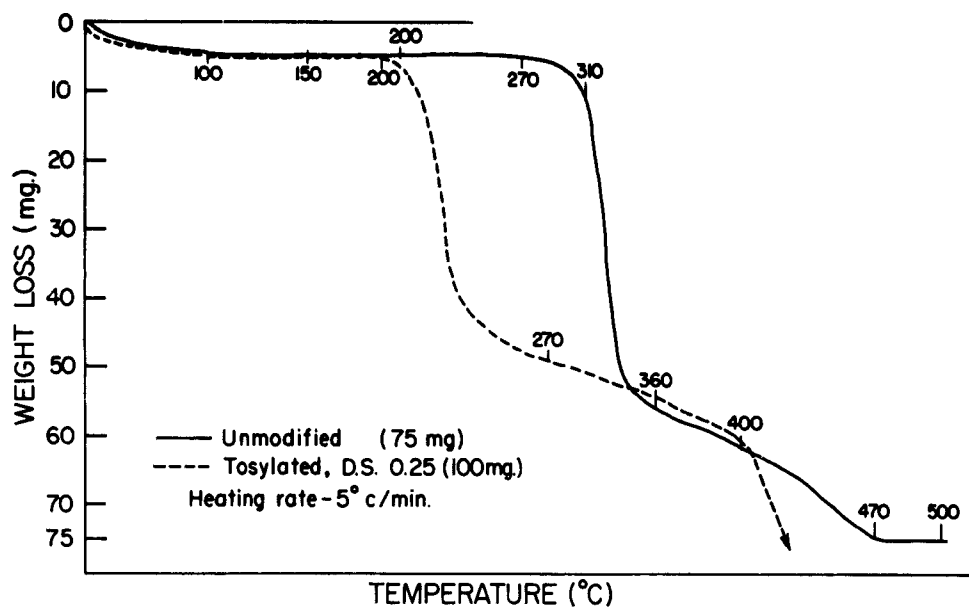
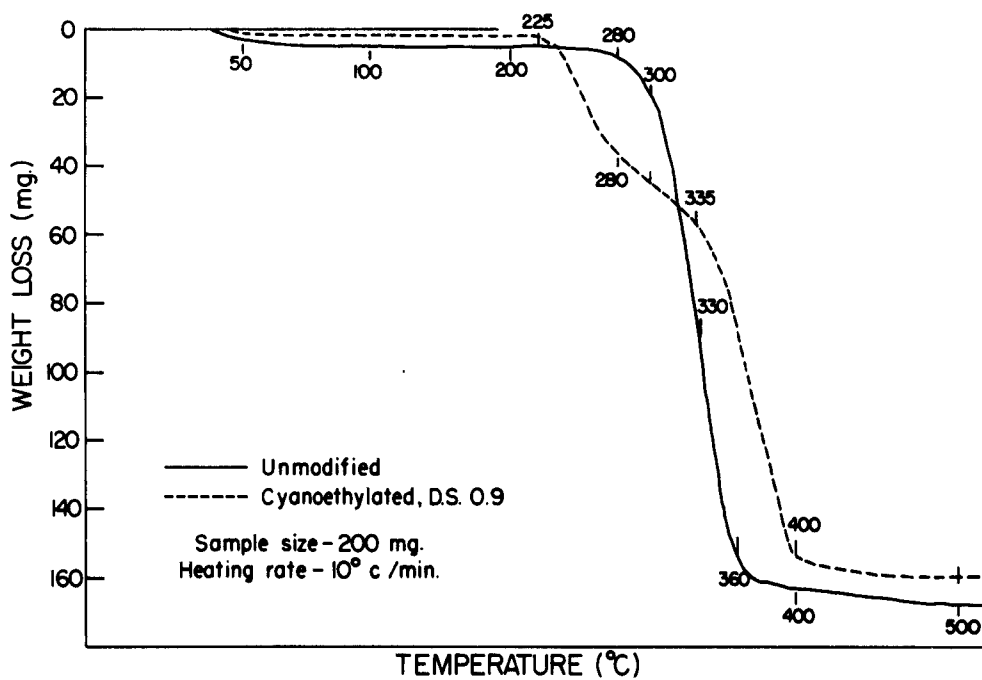


Fig. 3. TGA Curves of Textile Materials



THERMOGRAMS IN AIR



THERMOGRAMS IN NITROGEN

Fig. 4. TGA Curves of Chemically Modified Cotton Fabric

The effect of chemical modification on the thermal stability of cellulose is shown in Figure 4. Thus, tosylation to low D.S. is shown to reduce the thermal stability substantially, and also radically changes the path of thermal degradation from that of unmodified cotton cellulose. Cyanoethylation is also shown to give cellulose derivatives of reduced thermal stability. In Figure 5, the TGA curve for a cyanoethylated cotton is shown to correlate very well with the DTA (differential thermal analysis) curve of the same material. Cyanoethylation to D.S. 0.9 results in a theoretical weight gain of about 29.4% and the TGA reaction (220° to 330°C) corresponding to the DTA endotherm (230° to 335°C), found only for a cyanoethylated sample, results in a 29.2% weight loss. This result suggests that the DTA endotherm involves only the degradation of the cyanoethyl group followed by the depolymerization of the still unmodified cotton in the usual way during the next endothermic phase.

The rate processes involved in thermal degradation and other reactions at elevated temperature can be studied by means of TGA. Expressions have been derived for the case of irreversible reactions by Freeman and Carroll [6] that appear to be applicable to the catastrophic processes encountered in high polymer thermal degradation [7]. The relationship as derived by Freeman and Carroll is:

$$\frac{\Delta \log (dw/dt)}{\Delta \log W_r} = x - \frac{E^*}{2.3R} \Delta \left(\frac{1}{T} \right)$$

where

dw/dt = rate of change in sample weight
 W_r = weight of reactant at any time
 x = order of reaction
 E^* = activation energy
 R = gas constant
 T = absolute temperature.

A plot of $\Delta \log (dw/dt) / \Delta \log W_r$ as the ordinate versus $(\Delta T^{-1}) / \Delta \log W_r$ as the abscissa yields a straight line where the order of the reaction, x , is determined by the intercept and the activation energy, E^* , is calculated from the slope of the line. The kinetics of the major degradation reactions of cotton cellulose (320° to 380°C) and nylon 66 (380° to 480°C) in air have been explored by the Freeman-Carroll approach with the preliminary results shown in Table II.

Table II
Kinetic Data on the Thermal Degradation
of Cotton and Nylon in Air

Sample	TGA Reaction Zone (°C)	Activation Energy, E^* (Kcal/mole)	Order of Reaction
Nylon 66	380 - 480	50	~1
Cotton	320 - 380	56	~2

The plots from which the data were obtained are shown in Figure 6.

3. Coated Nylon Systems

a. Nylon-Butyl Rubber System

In Figure 7 the TGA curves of butyl rubber, nylon fabric, and coated fabric samples in air and in nitrogen are shown. In air, butyl rubber shows a single reaction zone beginning around 320°C and terminating about 440°C whereas nylon begins decomposition about 300°C with reaction completion about 490°C. The DTA curves indicate that in the case of nylon at least two reactions may occur: (1) 300° to 400°C and (2) 400° to 490°C [1], but TGA does not make such a distinction. In the case of the coated fabric the TGA curve is very similar in appearance to that of uncoated nylon showing one long continuous reaction zone from 300° to 490°C.

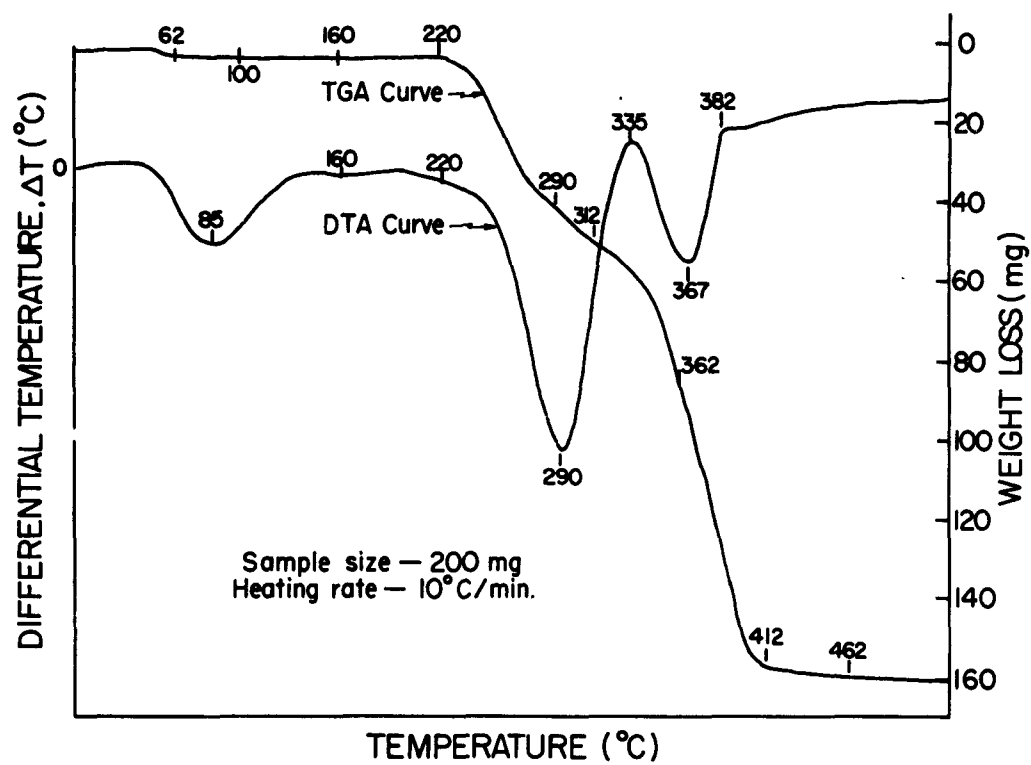
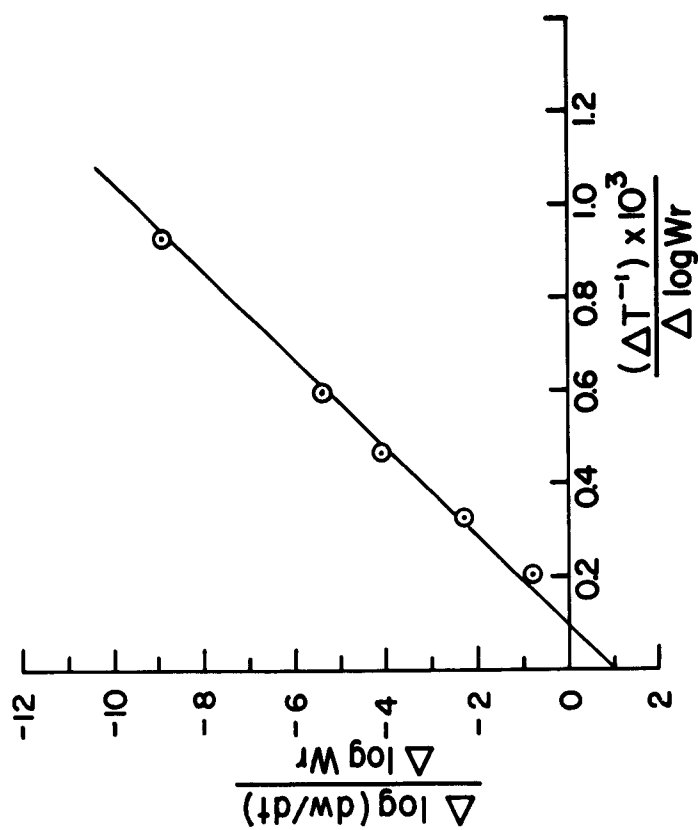
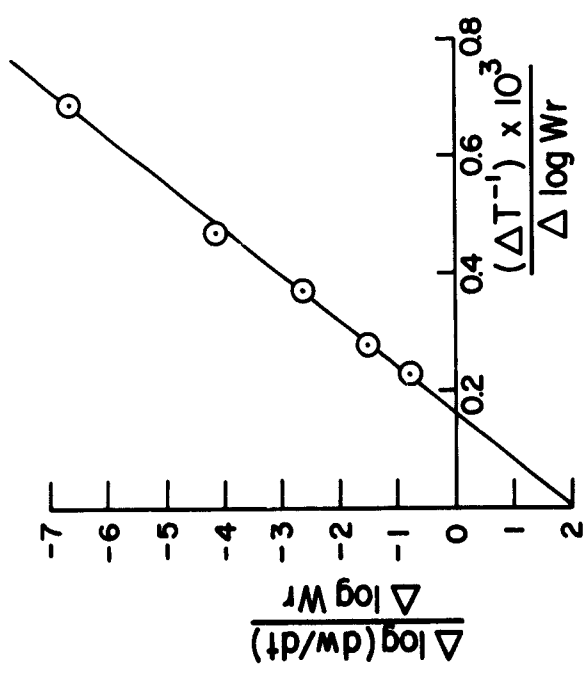


