STUDIES AND EXPERIMENTAL INVESTIGATIONS IN CONNECTION WITH CHEMICAL BONDING IN RESIN-TREATED CELLULOSE

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ABSTRACT

The nature of the interactions between methylolmelamine resins and cotton has been investigated. A new chemical analytical method for the elucidation of the chemical structure of resin-treated cotton has been developed. Data are presented for the degree of substitution of cellulose by trimethylolmelamine, and for the distribution of these substituents between the various hydroxyl groups of the anhydroglucose unit under various curing conditions. It has been shown by an investigation of weathered resin-treated cotton samples that periodate oxidation can be used as a sensitive index of the structural changes occurring during resin degradation. Microscopy and solubility studies in the cellulose solvent cadoxen, in connection with Smith degradations, have been found to provide a method for assessing any cellulose chemical treatment for uniformity and effectiveness of covalent cross-linking. Preliminary results are presented on the distribution of resin substituents along the cellulose chain, and considerable nonuniformity of resin substitution is indicated.

TABLE OF CONTENTS

CHAPTER I. INTRODUCTION

The resistance of cellulosic materials to microbiological degradation can be greatly enhanced by treatment of the fabrics with methylolmelamine resins, as was shown by Kaplan and co-workers [1,2] who studied the rot and weather resistance of methylolmelamine-treated cotton. Two methods of application of methylolmelamine resins as a finishing agent for cotton have been reported in this connection. The "dry cure" of Berard and co-workers [3] involves a short, high-temperature treatment of cotton padded with the formic acid colloid of the methylolmelamine, whereas Ruperti [4] used a "wet cure" process in which the curing is obtained at room temperature over prolonged periods of time or by the application of steam.

Although considerable research was conducted in the general field of the application of resins to cellulosic materials in connection with attempts to improve wrinkle recovery, flame resistance, and water repellency, little information is available about the chemical structure of the reaction products resulting from a resin treatment of cellulose. In this study, chemical methods have been developed which permit the elucidation of products arising from the direct chemical interaction between the resin and cellulose. The objectives involved: 1) determination of the incidence of covalent chemical linkages between the resin and cellulose; 2) the location, distribution, and nature of any covalent linkages; and 3) the establishment of analytical procedures for the quantitative assay of the degree of covalent resin-cellulose bonding.

CHAPTER II. CHARACTERIZATION OF RESIN-TREATED COTTON FABRICS

A number of resin-treated cotton duck fabrics, representing the various curing methods, have been used in these investigations. Most of these samples were supplied by the Fungicides and Germicides Laboratory, Pioneering Research Division, QM Research & Engineering Command. A series of special melamine resin samples with complete analytical data have been obtained from the American Cyanamid Company, and samples of commercial melamine resins have also been obtained from the CIBA Corporation. In certain special cases the fabrics were treated and cured at TRI. The characterization of these resin-treated samples by a variety of test methods will be described and discussed in this chapter.

The samples were analyzed for nitrogen by the Kjeldahl method and for formaldehyde by the chromatropic acid procedure [5]. Moisture regain was determined, and fabric wrinkle recovery was measured using the Monsanto test method [6]. A description of the samples and the characterization data are given in Table I.

Table I. Data on QM Melamine Resin-Treated Samples

Sample	Cure	Nitrogen (%)	HCHO (%)	Moisture regain (%)	Wrinkle Recovery W + F	
					wet	dry
QM-1 Untreated cotton duck	none	0	0	7.06	125	134
QM-2 "Statuff" resin-treated duck	wet	5.10	2.41	7.33	153	162
QM-3 "Arigal" C resin-treated duck	wet	4.60	0.52	8.25	192	151
QM-4 Formic acid colloid of MMA-treated duck	dry	7.30	0.81	6.85	237	234

It has been established that cross-linking and not resin deposition is primarily responsible for improved wrinkle recovery in modified cotton fabrics [7,8,9]. Thus, the wrinkle recovery data indicate that there is appreciable cross-linking in the "dry cure" sample, which is further supported by the decreased moisture content. The significant increase in wet wrinkle recovery and moisture regain for the Arigal C sample suggests that some wet-state cross-linking has occurred. It has been observed that cross-linking cotton fibers in the swollen state causes moisture regain to increase by fixing the structure in a more open configuration [7,8]. In the case of the sample wet-cured with Statuff resin, there is no indication of significant cross-link formation. The reason for the abnormally high formaldehyde content obtained from the Statuff resin-treated sample is not presently understood.

1. Resin Treatment of Cotton Print Cloth

A series of 80 x 80 cotton print cloth (bleached, desized, 3.5 oz/yd^2) samples treated with dimethylolmelamine and trimethylolmelamine were obtained by the "dry-cure" process of Berard et al. [3], and the "wet-cure" process of Ruperti [4], according to the following experimental procedures:

A. Dry-Cure Process

The methylolmelamine resin used was Aerotex Resin UM (American Cyanamid Company product) which is nominally a dimethylolmelamine. The aqueous treating solution contained 20% formic acid and 10% of the resin. Fabric samples were weighed, soaked in the treating solution, and passed through one set of squeeze rolls to give 100% pick-up on the weight of the fabric. The padded fabric samples were then placed on pin frames in a circulating air oven at 80°C for 4 minutes followed by curing in another circulating air oven at 140°C for 4 minutes. The products were then washed in hot water for 15 minutes and dried at room temperature.

B. Wet-Cure Process

The resin used was commercial Arigal C (CIBA product) which is nominally trimethylolmelamine. The procedures followed were similar to those described in CIBA Circular No. 2198 for Arigal C. The aqueous treating solution contained 24.7% resin and 1.2% of 30% hydrogen peroxide. Fabric samples were padded to 100% pick-up and cured in the wet state at room temperature by a batch method by wrapping the samples in lightweight plastic sheeting and storing them for four days. The samples were then washed in dilute ammonium hydroxide and dried at room temperature. The results of the treatments are given in Table II

Table II. Effects of Methylolmelamine Resin Treatment on 80 x 80 Cotton Print Cloth

Sample	Pad Bath Time (min)	Nitrogen (%)	Warp Wrinkle Rec. (deg) wet	dry	Warp Breaking str. (lbs)
Untreated	0	0	67	63	60.0
		Formic Acid Colloid-Dry-Cure Process			
FA-1a	15	5.16	140	145	41.5
FA-2a		5.36	137	149	40.0
FA-3a		5.04	136	141	38.8
FA-1b	30	6.13	132	134	43.4
FA-2b		4.86	140	144	39.4
FA-3b		5.50	130	143	39.1
		Wet-Cure Process			
A-1	10	5.38	93	94	-

C. Application of Pure Resin by Dry-cure

The methylolmelamines and other resins generally available tend to be chemically inhomogeneous, resulting in some ambiguities as to the exact chemical structures of resin-treated cotton products. A group of specially prepared resins of high chemical purity and unambiguous structure have been generously made available for this work by the American Cyanamid Co. The conditions of Berard and co-workers [3] for the preparation of formic acid colloid were not satisfactory for use with the pure trimethylolmelamine since that material is only sparingly soluble in 20% aqueous formic acid. In order to prepare suitable samples for evaluation, it was necessary that the resin be uniformly dispersed in a formic acid-water padding bath and that the resin be at such a concentration level that a 100% wet pick-up would give a final product containing at least 10% add-on. Preliminary experiments showed that these conditions could be met in the following way:

A 15.5% "solution" with respect to the TMM was prepared by adding 67 ml of formic acid to 33 g of TMM with stirring. Water (100 cc) was added to the resulting slurry and stirring was continued for one hour after which time a uniform, translucent mixture resulted. Five-gram pieces of scoured (2% caustic) cotton sheeting (80x80) were immersed in the TMM bath for 5 minutes and were put through a wringer set at a predetermined tension to give 100% wet pick-up. The samples were placed on pin frames and were dried at 107°C for 4 minutes and cured at 170°C for 4 minutes. After rinsing in hot running water for 10 minutes, the samples were allowed to dry under the standard conditions. Other cotton sheeting samples were prepared using exactly the same conditions for the sake of comparison but using, instead, the dimethylolmelamine (DMM). Some properties of the fabrics resulting from this application of TMM and DMM resins are shown in Table III.

Table III. Properties of TMM and DMM Dry-Cured Cotton Sheeting Samples

Resin	Weight Inc. (%)	Nitrogen (%)	Resin* Add-on (%)	Wrinkle Recovery (W+F deg) wet	dry
DMM	16.3	7.06	12.7	280	278
TMM	14.1	5.00	11.7	294	287

*Based on nitrogen content.

The high levels of wrinkle recovery obtained indicate that appreciable bonding in the cotton cellulose, probably involving covalent cross-linking, has occurred with the application of both the tri- and dimethylolmelamine.

2. Characterization by DTA

The fabric samples obtained from the U. S. Army Natick Laboratories (QM samples) were investigated by differential thermal analysis (DTA) in an effort to gain some insight into the nature of the chemical interaction of cellulose with the various resins. In this method thermally detectable transitions or reactions that a textile or other polymer material undergoes, as it is heated at a constant rate through the temperature range of interest, can be determined by measuring via thermocouples the differential temperature, ΔT, between the sample and an inert reference material [10,11]. It has been shown that the DTA curve is unique for a given composition of matter and that it may be used for positive identification and sample differentiation [10]. Samples in the range of 5 to 40 mg were run in air and in nitrogen atmosphere to obtain curves of the type shown in Figure 1.

The DTA curve of untreated cotton shows an early endothermic process which is the desorption of water, and a strong endothermic process with a peak at 381°C which has been attributed to the depolymerization of cellulose via thermal scission of the 1,4 links between the anhydroglucose units [12]. The thermogram for the

Statuff resin-treated cotton is almost identical with that of the untreated except for a small sharp reaction around 430°C, thus indicating no chemical modification of the cellulose. However, in the case of the Arigal C wet cure sample a small new exothermic peak appears at 320°C, and the size of the cellulose decomposition endotherm (peak at 375°C) is somewhat reduced. In the case of the dry-cure resin-treated sample, a thermogram with similar features, but considerably changed in size, is observed. There is a well defined exothermic peak at 314°C and the cellulose endotherm with a peak at 375°C has been drastically reduced. It may be suggested that, since the same sample size was used and the thermograms were found to be reproducible, these changes are due to chemical modification of the cellulose. Thus, as the cellulose hydroxyl groups are bonded, the size of the characteristic decomposition endotherm would be expected to decrease due to changes in the mode of thermal degradation. This has been observed in the case of other chemically modified celluloses. Therefore the Statuff resin-treated sample shows no alteration of the cellulose degradation pattern, indicating no chemical bonding, and the sharp peak at ca 430°C could be the decomposition of unbonded resin. The Arigal C resin-treated sample shows some chemical modification, whereas the acid colloid resin-treated sample shows the greatest change. These results are consistent with the data obtained on wrinkle recovery and moisture regain.

3. Gas Stream Pyrolysis

Samples of untreated and resin-treated cotton duck (QM samples) were pyrolyzed in the carrier gas stream of a gas chromatograph (F & M 500 High Temperature Programmed instrument equipped with thermal conductivity detector) and the decomposition products separated on the two columns as described below.

	Liquid Phase	Liquid Phase, %	Solid Support	Column Length
1. Column #18	Carbowax 20 M	3	Haloport F	12 ft.
2. Column #16	Silicone oil 550	10	Haloport F	12 ft.

Ten-milligram samples of fabric were placed in a loop of nichrome wire and positioned inside the injection port of the chromatograph. The samples were pyrolyzed by passing an electric current through the nichrome wire for 20 seconds. The carrier gas stream carried the decomposition products directly to the column for separation. The temperature of pyrolysis was measured by a thermocouple touching the nichrome wire and for these tests the temperature of pyrolysis was 450°C. The char was recovered from the nichrome wire after the completion of each run.

The chromatograms obtained using column 16 are reproduced in Figure 2. The chromatograms indicate qualitative similarity between samples, but a quantitative difference for some of the decomposition products. The lack of new peaks between untreated cellulose and resin-treated cellulose could mean that all the volatile decomposition products from the resin are of low molecular weight such as NH_3 and CH_2O which would come off the column in the first peak and are masked by the main component of this peak, which is water. The char residues of the pyrolyzed samples indicate that less material is being volatilized in the case of the resin-treated samples.

Each peak represents one or more compounds and the area under the peaks is directly related to the amount of the compound in the sample. Thus, the last peak in the chromatogram is an example of a compound that shows definite quantitative differences between samples. This peak has been identified as 1,6-anhydro-β-D-glucopyranoside (levoglucosan) which is formed during the thermal decomposition of cellulose [13]. The chromatograms indicate that on pyrolysis the Statuff resin-treated sample yields the largest amount. This means that more levoglucosan is volatilized during the pyrolysis of the resin-treated samples than in the case of cellulose alone. Such information might be used to indicate the process used and/or the amount of cross-linking in a sample.

It could also lead to information on the position of the cross link through considerations of structure that could give rise to the noted changes in the amounts of the decomposition products.

4. Infrared Spectra

It has been indicated that the infrared spectra (IR) of cotton cellulose and cellulose derivatives can provide information as to the nature and position of modifying substituents and, in many cases, the extent of chemical modification may be quantitatively estimated [14]. Therefore the infrared spectra of the resin-treated cotton samples have been investigated using a Perkin-Elmer Model 237 Double Beam Spectrophotometer equipped with a diffraction grating.

Using the potassium bromide (KBr) disc technique [15], spectra of untreated cotton duck and the QM resin-treated cotton duck samples have been obtained in the region between 4000 and 650 cm^{-1}. The fabrics were first finely cut and then admixed with spectral grade KBr in the proportion of 3 mg of sample to 597 mg of KBr, followed by milling for 4 minutes in a Spex Industries Mixer Mill to provide a sample concentration of 0.5%. Some 300 mg of this mixture was used to press out the KBr pellet for analysis.

The spectra are shown in Figure 3. O'Connor et al. [14], and Cleverly and Herrmann [16] observed that the ball milling of cellulose in the preparation of KBr pellets or Nujol mulls caused changes in the IR spectrum involving loss of definition and certain bands due to changes in crystallinity. These authors have specified Wiley milling cellulose to 20 mesh and hand mixing with KBr in a mortar to avoid such damage. However, in the present work a sharp spectrum for cotton cellulose comparable to that shown by O'Connor et al. [14], was obtained even though a high-speed vibrator-type ball mill was used in sample preparation. The untreated cellulose I spectrum (sample A) shows all characteristic bands previously reported [14,17]. The main bands observed and their assignments, based on literature data, are given in Table IV.

Table IV. Infrared Spectrum of Cotton Cellulose I

Band Maximum freq., cm^{-1}	Assignment	Literature reference
3380	OH stretching	14, 17
2890	CH stretching	14, 17
1630	adsorbed water	17
1450	OH in-plane bending	17
1365	CH bending	14, 17
1155	C-O stretching, antisym. bridge oxygen stretch.,COC	14 17
1110	Antisym. in-phase ring stretching	17
1050	C-O stretching	17
900	Antisym. out-of-phase ring stretching	17
660	OH out-of-plane bending mode	17

The spectra of the resin-treated samples (B, C and D) are significantly different from the spectrum of the untreated cotton in the region from about 1700 to 1250 cm^{-1}. Sample B shows three fairly broad and smooth bands with maxima at 1575, 1475 and 1350 cm^{-1}. Sample C shows a similar pattern except that a small fourth band is indicated around 1325 cm^{-1} and sample D also shows this same pattern. A prominent and sharp new band is observed at about 820 cm^{-1}, which is characteristic of nitrogen-containing resins. In the region from 1250 to 850 cm^{-1} the original untreated cotton cellulose spectrum is retained in detail. Thus the differences between the spectra of the resin-treated cotton samples appear to be slight and until further information is obtained no interpretation is possible. The variation in the size of the band at 820 cm^{-1} may be significant.

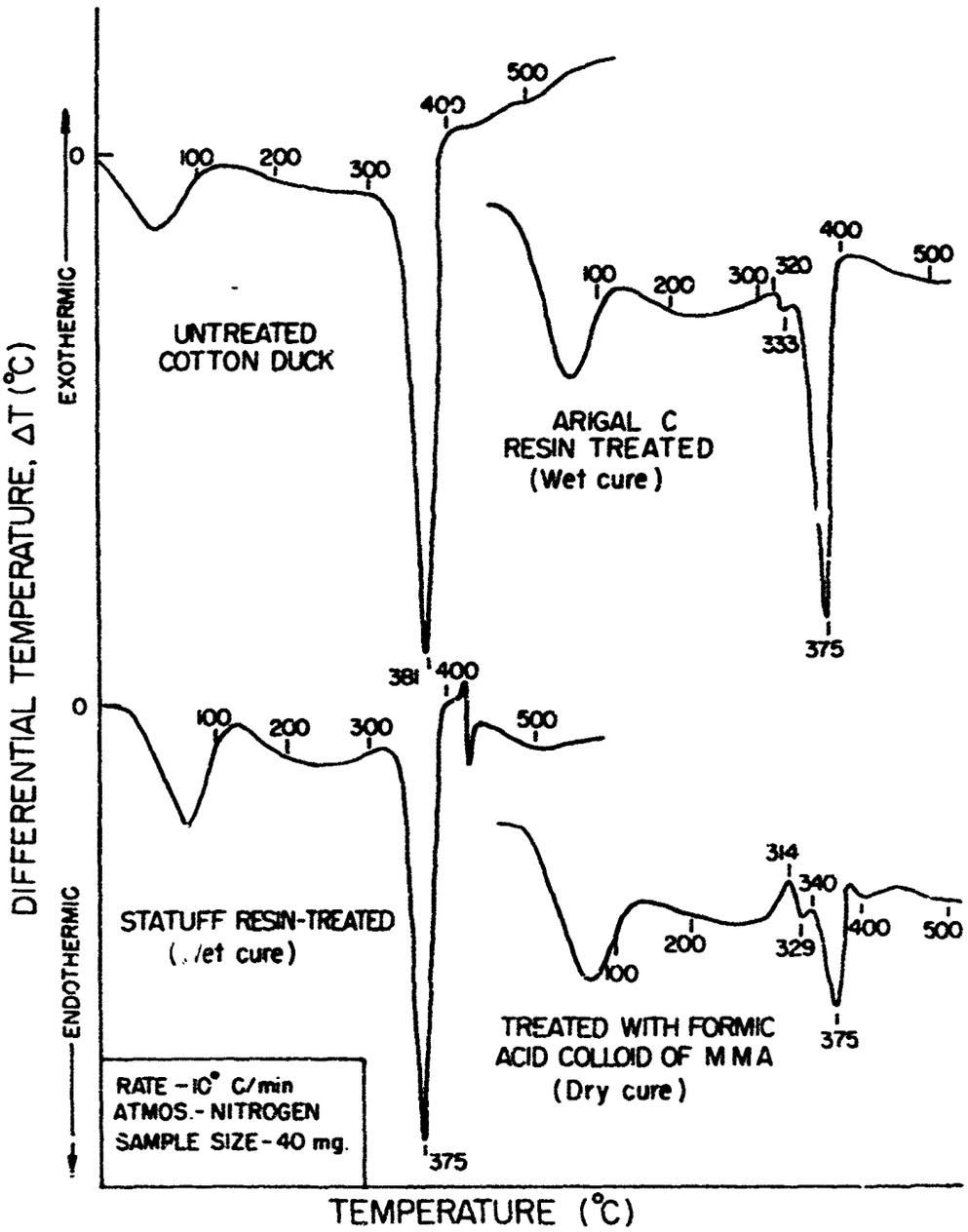


Fig. 1. DTA Curves of Untreated and Resin-Treated Cotton Duck.