Fig. 5. Thermograms of Cyanoethylated Cotton (DS 0.9) Fabric Obtained in Nitrogen Atmosphere



NYLON 66



COTTON CELLULOSE

Fig. 6. Kinetics of the Thermal Decomposition of Cotton and Nylon in Air

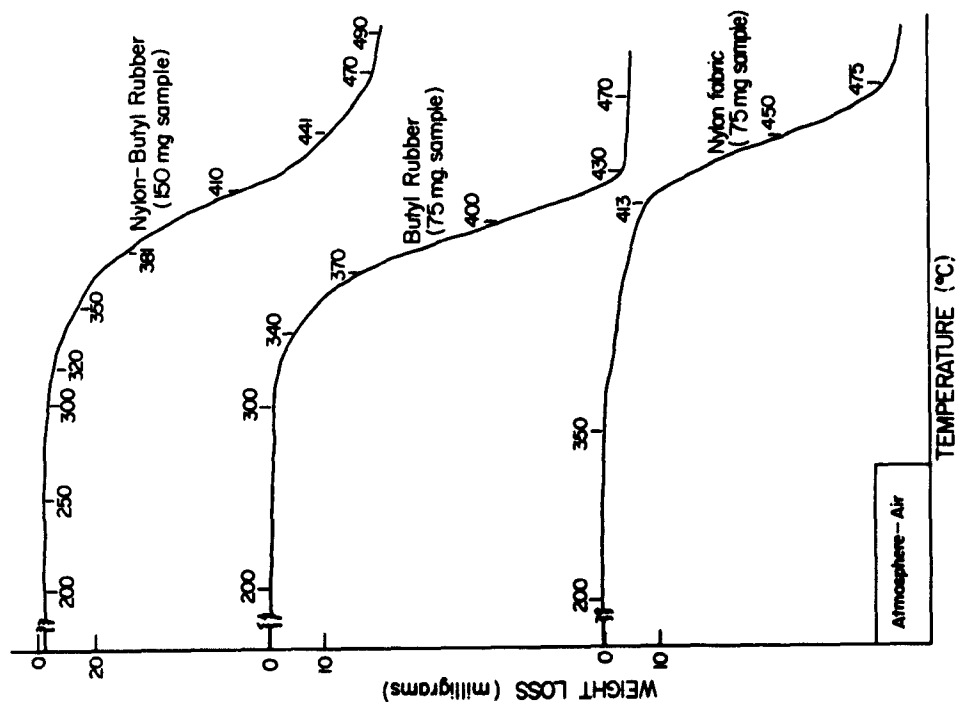
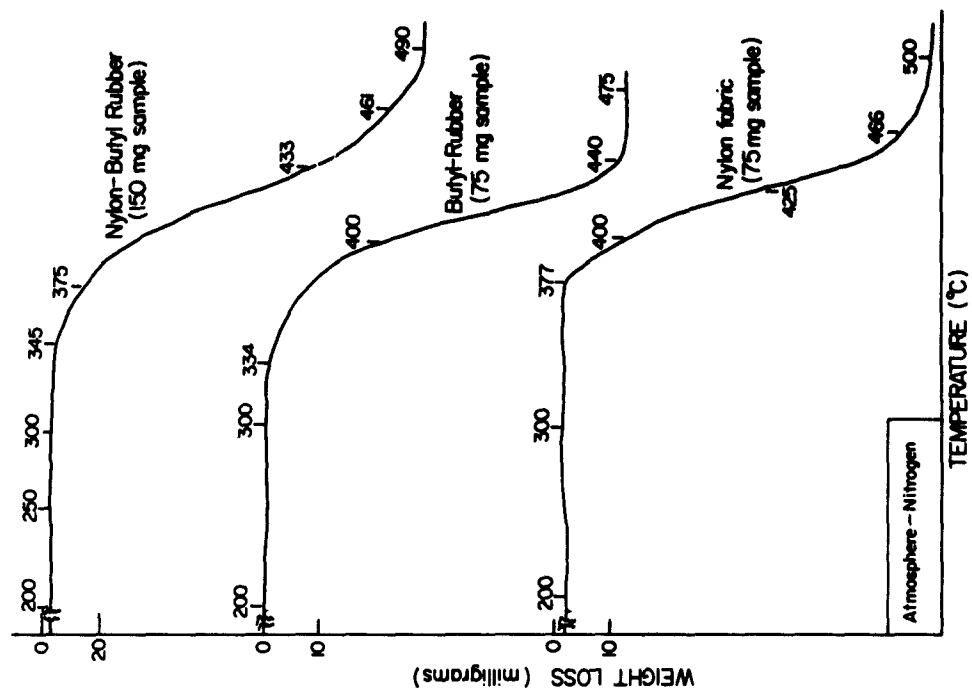


Fig. 7. TGA Curves: Nylon-Butyl Rubber System

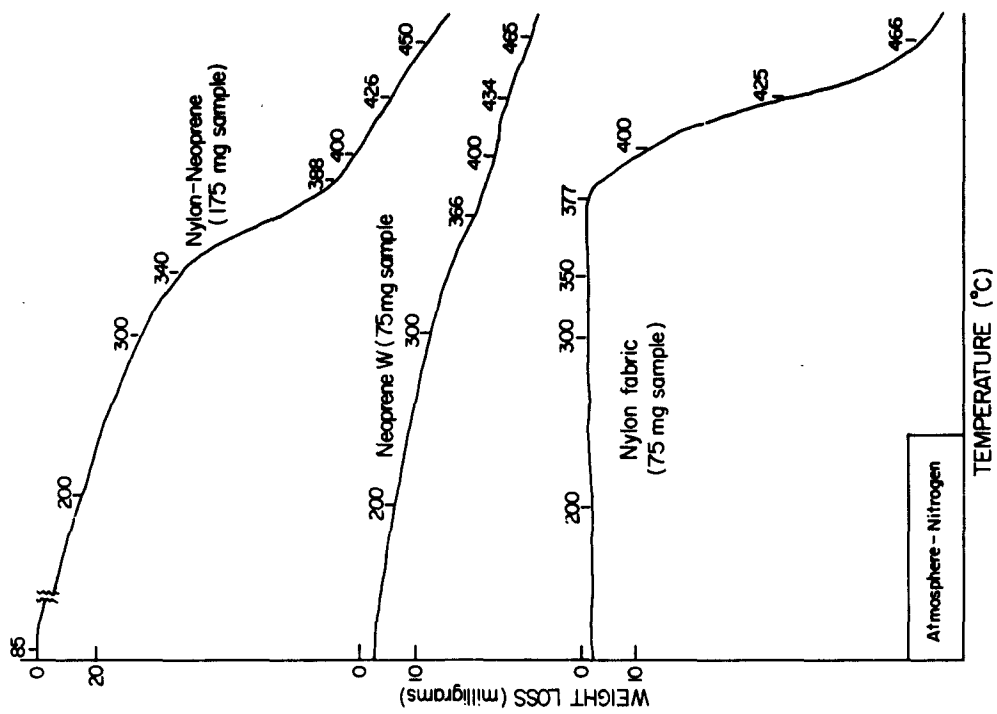
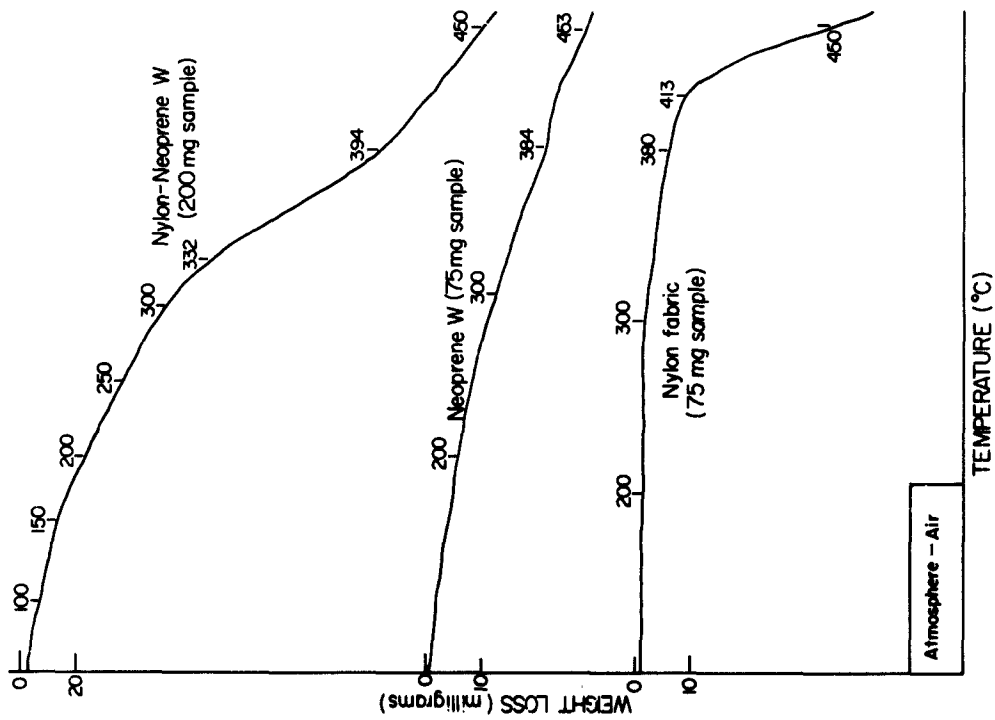


Fig. 8. TGA Curves: Nylon-Neoprene W System

The TGA curves for these materials in nitrogen atmosphere do not differ materially from those in air. Some of the data appertaining to the curves are shown in Table III.

Table III
TGA Data on the Nylon-Butyl System

Sample	IDT* (°C)	Max. Rate of Decomp. (mg/min.)	Wt. Loss (%) at		Heating Rate (°C/min.)
			400°C	500°C	
Air Runs					
Butyl Rubber	300	6.2	56.0	88.0	6.5
Nylon	280	5.7	40.0	73.2	6.0
Nylon-Butyl	313	10.0	38.6	84.0	6.0
Nitrogen Runs					
Butyl Rubber	319	7.8	34.6	86.7	6.2
Nylon	375	6.7	17.3	91.4	6.5
Nylon-Butyl	324	10.0	25.3	93.3	5.8

* Initial Decomposition Temperature.

The results from the air runs suggest that the coated fabric has slightly improved thermal stability based on the IDT (initial decomposition temperature) and weight loss at 400°C. In both atmospheres a chemical interaction is indicated by the marked increase in the maximum rates of decomposition for the coated samples over those of the component elastomer and fabric.

b. Nylon-Neoprene-W* System

The thermograms obtained for the components and coated samples in both air and nitrogen are presented in Figure 8.

* Du Pont Trademark.

Neoprene is indicated to undergo the same volatilization reactions in air or in nitrogen involving (1) a reaction initiating very early, about 60°C, and continuing slowly until about 400°C where (2) a second, slightly faster reaction takes over which terminates around 500°C. It is interesting to note that the DTA curves available [4] do not show significant activity prior to about 180°C and it is suggested that the rate of the first volatilization reaction (60° to 400°C) is initially so slow that the change in ΔT during DTA was not detected as a distinct reaction. These observations further indicate the need for TGA data wherever DTA data are obtained on polymeric materials.

The curves for the coated samples show at least three similar reaction zones in air and nitrogen: (1) 60° to 220°C, (2) 220° to 420°C, and (3) 420° to 500°C, and the behavior of the coated samples strongly reflects the influence of Neoprene. Decomposition rates and other numerical data for the system and its components are compared in Table IV.

Table IV
TGA Data on the Nylon-Neoprene W System

Sample	IDI* (°C)	Max. Rate of	Wt. Loss (%) at		Heating
		Decomp. ,mg/min.)	400°C	500°C	Rate (°C/min.)
Air Runs					
Neoprene-W	60	0.62 0.83	29.4	44.0	6.8
Nylon	280	5.7	40.0	73.2	6.0
Nylon-Neop.	60	6.7 3.3	68.1	95.0	8.0 5 to 6
Nitrogen Runs					
Neoprene-W	60	0.56 0.77	34.6	49.4	6.5
Nylon	375	6.7	17.3	91.4	6.5
Nylon-Neop.	60	8.0 3.3	66.3	93.7	6.0

* Initial Decomposition Temperature.