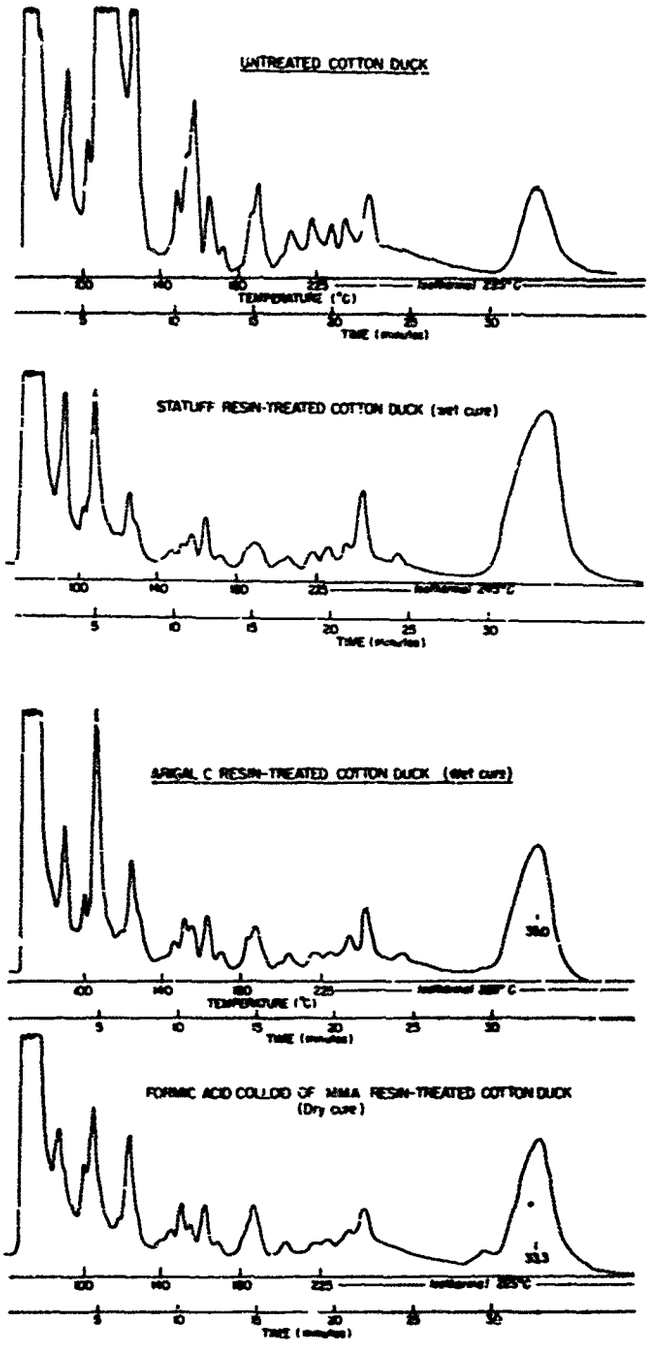


Fig. 2. Gas Chromatograms of the Gas Stream Pyrolysis Products from Untreated and Resin-Treated Cotton Cellulose. (Liquid Phase - Silicone Oil 550)

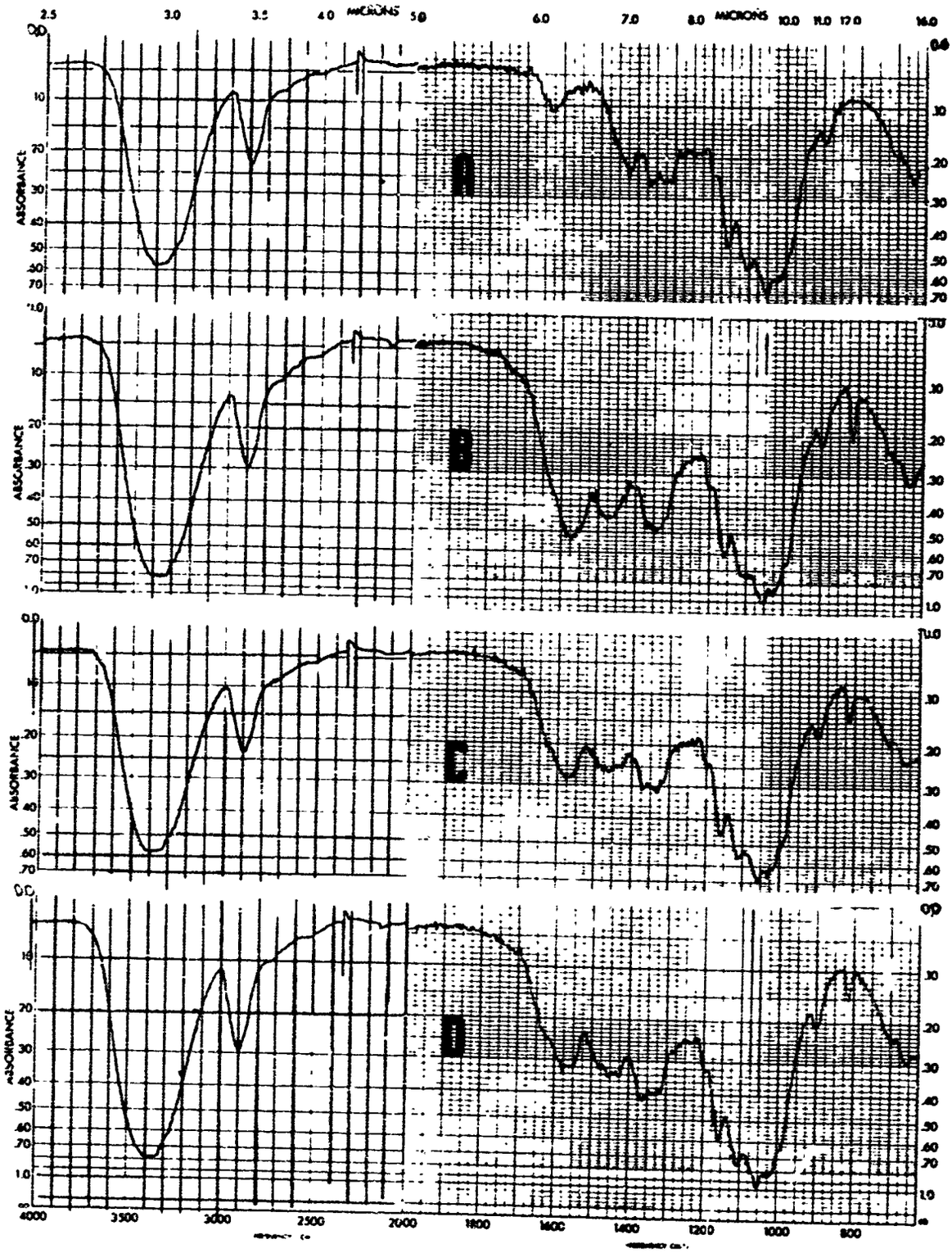


Fig. 3. Infrared Spectra of Methylol Melamine (MMA) Resin-Treated Cotton Duck Fabric (QM samples).

A. Untreated fabric.

B. Resin-treated fabric, formic acid colloid of MMA, dry cure, 7.30% nitrogen.

C. Arigal C resin-treated fabric, wet cure, 4.60% nitrogen.

D. Statuff resin-treated fabric, wet cure, 5.10% nitrogen.

CHAPTER III. DERIVATIVE FORMATION

1. Methylation of Resin-Treated Cotton

The initial approach for determining the number and position of cellulose hydroxyl groups involved in covalent bonding between methylolmelamine resins and cellulose was the direct methylation of all free hydroxyl groups. Experiments connected with attempts at exhaustive methylation of resin-treated cotton, and reasons why this approach had to be abandoned, are discussed in this section. The methylation procedures used, based on methods described by Steele and Pacsu [18], and Croon and St. John Manley [19], were as follows.

Method 1 - Sample was ground in a Wiley mill to 20 mesh, swollen in 20% sodium hydroxide under nitrogen, washed free of alkali, and suspended in a 1:1 mixture of 30% NaOH and acetone to which dimethylsulfate (DMS), $(CH_3)_2SO_4$, was added. Methylation was carried out at 60°C with stirring for 4 hours, the product was filtered and washed with hot water.

Method 2 - The sample was ground to 80 mesh, swollen in water, and after suction filtration, suspended in 45% NaOH followed by agitation for 1 hour under nitrogen. The alkali cellulose product was suction-filtered to 300% pick-up and methylated at 25°C in a 4:1 mixture of acetone and DMS for 18 hours with stirring. The product was washed in acetone followed by boiling hot water until free of alkali. Treatment and analytical data for various methylated products are given in Table V.

The blank treatment resulted in the loss of some resin as indicated by the loss of nitrogen which may be ascribed to the removal of unbound resin. Some further decrease in the nitrogen content of treated samples would be expected as a consequence of the increased molecular weight of the products due to the introduction of methyl groups. Thus, if the nitrogen content of 5.94%

Table V. Effect of Methylation on Resin-Treated Cotton Duck (QM Dry-Cure Sample - Formic Acid Colloid of Trimethylolmelamine)

Treatment	Methylation No. of times	Total time(hr)	Methoxyl* (%)	Nitrogen (%)
Untreated	-	-	-	7.46
Blank**	-	-	-	5.94
Method 1	4	16	41.4	1.01
at 60°C	7	28	-	0.18
Method 1	4	24	-	3.98
at 25°C	3	18	-	3.23
Method 2	1	18	-	4.36
at 25°C	3	54	41.6	1.62
Method 2	2	36	38.2	3.62
at 25°C;	3	54	40.3	1.63
1% HAc wash	4	72	41.8	1.01
Method 2	1	18	36.2	4.28
at 25°C;	2	36	38.2	3.74
cold 1% acid and H_2O wash	3	54	37.9	3.16

* Means of 3 to 5 determinations by the modified Zeisel method [20].
** Resin-treated sample ground to 80 mesh, treated in 45% NaOH for 1 hour, suction filtered and suspended in acetone at room temperature for 24 hours.

found for the blank represented covalently bound resin, the nitrogen content of a sample after methylation would be expected to be about 4.7% with an accompanying methoxyl content of ca 38%, i.e., the degree of substitution (DS) with respect to bonded resin would be about DS 0.35 and for methoxyl DS_{OCH_3} 2.65. However, the nitrogen losses shown after methylation were suprisingly large in many cases. Thus, where methylation was carried out at 60°C for 28 hours by Method 1 the nitrogen was almost completely lost and longer methylation times at 25°C resulted in substantial decreases in nitrogen content. The data also indicate that the degree of methylation increases as nitrogen content decreases, thus suggesting the possibility that more OH groups become available for reaction as nitrogen content decreases. This continued

loss of nitrogen on repeated methylation is difficult to reconcile with the postulate that appreciable amounts of resin monomer or dimer units are covalently bonded to the cellulose, primarily in the form of cellulose cross links since the conditions present in the methylation reaction would not be expected to bring about the rupture of cellulose ether linkages to methylolmelamine residues. Yet the high level of wrinkle recovery, shown in Chapter I to result from the dry cure treatment, as well as infrared and other chemical data developed by previous investigators [21-25], offer strong evidence that chemical reaction to include significant covalent cross-linking with the cellulose has taken place during such resin treatment. Nitrogen losses caused by alkali extraction alone are shown in Tables VI and VII for some QM samples and for the resin-treated cotton print cloth. After a loss of resin of about 30% the remainder appears to be stable to strong alkali at room temperature but under more severe conditions (60 hrs, 60°C) further resin losses of considerable magnitude occur. No explanation can be offered at this point for this surprising lack of stability of the presumably covalently bound resin to the action of strong alkali. Because of these difficulties encountered during methylation, an alternate approach was chosen which will be discussed in the following section of this chapter.

Table VI. Effect of Alkali Extraction on Nitrogen Content of QM Samples

Sample	Extractant	Time (hrs)	Temperature (°C)	Nitrogen (%)
	none	-	-	7.46
	water	60	60	6.46
FA-QM dry cure	20% NaOH	16	25	5.89
		24	25	5.80
		32	25	5.85
		48	25	5.63
		24	60	5.98
		60	60	3.22
Arigal C wet cure	none	-	-	4.60
	20% NaOH	24	25	3.12

Table VII. Effect of Alkali Treatment at 25°C on Dimethylolmelamine Resin-Treated Cotton Print Cloth*

NaOH (%)	Time (hr)	Nitrogen (%)
Untreated	-	5.16
20	16	5.46
	48	4.73
	72	4.71
40	16	4.59
	48	4.84
	72	4.72

*Formic acid colloid of aerotex resin UM-dry-cure process.

2. Periodate Oxidation of Resin-Treated Cotton

This approach is based upon the sodium periodate oxidation reaction as a means of determining the number of glycol groups in organic compounds [26]. This reaction has been applied in the case of cellulose to estimate the extent to which the adjacent secondary hydroxyl groups at C_2 and C_3 are substituted [27,28]. In periodate oxidation the C_2-C_3 bond is cleaved when both hydroxyls are unsubstituted, with the conversion of the hydroxyl groups to aldehyde groups. The oxidized products may then be characterized after sodium borohydride reduction of the aldehyde groups to alcohols [29]. If either or both the adjacent hydroxyls in an anhydroglucose unit of the cellulose chain are substituted there is no reaction with the periodate. The oxidation is followed titrimetrically to determine the amount of periodate consumed, providing quantitative data as to the number of unsubstituted glycol groupings in the sample.

The general reaction scheme involves 1) periodate oxidation of resin-treated cotton, providing data on the degree of secondary hydroxyl group involvement in covalent bonding; 2) reduction of the aldehyde groups arising from the oxidation to alcohols; 3) methylation and/or esterification of all hydroxyl groups not resin-bonded; and 4) hydrolytic degradation of samples followed

by analysis of the products by gas chromatography and other means. The periodate oxidation effectively causes the complete breaching of the highly organized structure of the cotton cellulose, thus rendering the structure so accessible that a wide range of reactions, such as methylation, can be readily carried out under milder conditions than possible in the case of unoxidized samples.

Experimental Method - Periodate oxidation: 1-g samples (5.2 millimoles anhydroglucose) of resin-treated cotton duck fabric (QM-4), as well as untreated cotton duck, were ground in the Wiley mill (20 mesh) and then treated with 100 ml of a 0.2 M buffered (pH 5.2) sodium metaperiodate solution (25 millimoles $NaIO_4$), in the dark. One ml aliquots were removed periodically and assayed as follows by the method of Müller and Friedberger [30]:

Five ml of saturated sodium bicarbonate and 5 ml of 10% potassium iodide solution were added. The solution was then kept in the dark for 15 minutes. During titration of the liberated iodine with 0.02 N sodium arsenite, 0.5 ml of starch indicator solution was added near the end point. The complete oxidation treatment required about 30 days. After the reaction was stopped, the products were recovered by filtration, washed, dried and weighed.

Borohydride Reduction of Oxidized Samples - 0.2 g of the oxidized sample was suspended in 20 ml of water and reduced with 0.2 g sodium borohydride for 6 hours at room temperature, a stream of CO_2 being introduced throughout to neutralize the sodium hydroxide formed. The solutions did not become strongly alkaline after that time and the mixtures were kept at 5°C overnight. The insoluble portions were recovered by filtration. The filtrates were acidified to pH 4.0 by addition of dilute HCl and precipitated into 540 times their volume of ethanol. The products were washed thoroughly (using water for the insoluble portions and ethanol for the soluble ones), dried, and weighed.

A secondary reaction commences in the case of the resin-treated sample, which results in a rapid exponential consumption of periodate after about 2 weeks. Since the oxidation was intended to be used as a quantitative analysis for anhydroglucose units unsubstituted in 2 and 3 positions, an independent determination of unoxidized glucose was necessary. The hexose assay method of Dische et al. [31] was found to serve this purpose.

Determination of Residual Glucose - Method [31]: QM-4 samples were oxidized for 5, 10, 15 and 20 days, reduced with borohydride as described above, and then investigated for residual glucose using the following method:

Approximately 2 mg of accurately weighed samples were weighed into pyrex test tubes of 4 ml capacity. To this was added 0.1 ml of 72% sulfuric acid and the mixture was agitated until the sample was wetted-out by the acid. It was then kept overnight at room temperature. Water (0.9 ml) was added, the tubes were sealed and placed in a boiling water bath for durations of one hour for CD and two hours for QM-4 samples. Clear solutions resulted. Treatment with 3 N sulfuric acid alone under the same condition did not effect complete solution of the QM-4 samples and the glucose contents found were lower than with the above procedure.

The tubes were cooled to room temperature and opened. Portions of the hydrolyzates were assayed directly for glucose. An aliquot of appropriate size (generally 0.1 ml) to give a result within the region of a standard curve, constructed simultaneously by running known amounts (20-125γ) of glucose, was removed and diluted to 1 ml with water in a 50 ml test tube. Cooling with an ice-bath, 5.0 ml of a mixture of sulfuric acid/water (6/1) was added. After cooling for 2 minutes more, the solutions were mixed by vigorous shaking and were placed in a room temperature bath for 2 minutes. They were then heated for exactly 3 minutes in a vigorously boiling water bath, protected with a cold water-filled glass bulk to serve as a condenser, and were finally cooled in a room temperature

water bath. A 3.0% solution of DL cysteine hydrochloride (0.1 ml) was added, followed by vigorous shaking to mix. The optical density (O.D.) of the yellow color which developed immediately (primary reaction) was measured at 412 mμ in the DB Beckman Spectrophotometer. During standing for 48 hours, a green color developed with a maximum absorption at 600 mμ (secondary reaction).

Contrary to the report of Dische, the secondary as well as the primary reaction were found to follow Beer's Law in the range of 20 to 100 micrograms. That author observed the Beer's Law relationship for the secondary reaction only at glucose levels greater than 100v. The results of the analyses as shown by the secondary cysteine reaction are shown in Tables VIII and IX, and are plotted in Figure 4.

Table VIII. Glucose Analyses
Secondary Cysteine Reaction (48 hours)

Time of oxid. (days)	Sample* Wt. (v)	O.D. (600 mμ)	Glucose found (v)	AHG (v x 0.9)	AHG (%) not oxid.	AHG (%) oxid.**
5	217	.366	150	135	62	44.0
	156	.209	87	78	50	
10	206	.267	111	100	48	53.5
	241	.289	119	107	45	
15	248	.308	127	114	46	53.0
	206	.288	119	107	48	
20	161	.167	70	63	39	62.5
	238	.228	95	85	36	

* Cellulose in resin-treated sample.
** Means of two values calculated by difference.

Equal glucose contents were found in those samples which had been oxidized for 10 and 15 days. This indicates that, although the periodate consumption is proceeding at an accelerating rate in that period of the oxidation reaction, all glucose units not blocked by substitution of methylol groups at a secondary hydroxyl have been cleaved during 10 days. Over-oxidation during an additional 5-day period resulted in a loss of only another 9% of the initial anhydroglucose. The unchanged nitrogen content

Table IX. Analyses of QM-4 Samples Oxidized for Different Lengths of Time

Time of oxid. (days)	Anhydro-glucose units oxidized (%)	Nitrogen in product (%)	Resin in product (%)	Sample (%) becoming soluble after reduction
0	-	7.30	14.3	-
5	44	6.74	13.2	-
10	53	7.20	14.1	0.9
15	53	7.37	14.4	1.2
20	62	7.73	15.2	2.0

indicates that no loss of resin occurs during the reaction. An investigation directed towards an elucidation of the mechanism of the secondary reaction, with the hope of finding the means of inhibiting it, was discontinued after it became clear that a detailed study would be necessary. It could be shown that an organic acid was formed during the secondary reaction stage (Table X), but since oxidant consumption curves were basically identical in buffered and unbuffered media it appeared that the organic acid formed was a by-product rather than a cause of the secondary reaction. Addition of 0.1 ml formic acid to a resin-treated sample (1 g) oxidizing in 30 ml of 0.2 M $NaIO_4$, however, resulted in a rapid consumption of periodate well over the

Table X. Formation of Organic Acid during Oxidation in 0.2 M Periodate

Oxidation time (days)	pH of solution		Moles of Acid formed per mole anhydroglucose unit	
	QM-4	CD	QM-4	CD
0	4.5	4.5	-	-
1	5.2	4.5	-	-
2	5.2	4.2	-	-
3	5.2	4.0	-	-
4	5.0	3.9	-	-
5	4.9	3.8	0	.011
10	4.5	3.5	.007	.022
15	4.3	3.4	.022	.030
20	3.9	3.3	.034	.044

theoretical amount. The curves in Figure 5 also show that addition of dilute HCl has the same effect on oxidation rates, and that this dependence of oxidation rate on the acidity of the oxidizing solution must be connected with the resin, since no effect could be observed with untreated cotton.

3. Exhaustive Substitution of Free Hydroxyl Groups

Methylation - Methylation of the free hydroxyl groups in the oxidized and reduced QM-4 samples was not as readily accomplished as had been anticipated. The QM-4 samples were subjected to various methylation procedures following periodate oxidation (0.2 M $NaIO_4$, 10 days) and reduction with sodium borohydride. The course of methylation was followed by methoxyl analyses (Zeisel) and thin layer chromatography to identify the methyl glucoses obtained from hydrolysis of the products. A thin layer chromatographic technique was developed for the purpose and the solvent system acetone-1,2 dimethyoxyethane-petroleum ether in a ratio 7:2:1 was found to give an excellent separation of glucose, mono-, di-, tri- and tetra-O-methyl glucoses when the mixture was irrigated on silica gel G.

Attempts were made to form the sodium cellulosate, as a preliminary step to methylation, by a variety of techniques. These included the use of the sodio-naphthalene complex [32], sodium in butanol [33] and other alcohols, and sodium hydride in various swelling and dispersing agents including tetrahydrofuran, dimethylformamide and N-methyl 2-pyrrolidone. Benzyl lithium was also prepared [34] in the hope that it could be used to form the lithium cellulosate which could subsequently be methylated. These methods introduced only low degrees of substitution of methyl ether groups even after prolonged reaction with methyl iodide. It was therefore decided to react the free hydroxyl groups via esterfication with phenylisocyanate (carbanilation) as an alternative approach which had been applied successfully by H. O. Bouveng [35] in an investigation of the location of acetyl groups in partially acetylated carbohydrates.

Carbanilation

The reaction involving substitution of the free hydroxyls in the resin-treated, oxidized-reduced sample (called hereafter OR-QM-4) with the phenyl carbamoyl (carbanilate) group has two immediately apparent points in its favor: 1) the reaction can be run in anhydrous pyridine which would not be expected to have degradative effects on the cellulose-melamine substrate even at elevated temperatures, and 2) the reaction involves a simple, one-step addition to the hydroxyl group requiring no catalyst.

$$R\text{-}OH + \phi N{=}C{=}O \longrightarrow R\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\phi$$

where $\phi = C_6H_5$.

The carbanilate ester group was chosen over other esters because of its known [35] relative stability, and because of the advantageous presence of nitrogen to assist in following the course of the reactions.

The carbanilation reaction can be used for the present purpose as the first step in the following reaction sequence: 1) carbanilation of all available hydroxyl groups with phenylisocyanate, 2) mild acid hydrolysis to effect removal of the bound resin, 3) methylation of the regenerated hydroxyl groups, 4) reductive (lithium aluminium hydride) removal of the carbanilate blocking groups, and 5) hydrolysis to glucose derivatives which contain a methyl ether group at each site previously substituted by methylolmelamine.

Method: 0.5 g of OR-QM-4 sample (oxidized-reduced containing 7.37% N) was suspended in 8 ml of anhydrous pyridine, and 3.0 ml of freshly distilled phenylisocyanate was added. The reaction mixture contained in a sealed tube was kept in boiling water for 10 hours with occasional shaking. After cooling, the mixture was added to a large excess of ethanol. The product was recovered by filtration and washed thoroughly with ethanol.

The results obtained with oxidized and reduced resin-treated samples are shown in Table XI.

Table XI. Carbanilation of Resin-Treated (Dry-Cured) Cotton

Time of periodate oxidation (days)	Initial Resin content (%)	Wt.Inc. (%)	Nitrogen Content (%) before*	after**
5	13.3	134	6.74	10.01
10	14.2	140	7.20	10.15
15	14.5	142	7.37	10.54
20	15.2	144	7.73	10.73
30	16.5	150	8.41	10.82

* Oxidized and reduced, insoluble fractions.
** Carbanilated products.