The incidence of a new reaction, the increased rates of decomposition, and the magnitude of the weight losses at 400°C and 500°C leave no doubt that marked chemical interactions occur even prior to nylon melting. The DTA curves show that the nylon component melts at the usual temperature (261°C) but that major decomposition occurs much earlier than normal in air and somewhat earlier in nitrogen [4]. Thus, new degradation paths are indicated, probably initiated by acid attack due to the generation of HCl from Neoprene decomposition [8].

c. Nylon-Hypalon* System

When the TGA curves for the system (Figure 9) are examined, the influence of the major reactions of the components is clearly visible in the combined sample but it is notable that contrary to the previous systems the rates of decomposition appear to decrease rather than increase. In the case of Hypalon, which is chlorosulfonated polyethylene, three major reaction zones are shown which appear much the same in both air and nitrogen: (1) 190° to 250°C, (2) 270° to 380°C and (3) 400° to 490°C. In the case of the coated samples reaction zones are observed as (1) 200° to 250°C, (2) 270° to 350°C, (3) 350° to 420°C, and (4) 420° to 500°C, which indicates a reaction, 350° to 420°C, not present in either component as a separate and distinct process. The reactions indicated from DTA curves, shown in Table V, are in good agreement with those indicated by TGA. The data from the TGA curves are shown in Table VI.

* Du Pont Trademark.

Table V

Comparison of Endothermic
Reaction Zones from DTA and TGA Curves

Sample	Reaction Zone	Temp. Range in °C DTA	TGA
Air Runs			
Hypalon	1	None	190 - 250
	2	270 - 340	270 - 380
	3	400 - 500	400 - 490
Nylon-Hypalon	1	170 - 250	200 - 250
	2	280 - 340	270 - 350
	3	340 - 400	350 - 420
	4	440 - 500	420 - 500
Nitrogen Runs			
Hypalon	1	None	190 - 250
	2	275 - 350	270 - 380
	3	380 - 450	400 - 490
	4	460 - 500	
Nylon-Hypalon	1	None	200 - 250
	2	280 - 350	270 - 350
	3	350 - 400	350 - 420
	4	450 - 500	420 - 500

Table VI

TGA Data on the Nylon-Hypalon System

Sample	IDT* (°C)	Max. Rate of Decomp. (mg/min.)	Wt. Loss (%) at 400°C	Wt. Loss (%) at 500°C	Heating Rate (°C/min.)
Air Runs					
Hypalon	260	2.0 5.7	38.0	93.2	6.0
Nylon	280	5.7	40.0	73.2	6.0
Nylon-	270	3.0	34.6	88.7	5.8
Hypalon		6.2			
Nitrogen Runs					
Hypalon	270	2.5 6.7	38.0	97.3	6.8
Nylon	375	6.7	17.3	91.4	6.5
Nylon-	275	3.6	34.6	97.2	6.0
Hypalon		6.2			

* Initial Decomposition Temperature.

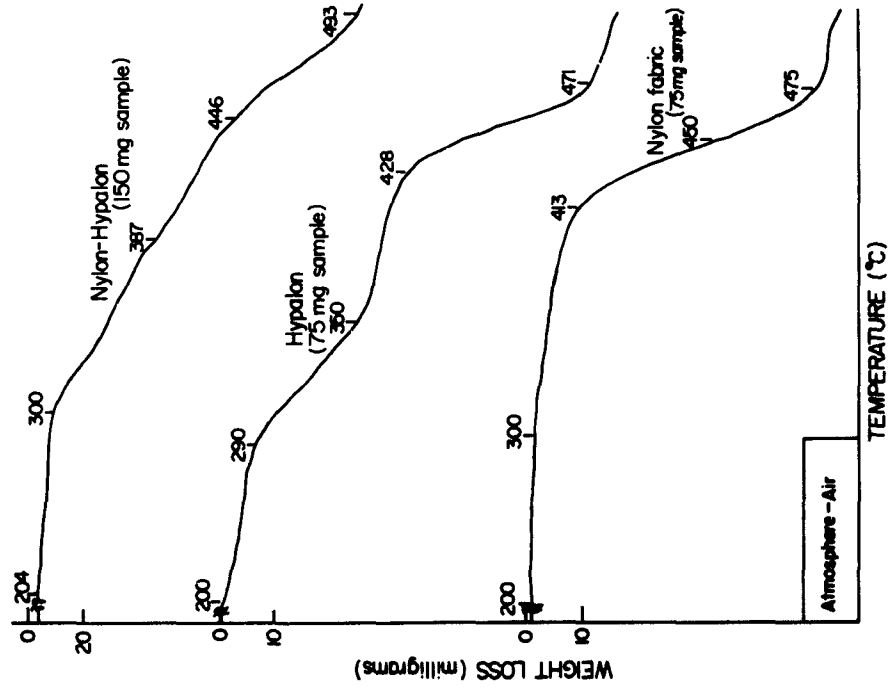
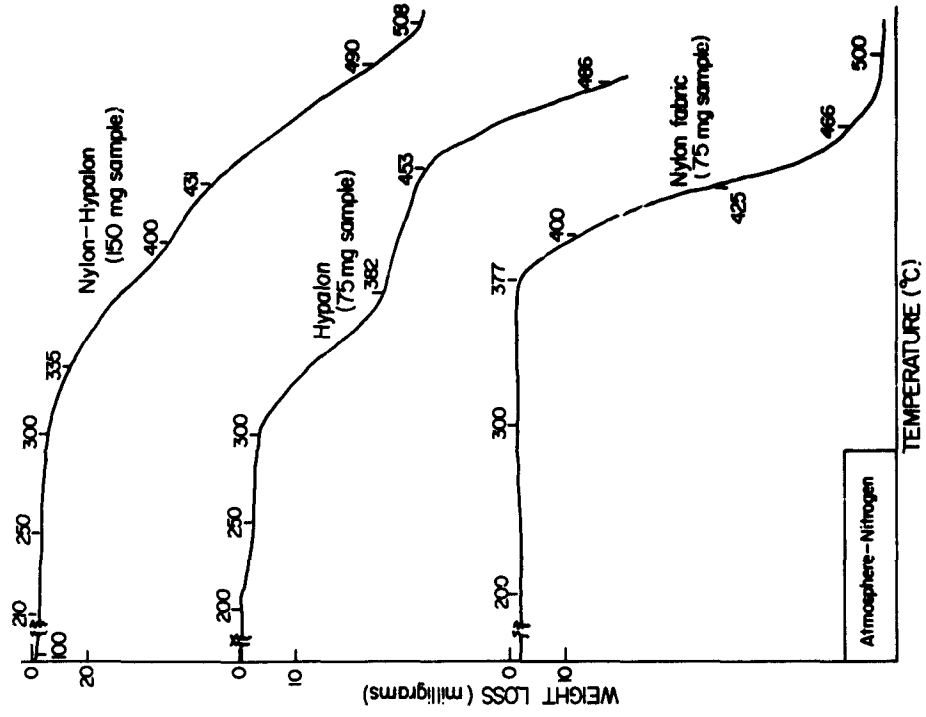


Fig. 9. TGA Curves: Nylon-Hypalon System

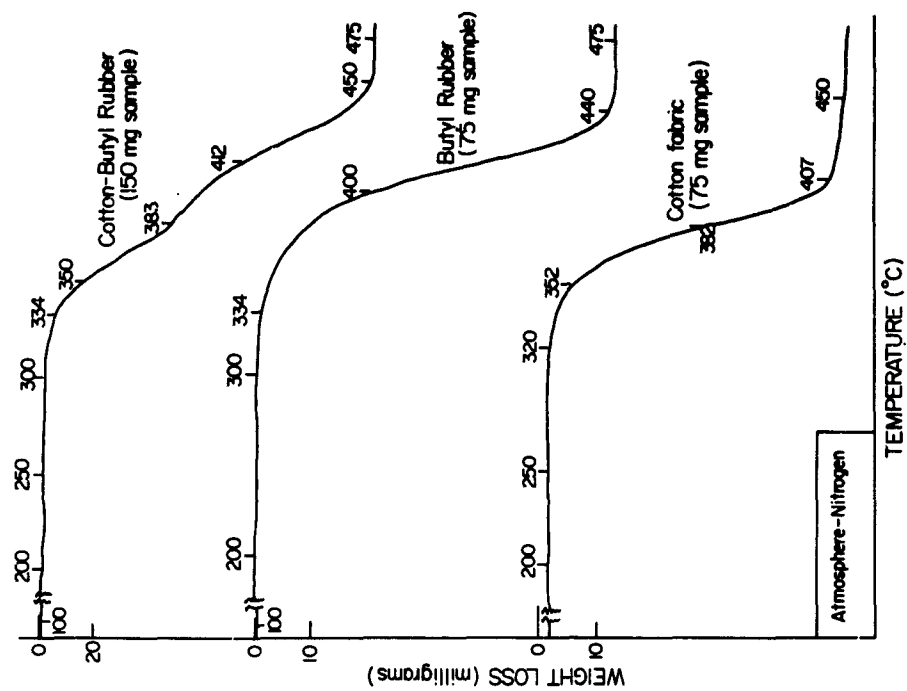
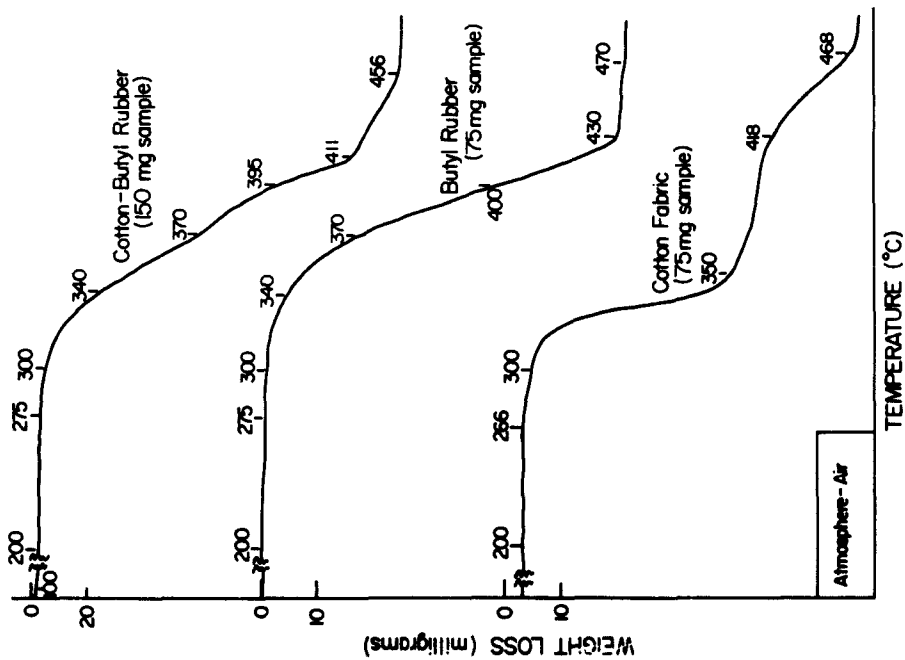


Fig. 10. TGA Curves: Cotton-Butyl Rubber System

These results indicate little or no interaction between the coating and the nylon base. Thus, it appears that the two materials react essentially independently, each making its anticipated contribution to the behavior of the coated sample.

4. Coated Cotton Systems

a. Butyl Rubber-Cotton System

The TGA curves from runs in air and nitrogen are shown in Figure 10 and the numerical data in Table VII.

Table VII

TGA Data on the Cotton-Butyl Rubber System

Sample	IDT* (°C)	Max. Rate of	Wt. Loss (%) at		Heating
		Decomp. (mg/min.)	325°C	475°C	Rate (°C/min.)
Air Runs					
Butyl Rubber	300	6.2	3.3	87.3	6.5
Cotton	290	10.0	18.7	86.8	6.3
Cotton-Butyl Rubber	290	7.5 13.3	9.3	89.3	6.2
Nitrogen Runs					
Butyl-Rubber	319	7.8	0	86.0	6.2
Cotton	310	7.5	2.7	75.3	6.4
Cotton-Butyl Rubber	303	6.7 8.6	3.3	82.7	6.2

* Initial Decomposition Temperature.