The DS of carbanilate groups in the cellulose portions were calculated on the assumption that the weight increases shown in Table XI reflect substitution of carbanilate groups in the cellulosic component alone. The results are shown in Table XII, together with calculations showing the expected nitrogen contents of the products based on the weight increase data.

Table XII Data on Carbanilated Products

Time of periodate oxidation (days)	Calc. Wt. Inc. of cellulosic component (%)	DS Calc.*	Nitrogen calc.* (%)
5	155	2.11	9.64
10	163	2.22	9.84
15	166	2.26	9.94
20	169	2.31	10.11
30	180	2.44	10.41

*Calculated from weight increase.

Comparison of the nitrogen contents calculated from weight increase data (Table XII) with the values found (Table XI) reveals that the values found were higher than those calculated in all

cases. The higher nitrogen contents found indicate that the actual DS of carbanilate groups in the cellulosic components of the products is somewhat higher than the calculated values shown in Table XII from weight increase data. The discrepancy can be rationalized if it is assumed that a small percentage of the carbanilated sample is soluble in the ethanol used to isolate the products from the pyridine reaction mixture and is therefore lost, giving a low value for weight increase. The data suggest that oxidation of the dry-cured material for 10 days or more has opened up the cross-linked polymer network sufficiently to permit carbanilation of all the free hydroxyl groups. Further oxidation did not result in a significant rise in the weight increase data or in the nitrogen content of the products on carbanilation. Apparently the carbanilation of TMM cured samples is readily carried to completion if the structure has been opened up by an oxidation-reduction treatment prior to carbanilation. The complete carbanilation of a dry cured QM-4 sample without prior degradation, however, appears to be impossible under these conditions, and if the rather involved degradation treatment is to be avoided, a new method of carbanilating these resin-treated samples must be established. It has been reported by Burkus [36] that triethylenediamine (TED) can be used effectively as a catalyst for the carbanilation of simple alcohols. In addition to TED as a catalyst, new solvent systems were investigated, and it appeared that dimethylsulfoxide (DMSO) was most promising as a solvent for the carbanilation of cellulose.

The results of a carbanilation treatment using TED as a catalyst and DMSO as a solvent are shown in Table XIII for untreated cotton duck and wet-cured resin-treated cotton duck. In about 30 minutes the cotton duck samples went into solution, forming a thick viscous gel and, as the weight increases in Table XII indicate, the reaction is almost complete after one hour, with little change occurring if the reaction time is extended to 48 hours. The resin-treated samples did not go into solution,

Table XIII. Carbanilation of Cotton Duck and Wet-Cured, Resin-Treated Cotton Duck in DMSO at 50°C in Presence of TED

Sample	Reaction time (hrs)	Weight increase (%)	Nitrogen content (%)	DS* based on wt.	Resin content (%)
Cotton duck	1	214		2.91	
	2	232		3.16	
	4	224	8.00	3.04	
	16	224	7.97	3.04	
	48	212		2.88	
Wet-cured cotton duck	0	0	4.43	0	9.6
	2	181	9.12	2.71	9.3
	4	214			
	16	215	9.33	3.18	8.4
	48	204			

* For substitution with phenylisocyanate only.

but did show considerable swelling. At the conclusion of the reactions, about 10 ml of DMSO were added to the solutions in order to decrease the viscosity of the gels. The resulting solutions were then poured into warm ethanol and a white precipitate formed which was extracted in a Soxhlet apparatus overnight. It appears that under these mild conditions the carbanilation of cotton duck, as well as cotton duck that had been resin-treated by a wet-cure process, can be accomplished quantitatively in a "clean" reaction, as the nearly theoretical DS values indicate. There appears to be a small loss in resin, which might be incompletely reacted with the cellulose, but which could not be removed after curing because of its molecular size. After almost complete carbanilation the fiber structure is essentially destroyed, and resin which is not covalently bound to the cellulose can be separated.

If the resin treatment was imparted by a dry-cure process, the carbanilation of free hydroxyl groups is considerably more difficult to accomplish, as the data in Table XIV indicate.

Table XIV. Carbanilation of Dry-Cured TMM-Treated Cotton Duck in DMSO in Presence of TED

Temperature (°C)	Reaction time (hrs)	Weight increase (%)	Nitrogen content (%)	DS* sed wt.	Resin content (%)
	0	0	7.3	0	15.8
50-55	2	18.4			
	24	64.7	8.27	1.01	12.9
	48	61.3	8.89	0.98	15.4
73	24	145	9.23	2.24	11.9
	48	150	9.38	2.30	12.5
	72	156	9.52	2.44	12.9
(without phenyl-isocyanate)	72	8.5	6.88		16.2
88	2	100			
	6	152	9.94	2.45	15.5
	24	186			
	48	178	9.65	2.76	12.5
(without phenyl-isocyanate)	48	9.0			

* For substitution with phenylisocyanate only.

This could be attributed either to the higher degree of cross-linking obtained by a dry-cure treatment which prevents the fiber structure from opening up during carbanilation, or to the concentration of resin near the surface of the fiber which could provide a diffusion barrier for the phenylisocyanate. The data in Table XIV indicate that there appear to be limiting levels of substitution depending on the reaction temperature. All these samples were shaken vigorously during the entire reaction period. Again, independent of the reaction temperature, a certain amount of resin apparently is lost during the reaction. At the highest temperature used so far a level of substitution is approached which corresponds to the theoretical degree of substitution of 2.83. This theoretical value is obtained from a DS of 0.17 for the substitution with resin, which was calculated under the assumption of a bifunctional reaction of the resin monomer with cellulose and is, therefore, probably too high.

4. Hydrolytic Removal of Bound Resin

The next step in the sequence of reactions is the removal of the bound resin in order to make available the regenerated hydroxyl groups for subsequent methylation. Removal of the resin is accomplished by heating the carbanilated OR-QM-4 samples in 95% dioxane which is 0.01 N in HCl. A hydrolysis time of 6 hours at 100°C and a liquor ratio of 100:1 were found to be optimum. If insufficient acid was used, neutralization resulted during the course of reaction and hydrolysis did not go to completion. Free amino groups can arise in the resin portion of the sample during the hydrolysis, which could account for the observation that the HCl was neutralized when 10 or 30 ml of solution per gram of material was used. During the hydrolytic removal of the resin the major part of the sample becomes soluble, this portion containing most or all the cellulose, whereas the insoluble fraction seems to consist mainly of resin. The insoluble resin portion of the product obtained by the usual procedure was subjected to total acid hydrolysis. The hydrolyzate was investigated after neutralization by gas chromatography, and the presence of glucose could not be detected. Therefore the cellulosic portion of the sample must have been entirely solubilized, and it is probable that all of the resin-cellulose bonds were broken by the treatment.

The products obtained after hydrolysis (6 hours) of 1.39 g of carbanilated (10 hours) material were recovered as 0.065 g (4.7%) of insoluble product and 1.134 g (82%) of soluble material recovered by precipitation with water. The latter sample was further fractionated by precipitation into ethanol as follows:

Dissolved in 10 ml of dioxane and added to one l. of ethanol, there was precipitated 0.598 g (53%). The ethanol filtrate was concentrated to 20 ml i.v. and a further 0.046 g (4%) was deposited when the solution was kept at 0°C overnight. The clear filtrate was added to one l. of water which precipitated 0.464 g (41%). Total recovered, 98%.

The infrared spectra of the two major fractions were very similar, and the results of nitrogen analyses showed 6.96% in the ethanol insoluble fraction and 7.68% in the ethanol soluble fraction. The similarity in the infrared spectra and the nitrogen analyses indicate that the difference in these two fractions may be one of molecular weight alone. The ethanol insoluble material gives a solution of noticeably greater viscosity in dioxane or in chloroform than a comparable solution of the ethanol soluble material.

5. Methylation of Regenerated Free Hydroxyl Groups

Methylation of the regenerated hydroxyl groups was initially attempted by using methyl iodide and sodium hydride. It was learned, however, that a migration of carbanilate groups results when methyl-3,4,6-tri-O-(phenylcarbamoyl)-α-D-glucopyranoside (I) is methylated using this procedure. The product thus obtained was shown by thin layer chromatography to consist of several products with different migration rates. This methylation procedure has therefore been abandoned and the Kuhn [37] methylation technique (silver oxide and methyl iodide in dimethylformamide solution) has been adopted and proved suitable. Complete methylation of (I) was achieved without concomitant migration of carbanilate groups. This was proved by gas chromatographic analysis of the product obtained on methylation.

Reductive removal of the carbanilate groups afforded a chromatographically pure product. Hydrolysis of the glycosidic methyl group gave a product showing only two peaks having the same retention times as the α- and β-anomers of 2-O-methyl-D-glucose. Therefore no migration of carbanilate groups was indicated during the methylation by this procedure, and it can be assumed that the same would be true in the case of partially carbanilated cellulosic samples.

The soluble, carbanilated, cellulosic portions of the samples resulting from the mild acid hydrolysis of resin were

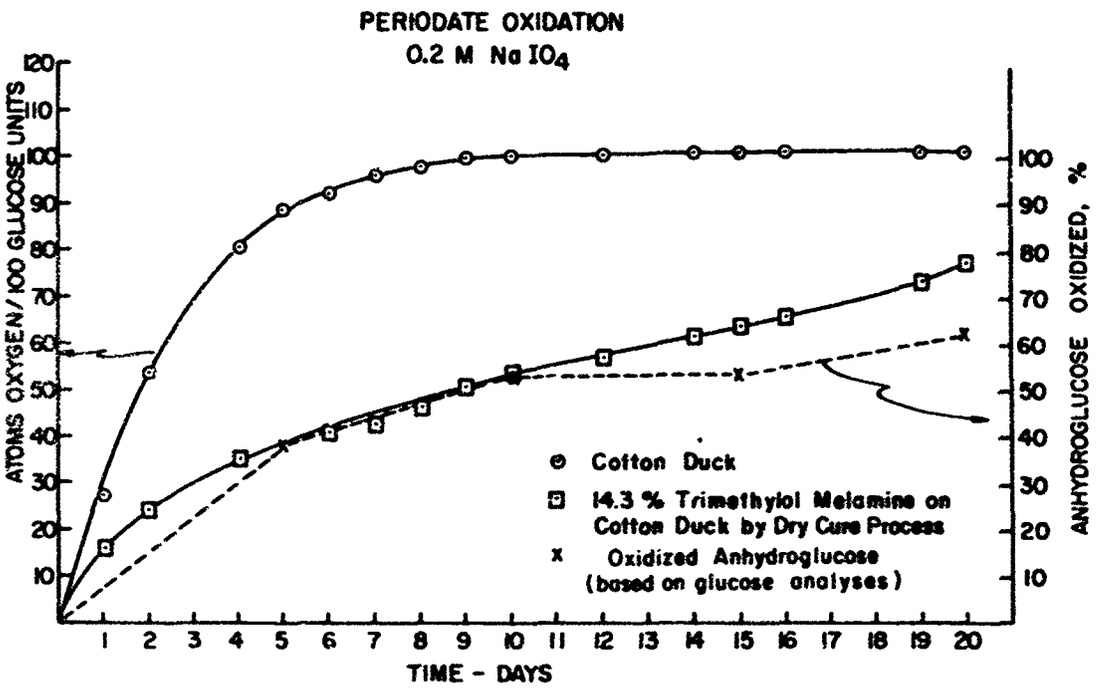


Fig. 4. Results of Periodate Oxidation (0.2 M) of Untreated and Resin-Treated Cotton

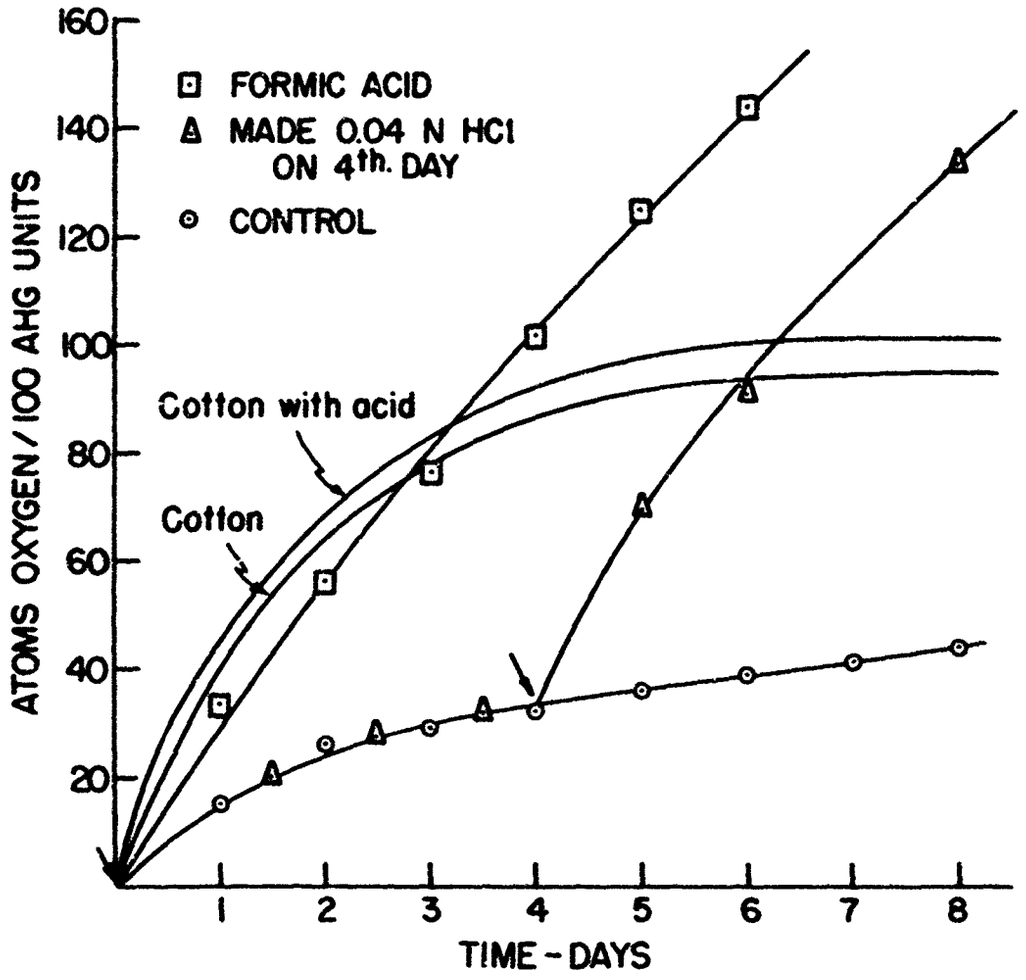


Fig. 5. Effect of Acid on Oxidation Rate of Dry-Cured Sample.

therefore methylated according to the method of Kuhn. Isolation of the products was accomplished using the procedure described by Bouveng [35] involving precipitation of the product into an aqueous-ethanolic solution containing excess potassium cyanide, after the excess of methyliodide had been removed in vacuo. Two Kuhn methylations (48 hours reaction time each) afforded a product which did not show O-H or N-H absorption in the infrared spectrophotometer, showing that methylation was complete. Yields ranged in the order of 80-90%.

6. Removal of Carbanilate Groups

The methylation of carbanilate groups which occurs in the previous step of the reaction sequence increases the resistance of this protective group to alkaline hydrolysis. The reductive removal of carbanilate groups with lithium aluminium hydride [38] occurs smoothly within a few hours, as pointed out by Bouveng [35].

Method - Approximately 3 mg of sample were weighed into 4 ml pyrex test tube and 0.5 ml of anhydrous dioxane and 3 mg of lithium aluminium hydride were added. The tube, protected with a drying tube, was heated at 99°C in a water bath for 6 hours, with periodic replacement of dioxane lost by evaporation. The dioxane was allowed to evaporate to dryness in vacuo, and the sample was then submitted to total hydrolysis.

7. Total Hydrolysis

Total hydrolysis of the partially methylated cellulose was carried out by adding 72% sulfuric acid (4 ml per gram of starting material) to the residue and keeping it overnight at room temperature. The mixture was then diluted tenfold with water and refluxed for 6 hours. The cooled hydrolyzates were neutralized with $BaCO_3$, the filtrate was evaporated in vacuo, and the sirup was then investigated chromatographically.

CHAPTER IV. SEPARATION AND IDENTIFICATION OF METHYL DERIVATIVES BY GAS LIQUID CHROMATOGRAPHY

1. Synthesis of Authentic Samples

Since positive identification of the separated methyl-glucoses can only be accomplished by comparison with authentic derivatives, it was necessary to synthesize derivatives which were not available from other sources.

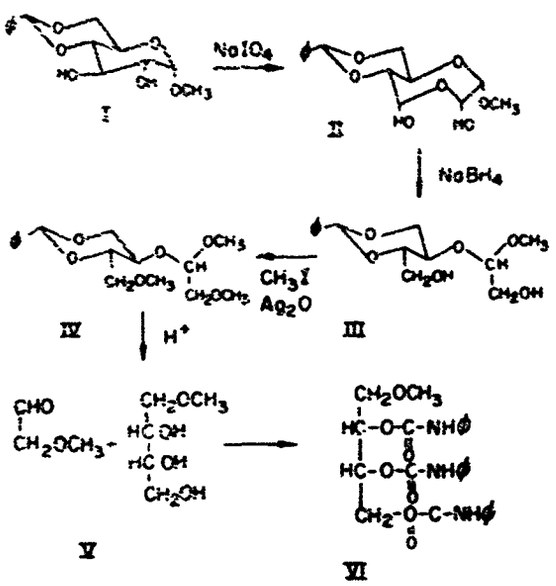
A. 4-O-Methyl-D-Erythritol

Anhydroglucose units substituted by a resin component at the primary (C6) hydroxyl would be cleaved by periodate at the secondary hydroxyls and would be recovered in the final hydrolyzate as 4-O-methyl-D-erythritol. An authentic sample of that compound was synthesized from cellulose by the scheme shown in Figure 6. Advantage was taken of the specificity of the triphenylmethyl (trityl) ether group to block the primary (C6) hydroxyl group. The secondary hydroxyls were then carbanilated to give II. Removal of the trityl group by treatment of II in chloroform solution with hydrogen chloride gave III. The 2-O-phenylcarbamoyl cellulose was methylated with methyl iodide and sodium hydride giving IV, and reductive removal (lithium aluminium hydride) of the carbanilate groups gave a water soluble product, 6-O-methyl cellulose. This product was characterized after hydrolysis by paper chromatography and paper electrophoresis [39], which showed that 6-O-methyl-D-glucose was the predominant component. The synthesis of 4-O-methyl-D-erythritol from 6-O-methyl cellulose was accomplished by periodate oxidation followed by sodium borohydride reduction and hydrolysis to give a mixture of 4-O-methyl-D-erythritol and glycol aldehyde; the latter compound was reduced to ethylene glycol by a second reduction with sodium borohydride.

B. Synthesis of 1-O-Methyl-D-Erythritol

The compound 1-O-methyl-D-erythritol was reported in 1959 by Goldstein, Hamilton and Smith [40] after its isolation

from periodate oxidized and borohydride reduced amylopectin. The crystalline tri-O-p-nitrobenzoate derivative was described. A synthesis of authentic 1-O-methyl-D-erythritol has not been reported. In the present work the compound was synthesized starting with methyl-4,6-O-benzylidene-α-D-glucopyranoside (I) [41] as follows:



Periodate oxidation of I furnished the known [42] hydrated derivative II, m.p. 143-145°, $[\alpha]_D^{24}$ +63.8° (c 0.5, pyridine). Reported [42] for II: m.p. 143-144°. Reduction of II with sodium borohydride gave a crystalline product (from water) III having m.p. 51-53° and $[\alpha]_D^{24}$ -3.7 (C2, $CHCl_3$). Analysis calculated for $C_{14}H_{20}O_6$: C, 59.15; H, 7.04. Found: C, 58.83; H, 7.18%. This product gave a crystalline (from ethanol) dicarbanilate derivative m.p. 167-168° $[\alpha]_D^{24}$ -68.55° (C2, $CHCl_3$), after treatment with phenylisocyanate in pyridine solution. Analysis calculated for $C_{29}H_{30}O_6N_2$: C, 64.37; H, 5.75; N, 5.37. Found: C, 64.01; H, 5.94; N, 5.23%.

Methylation of III was accomplished by the procedure of Kuhn [37] and the reaction was shown by gas-liquid (GLC) and thin-

layer chromatography (TLC) to be completed after 20 hours of shaking at room temperature. The isolated sirupy product was purified by distillation in high vacuum and had $[\alpha]_D^{24}$ -34.15° (Cl, $CHCl_3$). Analysis. Calculated for $C_{16}H_{24}O_6$: C, 61.54; H, 7.69. Found: C, 61.53; H, 7.80%.

1-O-methyl-D-erythritol (V) was obtained by hydrolysis in two stages of the benzylidene and the 1,2-dimethoxyethyl groups from IV. Compound IV (4.8 g) was refluxed one hour in 50 ml 0.3 N sulfuric acid. The cooled solution was extracted twice with chloroform, neutralized with barium carbonate and the filtrate concentrated in vacuo to a sirupy product. After a second hydrolysis (one hour reflux) in 9 ml of 1 N sulfuric acid and isolation of the product as above, the product V was further purified. The 2-methoxyacetaldehyde was eliminated after treatment with sodium borohydride to reduce it to 2-methoxyethanol. This volatile product was removed by storing the mixture at 50°C in vacuo for three days. The GLC showed a single peak (trimethylsilyl ether derivative) at 16.2 minutes using the GLC procedure which will be described later. Analysis: Calculated for $C_5H_{10}O_4$: C, 44.12; H, 8.83; molecular weight: 136. Found: C, 42.81; H, 8.63, molecular weight: 145.

A crystalline tricarbanilate derivative VI was prepared from the sirupy product V by treatment with phenylisocyanate in the usual way and had m.p. 220-221° and $[\alpha]_D^{24}$ +15.8° (c 0.5 pyridine). Analysis. Calculated for $C_{26}H_{27}O_7N_3$ (VI): C, 63.29; H, 5.48; N, 8.52. Found: C, 63.05; H, 5.70; N, 8.32%.