It is apparent from a perusal of the curves that in the case of the coated sample a new reaction is evident in the range of 375° to 420°C in air and 390° to 460°C in nitrogen which betokens a chemical interaction probably resulting between the degradation products of the components. The overall thermal stability of the coated fabrics is not, however, very different from that of the components.

b. Cotton-Neoprene W System

In Table VIII the data from the TGA curves (Figure 11) are given.

Table VIII
TGA Data on the Cotton-Neoprene W System

Sample	IDT* (°C)	Max. Rate of Decomp. (mg/min.)	Wt. Loss (%) at 325°C	Heating Rate (°C/min.)	
Air Runs					
Neoprene W	60	0.62 0.83	9.3	40.0	6.8
Cotton	290	10.0	18.7	86.8	6.3
Cotton- Neoprene	200	4.6 2.0	46.6	90.0	6
Nitrogen Runs					
Neoprene W	60	0.56 0.77	11.3	43.9	6.5
Cotton	310	7.5	2.7	75.3	6.4
Cotton- Neoprene	200	5.0 4.0	42.0	68.0	8.0

* Initial Decomposition Temperature.

The data indicate that the thermal stability of the coated samples has been substantially reduced from that of the cotton base fabric. This can be due to nothing other than chemical interaction. It is suggested that the cotton undergoes degradation via acid attack involving HCl produced from the thermal degradation of the Neoprene. The curves also clearly show a new reaction that occurs in the region from 200° to about 320°C. The change in the magnitude of the decomposition rates is also evidence for chemical interaction at relatively low temperatures.

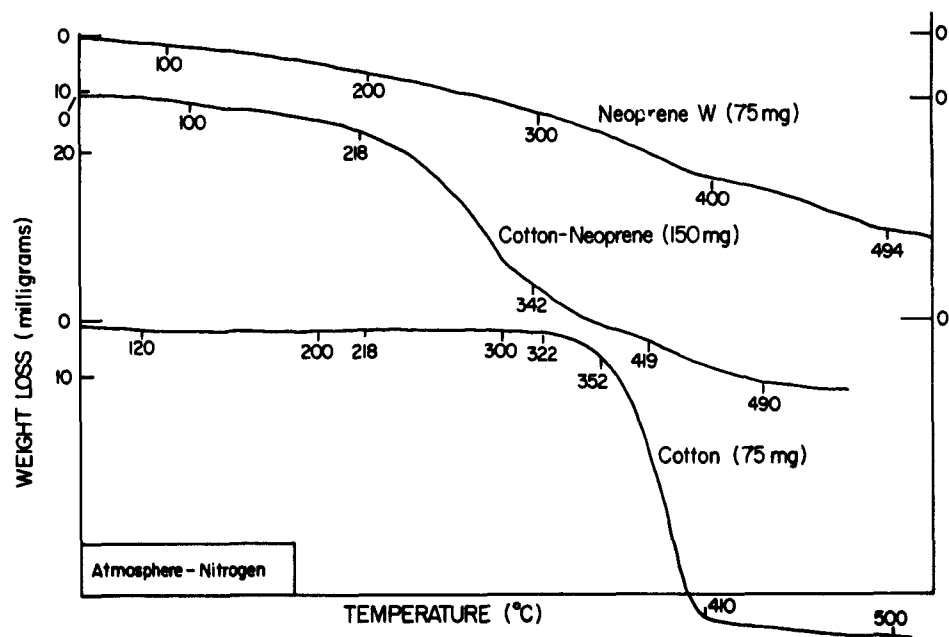
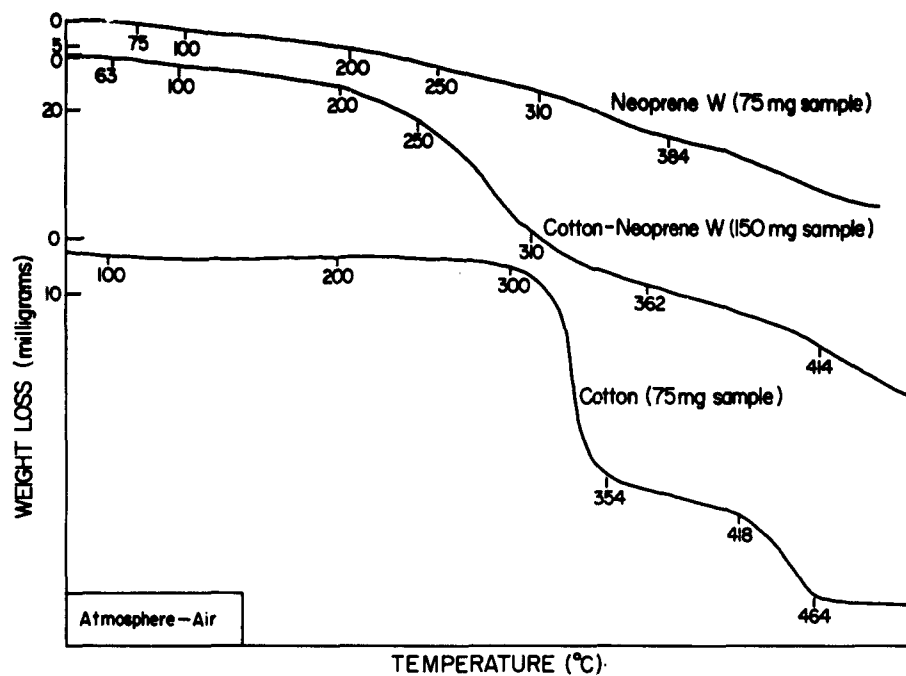


Fig. 11. TGA Curves: Cotton-Neoprene W System

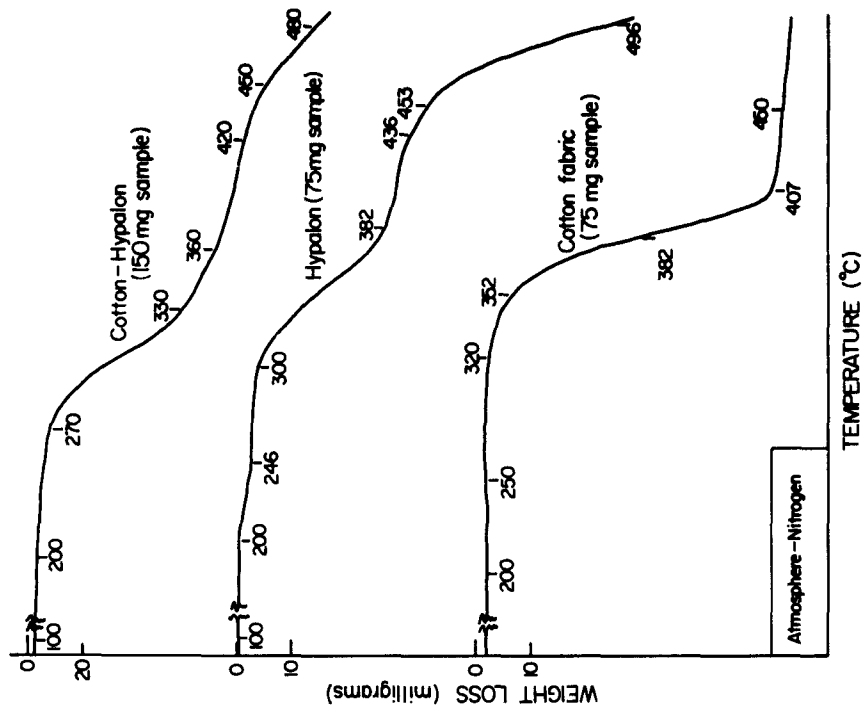
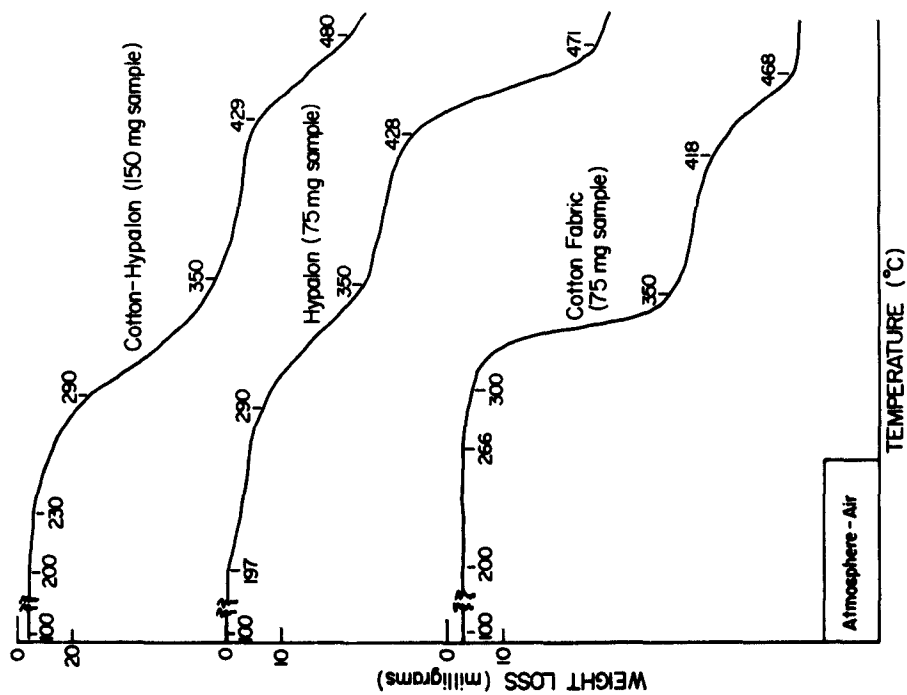


Fig. 12. TGA Curves: Cotton-Hypalon System

c. Cotton-Hypalon System

In Figure 12 the thermograms for the coated samples indicate reduced thermal stability and some of the data obtained from the curves are presented in Table IX.

Table IX

TGA Data on the Cotton-Hypalon System

Sample	IDT* (°C)	Max. Rate of Decomp. (mg/min.)	Wt. Loss (%) at 325°C	475°C	Heating Rate (°C/min.)
Air Runs					
Hypalon	260	2.0 5.7	20.6	89.2	6.0
Cotton	280	10.0	18.7	86.8	6.3
Cotton- Hypalon	220	6.0 5.0	37.3	80.2	6.1
Nitrogen Runs					
Hypalon	270	2.5 6.7	10.6	60.0	6.8
Cotton	310	7.5	2.7	75.3	6.4
Cotton- Hypalon	227	6.0 4.4	41.3	66.8	6.1

* Initial Decomposition Temperature.

The initial decomposition temperatures indicate reduced thermal stability for the coated samples and this is confirmed by the weight losses found at 325°C. The DTA curve in nitrogen for the coated sample shows three major endothermic reactions of (1) 260° to 300°C, (2) 310° to 380°C, (3) 380° to 500°C compared with TGA reactions of (1) 230° to 380°C and (2) 380° to 500°C. In the case of Hypalon the nitrogen DTA curve shows an endothermic reaction starting around 260°C with a peak at 334°C and in this area the polymer is shown by TGA to lose appreciable weight (about 25%). This may involve the loss of the sulfonyl chloride and chlorine which could initiate acid degradation of the cellulose substrate.

DIFFERENTIAL THERMAL ANALYSIS

A continuing effort was made to further develop improved DTA techniques for the characterization and study of the reactions of textile materials at elevated temperatures. In the preferred technique of sample packing for high temperature DTA, the reference material is admixed with the sample primarily in order to minimize baseline shift [4]. In this connection recent work in the program indicated that under certain circumstances interactions could occur between the reference materials, alumina, and certain cotton cellulose derivatives. It is readily apparent that any appreciable proclivity for a particular reference substance to enter into reaction with sample degradation products or to otherwise respond to sample behavior seriously imperils the usefulness of that substance as a reference material. Sutherland and Drechsel [9] have suggested that quartz microfiber be considered as a DTA reference substance. These workers found the quartz material to have more favorable thermal conductivity than aluminum oxide and better stability at the high temperatures (1000°C) used in their DTA experiments. A brief investigation was made using quartz microfiber as a DTA reference material in place of alumina. The results obtained indicated very satisfactory performance as shown by the data in Table X.