The structure of 1-O-methyl-D-erythritol (V) was proved by treatment with sodium periodate. The material should consume two moles of periodate with the generation of one mole of formic acid. The structure and its purity were confirmed when it was found to consume 1.98 moles of periodate (15 min) and 2.1 moles (15 hr) with the production of 1.03 moles of formic acid. The compounds 1-O-methyl-D-erythritol and 1-O-methyl-L-erythritol cannot be separated by gas chromatography and both can be used for identification purposes.

C. 6-O-Methyl-D-Glucose

Hydrolysis of the 6-O-methyl cellulose previously described furnished 6-O-methyl-D-glucose. The major product obtained was found to have the expected [39] mobilities when studied by paper chromatography and electrophoresis.

D. 2-O-Methyl-D-Glucose

A new synthesis of 2-O-methyl-D-glucose was developed which is an improvement over existing methods [43,44]. The compound methyl 2-O-[(benzylthio)carbonyl]-α-D-glucopyranoside has been described [45], and it was shown that the (benzylthio)-carbonyl group, $C_6H_5CH_2S$-CO-, can be removed under mild conditions which do not disturb other ester groupings. That compound, therefore, serves as a convenient precursor to 2-O-methyl-D-glucose.

The 3,4,6-tri-O-benzoate and tri-O-phenylcarbamate derivatives of methyl 2-O-[(benzylthio)carbonyl]-α-D-glucopyranoside were prepared and the (benzylthio)carbonyl group was removed oxidatively [46] to furnish methyl 3,4,6-tri-O-benzoyl-α-D-glucopyranoside and methyl 3,4,6-tri-O-phenylcarbamoyl-α-D-glucopyranoside. The former of these compounds has been described [42] and its structure proved. The latter, which had melting point (m.p.) 249-251° and $[\alpha]_D^{24}$ +112.0° (acetone), gave a mono-acetate derivative (m.p.) 212-214°, $[\alpha]_D^{24}$ +103.0° ($CHCl_3$) and a mono-benzoate (m.p.) 215-217°, $[\alpha]_D^{24}$ +118.9° ($CHCl_3$). Methylation of the tribenzoate or tricarbanilate derivative using silver oxide and methyl iodide was followed by removal of the benzoate or carbanilate groups by reaction with barium oxide in methanol. Hydrolysis gave a product which was shown by paper electrophoresis to be comprised solely of 2-O-methyl-D-glucose.

E. 3-O-Methyl-D-Glucose

An authentic specimen of the compound 3-O-methyl-D-glucose was prepared in the usual way [47] by using as a precursor 1,2-5,6-di-O-isopropylidene-α-D-glucofuranose. Methylation of the latter followed by acid hydrolysis of the isopropylidene groups provided 3-O-methyl-D-glucose.

2. Separation of Methylglucoses by GLC

One of the problems that arises in the gas chromatographic analysis of organic compounds is possible thermal degradation at the temperatures required to assure complete compound volatilization on injecti and subsequent to movement of the products on the GC column. Sugars and their derivatives are known to be especially sensitive to high temperatures and tend to form anhydrides in addition to fragmenting to form aldehyde degradation products [48,49]. Where the objective is the quantitative estimation of products, essentially complete volatilization of the injected sample, without significant degradation, is required. Neely et al. [50] used methylglucosides rather than the original glucose derivatives, and in general these compounds have been used because of their greater volatility. In 1963 Sweeley and co-workers [51] developed a method for the quantitative estimation of glucose derivative which made use of the even more volatile trimethyl silyl ether derivatives. A considerable amount of work in this investigation was done using methylglucosides until finally the method of Sweeley et al. [51] was adopted for the separation of the methylglucoses.

A. Separation Using Methyl Glucosides

Gee and Walker [52] have compared the resolution of methyl tri-O-methyl-D-glucosides (trimethyl glucosides) on three different polar, liquid phases. These authors found the best resolution using neopentyl glycol succinate as the liquid phase with Carbowax 20M as intermediate, and diethylene glycol succinate as the poorest. Jones and Perry [53] found that an

equal mixture of a polar polyester (butanediol succinate) and a non-polar grease (Apiezon M) gave a satisfactory separation of glucosides, whereas Neely, Nott and Roberts [50] obtained good separation of the methyl glucosides, obtained from the hydrolysis of methylated cellulose and subsequent methanolysis of the glucose derivatives, on a column containing 25% of a polar polyester LAC-2R-446 (polydiethyleneglycopentaerythritol adipate) and 2% phosphoric acid as the liquid phase on the 8-100 mesh Chromosorb W as the solid support.

The work of Neely, Nott and Roberts [50] was felt to be the most complete and pertinent to the present study. Accordingly, one series of columns was made similar to that used by these workers according to preparative procedures described by Metcalfe [54]. A known mixture containing (1) methyl 2,3,4,6-tetra-O-methyl-D-glucoside, (2) methyl 2,3,6-tri-O-methyl-D-glucoside, and (3) methyl 2,3-di-O-methyl-α-D-glucoside in chloroform was used for testing. In Table XV the experimental conditions and instrument settings are shown. The results obtained are shown in Table XVI along with column characteristics. Although reasonable separation was achieved, the peaks tended to be quite small and the resolution was not as good as that shown in the literature [50] even though samples of comparable size were injected.

Table XV. Experimental Conditions and Instrument Data

	Neely, Nott & Roberts [50]	TRI
Instrument	aerograph Hi Fi 600	F & M 500
Injection port, T(°C)	240	240
Carrier gas	nitrogen	helium
Gas flow		60 cc/min
Detector	flame ionization	thermal conductivity
Inlet pressure (psi)	30	30
Run condition	isothermal	isothermal
Column temperature, °C	200-210°C	200°C

Table XVI. Comparison of Columns and Retention Data on Methyl Glucosides

Column Description				Glucoside Retention Time (mins)		
No.	Length (ft)	Dia. (in)	% Liq. phase*	Tetra-methyl	Trimethyl	Dimethyl (2,3-di)
23	2	1/4	25	2.8	4.7	8.4
24	2	1/4	10	1.3	2.5	3.7
22	3	1/8	25	1.8	3.8	5.6
27	4	1/8	25	2.3	5.4-6.9	no peak
Lit.**	1	1/8	25	-	ca 1.5	ca 3.0
Lit.**	3	1/8	25	ca 3.0	ca 5.5-7.0	ca 17.0

* LAC-2R-446 was the liquid phase plus 2% H_3PO_4. The solid support was acid washed Chromosorb W.

** Neely, Nott and Roberts [50].

Another series of columns, prepared with Haloport F, a perfluorcarbon, as the solid support and featuring some of the other liquid phases previously mentioned, is described in Table XVII. The columns were tested with a mixture of methyl glucosides derived from the hydrolysis of the same methylated cellulose material (Dow Methocel, DS 1.86) used by Neely, Nott and Roberts [50]. Haloport F was used as the support so that water solutions of the glucoses and glucosides could be used, since water is superior to chloroform as a solvent for the entire range of methylated products. Haloport F is a poor absorbant for water, so that water emerges from the column quickly and as a sharp peak, whereas Chromosorb W holds water tenaciously resulting in tailing, thus obscuring some of the peaks. The methylated cellulose samples (DS 1.86) were hydrolyzed in 72% sulfuric acid according to the method of Monier-Williams [55] and Croon and Lindberg [56]. The hydrolysis products, glucose and methyl glucoses, were converted to the methyl glucosides by a standard methanolysis procedure [57] involving refluxing the products in 2% methanolic HCl for 4 hours followed by evaporation to dryness

Table XVII. Gas Chromatographic Columns

No.	Liquid Phase Compound	%	Length	Dia. (in)	Operating limit, T(°C)
18	Carbowax 20M	3	12 ft	1/4	245
19	Neopentyl glycol succinate	3	22 in	1/4	245
20 & 21	Carbowax 20M	3	22 in	1/4	245
28	LAC-2R-446	3	2 ft	1/4	225
29	Butanediol succinate plus Apiezon M	6	2 ft	1/4	215

and solution in a known amount of water. This treatment causes the C-1 position to be methylated. A comparison of the chromatograms shows general similarity but Carbowax 20M (polyethylene glycol) appeared to offer the best balance and resolution of isomers, in that only in the case of this liquid phase were three distinguishable peaks found in both the dimethyl and monomethyl glucoside region. Therefore, this liquid phase was selected for further study.

In Figure 7 are shown the results obtained on a much longer column (12 ft.) The separation has been greatly improved by lengthening the column, and peak resolution has been enhanced. One drawback in the long column is that the α-methyl-D-glucoside representing the unmethylated glucose component has a much longer retention time than any of the methylated glucosides, so that a shorter column may be required to effect reliable detection and measurement of this compound.

In the gas chromatographic separation of methyl glucosides Neely et al. [50] used an injection port temperature of 240°C, and a column temperature of 210°C. The same injection port temperature has been used previously in this work, but a column

temperature of 245°C was used to achieve the removal and separation of the monomethyl glucosides. In order to elucidate the effect of injection port temperature, the methyl glucosides of the hydrolysis products from methyl cellulose (DS 1.86) were chromatographed using injection port temperatures of 150°C, 200°C and 300°C with column temperature programming from 100°C to 245°C. The results, shown by the chromatograms in Figure 8, indicate that as injection port temperature increases a number of small peaks appear before the peaks for trimethyl glucoside, thus revealing the incidence of volatile, low molecular weight compounds. When the injection port temperature is at 150°C, these appear to be negligible but at 300°C several significant peaks are observed accompanied by considerable base line displacement. However, at the intermediate temperature of 200°C fewer and smaller peaks appear and the base line is well maintained. Sample volatilization was checked by raising the injection port temperature to 250°C at the conclusion of a run and making another run without adding further sample. The results of this procedure showed some sample was not being volatilized at 150°C, but that at 200°C only trace amounts of products were found. These results indicate that the maximum injection port temperature should not exceed 200°-210°C for best results.

B. Separation Using Silyl Derivatives

The results obtained to this point indicated that the identification (inclusion of known compounds in the unknown mixture) and determination of the hydrolysis products of methylated cellulose in the form of their methyl glucosides can be achieved via gas chromatography. The method introduced by Sweeley [51], however, which was published in 1963 appeared to be preferable.

As mentioned above, this technique makes use of the trimethyl silyl derivatives which are readily prepared by adding hexamethyl disilazane and trimethylchlorosilane to the sugar in pyridine solution. An F & M Model 500 gas chromatograph, equipped with a 12-foot column of $\frac{1}{4}$-inch O.D. aluminum tubing packed with 6%

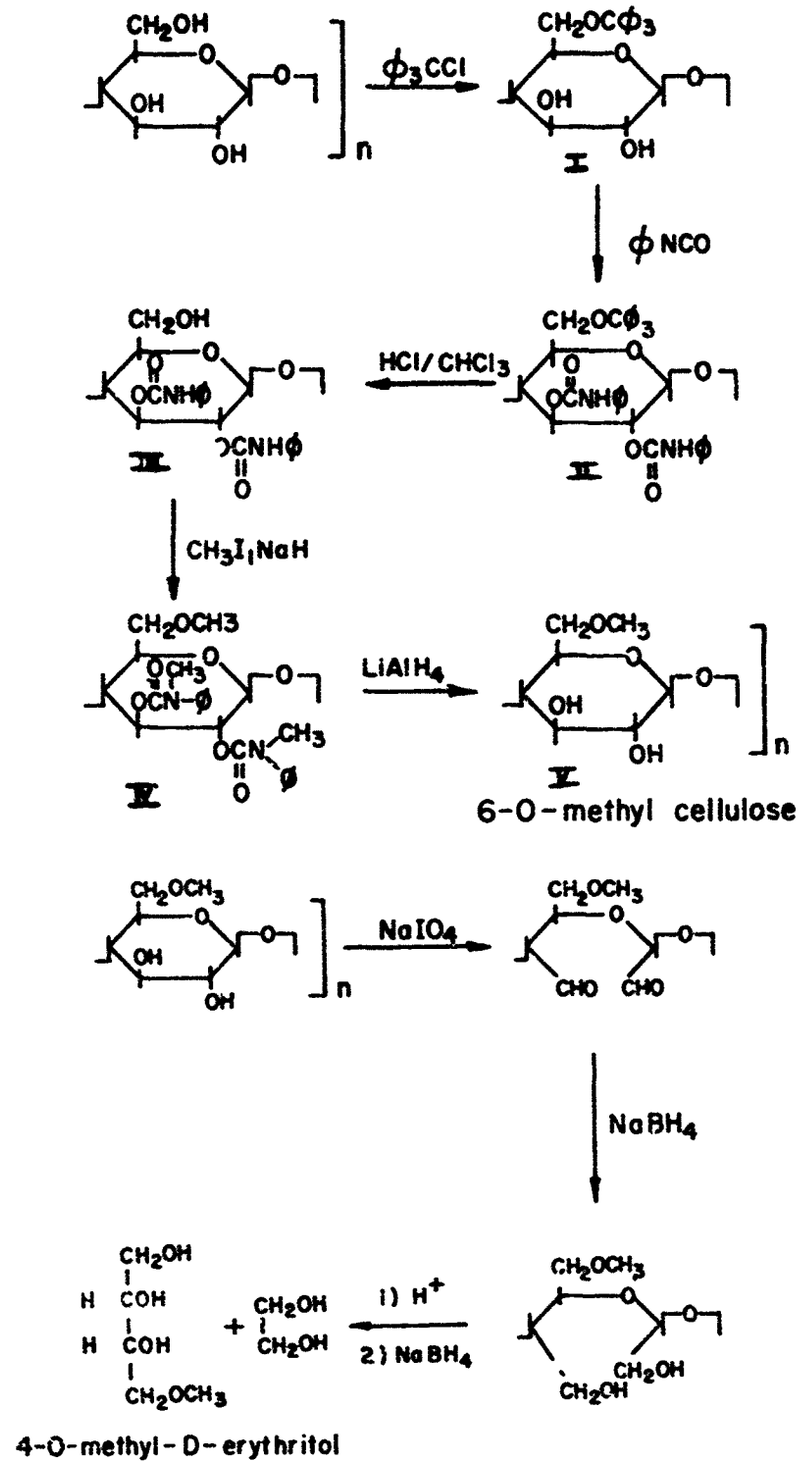


Fig. 6. Synthesis of 4-O-Methyl-D-Erythritol via 6-O-Methyl Cellulose.

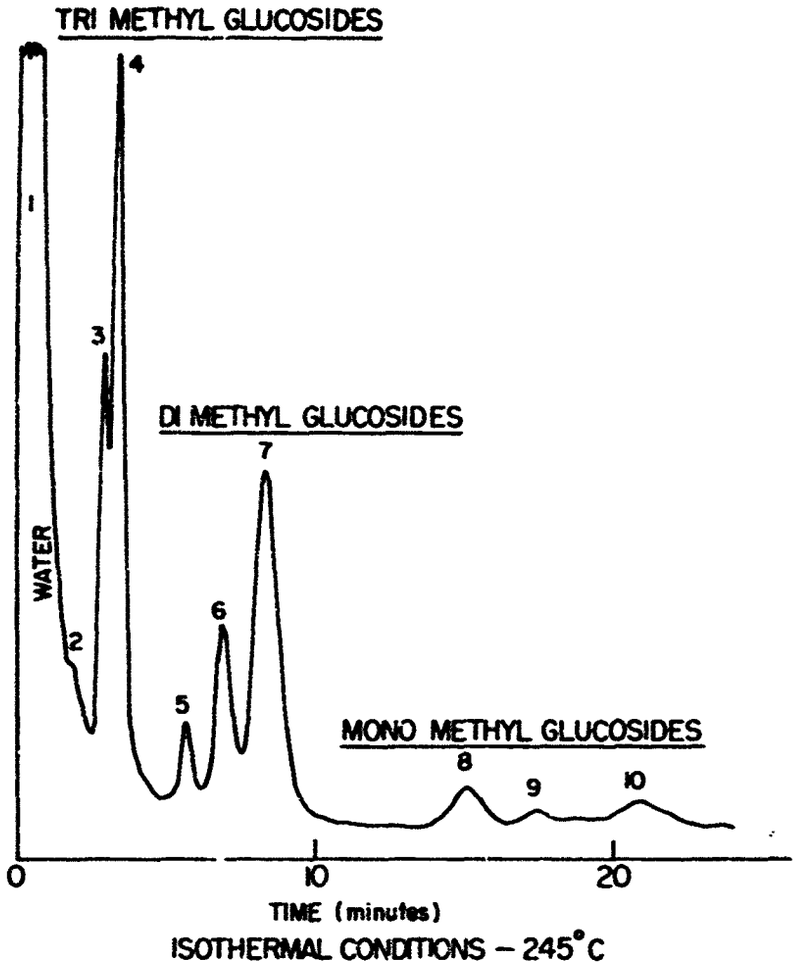


Fig. 7. Gas Chromatogram Showing Separation of Methyl Glucosides. (Col. 18: 3% Carbowax 20M on Haloport F)

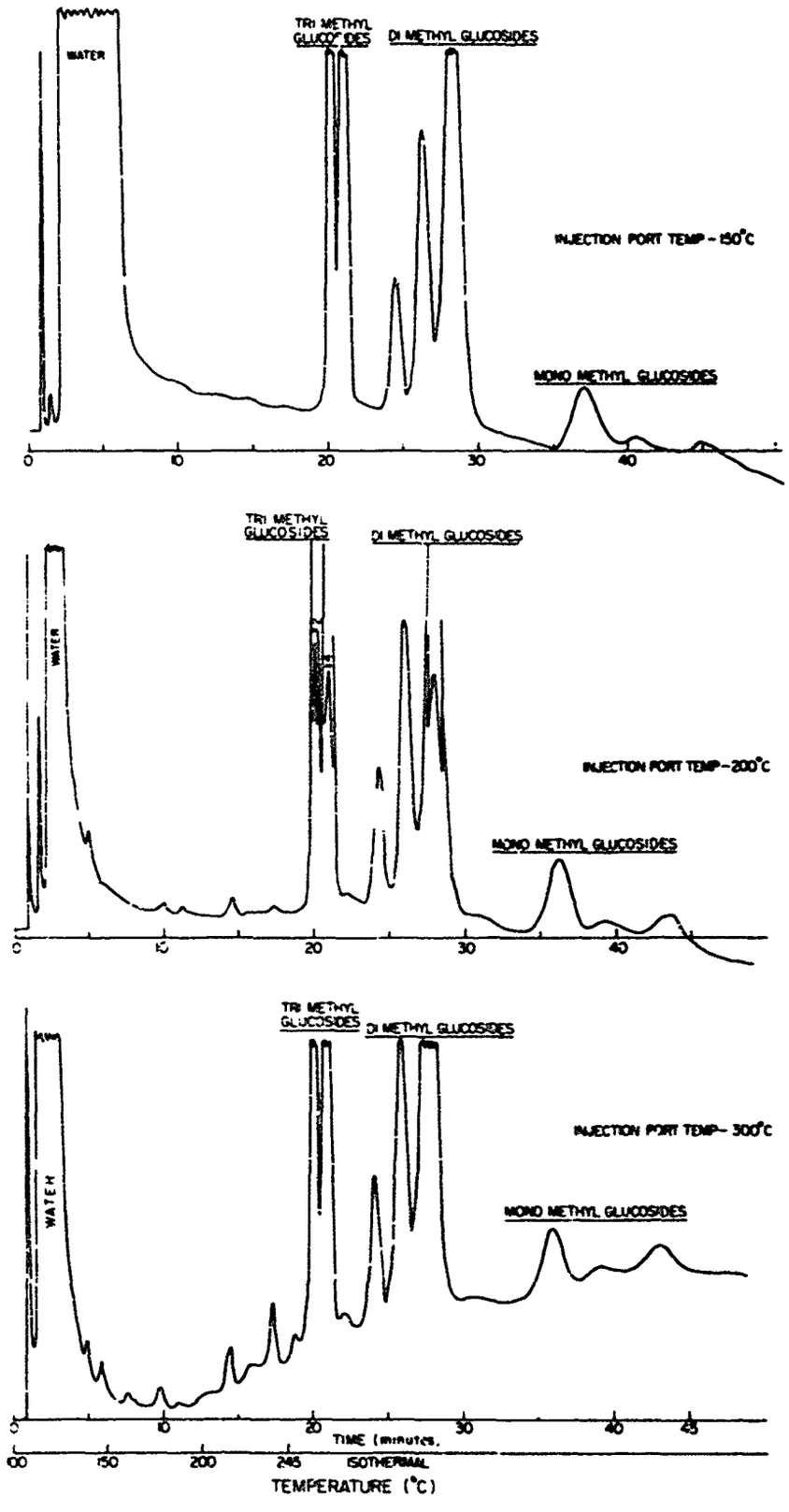


Fig. 8. Gas Chromatograms of Methyl Glucosides (Derived from Methylated Cotton Cellulose, DS 1.86) Showing the Effect of Varying the Injection Port Temperature. (12 ft. Col. - 3% Carbowax 20 M on Haloport F)

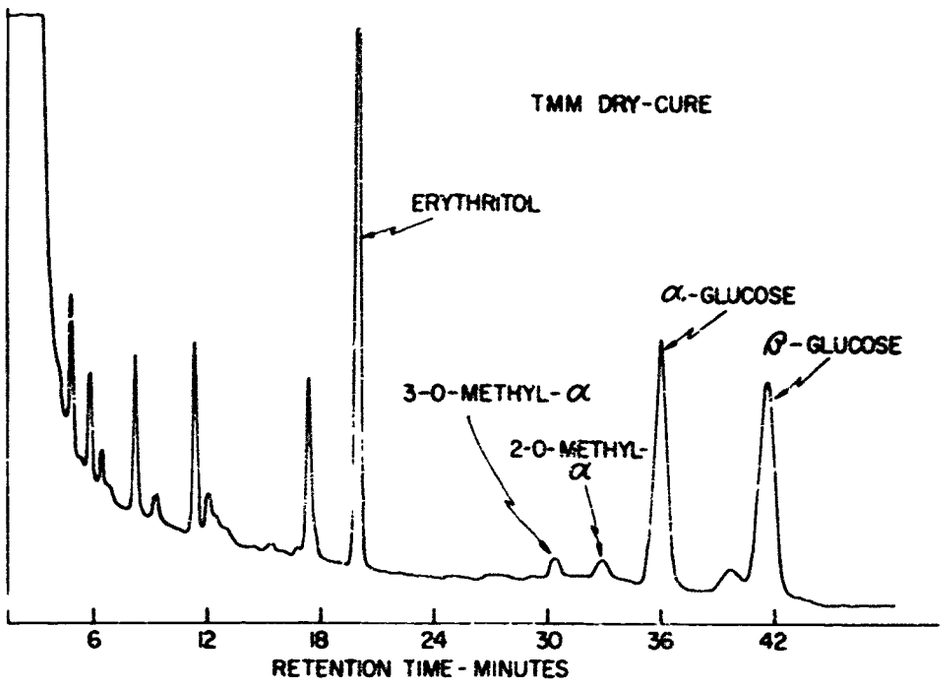


Fig. 9. Gas Chromatogram of Products of Total Hydrolysis.

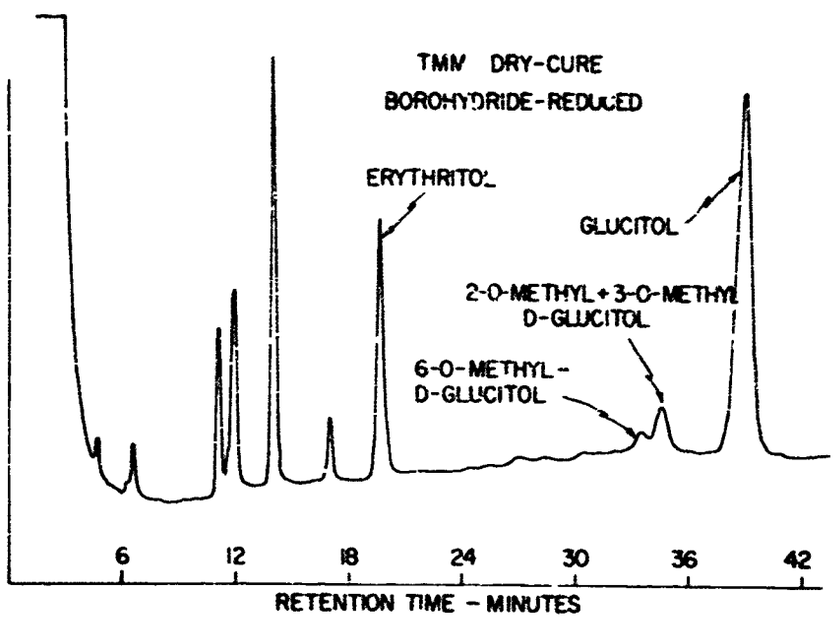


Fig. 10. Gas Chromatogram of Glucitol Derivatives of Total Hydrolysis Products.

G. E. Silicone Oil 52 (liquid phase) on hexamethylene disilane pretreated 80 mesh Chromosorb (solid support), was used. The experimental conditions were as follows:

carrier gas	helium
flow rate	60 cc/min
injection port temp.	220°C
column temp.	programmed heating to 180°C
heating rate	4°C/min
detector temp.	270°C

Figure 9 shows a GLC chromatogram of the total hydrolyzate from the dry-cured sample which had been periodate oxidized for 20 days. A GLC chromatogram of the methyl glucitol derivatives obtained by borohydride reduction of the dry-cured sample (oxidized 15 days) is shown in Figure 10. All the peaks indicated were identified using the known addition method. The presence of 6-O-methyl-D-glucitol indicated in Figure 10 could not be confirmed in later experiments, and all substitutions of resin at the carbon 6-hydroxyl is represented by the 4-O-methyl-erythritol peak, which appears just prior to the erythritol peak with a retention time of about 17 minutes.

CHAPTER V. APPLICATION OF DERIVATIVE FORMATION AND CHROMATOGRAPHIC SEPARATION METHODS

The experimental method for determining the extent and the position of covalent bonding between methylolmelamine resins and cotton cellulose was discussed in the previous chapters. This method was essentially followed to yield the results which will be reported in this chapter. Minor modifications in method will be mentioned at the appropriate place. The following samples were studied:

(1) TMM Wet-Cured Cotton Duck (QM-3)

Periodate oxidation, 10 days; 108 moles of periodate consumed per 100 anhydroglucose units (see Fig. 11). According to the determination of unoxidized anhydroglucose units, 95% of these units have been oxidized. After borohydride reduction, 94% of the material was recovered of which 67% was insoluble in water. Only the insoluble fraction contained nitrogen (5.26%) and was therefore investigated further.

(2) TMM Dry-Cured Cotton Duck (QM-4)

Periodate oxidation, 15 days; 65 moles of periodate consumed per 100 AHG units (see Fig. 4). According to the determination of unoxidized AHG units, 53% of these units have been oxidized. Only 1.2% of the sample was soluble in water after borohydride reduction and consequently the nitrogen content of the insoluble fraction was almost unchanged (7.37% N_2)

(3) Aerotex - M-3 Dry-Cured Cotton Sheeting

Cotton sheeting (80 x 80) was dry-cured with methylated trimethylolmelamine (Aerotex resin) in the usual pad, dry (4 minutes at 80°), and cure (4 minutes at 140°) manner [3]. The treated product, containing 4.77% nitrogen (9.36% resin),

was periodate oxidized, 33 moles of periodate being consumed per 100 anhydroglucose units after 10 days. Some of the properties of this dry-cured material are reported in Table XVIII.

Table XVIII. Properties of Aerotex M-3 Treated (Dry Cure) Cotton

Sample	Moisture Regain (%)	Wrinkle Recovery (W+F deg) Dry	Wet
Control	7.2	149	154
Resin-treated	5.5	286	276

The results of gas chromatographic analysis of the products obtained after the final total hydrolysis (carried out with 0.02 N HCl) and borohydride reduction are compiled in Table XIX.

Table XIX. Substitution in Methylated Cellulose Products from Resin-Treated Cottons

Component	Percent of Component Aerotex M-3 dry cure	TMM Colloid dry cure	Arigal C wet cure
D-glucitol	50.0	21.7	10.4
Erythritol	20.3	62.4	85.4
2-O- & 3-O-methyl-D-glucitol	20.8	8.5	1.6
4-O-methyl-erythritol	9.0	7.3	2.5

The separation of 2-O- and 3-O-methyl-D-glucitol was not possible under the conditions employed. Ordinarily the ratio of these two compounds could be obtained from the chromatograms of the reducing products resulting from hydrolysis prior to borohydride reduction. However, although a gas chromatographic analysis was carried out for these products, the assignment of peaks representing the several anomers of the mono-O-methyl-D-glucoses could not be made with confidence. The DS value of

the Arigal C wet-cured sample, shown in Table XX, has been corrected for the fact that only the insoluble fraction (67%) was investigated.

Table XX. Fraction of Material Oxidized as Revealed by Periodate Oxidation, Glucose Analysis and Subsequent GL Chromatogr phy

	Resin Treatment		
	Arigal C wet cure	TMM Colloid dry cure	Aerotex M-3 dry cure
Periodate consumption, atoms oxygen/100 AHG units	104	68	48
Glucose analysis, % of oxidized AHG units	95	53	-
% of AHG units subsequently found as erythritol	88	70	29
Degree of substitution	0.030	0.156	0.298

A comparison of the fraction of the final sample present in the form of oxidized anhydroglucose units (erythritols) to that of intact glucose units (glucitols), as revealed in the gas chromatograms of the final hydrolyzates, and to the values expected from the periodate consumption data of the materials studied is shown in Table XX. The results of glucose analyses are included for comparison.

1. Studies on DMM and TMM Dry-Cured Print Cloth

The cotton sheeting (80 x 80) samples which were dry-cured with pure TMM and DMM as reported above were subjected to two successive periodate oxidation treatments in fabric form. Duplicate samples were treated with one molar excess of 0.2 M $NaIO_4$. One sample was recovered when the periodate consumption reached 40 moles per 100 AHG units at which time the rate of consumption appeared to be accelerating. These samples were

then reduced with borohydride. Oxidation was continued with the second sample until 75 moles of periodate per 100 AHG units had been consumed. Portions of the former samples were subjected to a second treatment with periodate, basing the amount of periodate used on the AHG contents of the once-oxidized products as shown by analysis.

As shown by the oxidation curves in Figure 12, the TMM sample reacted initially somewhat more readily than the DMM, the two samples requiring 16 and 21 days, respectively, to consume 40 moles of periodate per 100 AHG units. An increasing rate of periodate consumption then followed with each of the samples. The samples recovered and borohydride reduced after 16 and 21 days for the TMM and DMM materials, respectively, also responded to the second oxidation treatment in a similar manner, the two samples consuming a total of ca 100 moles periodate per 100 AHG units after an additional 4 days of oxidation. After the intermittent borohydride reduction, periodate oxidation occurs at a much faster rate, as shown in Figure 12.

Analytical data obtained for the six products after borohydride reduction are compiled in Table XXI. The percent of nitrogen found in the water-insoluble fraction is shown together with the percent of AHG units oxidized. The latter was calculated after analyzing the hydrolyzed insoluble fractions for percent of glucose as determined from the ratio of peak areas representing the trimethylsilyl ether derivatives of erythritol and glucose in gas-liquid chromatograms. A correction for the unidentified, two-carbon fragment glycolaldehyde was included. These values represent the total sample, assuming that the water-soluble portion of the products contained oxidized cellulosic materials only. The weight percent of insoluble product found experimentally is also shown. The fraction of insoluble product expected, calculated from the percent nitrogen found in that portion and assuming that all the resin is contained therein, is shown in the last column.

Table XXI. Analysis of TMM and DMM Dry-Cured Samples (Insoluble Fractions) after Oxidation-Reduction

Sample and no. of treatments	Oxidation time (days)	Periodate consumed (moles per 100 AHGU)	Nitrogen found, % (insol. fraction)	AHG* units oxidized (%)	Insol. Fraction** wt. % found	calc'd
TMM	(control)		6.02			
1	16	39	6.08	17	92	99
1	25	75	7.17	36	82	84
2	16 + 4	94	6.40	54	85	94
DMM	(control)		7.05			
1	21	42	7.24	23	95	97
1	29	74	8.22	34	88	86
2	21 + 4	100	8.43	73	73	83

* Based on glucose analysis of insoluble fraction.
** Calculation based on percent nitrogen found in insoluble fraction.

The portion of insoluble products found generally agreed well with the calculated values in the case of the samples oxidized only once. When compared to the periodate consumption data, glucose contents of the insoluble products showed that the secondary oxidation reaction had occurred to an appreciable extent during the relatively long oxidation times required. Extending the oxidation time from 16 and 21 to 25 and 29 days for the TMM and DMM samples, respectively, approximately doubled the percent of AHG units oxidized. The fraction of cellulose becoming soluble after reduction was also approximately doubled. Intermittent reduction resulted in a sharp increase in the fraction of cellulose oxidized when followed by 4 days of additional oxidation. The observation that the insoluble fraction found after the two oxidations was ca 10% less than the value calculated from the nitrogen contents of the insoluble products may mean that some of the resin was contained in the soluble fractions of the twice-oxidized samples. This point will be clarified in future work.

TMM and DMM samples oxidized for 16 and 21 days, respectively, together with the portions oxidized after reduction for an additional 4 days were treated with excess phenyl isocyanate (sealed tube) for 16 hours in a boiling water bath. The resulting weight increase data and nitrogen contents of the products are shown in Table XXII.

Table XXII. Data from Carbanilation and Hydrolysis Treatments of Oxidized TMM and DMM Samples

Sample & oxidation time (days)	Carbanilation		Hydrolysis of Resin		
	Wt. inc. (%)	Nitrogen (%)	Insol. (%)	Sol. (%)	Nitrogen %, sol. fraction
TMM					
16	176	10.09	13	65	8.15
16 + 4	196	10.14	12	64	8.34
DMM					
21	184	10.55	15	66	8.21
21 + 4	195	10.72	14	52	8.49

The carbanilated products were hydrolyzed in 0.05 N HCl (95% aqueous dioxane) for 18 hours. The soluble fractions were precipitated into a large excess of water, the percent of sample thus recovered being shown in Table XXII together with the nitrogen content of the soluble fraction. As seen from the data, a significant portion of the sample was not precipitated by water. That fraction must consist of very low molecular weight fragments arising from the oxidized-reduced regions of the cellulose. If the hydrolytic removal of the resin is accomplished with acid of a lower concentration (0.02 N HCl), the fraction that cannot be precipitated in water at this point is considerably smaller as can be seen in Table XXIII, which shows yields and nitrogen contents for samples with periodate oxidation times similar to the ones reported in Table XXII.

Table XXIII. Mild Acid Hydrolysis of Carbanilated TMM Products

Sample oxidation time days	Yields insol. (%)	sol. (%)	total	Nitrogen Content (%) insol. fraction	sol. fraction
16	12.4	82.9	95.3	13.90	7.30
16 + 4	16.8	76.2	93.0	22.13	7.82
24	3.4	84.4	87.8	19.37	8.43
24 + 9	3.2	88.8	92.0	20.53	8.61

An understanding of the nature of the fractions remaining insoluble during the mild acid hydrolysis experiments has posed a problem of considerable importance from the beginning of these studies. The nitrogen contents of those fractions have generally been of the order of 20%. Fully carbanilated cellulosic materials are calculated to contain ca 8% of nitrogen, and the insoluble products must therefore contain an appreciable amount of material derived from the melamine, TMM containing 50.9% of nitrogen. The insoluble fractions described in Table XXIII were also examined by x-ray diffraction techniques, powder diagrams being obtained using a Debye-Scherrer camera. In addition to considerable scatter representing amorphous material, the presence of arcs having spacings identical to those of native cellulose were observed in the insoluble residue specimen, showing that uncarbanilated, crystalline cellulose is present in those residues. This was confirmed when completely carbanilated cellulose gave only the scatter of an amorphous material after prolonged exposure.

2. Periodate Consumption of Weathered Samples

Preliminary results suggested that periodate oxidation could provide a sensitive index of chemical structure changes involving resin degradation. Therefore a series of TMM resin-treated samples, exposed to outdoor weathering for different periods up to 21 months, were obtained from the Natick Laboratories and was subjected to periodate oxidation for 8 days

in the fabric form. The periodate consumption data obtained are shown in Table XXIV and the data from representative samples are plotted in Figure 13.

Table XXIV. Periodate Oxidation of Weather-Exposed TMM Dry-Cured Cotton Duck

Exposure time (mos)	Atoms Oxygen/100 AHG Units with increasing oxidation time (days)							
	1	2	3	4	5	6	7	8
0	19	27	32	38	41	43	46	60
2	30	36	44	60	78	100	124	157
4	35	43	61	88	98	117	135	158
6	38	51	73	99	107	122	136	156
8	39	56	73	94	105	121	134	151
10	45	59	87	105	110	120	131	146
12	42	62	86	107	112	118	130	148
14	44	62	84	103	109	118	130	144
16	48	66	91	106	107	115	122	136
18	55	73	91	104	104	110	117	126
21	55	71	88	98	102	107	114	122

As shown in Figure 13, the initial oxidation rate increased dramatically with increasing exposure time. As exposure reached the final 21 months the rate of oxidation became indistinguishable from that of untreated cotton fabric, and the "resistance" to periodate oxidation exhibited by TMM dry-cured samples had been completely lost.* When the periodate oxidation time had reached about the 5th day, the situation began to be reversed until ultimately the final periodate consumption values decreased with increasing time of exposure. This reversal in periodate consumption can be attributed to the occurrence of the secondary

* In all cases cotton treated with melamine resins by dry-curing processes have shown a resistance to periodate oxidation, i.e., a major portion of the cellulose which has been shown not to be involved in bonding with resin will react with periodate only after intermittent borohydride reduction or with the occurrence of an extensive secondary oxidation reaction.

oxidation reaction customarily observed with TMM-treated cotton. The nitrogen contents of the samples are shown in Table XXV, and these decreased with increasing exposure time. The secondary oxidation reaction is not observed with cotton cellulose, and therefore must involve the resin in some way. The decreasing resin content of the samples exposed longer would then explain the decreasing rate of oxidation after the 5th day, when the secondary reaction becomes important. Wrinkle recovery (warp direction) values obtained on the weathered samples are also shown in Table XXV. The original resin treatment resulted in an increase in dry wrinkle recovery (warp direction) from 67° (cotton control sample) to 116°. This improvement in wrinkle recovery had been almost completely lost during exposure for only 4 months, and after 10 months the fabric showed no significant difference in wrinkle recovery from the untreated cotton.

Selected samples were reduced with borohydride for subsequent analysis and pertinent data obtained are shown in Table XXVI. The fraction of sample remaining insoluble after borohydride reduction is shown together with nitrogen and

Table XXV. Analysis of TMM Dry-Cured Cotton Duck after Different Weathering Exposure Times

Exposure Time months	Nitrogen (%)	Wrinkle Recovery (warp) degrees
0	7.30	116
2	4.43	101
4	4.09	84
6	3.87	83
8	3.84	82
10	3.42	74
12	3.40	79
14	2.93	79
16	2.46	76
18	1.78	73
21	1.21	-
Cotton control	-	67

Table XXVI. Analysis of Insoluble Fractions after Oxidation-Reduction of Weathered Samples

Exposure time months	Insoluble Fraction Weight % Found	Calc'd from % N	AHG Units remaining (%)	Nitrogen, % initial insol. fraction	
0*	99.0	-	47	7.30	7.20
2	66.8	65.6	20	4.43	6.75
4	63.0	64.4	14	4.09	6.35
8	58.3	68.4	19	3.84	5.61
12	58.0	64.8	15	3.40	5.25
18	none	-	3	1.78	-

*These data, taken from Progress Report No. 5, pertaining to the unexposed dry-cured material oxidized for 10 days, are included for comparison.

glucose analyses of those fractions and the expected insoluble fraction calculated from the nitrogen contents. Considering the marked increase in the initial rate of periodate consumption with concomitant loss in wrinkle recovery as exposure time increased, the water insolubility of the product after borohydride reduction remained remarkably high through 12 months of exposure. After only 2 months exposure the insoluble fraction had dropped from 99% (no exposure) to 67%, and this value had dropped only another 9% after 12 months exposure. After reduction of the 18 months exposed sample it was not possible to recover an insoluble fraction by filtration, the sample being almost completely soluble in water. Nitrogen analyses showed that the resin was contained in the insoluble fraction of the products when the values found were used to calculate the expected weight percent of insoluble fraction, and the results agreed generally with the weight percent of insoluble fraction found.

The gradual loss of "resistance" to periodate oxidation and of wrinkle recovery which are observed with increasing

exposure time could be attributed to a breaking of effective chemical crosslinks during exposure. These samples have been noted [58] to show a gradually increasing solubility in cuprammonium hydroxide with increasing exposure time until complete solubility was reached after 14 months exposure. These results suggest that periodate oxidation might serve as a useful method for gaining information regarding the degradative reactions occurring during exposure. In the periodate study the significance of the plateau between 2 and 12 months in the solubility vs exposure time curve as compared to the gradual increase in cuprammonium solubility with increasing exposure time during that period might provide an insight into the nature of the incident actinic degradation.

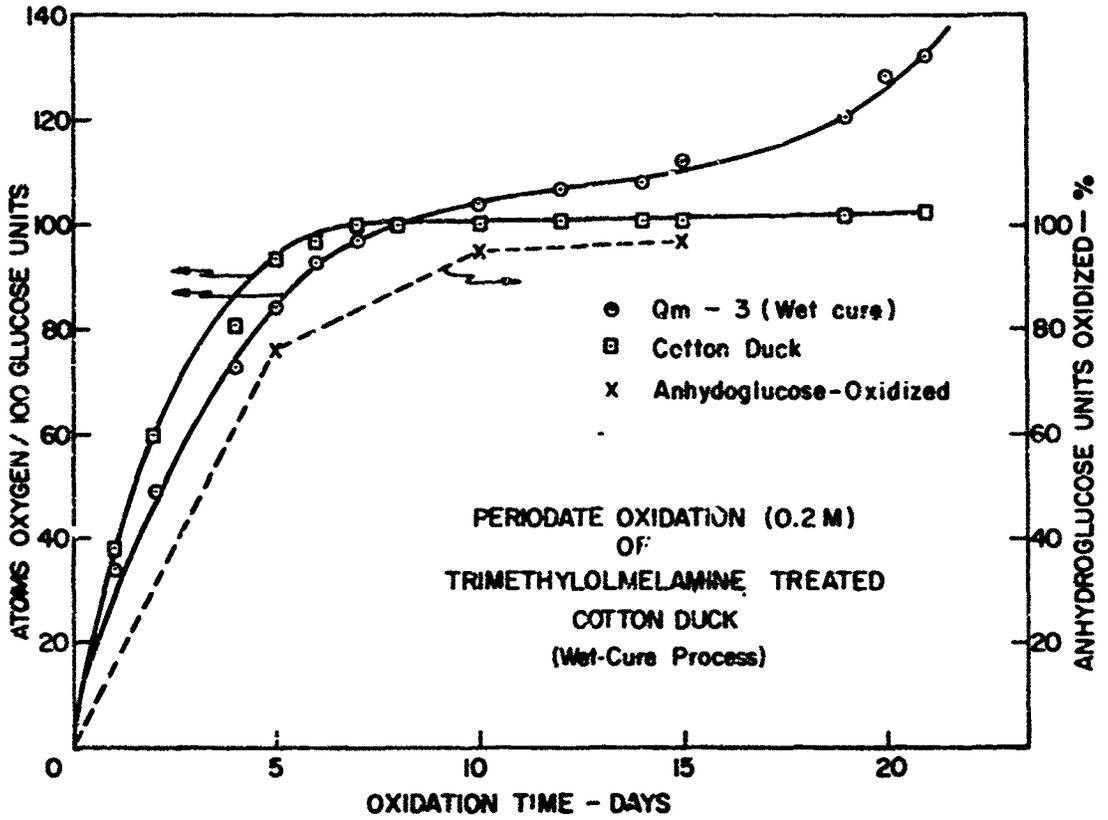


Fig. 11. Periodate Oxidation (0.2M) of Trimethylolmelamine Treated Cotton Duck.