Since the difficulties with alumina became manifest during DTA analysis of the sulfonic esters of cellulose, thermograms of these materials were obtained using quartz instead of alumina with the result that the interaction did not occur. The data in Table X indicate that qualitatively the same results are obtained for both reference materials for the base fabrics used in this study. The results in certain instances, notably the melting transition of nylon and

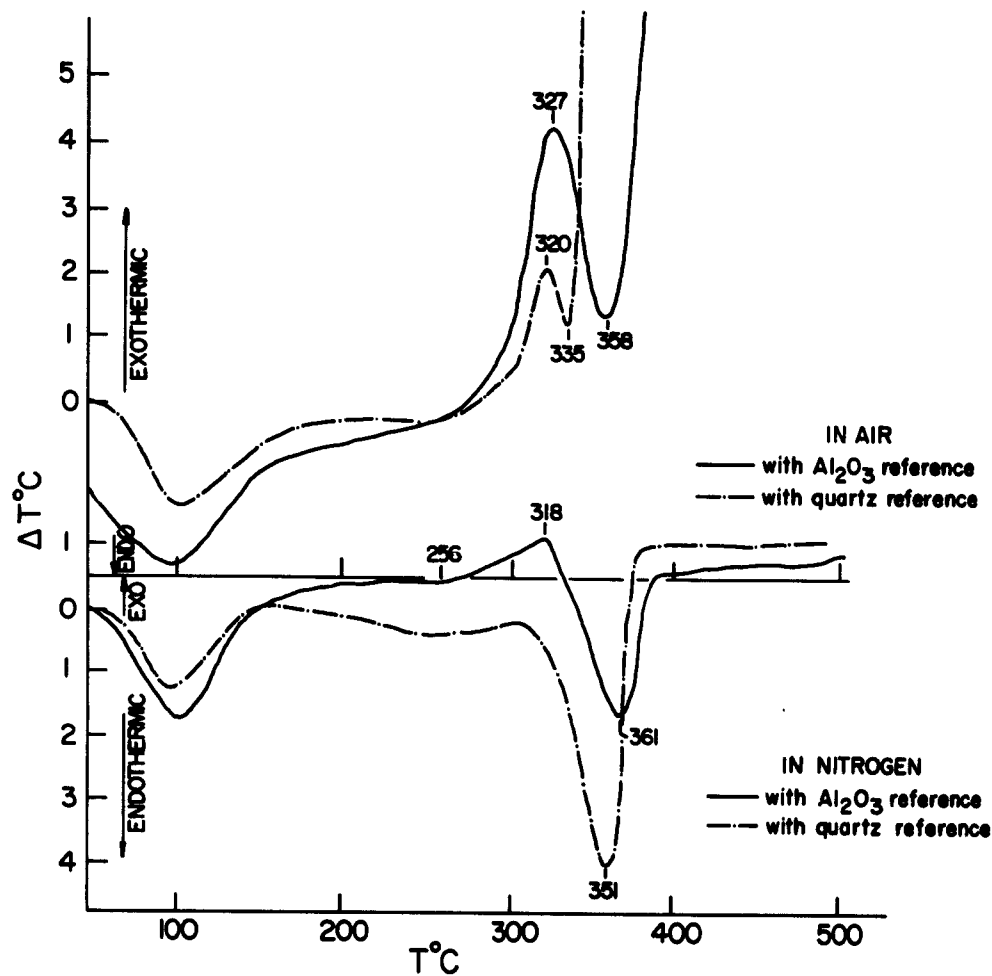


Fig. 13. DTA Curves of Cotton Fabric

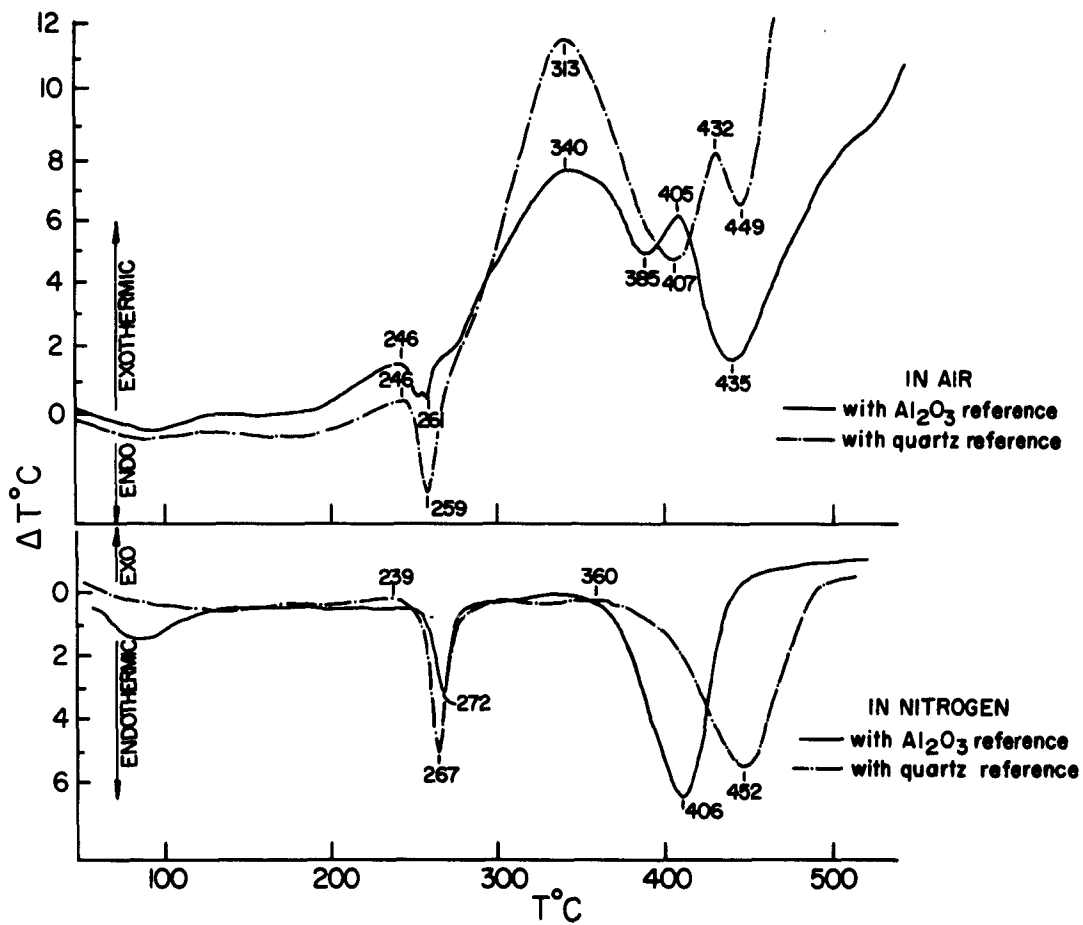


Fig. 14. DTA Curves of Nylon Fabric

the characteristic exothermic reaction for Orlon, are quantitative whereas in the case of the nylon endotherm, believed to be associated with depolymerization, a substantial shift of peak temperature upward has occurred. In Figures 13 and 14 thermograms prepared with the two reference materials are shown. In nitrogen the peaks appear to be of somewhat greater magnitude where quartz fiber was used as the reference material. In air, differences in peak heights are also shown. Curve configurations remain the same in both nitrogen and air but some shifts in peak temperatures appear to occur. These and other results indicate that aluminum oxide was a satisfactory reference substance for the materials involved in this investigation and no interactions appear to occur within the temperature range studied.

Table X

Comparison of Quartz Microfiber and
Alumina as DTA Reference Materials

Sample	Wt. (mg)	Atmos.	Ref. Mat. ^a	Peak Temperature and Type					
				T(°C)	Type ^b	T(°C)	Type ^b	T(°C)	Type ^b
Cotton	100	Air	Al	100	En	327	Ex	358	En
	100	Air	Q	100	En	320	Ex	335	En
Fabric	100	N ₂	Al	100	En	318	Ex	361	En
	100	N ₂	Q	100	En	c	c	351	En
Nylon	75	Air	Al	98	En	259	En	340	Ex
	75	Air	Q	95	En	259	En	343	Ex
	75	N ₂	Al	95	En	266	En	406	En
	75	N ₂	Q	100	En	267	En	452	En
Fabric	100	N ₂	Al	90	En	266	En	400	En
	100	N ₂	Q	105	En	270	En	451	En
Orlon	75	Air	Al	—	—	308	Ex	—	—
Fabric	75	Air	Q	—	—	310	Ex	—	—

a-Al = aluminum oxide; Q = quartz microfiber

b-En = endothermic reaction; Ex = exothermic reaction

c-No peak observed.

GAS CHROMATOGRAPHY STUDIES

Since detailed knowledge of the products arising from the thermal decomposition of a polymer would seem essential for the complete elucidation of the degradation mechanisms involved, it was decided to study the degradation products arising from the exposure of the base fabrics, coatings, and coated fabrics to decomposition temperatures by gas-liquid chromatography. Gas chromatography is the most sensitive and versatile method yet devised for the separation and determination of organic volatiles and was, therefore, uniquely suited to this most difficult task.

Samples of cotton, nylon, butyl rubber and butyl rubber-coated cotton were pyrolyzed in the pyrolysis apparatus previously described. Samples (ca. 10 g) were preheated at 110°C to drive off sorbed moisture and then heated at ca. 15°C/min. to decomposition temperatures (up to 450°C) either in air or purified nitrogen. The volatile products were trapped at 75°C, 0°C, and -78°C to yield tarry pyrolyzates which were subsequently taken up in appropriate solvents for injection into the gas chromatograph. Samples were also degraded within the injection port of the gas chromatograph on a hot wire loop to afford a more direct examination of the degradation products as suggested by the work of Lehrle and Robb and others [11,12].

The primary method of component identification was by comparison of the retention volumes for unknown peaks with those of known compounds. In addition, the effluents for various unknown peaks, trapped and collected as they emerged from the column, were tested with various qualitative organic reagents for the presence of aldehydes, ketones, alcohols and acids [10]. The retention volumes for unknowns and knowns were determined on different columns to provide a cross-check.

Another identification aid involved the inclusion of suspected knowns in the unknown mixtures in the case of liquid pyrolyzates.

1. Instrumentation and Procedures

The F & M Gas Chromatograph and pyrolysis equipment used were described earlier herein. A variety of chromatographic columns was required and all columns were made in the laboratory using 1/4 inch O.D. aluminum tubing and hand-packed. In Tables XI and XII the various liquid phases, packings, and the columns are described.

Table XI
Liquid Phases and Packing Materials

Trade Name	Compound
Haloport F	Perfluorocarbon Polymer
Octoil S	Di(2 Ethyl Hexyl) Sebacate
Carbowax 20M	Polyethylene Glycol (mol. wt. 15000-20000)
Silicone Gum	
Rubber	
Chromosorb P	Diatomaceous earth
Chromosorb W	Diatomaceous earth
Polyester	Diethylene Glycol
LAC 728	Succinate
Carbowax 1500	Polyethylene Glycol Succinate
D-C Silicone	
Oil 550	

The analysis of polymer degradation products by decomposing the polymer directly in the gas stream of the gas chromatograph is a new and useful technique [11,12,13]. This technique facilitates the removal of primary reaction products from the hot pyrolysis zone while minimizing the occurrence of secondary and tertiary reactions. Subsequent analysis is not complicated by solvents or the need for

condensing the products. These reasons, plus the speed with which the analysis can be completed, made it important that a suitable technique for this type be developed for use with TRI instrument.

Table XII
Description of Columns

Col. No.	Liquid Phase Name	%*	Solid Support	Solid Support Mesh Size	Column Length	Col. Temp. Limit
1	Silicone Gum Rubber	—	Chromosorb P	—	2 ft.	375°C
2	Octoil S	11	Haloport F	30-60	12 ft.	175°C
3	Octoil S	11	Haloport F	30-60	3 ft.	175°C
4	Carbowax 20 M	14	Basic Chromosorb W	60-80	12 ft.	225°C
5	Silicone Gum Rubber	10	Chromosorb P	40-60	6 ft.	375°C
6	Silicone Gum Rubber	10	Chromosorb P	40-60	12 ft.	375°C
7	Polyester LAC 728	10	Chromosorb W	60-80	12 ft.	225°C
8	Carbowax 20 M	15	Basic Chromosorb W	60-80	12 ft.	225°C
9	Octoil S	10	Haloport F	30-60	18 ft.	175°C
10	Octoil S	10	Haloport F	30-60	12 ft.	175°C
11	Carbowax 20 M	10	Haloport F	30-60	12 ft.	225°C
12	Carbowax 1500	20	Chromosorb P	40-60	12 ft.	200°C
13	D-C Silicone Oil 550	10	Haloport F	30-60	11 ft.	225°C
14	Carbowax 20 M	10	Haloport F	30-60	12 ft.	225°C

* % of liquid phase in total weight of packing.