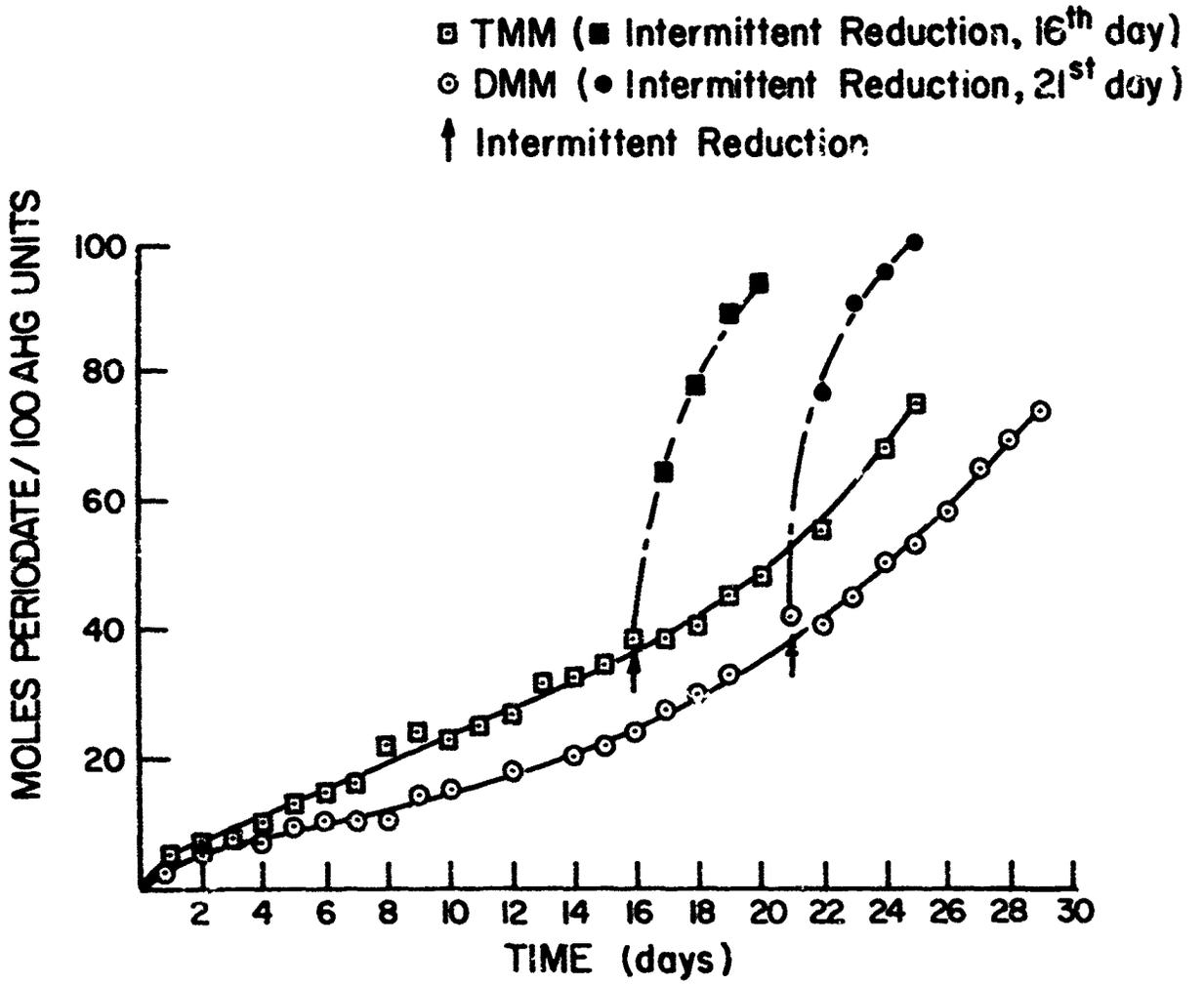


Fig. 12. Periodate Oxidation of TMM and DMM Dry-Cured Cotton Print Cloth with Intermittent Reduction.

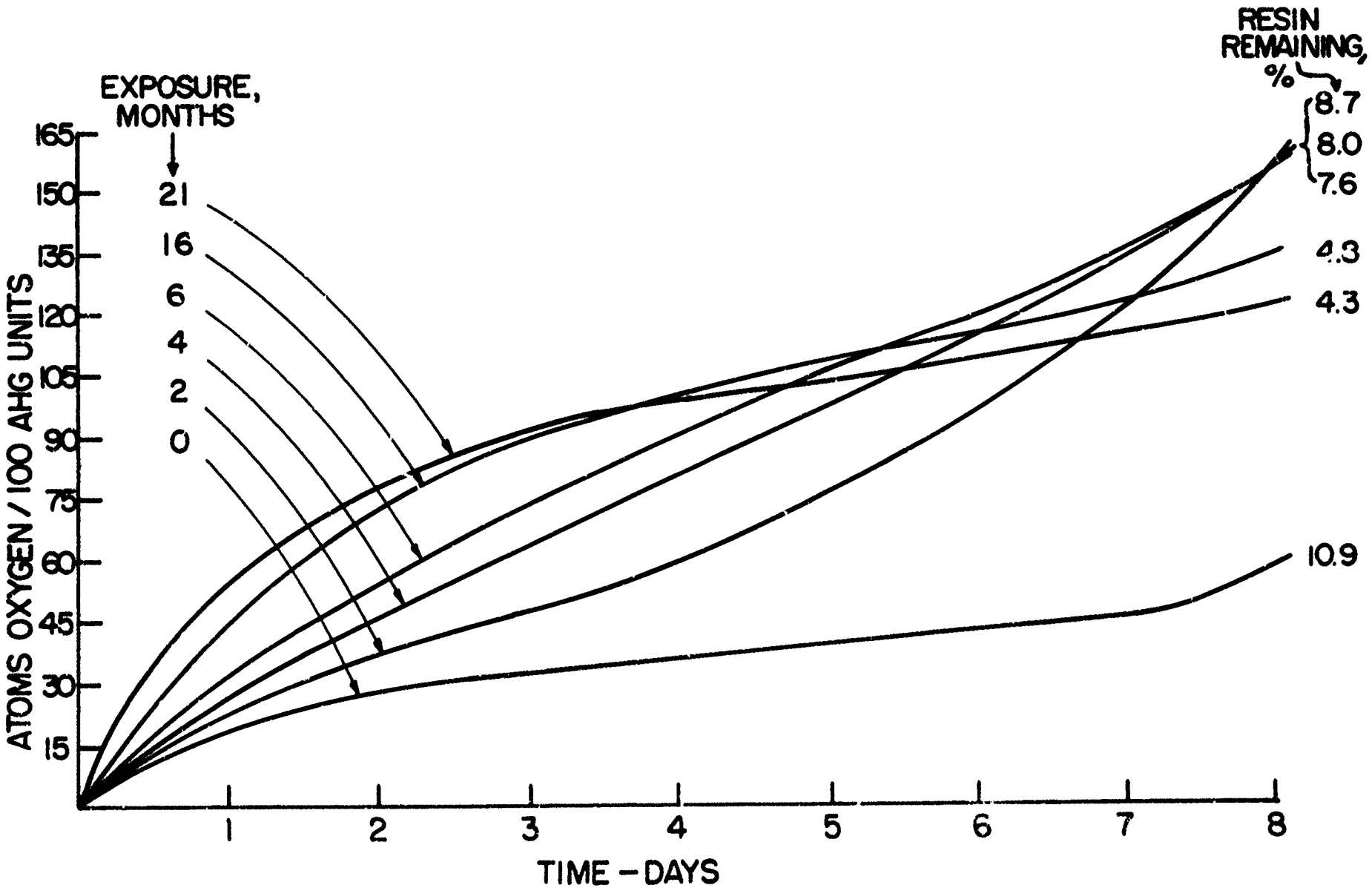


Fig. 13. Periodate Oxidation of Exposed, TMM Dry-Cured Cotton.

CHAPTER VI. MICROSCOPIC INVESTIGATIONS

A microscopic investigation of yarns removed from treated fabrics was undertaken in order to obtain information about the distribution of resin among the various fibers in the yarn. Since the yarns do not retain sufficient strength after oxidation for mounting for a microscopic investigation, they were carefully removed from the resin-treated fabrics (TMM dry-cured cotton sheeting) prior to oxidation. Analytical data obtained on the separated warp and filling yarns from three fabric samples are compiled in Table XXVII.

Table XXVII. Data on Warp and Filling Yarns Removed from TMM-Treated Cotton Sheeting and Cotton Sheeting Control

	Warp wt. %*	Nitrogen % *	Moisture regain %*	Filling wt. % **	Nitrogen % **	Moisture regain %**
TMM-treated	56.55	7.23	5.86	43.45	6.65	6.05
Control	57.52	-	6.36	42.48	-	6.36

* Warp yarns
** Filling yarns

In all the samples tested the warp yarns, heavier than the filling yarns, were found to contain a small but significantly greater proportion of resin, based on nitrogen contents. The moisture regain values of the warp yarns were reduced further from the cotton control values. The fact that the warp showed a relative weight loss of 1% on resin treatment, in spite of having a larger proportion of resin based on nitrogen, probably results from a removal of sizing during an alkali scouring treatment given the fabric before resin treatment but omitted in the cotton sheeting control.

Periodate oxidation curves obtained on the warp and filling yarns in solutions buffered at pH 5.2 are shown in Figure 14. After an induction period of 2-3 days, the reaction proceeded smoothly to the 11th day without evidence of appreciable over-oxidation. Subsequent oxidations for 3-day intervals showed a reduced reaction rate. A comparison of the relative oxygen consumption by warp and filling yarns does not reveal significant differences.

1. Microscopic Examination of Treated Yarns

Microscopic examination of 3 to 6μ cross sections of yarns of the different reaction products was accomplished by phase contrast microscopy. When possible, the yarn was mounted on an aluminum supporting frame and embedded in polymethacrylate or epoxy resins by conventional techniques [59]. When a reaction causes a severe loss of yarn strength, it becomes necessary to carry out subsequent reactions on previously mounted yarns. Untreated control cotton yarns from the fabric and yarns oxidized during three successive treatments (Figure 14) were embedded in methacrylate for examination. Photomicrographs of typical cross sections are shown in Figure 15. The majority of the fibers in the yarns maintain their identity through the first two oxidation treatments, although evidence of dissolution of portions of some fibers is apparent in C. After the third oxidation many of the fibers have lost the smooth contour of their outer surface, and in some instances it appears that only fragments of given fibers remain. Some fibers remain, however, that appear to be unchanged by the oxidation and reduction treatments.

The phenomenon sometimes called the "methacrylate explosion", in which a fiber immersed in methacrylate becomes enormously expanded in size during the polymerization process, has been known for several years [60,61]. As demonstrated by the photomicrographs in Figure 15, dry cotton fibers do not expand in size when embedded in methacrylate. However, recent work in the

TRI laboratories has shown that when esterified cotton fibers are embedded in methacrylate in the dry state, they undergo an expansion in size up to two orders of magnitude. Thus, it has been possible to appraise qualitatively the uniformity of an esterification reaction among the numerous fibers in a cotton yarn. The "methacrylate explosion" phenomenon is demonstrated by the photomicrographs in Figure 16. Cotton yarns were swollen at 5°C in 10% sodium hydroxide and solvent exchanged to the desired embedding medium. A cotton yarn thus embedded in an epoxy resin is shown in E, the fibers having the customary appearance of a cross section of a cotton yarn in its natural state. A portion of an identically treated yarn embedded in methacrylate is seen in F, where an enormous swelling has occurred and separation of the lamellae of each fiber is distinctly visible. Based on the work of Dlugosz [60], who used dissolution techniques for the cellulose and the polymethacrylate in turn on cross sections similar to those in F, it may be concluded that the lighter areas of this picture correspond to the cellulose. A cross section of a portion of a yarn from cotton sheeting benzoylated to DS 1.4 is seen in C. This photomicrograph demonstrates the swelling which results when esterified cotton is embedded in methacrylate. Evidence for the separation of cellulose growth layers, or lamellae, is again apparent although less distinct than in the alkali-swollen fibers seen in F.

The oxidized and reduced samples shown in Figure 15 were mounted on aluminum frames, placed in sealed pyrex tubes containing anhydrous pyridine and phenyl isocyanate and carbanilated for 24 hours at 100°C to insure complete reaction. The specimens were carefully removed, washed thoroughly with ethanol, and dried. It can be expected that portions of the carbanilated products were lost in this way since it has been found that carbanilated products are recovered in high yield only when precipitated into aqueous ethanol, which was not possible in this instance. The carbanilated yarns were embedded in polymethacrylate, and views of two typical cross sections are seen in Figure 17.

Photomicrographs H and I demonstrate two distinctly different situations. Several fibers in the yarn have undergone the swelling characteristic of esterified fibers. Many other fibers, however, appear identical to those in Figure 15 which show the same oxidized samples prior to carbanilation. The samples oxidized two and three times prior to carbanilation are seen in pictures J and K, L and M, respectively. Although evidence of "exploded" fibers, or portions of fibers, is abundant, a few fibers remain which are clearly unaltered even after the three oxidation treatments.

As described earlier, x-ray diffraction results and nitrogen analyses show that the insoluble residues after the mild acid hydrolysis reaction are comprised of a large proportion of resin and some crystalline cellulose. Therefore, even in the case of highly oxidized samples, a small portion of the sample was not carbanilated. This small insoluble residue is logically associated with the fibers seen in these photomicrographs, since a failure of certain fibers to carbanilate would result in a failure of those fibers to undergo the explosion in polymethacrylate. Two identical fibers would not be expected to respond in a grossly different way to the carbanilation treatment, and since the samples only partially react with sodium periodate in the first instance, it is reasonable to assume that the distinction arises from the oxidation reaction. Taken together, these observations indicate that some fibers in the treated yarns contain enough resin to render them highly resistant to periodate oxidation. Although the carbanilated fibers seen in Figure 17 have undergone a large swelling, nowhere is a clear separation of the lamellae visible, as is distinctly clear in the swollen cotton sample and the benzoylated yarn seen in Figure 16. This situation may be due to the presence of effective chemical cross-linking of the lamellae of the fibers by the TMM.

An understanding of the gross effect of Smith degradations (periodate oxidation followed by borohydride reduction) is

prerequisite for a complete chemical analysis of the location and distribution of resin-substituted groups. A microscopical examination of the course of the periodate attack, within and among the resin-treated fibers, was therefore performed. Cotton print cloth (80 x 80) was treated with pure TMM and DMM resins following the Berard [3] dry-cure method to yield samples with low resin contents (6.9% TMM and 7.6% DMM). A cotton duck sample, obtained from the U. S. Army Natick Laboratories, wet-cured by the Arigal C process (9.0% resin) was also used in the study.

Yarns separated from the treated fabrics were oxidized with 1 M excess of 0.2 M sodium periodate solution buffered at pH 5.2 followed by borohydride reduction. This procedure was repeated three times. At each stage during the Smith degradation treatments fibers were removed from the yarns, mounted in water, and photomicrographs were prepared using transmitted light. The water was then removed by blotting, and was replaced by cadoxen [62], and photographs were taken again after 20 minutes. Changes in fiber appearance occurred after that time only in the cases of the DMM and Arigal C control samples. Periodate consumption data and oxidation times, as well as the solubility of fractions during reduction, are shown in Table XXVIII.

Table XXVIII. Periodate Oxidation of Melamine-Formaldehyde Dry- and Wet-Cured Cotton during Successive Smith Degradations

Sample	Cure	Successive oxidation times, hrs	Moles periodate/ 100 AHG units	Fraction of sample sol. during reduction, %
TMM (6.9% resin)	dry	47	29	12
		51	66	28
		46	60	ca 70
DMM (7.6% resin)	dry	47	25	10
		51	64	24
		46	70	72
Arigal C (9.0% resin)	wet	41	35	62
		81	67	6.

Photomicrographs of fibers from the TMM, DMM and Arigal C samples are shown in Figures 18 to 20, respectively. Insolubility in cellulose solvents has been used commonly as a criterion of cross-linking in chemically modified cellulose. The DMM and Arigal C samples, contrary to the TMM sample, exhibited pronounced swelling at intervals along some fibers after 20 minutes in cadoxen. This swelling was more pronounced, involving most fibers in the sample, after 2 hours in cadoxen. The aldehyde groups formed by periodate cleavage in cellulosic fibers lend high sensitivity to alkaline degradation. The oxidized regions of fibers degrade rapidly in cadoxen, which is 0.35 N in sodium hydroxide, while fibers not oxidized would appear unaltered. The first oxidation treatment clearly penetrated all the fibers in the DMM and TMM samples as shown by the extensive degradation which occurred in cadoxen. This would not necessarily be expected in view of the fact that only one in five anhydroglucose units was oxidized during the treatment.

Little or no swelling in water was evident after the borohydride treatment. Reduction of the aldehydes to alcohols confers alkali stability to the modified cellulosic fibers. Most fibers showed appreciable swelling and all fibers remained intact in cadoxen after the reduction. The Arigal C sample exhibited far more pronounced swelling than the dry-cured samples, reflecting marked differences in the nature and/or the extent of cross-linking. Following the second Smith degradation, fiber appearance of the dry-cured samples followed the same general pattern exhibited after the first treatment. Some swelling in water had become evident after the reduction step; attention should be called to the nonrepresentative fibers which appeared unswollen in cadoxen after that reduction. Significant portions of the samples (28 and 24%, respectively, for TMM and DMM) dissolve during the reduction step.

In view of the fact that the DMM and TMM samples consumed 60 and 70 moles, respectively, of periodate during the third oxidation treatment, the chemical stability to alkali observed when the fibers were examined in cadoxen was unexpected. No evidence of fiber degradation was found with either sample. Portions of some fibers in the Arigal C sample also exhibited alkali stability after each of two oxidation treatments. At no point, however, was complete retention of fiber form observed in the case of the wet-cured sample. The retention of total fiber integrity in cadoxen can only be explained by the formation of high uniform levels of conversion to the alkali-stable, modified cellulose during the first two Smith degradations. This degraded cellulose, known to be water soluble, must be cemented together by resin bridges, providing cadoxen stability and insolubility.

During the reduction step of the third sequence of reactions, a drastic change in the physical state of the dry-cured samples occurs. (This change resulted after the second Smith degradation with the Arigal C sample.) As a whole, the samples lose their fibrous nature almost completely and become highly swollen, gelatinous materials which are recovered after drying as horny residues. Approximately 70% of each sample dissolved in the reducing medium, showing that extensive degradation had occurred. This degradation is indicated to be something other than alkaline degradation, since the oxidized fibers appeared stable in cadoxen. Since these photographs were taken, it has been observed that fiber segments are clearly visible microscopically after the reduced products are swollen in water overnight. The intact fibers appearing at this high level of oxidation probably resisted oxidation by periodate and were not apparent after earlier stages of oxidation due to nonrepresentative sampling. These fiber residues are probably associated with those which were not swollen by cadoxen after the second Smith degradation.

The insoluble residues encountered after acid hydrolysis treatments of carbanilated samples can probably be correlated with the intact fibers seen to resist three Smith degradations. X-ray diffraction patterns revealed the presence of unmodified crystalline cellulose in those residues, and it was estimated previously that they comprise up to 20% of the original cellulose and 50% of the total resin in certain samples. Before definitive analyses of the location and distribution of substituent groups can be accomplished, a means of incorporating these resistant fibers into a suitable analysis scheme must be accomplished.

The sharp contrast between wet- and dry-cured samples in cadoxen following sequential Smith degradations is indicated to provide a rapid and convenient method for establishing the nature and the extent of cross-linking in cellulose. The retention of a swollen, fibrous form in cadoxen following the third oxidation treatment shows clearly that the modified cellulose in the fibers is cemented together by resin cross links. Examination by these techniques is indicated to provide a rapid method for assessing any cellulose chemical treatment for uniformity and effectiveness of covalent cross-linking.

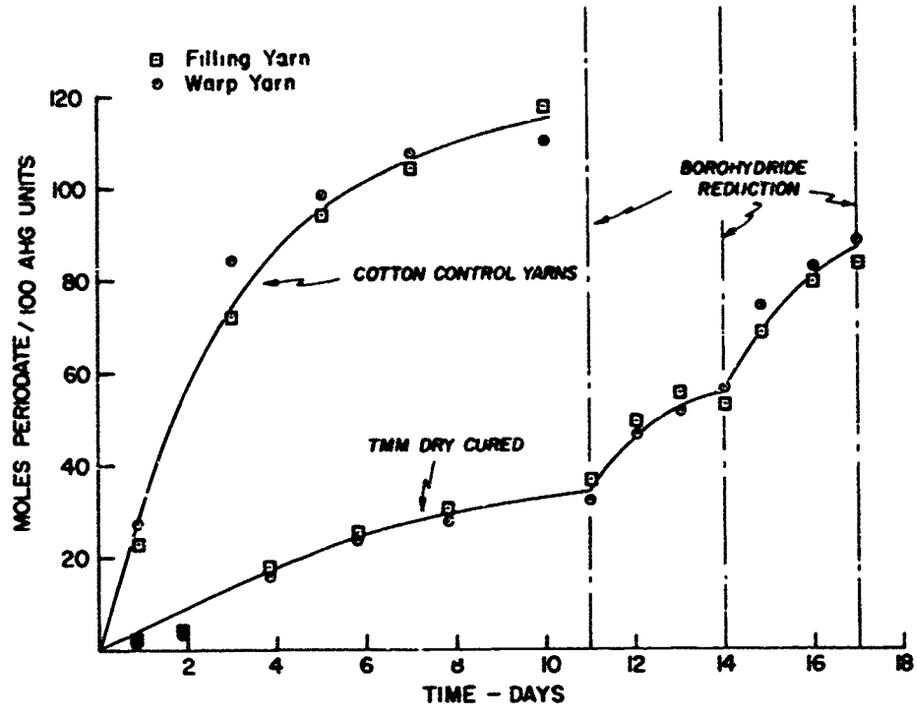


Fig. 14. Periodate Oxidation of TMM-treated Cotton Sheeting, Buffered at pH 5.2.