A hot wire pyrolyzer was made consisting of a specially designed brass fitting with copper leads passing through Kovar seals into the fitting and connecting to the ends of a loop of 26 gauge nichrome wire which projected from the opposite end of the fitting. The copper wires connect to a

variac which controls the electric current whereby the loop is heated. In operation a fiber sample is wrapped around the loop and the assembly screwed into the injection port with the loop containing the sample intruding into the carrier gas stream. A silicone rubber septum holds the injection port pressure.

The normal running procedure is to insert the apparatus into the injection port then wait for the helium flow to return to normal; the temperature of the injection port drives off the absorbed water in the sample. After this absorbed water comes off the column and the baseline is stable, the sample is ready for pyrolysis. The variac is set at a preset value and current fed into the 6 inch length of 26 gauge nichrome wire for 10 to 15 seconds. The sample size was 5-15 mgs. The temperature of the wire was calibrated with thermocouples and "Templac."

The nichrome wire heater is capable of decomposing polymers very quickly and since the sample is positioned in the carrier gas stream the decomposition products are immediately carried away from the pyrolysis zone. The sample in the hot wire method is vaporized at the same place, the same injection port temperature, and same helium flow conditions as a normal syringe injection, but there is a steep temperature gradient outward from the wire which limits the size of the sample that can be pyrolyzed under uniform temperature conditions. A disadvantage of the method of pyrolysis in the gas stream of the chromatograph is that the comparison of V_R (retention volume) between liquid samples of known components and unknown peaks from a pyrolysis in the gas stream, can vary slightly because the known sample is volatilized instantly, whereas the polymer volatilizes over a longer period.

2. Volatile Products from Cotton Pyrolysis

Columns 9, 13, and 14 (Table XII) were employed. Helium, at a tank pressure of 30 psi, was used as the carrier gas and the gas flow rate was 30 cc/min. for column 13 and 60 cc/min. for columns 9 and 14. The detector block temperature was 275°C. Since there was a wide range of boiling points of the pyrolysis products, runs were usually initiated at a column temperature of 60°C and then programmed, at 4.0°C/min. for the Octoil-S and Silicone Oil columns and 7.9°C/min. in the case of the Carbowax column, to the maximum safe operating temperature for each column and then continued isothermally until the run was completed.

Purified cotton fabric was pyrolyzed by heating at ca. 15°C/min. to 370°C in an atmosphere of air or purified nitrogen. Samples of cotton yarn (10 mg) were also pyrolyzed for 10 to 12 seconds on the Nichrome wire loop.

Typical chromatograms obtained from the analysis of cellulose pyrolysis products on the Carbowax 20M column are shown in Figure 15. Chromatogram A was obtained by direct analysis of the degradation products. Chromatograms B and C were obtained on liquid pyrolyzates. Corresponding peaks in the three chromatograms are indicated by the same number and the products that have been identified are listed by peak number in Table XIV.

A minimum of 37 different volatile products is indicated whereas earlier studies using other analytical methods have indicated from 8 to 18 products [14,16] and the recent studies on cellulose pyrolysis by isothermal gas chromatography [17,18] have indicated no more than 18 decomposition products. These results indicate the same products irrespective of the pyrolysis conditions but significant differences in product distribution are shown. The pyrolyzate condensed at 75°C from cellulose pyrolysis in nitrogen shows the more volatile components as minor constituents with the intermediate and high boiling compounds as the most significant, whereas in

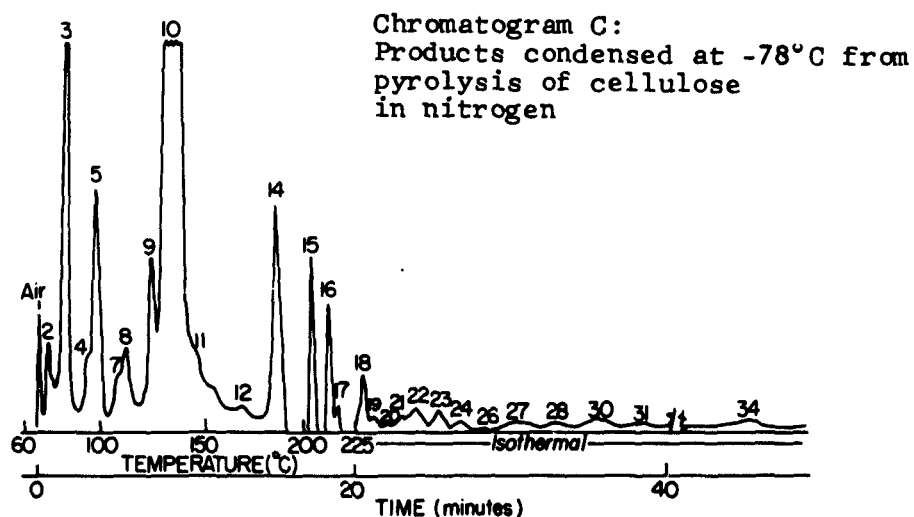
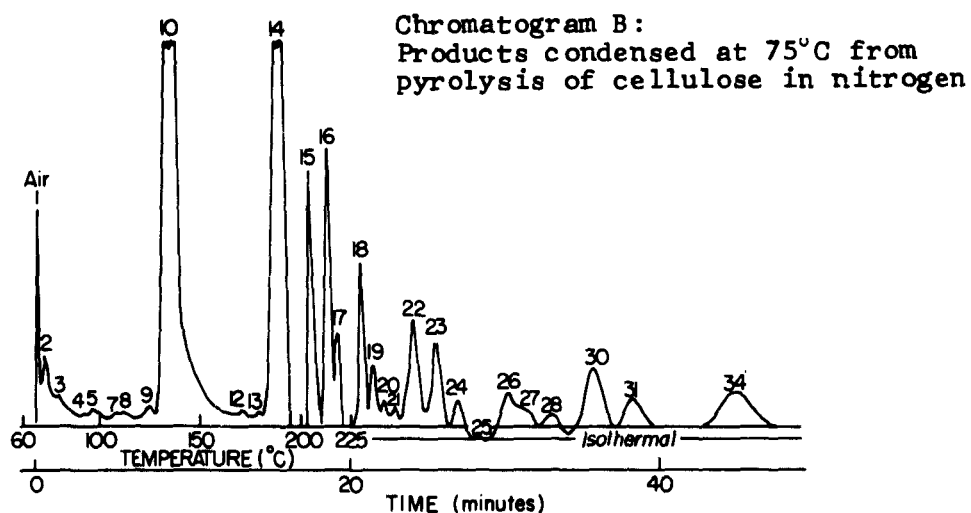
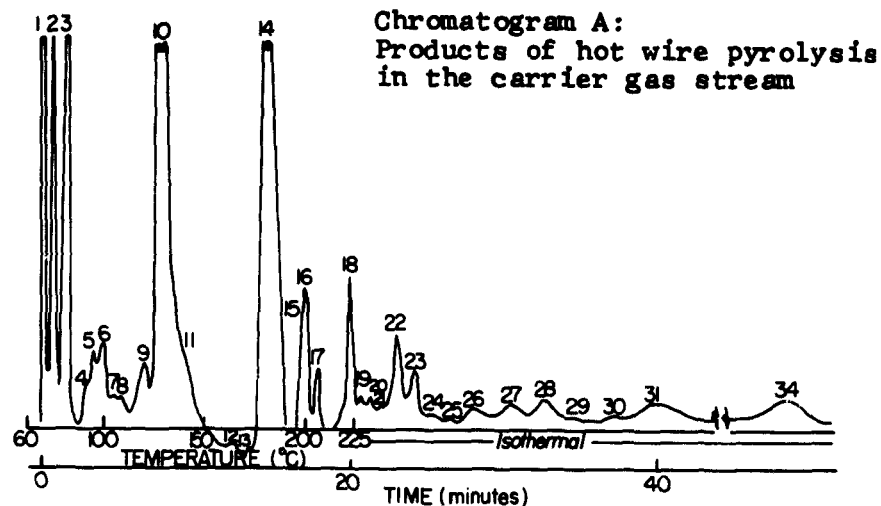


Fig. 15. Gas Chromatograms of Cellulose Pyrolysis Products (Column 14 - Carbowax 20M)

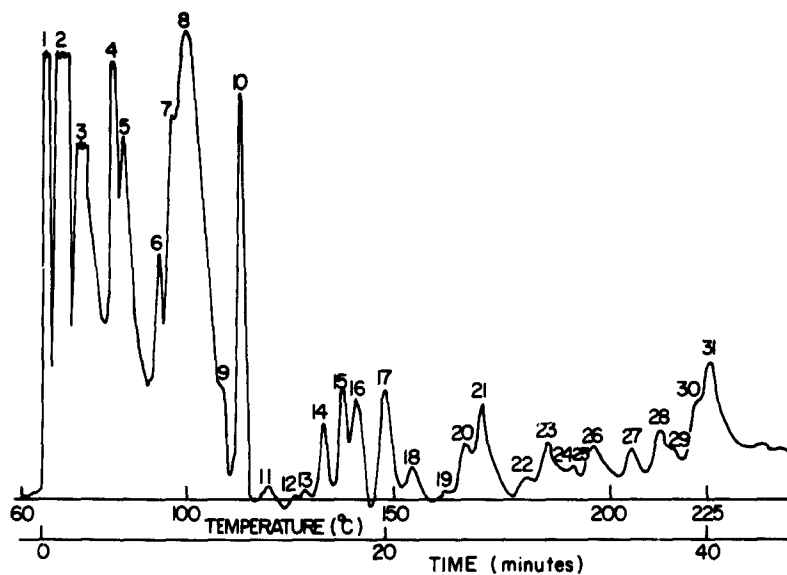


Fig. 16. Gas Chromatogram of Cellulose Products from Hot Wire Pyrolysis (Column 13 - Silicone Oil 550)

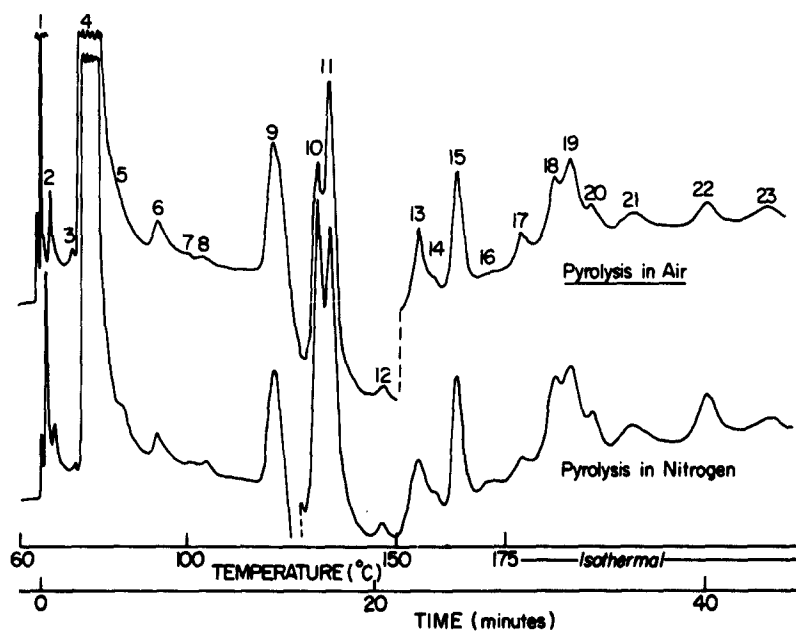


Fig. 17. Gas Chromatograms of Cellulose Pyrolysis Products (Column 9 - Octoil S)

the case of products condensed at -78°C the converse is indicated. These variations reflect the expected effect of condensation temperature as well as the difficulty in quantitatively trapping all products from conventional pyrolysis for subsequent analysis. Direct analysis of products from hot wire pyrolysis shows an intermediate distribution which could be expected to approximate the true distribution of products.

Intuitively, controlled pyrolysis in the carrier gas stream as described by Lehrle and Robb [11] and others [12,13] would seem to constitute the most realistic conditions for polymer degradation studies. Under ideal conditions a thin layer of polymer can be rapidly decomposed so that the effects of thermal gradients in the sample and of the diffusion of products are minimized. The carrier gas stream flowing past the sample removes the products from the hot reaction zone as they are formed thus reducing the opportunity for interactions between products. Further, no appreciable loss of products is possible and the analysis is not complicated by the presence of solvents frequently required to handle the condensed products obtained in conventional pyrolysis procedures.

The results of analysis with other columns are indicated by the chromatograms in Figures 16 and 17. Figure 16 is a typical chromatogram of hot wire pyrolysis products analyzed on the Silicone Oil-550 column (Column 13) with component identifications given in Table XIII. Cotton cellulose samples were pyrolyzed in air as well as in nitrogen with temperature programming to 370°C and the decomposition products, condensed in two fractions as previously described, were analyzed on the Octoil S column (Column 9) with temperature programming at $4^{\circ}\text{C}/\text{min.}$ to 175°C . The chromatograms (Figure 17) were found to be essentially identical with respect to the number, shape and occurrence of peaks. This

Table XIII

Identification of Cellulose Pyrolysis Products

Column 9 (Octoil-S)		Column 13 (Silicone Oil-550)		Column 14 (Carbowax-20M)	
Peak No.	Compound	Peak No.	Compound	Peak No.	Compound
1	Fixed gases	1	Fixed gases	1	Fixed gases
2	Formaldehyde	2	Water/Formaldehyde	2	Formaldehyde
3	Acetaldehyde	3	Acetaldehyde	3	Acetaldehyde
4	Water	4	Propionaldehyde/ Acrolein/Acetone	4	Propionaldehyde
5	Propionaldehyde/ Acrolein/Acetone	6	Acetic acid	5	Acetone
6	Carbonyl containing	7	Methyl Ethyl Ketone/ n-Butyraldehyde	6	Acrolein
7	Methyl Ethyl Ketone/ n-Butyraldehyde	8	Glyoxal	7	n-Butyraldehyde/Methanol
9	Glyoxal	10	Unidentified carbonyl compound	8	Methyl Ethyl Ketone
10	Formic acid	17	Furfural	10	Water
11	Acetic acid	31	5-Hydroxymethyl Furfural	14	Glyoxal
13	Carbonyl containing			15	Acetic acid
15	Furfural			16	Formic acid/Furfural
23	Lactic acid			18	Carbonyl containing
				30	Lactic acid
				34	5-Hydroxymethyl Furfural

result indicates that the same products are formed irrespective of whether the pyrolytic degradation of cellulose is carried out in an oxidizing or a nonoxidizing atmosphere. Consequently, the degradation mechanism must be nonoxidative in character. Peak identifications for these chromatograms are also given in Table XIV.

It has been indicated that the identification of the components of a heterofunctional mixture separated by gas chromatography by retention data from a single column is open to question [10]. Therefore, data have been obtained on three columns differing in liquid phase and in phase polarity. The retention volume data obtained on unknown components are compared in Table XIV with similar data on suspected, known compounds. According to Walsh and Merritt [10] data on qualitative functional group analysis of gas chromatographic effluents when combined with retention volume data can provide positive identification of the components in a mixture. Accordingly, the effluent gases for certain of the unknown peaks were condensed as they come off the columns and the condensates analyzed for functional groups by qualitative reagents.

Levoglucosan, a major volatile product from cellulose pyrolysis, was not found in any of the chromatograms obtained on the columns described earlier. The melting point of levoglucosan is 180°C [19], which indicates a boiling point well above the maximum operating temperature, 225°C, of any of the columns involved. Apparently levoglucosan was not eluted from the column due to relatively low volatility. However, preliminary results on a column containing 3% by weight of polyethylene glycol (Carbowax 20M) as the liquid phase instead of the usual 10% have indicated a product that has been tentatively identified as levoglucosan. Chromatograms on the pyrolysis products of cellulose and starch obtained on this column with temperature programming to 245°C showed a very high-boiling component. The effluent gas yielded a crystalline product soluble in water, relatively insoluble in acetone, and melting at 179°C.

Table XIV

Comparison of Retention Volume Data* of Known
Compounds and Unknown Components

Compound	Column 9			Column 13			Column 14		
	Known	Unkn.	Peak No.	Known	Unkn.	Peak No.	Known	Unkn.	Peak No.
CO,CO ₂	12	12	1	6	6	1	12	12	1
Formaldehyde	48	48	2	21	24	2	42	42	2
Acetaldehyde	132	132	3	51	57	3	96	84	3
Propionaldehyde	294	282	5	120	114	4	192	174	4
Acetone	294	282	5	120	114	4	222	198	5
Acrolein	294	282	5	120	114	4	240	252	6
Methyl Ethyl Ketone	546	540	7	222	225	7	342	312	8
n-Butyraldehyde	546	540	7	222	225	7	306	286	7
Water	168	198	4	78	75	2	463	462	10
Glyoxal	856	840	9	282	261	8	912	858	14
Formic acid	990	1008	10	—	—	—	1056	1050	16
Acetic acid	1032	1062	11	204	207	6	978	978	15
Lactic acid	2652	2628	23	—	—	—	—	—	—
Furfural	1512	1512	15	597	609	17	1056	1050	16
5-Hydroxymethyl Furfural				1230	1194	31	3360	3360	34

* Uncorrected; V_R = Retention Volume.

In Table XV the results on component identification are summarized. There is some evidence to indicate that isobutyraldehyde, valeraldehyde, ethylene glycol, methyl propyl ketone and glycolic acid may be among the products but more data are required to establish any of these as pyrolytic degradation products of cellulose.

Table XV
Pyrolytic Degradation Products of Cellulose
Indicated by Gas-Liquid Chromatography

Compound	Columns Indicating ^a	Identification ^b
Volatile gases-CO,CO ₂	9,13,14	P
Formaldehyde	9,13,14	P
Acetaldehyde	9,13,14	P
Acrolein	9,13,14	P
Propionaldehyde	9,13,14	P
n-Butyraldehyde	9,13,14	T
Glyoxal	9,13,14	P
Furfural	9,13,14	P
5-Hydroxymethyl Furfural	13,14	P
Acetone	9,13,14	P
Methyl Ethyl Ketone	9,13,14	P
Methanol	9,14	T
Formic acid	9,14	T
Acetic acid	9,13,14	P
Lactic acid	13,14	T
Water	9,13,14	P
Levogluconan	3% Carbowax-20M	T

a 9-Octoil S, 13-Silicone Oil, 14-Carbowax-20M

b P-positive identification, T-tentative identification.

3. Cotton-Butyl Rubber System

The results of pyrolysis of polyisobutene have shown [20] that this polymer decomposes mainly into the monomer isobutene, dimer, trimer, and small fragments of the polymer. A normal pyrolysis in an air atmosphere of the butyl rubber sample (Enjay 365) resulted in a liquid pyrolyzate that did not need solvent to remove it from the collection traps. This pyrolyzate was run on Column No. 2 and the chromatogram obtained indicated at least thirty-six peaks of wide boiling point distribution.

A comparison of chromatographic curves were made of the pyrolysis products from butyl rubber, and cotton coated with butyl rubber (50% cotton-50% butyl) to test the feasibility of detecting chemical interactions by means of gas chromatography. The samples were all pyrolyzed in air at approximately 400°C and the pyrolysis products (Figure 18) were analyzed under similar conditions. Column 2 proved satisfactory for the pyrolysis products of cotton and butyl rubber. The conditions were helium flow 28 cc/min., injection port temperature 250°C, block temperature 250°C. The experiment was started at 50°C and programmed at a rate of 4°C/min. to 175°C and held at this temperature to the end of the run. A comparison of peaks from the chromatograms of cotton and butyl rubber along with the peaks resulting from the pyrolysis of the coated sample indicates that some of the major peaks are similar but also clearly shows major peaks which represent new products not present in either component. This confirms the earlier conclusion [1] of chemical interaction.

4. Nylon

The variety of products produced in the thermal degradation of nylon polymers indicates a random breakdown of the polymer [21]. Ammonia, carbon dioxide, ammonium

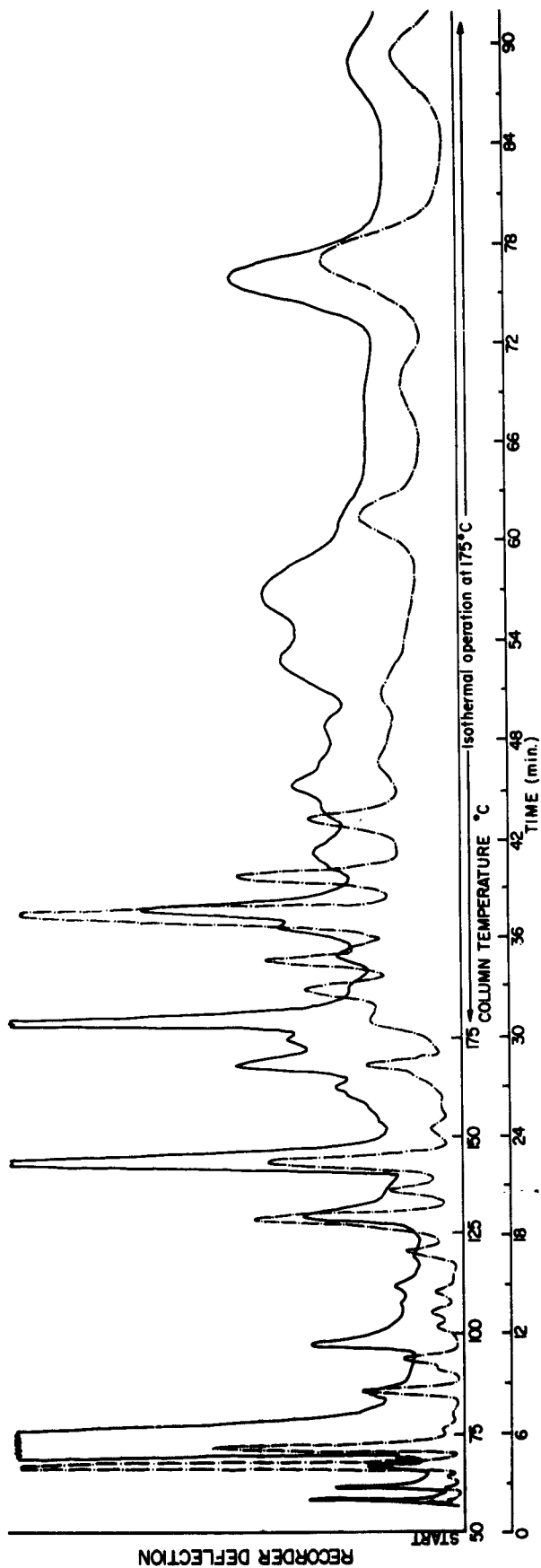


Fig. 18. Gas Chromatograms of Cotton-Butyl Rubber (—) and Butyl Rubber (---) Pyrolysis Products (Pyrolysis in Air)

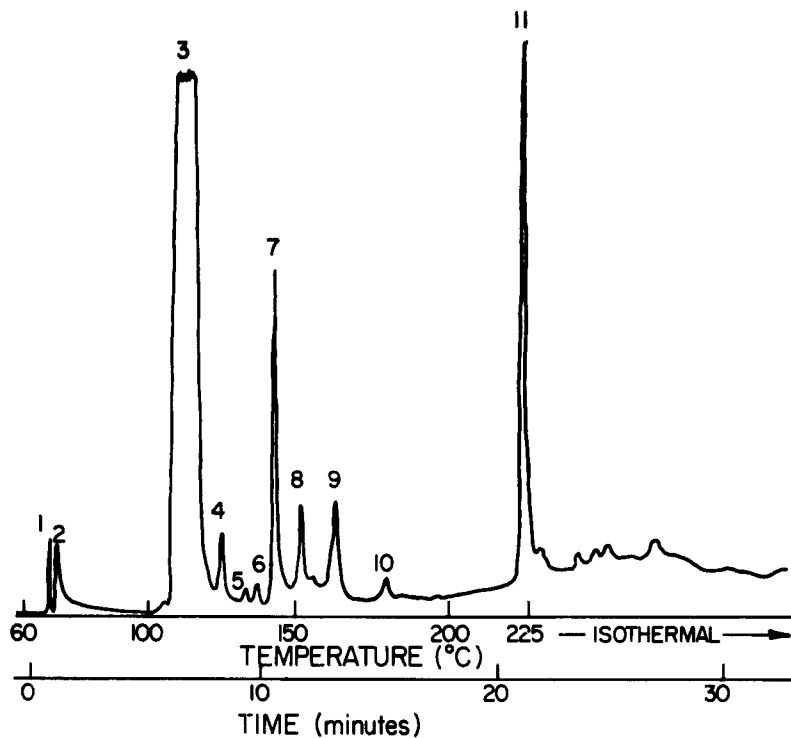


Fig. 19. Gas Chromatogram of Nylon Pyrolysis Products (Pyrolysis in Nitrogen; Column 8)