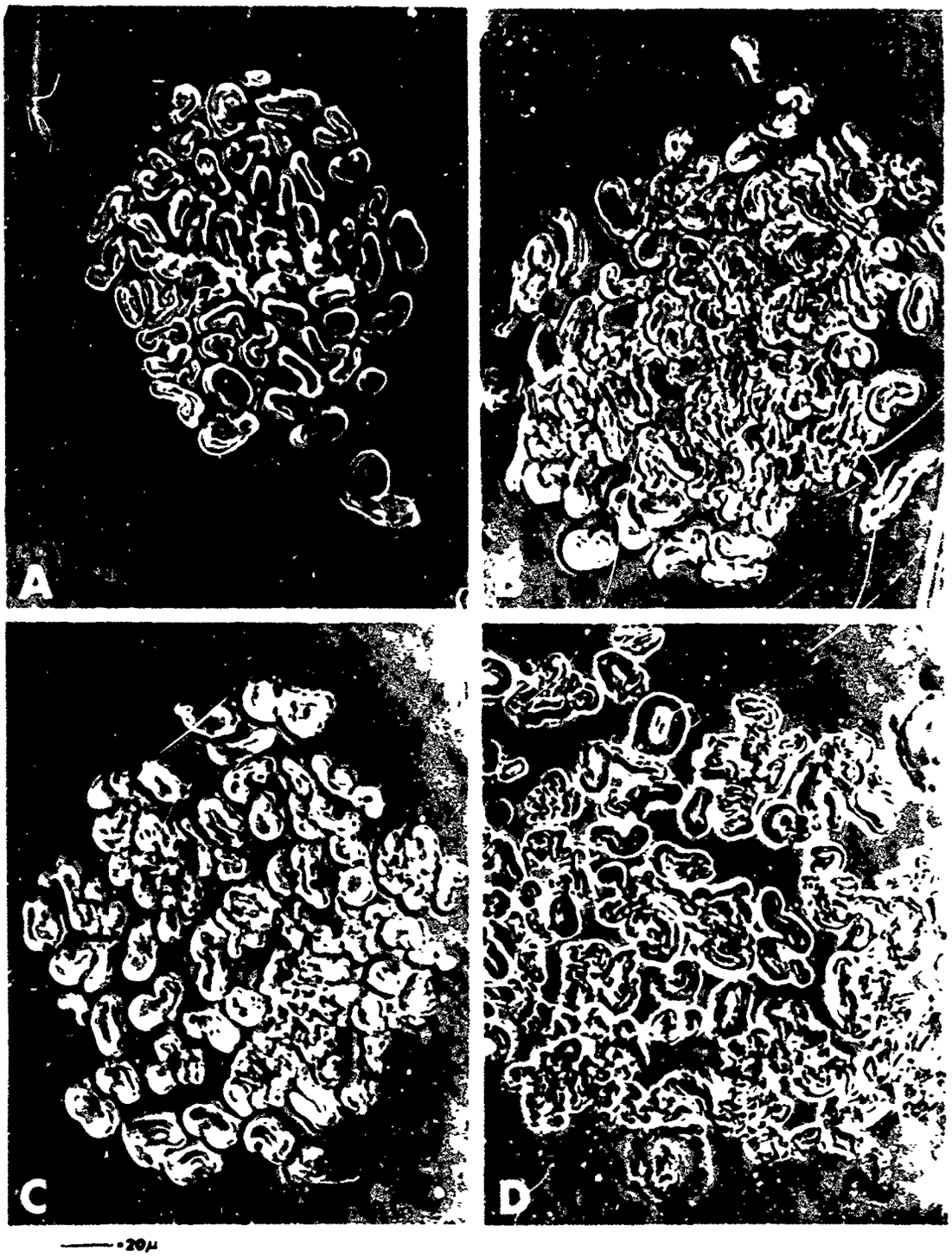


Fig. 15. Photomicrographs of Oxidized-reduced Yarns from TMM-treated Cotton Sheetings (A) unoxidized; (B) one oxidation treatment; (C) two oxidation treatments; (D) three oxidation treatments.

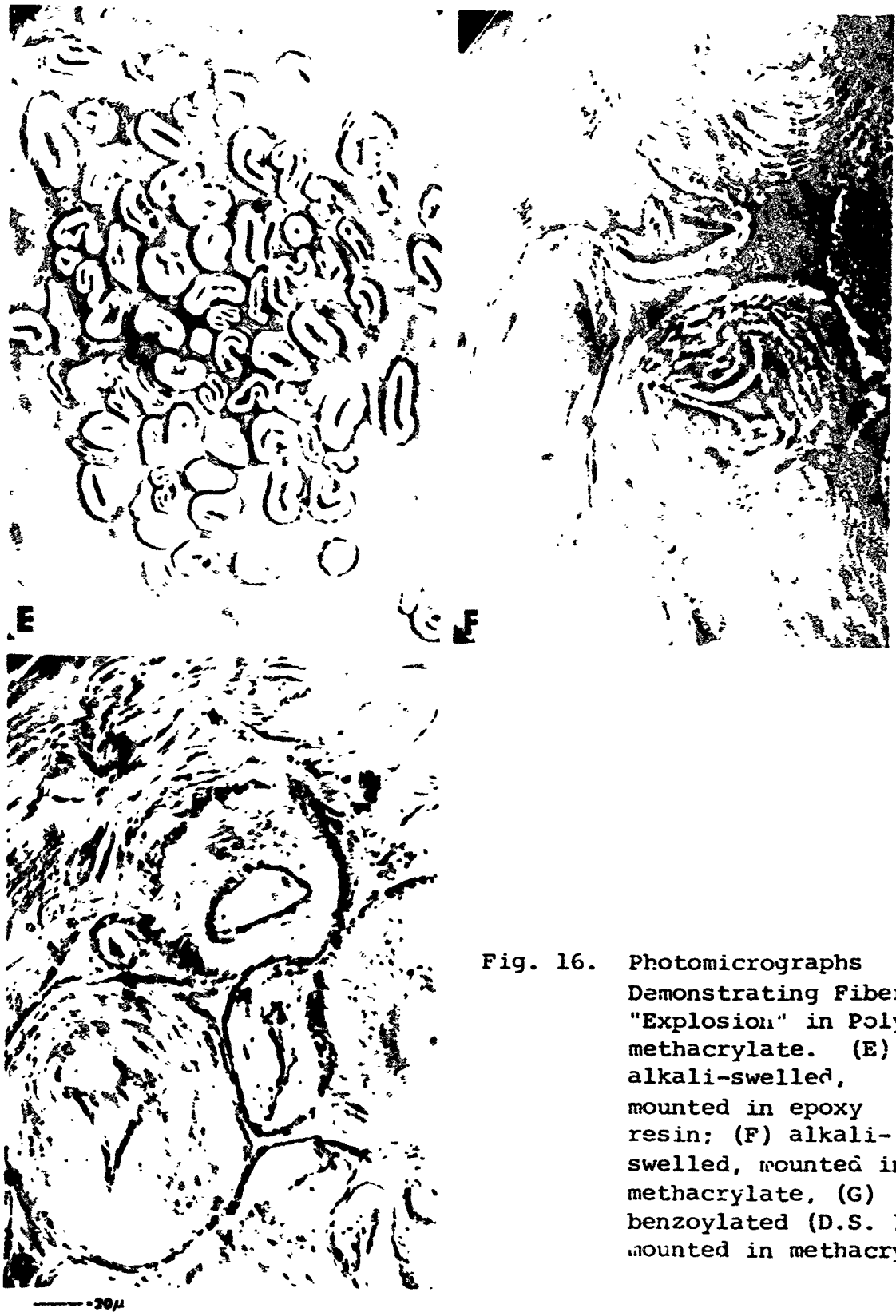


Fig. 16. Photomicrographs Demonstrating Fiber "Explosion" in Polymethacrylate. (E) alkali-swelled, mounted in epoxy resin; (F) alkali-swelled, mounted in methacrylate, (G) benzoylated (D.S. 1.4) mounted in methacrylate.

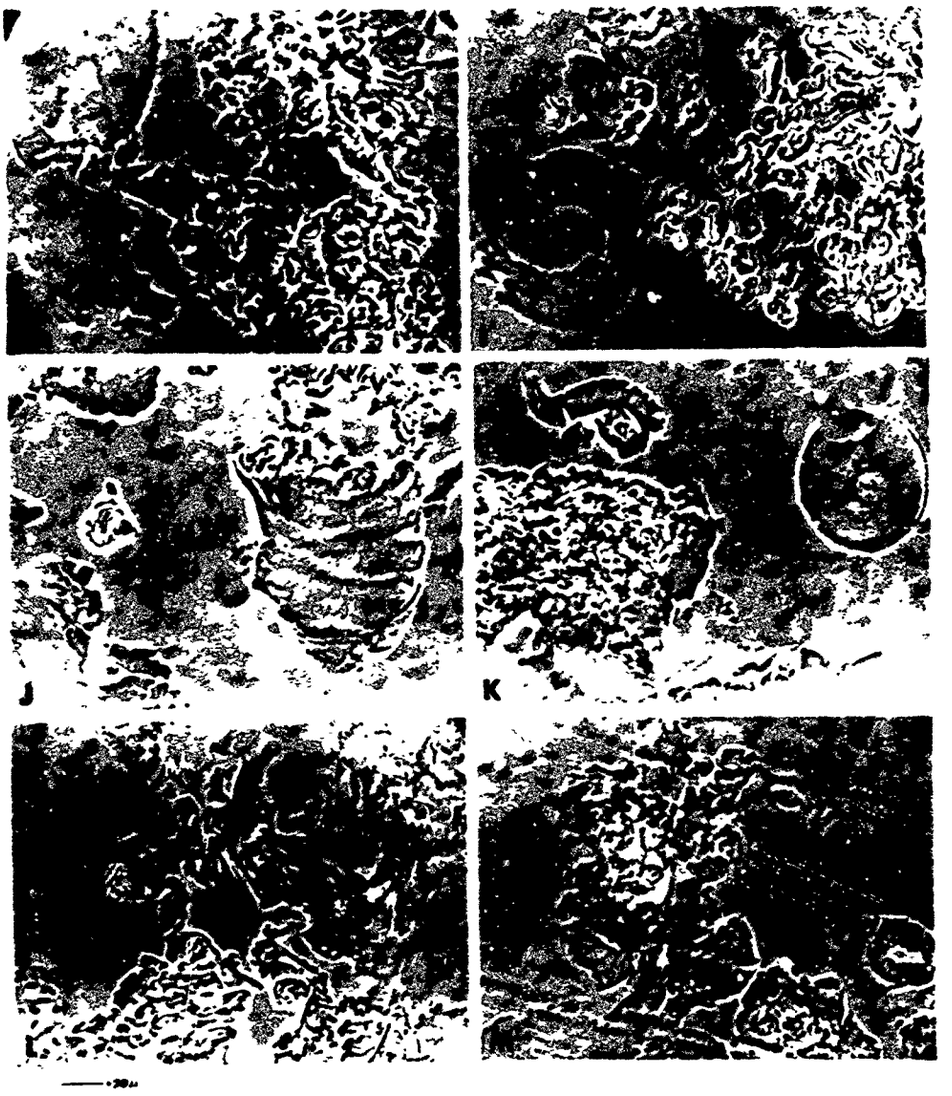


Fig. 17. Photomicrographs of Yarns at Different Oxidation Levels after Carbanilation (H,I) one oxidation treatment; (J,K) two oxidation treatments; (L,M) three oxidation treatments.

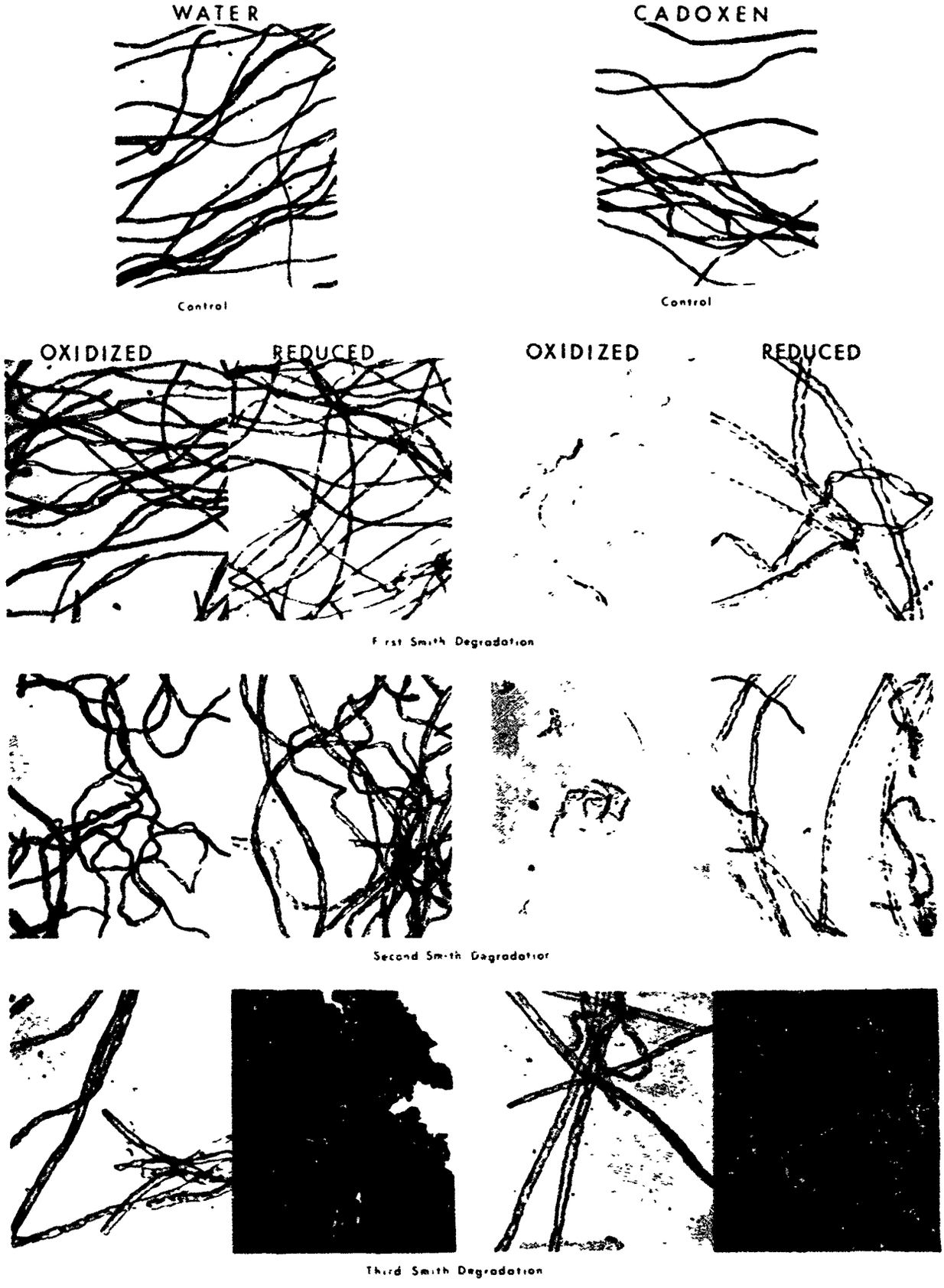


Fig. 18. Fibers from TMM Dry-Cured Fabric, in Water and in Cadoxen, after Sequential Smith Degradations.

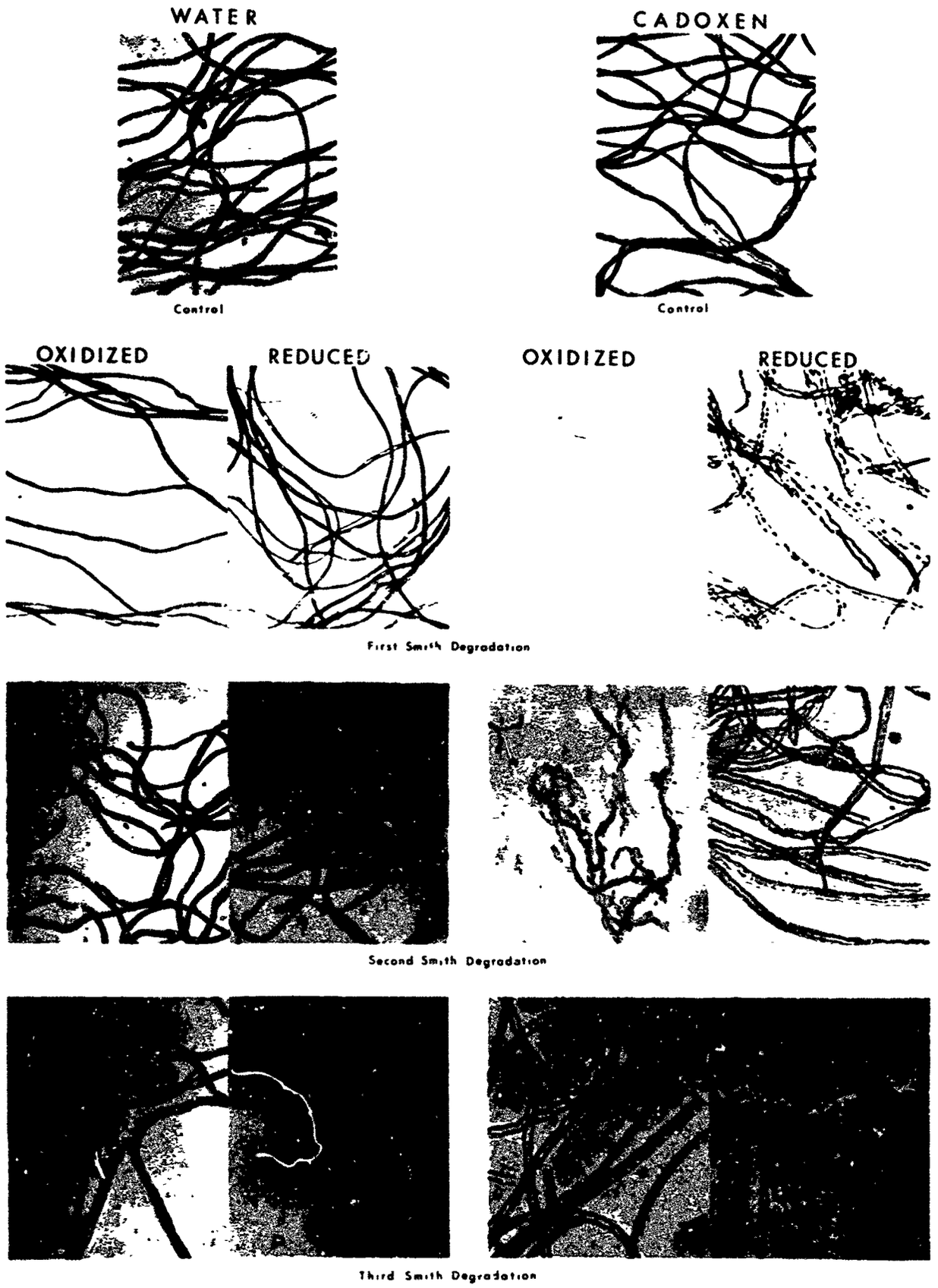


Fig. 19. Fibers from DMM Dry-Cured Fabric, in Water and in Cadoxen, after Sequential Smith Degradations.

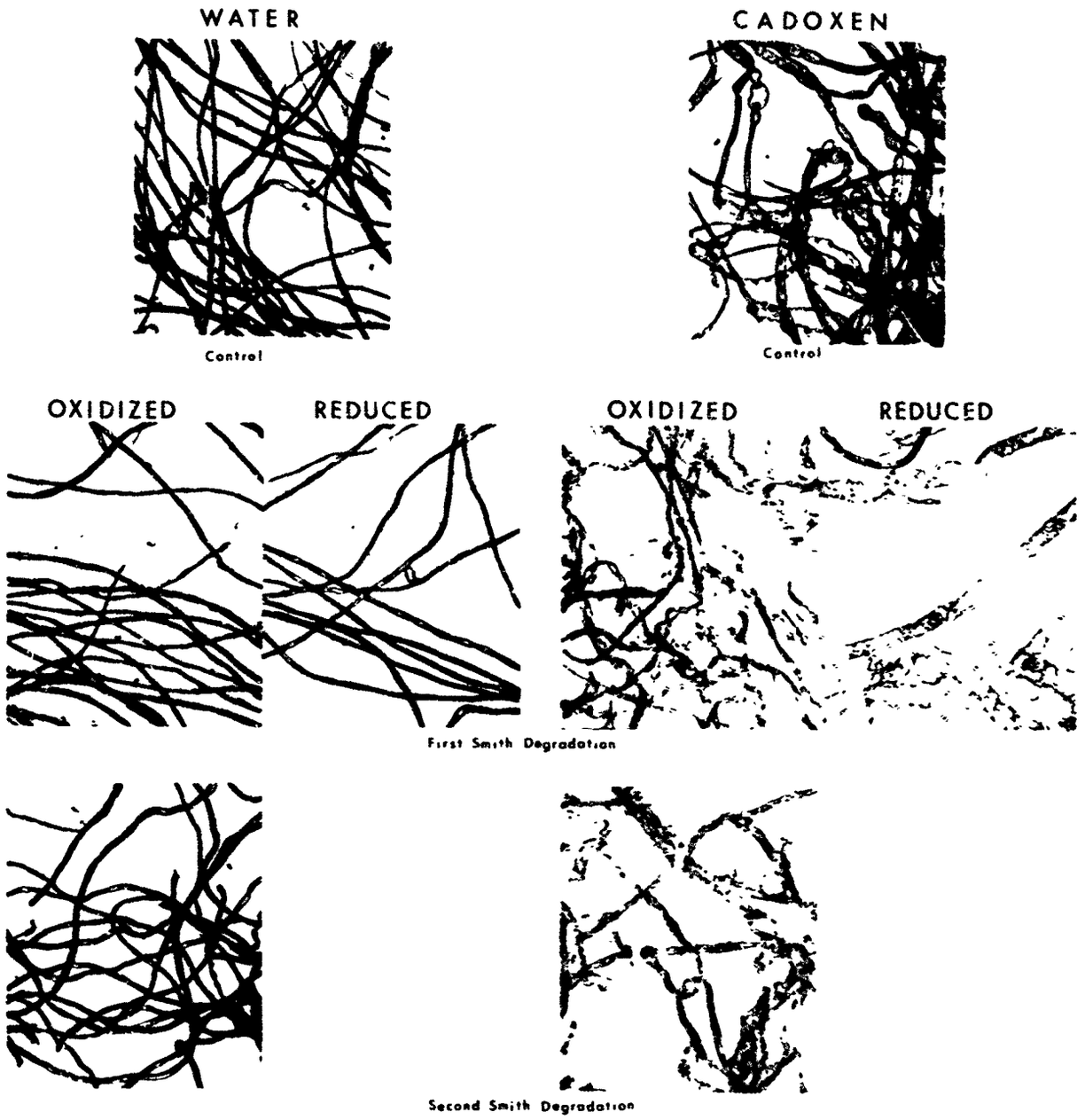


FIGURE 20.