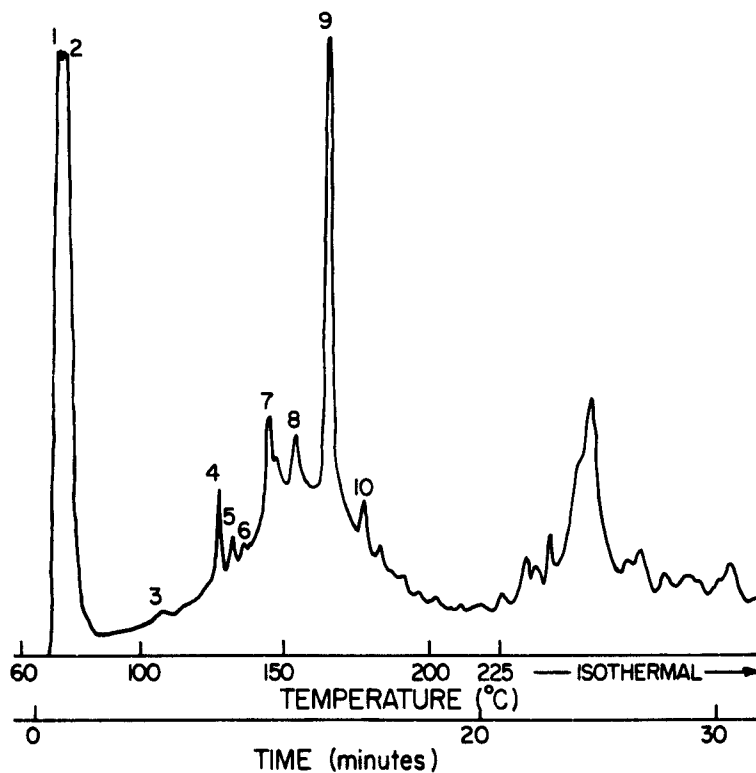


Fig. 20. Gas Chromatogram of Nylon Products from Hot Wire Pyrolysis (Column 8)

carbonate and butene have been identified in the decomposition products of nylon 66 [22]. The results of chemical separation and identification of the degradation products of a model compound, indicated that the nylon 66 decomposition products contained n-amines, and substituted cyclopentanone type compounds [23,24]. There have also been indications of cyclopentanone, alkyl amines, the possibility of hexamethylene diamine adipic acid salt, and of a dimer of adipic acid salt [25]. Pyrolysis data of nylon pyrolyzed in an air and in a nitrogen atmosphere in these laboratories [1] indicated the presence of carbonyl compounds, ammonia, carbon dioxide, primary amines, and water. Straus and Wall [21,25], investigated the decomposition of nylon mixtures by experiments on the rate of volatilization. They concluded that the decomposition is a thermal free-radical decomposition complicated by the residual polymerization catalysts and water strongly bonded to the peptide links. They also concluded that the cyclopentanone found in the nylon pyrolyzate is an initial product of the decomposition of the polymer chain and is produced by a free radical mechanism.

Four columns were used in separating the products from the decomposition of nylon in air and in nitrogen. The four columns tested were column 4, column 2, column 7, and column 6. The conditions for the series were kept the same from column to column and included a helium flow of 60 cc/min. a block temperature of 280°C and an injection port temperature of 275°C with programming at 60°C at 7.8°C/min. to the column temperature limit. Figure 19 shows a typical chromatogram of nylon pyrolyzate on Column 8 indicating ammonia and amines coming off early, then water, cyclopentanone and other cyclic compounds, hexamethylene diamine plus many unidentified high boiling basic compounds. Samples (Figure 20) were pyrolyzed in the gas stream of the chromatograph with the hot wire apparatus previously described.

Hot wire pyrolysis on column 9 indicated two early gas peaks, probably carbon dioxide and/or carbon dioxide and methane, a strong ammonia peak, and a strong water peak plus six medium peaks representing low molecular weight hydrocarbons.

Table XVI shows a comparison of corrected retention volume data of nylon decomposition products with the peak numbers corresponding to those in Figures 19 and 20.

Table XVI
Comparison of Retention Volume Data* of
Known and Unknown Compounds on Column 8
 V_R Data of Unknowns

Compounds	Peak No.	V_R Known	Nitrogen Pyrolysis	Air Pyr.	Hot Wire Pyrolysis
CO and CO ₂	1	12	a	a	12
Ammonia	2	30	30	36	24
Ethanol	3	276	276	282	288
b	4	—	372	378	438
b	5	—	438	438	474
b	6	—	468	468	504
Water	7	498			
Hexylamine		504	510	510	564
b	8	—	576	576	636
Cyclopentanone	9	672	666	666	720
b	10	—	792	786	816
Hexamethylene diamine	11	1158	1152	1170	1176

* V_R = Retention Volume
a = No peak
b = No known compound.

Peak No. 1 is a large peak in the hot wire pyrolysis and represents volatile gases such as CO and CO₂. These gases would not be trapped as well in the regular pyrolysis experiments unless they were adsorbed in the pyrolyzate so that the liquid pyrolyzates do not show any peak in this area. Peak No. 2 is a major decomposition product and the measurements and odor indicate that this peak is ammonia.

The area between peak 2 and peak 3 shows a number of small peaks. The order and retention volumes of these peaks indicate that they are low molecular weight amines up to four carbon atoms. Peak No. 3 is the solvent (ethanol) used to extract the pyrolyzate from the pyrolysis traps but the pyrolysis of nylon in the gas stream shows a small peak at this retention volume like that of the solvent used for pyrolyzates. Peak No. 9 has the odor of an aromatic hydrocarbon and the retention volume data indicate cyclopentanone. Peak No. 11, identified as hexamethylene diamine, is small for hot wire pyrolysis and pyrolysis in air, but large in the case of pyrolysis in a nitrogen atmosphere. Thus, a number of nylon decomposition products are confirmed, such as carbon dioxide, carbon monoxide, ammonia, cyclopentanone, hexamethylene diamine, amines, water, high boiling basic compounds, and low molecular weight hydrocarbons.

The chromatograms for nylon 66 pyrolyzed in an air and nitrogen atmosphere indicate that ammonia and water may occur in different amounts depending on the pyrolysis atmosphere and the occurrence of hexamethylene diamine appears to be atmosphere dependent. The fast, hot wire pyrolysis experiments do not indicate that this method is altering the major decomposition products. The data showing a large cyclopentanone peak in the hot wire experiments supports the conclusion [21] that cyclopentanone may be a primary product from thermal decomposition of nylon

SUMMARY AND CONCLUSIONS

Due to the exigencies of the situation, this work is characterized by a dichotomy that precludes an integrated treatment. On the one hand there is the central theme of fabric-coating interactions, whereas on the other the investigation and development of novel analytical methods constitutes an almost separate study. In addition, this latter phase of the program gave rise to a complete study of the pyrolysis of cellulose via gas-liquid chromatography.

The effect of coatings in the thermal behavior of coated textiles may involve (1) the coating acting as a physical barrier, (2) the absorption of melt in synthetic systems, and (3) chemical interaction of the coating with the textile substrate. Certainly, chemical interaction must ultimately occur when massive thermal decomposition of both components occurs. However, it is the early interactions that can greatly alter system performance. It has been shown by previous work in this program that nylon fabric structure begins to be seriously affected around 230°C by softening and melting processes. With any of the coatings studied the overall thermal performance in coated nylon systems is better than that of uncoated nylon. In the case of cotton, a nonfusible fiber, the same is not true.

The results on butyl rubber-coated fabrics show that butyl rubber enters into a chemical interaction with both the nylon and cotton fabrics, but only at temperatures above 300°C. The interaction mechanism is nonoxidative in both cases and is believed to involve the major decompositions of the coating and substrates. Thus, the early interaction of low molecular weight degradation products results in new reactions and accelerated decomposition rates.

The interaction of Neoprene W with the two substrates is also chemical, but quite different in mechanism, and occurs at much lower temperatures (below 200°C for nylon and around 225°C for cotton). The thermal stability of the coated cotton is substantially reduced from that of uncoated cotton and in the case of coated nylon serious fabric distortion occurs by 200°C and weight losses begin around 75°C. The interaction mechanism, which is also nonoxidative, is believed to involve acid attack upon the textile substrates due to the gradual formation of small amounts of gaseous HCl from the degradation of the Neoprene coating.

In the case of Hypalon little significant interaction is indicated with nylon fabric in either air or nitrogen atmosphere. Thus, the coating appears to act essentially as a protective barrier preserving the system structure appreciably beyond the deterioration point of uncoated nylon. However, in the case of cotton significant chemical interactions are indicated in both air and nitrogen atmospheres. The interaction initiates around 220°C, is indicated to be nonoxidative in character, and the mechanism may involve the action on cotton of early degradation products of the sulfonic acid type from Hypalon.

The work on dynamic thermal methods has shown that both TGA and DTA are extremely useful for characterizing the thermal behavior of textiles and other polymeric materials. TGA has provided quantitative data on (1) thermal stability (2) thermal degradation rates (3) relative activation energies and (4) estimated orders of reaction. A high degree of correlation has been shown between TGA and DTA results. It has also been shown that gas chromatography is applicable to the study of thermal degradation processes in polymers and a special technique was developed to facilitate such investigation.

Gas chromatography indicates a greater number of products from the thermal decomposition of cellulose than has previously been reported. At least 37 different compounds, consisting largely of levoglucosan and water plus a variety of low molecular weight aldehydes, ketones and organic acids were found. Many of these products appear to be present only in trace amounts and have not yet been identified.

The remarkable identity of the gas chromatograms of the volatile products arising from the pyrolytic decomposition of cellulose in different atmospheres and at different rates suggest a common degradation mechanism that is non-oxidative and essentially thermal in nature. This finding is entirely consonant with, and offers strong support to, the mechanism for the pyrolytic decomposition of cellulose involving cellulose depolymerization at elevated temperatures by scission of the 1,4 glycosidic linkages followed by intramolecular rearrangement of the monomer units to levoglucosan.

References Cited

1. Schwenker, R. F. Jr. and Beck, L. R. Jr., Summary Report I, Contract No. N140(138)67979B, Textile Research Institute, 30 November 1961.
2. Gordon, S. and Campbell, C., Anal. Chem. 32, 271 (1960).
3. Hooley, J. C., Can. J. Chem. 35, 374 (1957).
4. Schwenker, R. F. Jr., Beck, L. R. Jr., and Kauzmann, W., Final Report, Contract No. N140(132)57442B, 15 February 1960.
5. Newkirk, A. E., Anal. Chem. 32, 1566(1960).
6. Freeman, E. S. and Carroll, B., J. Phys. Chem. 62, 394 (1958).
7. Anderson, D. A. and Freeman, E. S., J. Applied Poly. Sci. 1, 192 (1959).
8. Roff, W. J., Fibres, Plastics and Rubbers, Butterworths Scientific Pub., London, 1956.
9. Sutherland, G. and Drechsel, P. D., Anal. Symp. on Thermal Methods, Abstracts of the 137th A.C.S. Meeting, Cleveland, Ohio, April 1960.
10. Walsh, J. T. and Merritt, C., Anal. Chem. 32, 1378 (1960).
11. Lehrle, R. S. and Robb, J. C., Nature 183, 1671 (1959).
12. Strassburger, J., Brauer, G. M., Tryon, M. and Forziati, A. F., Anal. Chem. 32, 454 (1960).
13. Barlow, A., Lehrle, R. S. and Robb, J. C., Polymer 2, 27 (1961).
14. Madorsky, S. L., Hart, V. E., and Strauss, S., J. Res. NBS 56, 343 (1956).
15. Schwenker, R. F. Jr. and Pacsu, E., Chem. and Eng. Data Ser. 2, 83 (1957).
16. Madorsky, S. L., Hart, V. E. and Straus, S., J. Res. NBS 60, 343 (1958).
17. Martin, S. B. and Ramstad, R. W., Anal. Chem. 33, 982 (1961).

18. Greenwood, C. T., Knox, J. H. and Milne, E., Chem. and Ind., Nov. 18, 1961.
19. Montgomery, E. M., Richtmeyer, N. K. and Hudson, C. S., J. Am. Chem. Soc. 65, 3 (1943).
20. Madorsky, S. L., Straus, S., Thompson, D. and Williamson, L., J. Res. NBS 42, 499 (1949).
21. Straus, S. and Wall, L. A., J. Res. NBS 63A, 269 (1959).
22. Hasselstrom, T., Coles, H. W., Bolmer, C. E., Hannigan, M., Kieler, M. M. and Brown, R. J., Textile Research J. 22, 742 (1952).
23. Goodman, I., J. Polymer Sci. 13, 175 (1954).
24. Ibid, 17, 587 (1955).
25. Straus, S. and Wall, L. A., J. Res. NBS 60, 39 (1958).