FIBERS FROM ARIGAL C WET-CURED FABRIC, IN WATER AND IN CADOXEN, AFTER SEQUENTIAL SMITH DEGRADATIONS

CHAPTER VII. DISTRIBUTION OF RESIN SUBSTITUENTS ALONG THE CELLULOSE CHAIN

1. Solubility Studies on Degraded Resin-Treated Cellulose

One aspect of the problem of the distribution of resin and resin substituent groups in the cellulose lies in determining the fraction of the cellulose molecules involved in such bonding and their location in the cotton fiber. If that portion of cellulose not involved in bonding could be physically separated from that which is bonded, the problem of the distribution along the individual cellulose macromolecules would be simplified. Although cotton fabrics treated with melamine resins by dry-curing processes are completely insoluble in cellulose solvents [1], it has been found that periodate oxidation followed by reduction renders considerable portions of the cellulose soluble in cadoxen.

Numerous solvents for cellulose are widely used, but the solvent cadoxen appears to have several distinct advantages over others, including the following: 1) it is easily prepared and it is stable during storage at room temperature, 2) the solution is transparent before and after the cellulose is dissolved, 3) oxidative degradation of cellulose is generally negligible, and 4) the cellulose is readily regenerated from solution. Cadoxen consists of a solution of cadmium oxide (5% Cd) in 28% aqueous ethylenediamine which is 0.35 N in sodium hydroxide. A cadoxen solution was prepared according to the method of Henley [63] and was found to dissolve cotton linters or yarns readily. The oxidized TMM samples were treated with the solvent for 24 hours at room temperature. The insoluble portions, still having the appearance of intact yarns, were removed by filtration and the soluble portions were recovered by the addition of a small quantity of concentrated HCl to the filtrate. Data obtained from the solubility experiments are compiled in Table XXIX.

Table XXIX. Solubility of Oxidized-Reduced TMM Yarns in Cadoxen

Sample oxidation time (days)	Nitrogen of yarns (%)	Cadoxen insol wt (%)	Nitrogen in insol fraction(%)	Resin* found (%)	Resin** calc'd (%)
Warp					
none#	7.01	104.5	6.57	-	-
none	7.10	-	-	-	-
11	7.02	78.7	8.39	16.48	17.73
11+3	7.28	64.7	9.75	19.16	22.11
11+3+3	6.53	43.1	16.77	32.95	29.75
Filling					
none#	6.27	104.2	6.22	-	-
none	7.03	-	-	-	-
11	7.02	78.4	9.29	18.25	17.58
11+3	6.87	67.6	10.26	20.16	19.96
11+3+3	6.58	34.1	19.35	38.02	37.94

* Based on nitrogen content of insoluble product.
** Based on weight of insoluble product assuming all resin was contained therein.
\# These yarns were taken from a different fabric.

The reason for the small increase in weight of unoxidized yarns treated with cadoxen is not clear. As the oxidation level increased, an increasing portion of the sample became soluble in cadoxen. After three oxidation treatments the filling yarns were only 34.1% insoluble compared with 43.1% of the warp yarns. This difference is consistent with the observation that the warp yarns contain a slightly larger proportion of resin than the filling yarns (see Table XXIX). The resin content in the insoluble fraction was calculated from the nitrogen contents. Assuming that all the resin remains insoluble, the percent of resin expected, based on the weight percent remaining insoluble, was also calculated. The values obtained were similar to those calculated from nitrogen content data and show that virtually all of the resin is in the insoluble portion of the sample.

The insoluble residues remaining after the mild acid hydrolysis treatment of carbanilated TMM products (Table XXIII)

were found to contain high proportions of resin. Combined evidence of the x-ray diffraction and the photomicrographs suggest that they represent primarily cellulose fibers which had not responded to the periodate treatments. If it is assumed that the residues are comprised of resin and cellulose only (no carbanilated cellulose or carbanilated resin), the percent of the resin and cellulose in the original sample appearing as this insoluble residue can be calculated. In view of the large weight increases resulting from the carbanilation treatment, a small residue from the acid hydrolysis assumes considerable importance if comprised of cellulose and resin only. Some calculations are compiled in Table XXX.

Table XXX. Calculated Percent of Original Cellulose and Resin Remaining in Insoluble Residues after Mild Acid Hydrolysis

Sample oxid. time (days)	Insol. residue, % of carbanilated product	Resin in residue (%)	Original resin (%)	Original cellulose (%)	Resin to cellulose ratio remaining
none	-	11.7	-	-	-
16	12.4	27.3	69.8	24.6	2.84
16+4	16.8	43.5	56.5	18.4	3.70
none	-	11.6	-	-	-
24	3.4	38.1	30.1	8.0	3.76
24+9	3.2	40.3	21.8	6.4	3.41

Based on nitrogen content.

The ratio of resin to cellulose from the original sample found in the insoluble residue is of the order of 3.5. Considering, for example, the sample oxidized a total of 20 days, the data suggest that 56.5% of the original resin remains and is associated with 18.4% of the original cellulose. Finally, the sample oxidized for 33 days gave a residue containing 21.8% of the resin associated with 6.4% of the cellulose.

These data indicate that the first mild oxidation treatment modified 75.4% of the cellulose, permitting its subsequent carbanilation, but that this major fraction of cellulose was associated with only 30.2% of the total resin. As the oxidation is continued to higher levels, the ratio of resin to cellulose in the diminishing insoluble residue is essentially unchanged (ca 3.5), indicating a uniformity of distribution of resin in the 24% cellulose not reacted with periodate in the first instance.

2. Solubility Studies on Cellulose with Lower Resin Content

Cotton sheeting was cured with di- and trimethylolmelamine (DMM and TMM) to provide products having ca 7% resin add-on. Properties of these fabrics are compared in Table XXXI with those used previously, with higher resin add-ons, treated under identical drying and curing conditions.

Table XXXI. Properties of Resin-Treated Cotton Sheeting

Resin	Resin add-on*	Moisture regain %	Wrinkle Recovery (W+F)** dry	wet
TMM	6.8	5.24	302	293
	11.7	5.71	287	294
DMM	7.4	5.24	290	283
	12.7	-	278	280
Cotton Control	-	7.15	134	169

* Based on nitrogen content.
** Mean of 6 determinations by the Monsanto test method.

Cadoxen treatment of the yarns from the resin-treated fabrics resulted in no significant weight loss from either the DMM or TMM samples. The cadoxen-treated yarns consumed periodate at an appreciably faster rate, however, particularly in the case of the DMM sample (Fig. 21). Oxidation of yarns from resin-treated

fabrics for only 4 days, followed by borohydride reduction and cadoxen treatment, gave products which oxidized very rapidly but smoothly during a second oxidation treatment for 4 days. In all cases, the additional periodate consumed by the cadoxen-treated samples was consumed during the first day, after which the rates of oxidation were similar to those of samples not treated with cadoxen. Warp yarns generally tended to consume a significantly greater quantity of periodate than the filling yarns. DMM warp yarns treated with cadoxen oxidized to an appreciably greater extent than the filling yarns. A sample oxidized and reduced only was also reoxidized for comparison. These results clearly show that cadoxen treatment has a pronounced effect on the cellulose in these resin-treated samples, undoubtedly involving decrystallization, to provide a product which then responds very satisfactorily to periodate oxidation. After two oxidation periods for 4 days, with intermittent borohydride reduction and cadoxen treatment, slightly more than 100 moles of periodate were consumed per 100 AHG units.

Solubility data obtained concurrently during the several treatments (see Fig. 21) are shown in Table XXXII. With each operation the weight percent of sample taken, which became soluble, is shown together with the percent of resin remaining in the insoluble fraction based on nitrogen contents. Oxidation for 4 days caused 2-3% of the product to become soluble in water during reduction. A second oxidation treatment caused only an additional 3.3 - 5.6% of the sample to dissolve. Significant differences appeared when the once oxidized and reduced samples were treated with cadoxen. About 14% of the DMM samples dissolved in the solvent compared to 6% of the TMM samples. Reoxidation of the cadoxen-treated samples, resulting in the rapid consumption of periodate, gave products from which large fractions dissolved in water during borohydride reduction. Again, more of the DMM sample dissolved than the TMM. A final cadoxen treatment of this product dissolved about 75% of the

Table XXXII. Weight Percent of TMM- and DMM-Treated Cotton Yarns Soluble after Oxidation-Reduction and Cadoxen Treatment

Resin-Yarn Samples			Treatments	Soly. of Treated Samples and resin content** of insol. residues			
no.	resin	yarn*	oxid.-red. & cadoxen	Water soly. %	Resin %	Cadoxen soly. %	Resin %
1	TMM	W	none	0	6.94	0.6	-
		F		0	7.54	0.3	-
	DMM	W		0	~ 7	1.6	-
		F		0	6.30	0.6	-
2	TMM	W	oxidized 4 days & reduced	2.3	6.98	5.9	6.23
		F		3.1	7.82	6.0	6.85
	DMM	W		2.1	7.20	14.1	7.92
		F		2.3	4.45	13.7	8.10
3	TMM	W	twice oxidized 4 days & reduced	4.2	5.99	-	-
		F		3.3	6.61	-	-
	DMM	W		5.6	7.92	-	-
		F		4.9	7.28	-	-
1	TMM	W	(1) cadoxen	0.4	5.73	-	-
		F		3.9	6.70	-	-
	DMM	W	(2) oxidized 4 days & reduced	16.5	5.53	-	-
		F		14.3	5.22	-	-
2	TMM	W	(1) oxidized 4 days & reduced (2) cadoxen (3) reoxid. 4 days & reduced	33.0	8.70	64.8	11.96
		F		33.2	9.23	76.0	11.57
	DMM	W		56.8	16.48	75.6	16.29
		F		43.8	14.91	74.0	20.54

* W - warp; F - filling.
** Resin percent of insoluble residues based on nitrogen contents.

reduced sample. The fractions of the original samples recovered after two oxidation-reductions, with the subsequent cadoxen treatments together with the respective resin contents, are shown in Table XXXIII. Although the insoluble fractions recovered after each operation in the series become increasingly richer in resin, the percents of original resin recovered show that large proportions of resin are associated with the soluble

fractions. This fractionation of resin between the insoluble and soluble fractions occurred almost entirely during the last oxidation reduction and cadoxen treatments. The data also show that 22-40% of the original resin remains in the final insoluble residue comprised of only 12-22% of the original sample. The 4-day oxidation periods used in conjunction with cadoxen treatments represent relatively extensive modifications of these materials. For the purpose of providing cadoxen soluble fractions for molecular weight studies to define substituent group distribution in the cellulose, milder oxidation conditions could be used to provide additional cellulose fractions prior to the onset of resin loss.

Table XXXIII. Resin Contents of Sample Residues after Two Oxidation-Reduction and Cadoxen Treatments

Resin Content, % untreated	treated	Original Sample % remaining	Orig. Resin % remaining
6.94	11.96	21.7	37.6
7.54	11.57	14.6	22.4
ca 7.0 *	16.29	16.3	ca 24 *
6.30	20.54	12.3	40.1

* Estimated on the basis of values from other comparable samples.

3. Molecular Weight of Soluble Cellulose Chain Segments

If not bonded by resin, chain segments produced by cleavage (probably random) during borohydride reduction are free to pass into cadoxen solution. The fractions soluble in cadoxen after 4 days of oxidation were isolated and found to contain no nitrogen. Viscosity measurements were made in cadoxen solutions at 20.1 ± .01°C. Intrinsic viscosities, $[\eta]$, of 1.62 and 1.43 for the soluble fractions from DMM warp and filling yarns, respectively, were obtained by extrapolation of the specific viscosities plotted against concentration, shown in Figure 22.

The following equation was developed by Henley [62] for degree of polymerization (DP) determination of cellulose in cadoxen from viscosity measurements:

$$[\eta] = 2.5 \times 10^{-2} \bar{Z}_{ww}^{0.75}$$

where $\bar{Z}_{ww}$ = average DP. Neglecting at present any different contribution to viscosity of those anhydroglucose units in the cellulose modified by periodate oxidation, use of this equation gives average DP values of 260 and 220 for the cadoxen-soluble fractions from DMM warp and filling yarns, to a first approximation, respectively.

Specific viscosities in 0.5% solutions of the comparable soluble fractions from warp and filling yarns from the TMM samples were 1.29 and 1.30, respectively. Comparison of these values with those obtained with DMM samples (Fig. 2) indicates that the DP of the soluble chain segments from the TMM samples is somewhat less than those from the DMM yarns. Assuming similar extrapolation curves for $[\eta]$ determination, DP values of 180 are obtained for the TMM soluble fractions using the equation of Henley. These data indicate that the method outlined above can serve as a means for a very rough estimate of the distribution of substituent groups in resin-treated cellulose. Partial periodate oxidation followed by borohydride reduction affords cellulose chain segments which can be dissolved in the cellulose solvent, cadoxen. These segments represent sections of the macromolecule which were not bonded to the resin in the early stages of oxidation, as evidenced by the absence of nitrogen. To a first approximation molecular weight determination showed an average DP of ca 240 for the fractions from the DMM sample and 180 from a comparable TMM sample. It is thus seen that the materials contained relatively long cellulose chain segments which were not bonded by resin. A degree of substitution (DS) of resin of 0.1 signifies a resin substituent group on the average of one in every ten

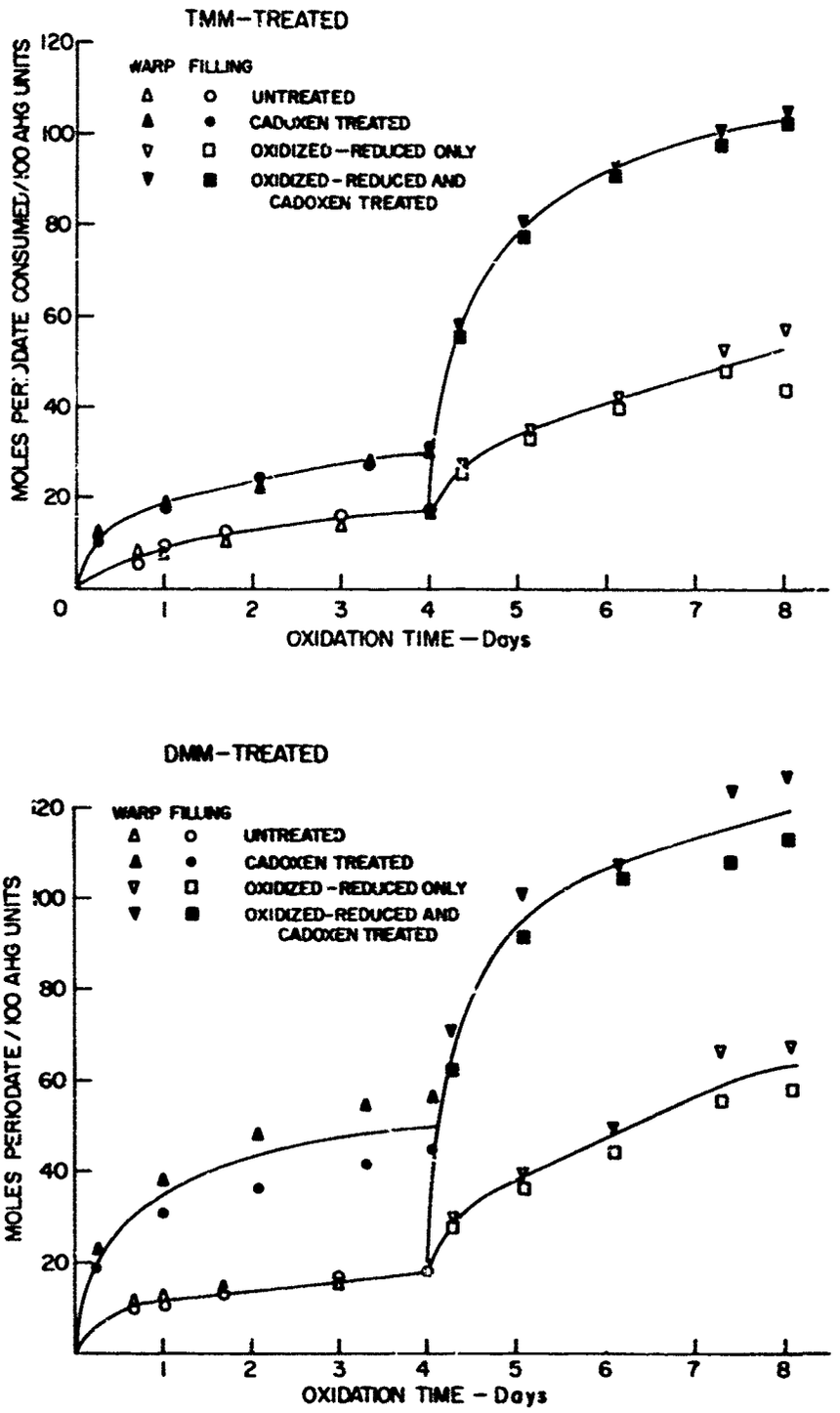


Fig. 21. Effect of cadoxen treatment on periodate oxidation.

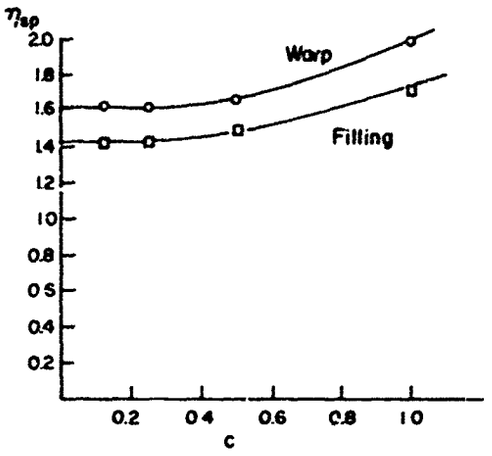


Fig. 22. Viscosity of cadoxen soluble fraction from 4 days oxidized DMM treated cotton.

anhydroglucose units. In the light of earlier DS determinations, this is not an unreasonable minimum DS to expect. The isolation of unsubstituted chain segments with a DP of the order of 200 therefore suggests that these products contain a very non-uniform distribution of resin substituent groups.

CHAPTER VIII. CONCLUSIONS AND RECOMMENDATIONS

The experiments which were conducted in connection with this research program were designed to shed some light on the chemical structure of the products resulting from the application of methylolmelamine resins to cotton materials under various curing conditions. The main objectives were to develop an analytical procedure to determine the degree of substitution of the resin cellulose products, and to obtain information about the distribution of the covalent linkages between resin and cellulose among the various hydroxyl groups of the anhydroglucose unit. Essentially, these objectives have been accomplished although there appears to be some doubt as to the reliability of the quantitative nature of the data that were obtained. Some of these results have been published [64,65], and it can be said with some confidence that covalent bonding occurs between the methylolmelamine resin and cellulose.

The chemical analytical method which was developed for the structural analysis is essentially a replacement of the resin substituents with methyl groups and analysis of the resulting methyl glucoses. For this replacement reaction all free hydroxyl groups of the resin-treated cellulose must be protected by an exhaustive substitution. This exhaustive substitution is one of the major problems of the method, and as a solution to the apparent lack of accessibility of certain hydroxyl groups, the prior degradation of the cellulose by periodate oxidation followed by borohydride reduction was chosen. The degradation treatment, however, which was designed to open up the cellulose structure sufficiently to guarantee quantitative carbanilation of all free hydroxyl groups, apparently is not able to accomplish this in regions of high resin content and, in addition, introduces new problems connected with the solubility and quantitative recovery of the degradation products. A new method of carbanilation without prior degradation was developed at the end of this

research program, and showed promising results. However, it was not tested in conjunction with the complete structural analysis due to lack of time. The degrees of substitution, as well as the distribution of resin between the various hydroxyl groups of the anhydroglucose unit which have been reported here, should therefore be treated with caution, especially in the case of the dry-cured samples, and it is strongly recommended that the quantitative nature of the various steps of the structural analysis be reinvestigated.

The investigation of weathered resin-treated samples indicated that periodate oxidation can be used as a sensitive index of the structural changes occurring during resin degradation. Phase contrast microscopy and solubility studies in connection with Smith degradations have been found to provide a rapid method for assessing any cellulose chemical treatment for uniformity and effectiveness of covalent cross-linking. The solubility studies on degraded resin-treated cellulose indicated considerable non-uniformity of the resin treatment and, together with a molecular weight determination, this can serve as a first attempt to gather information about the distribution of resin substituents along the cellulose chain. Since this distribution would seem to have important implications for the understanding of the mechanism by which resin-treated cotton fabrics are protected against microbial and actinic degradation, it is recommended that this approach be fully explored.

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13. ABSTRACT

The nature of the interactions between methylolmelamine resins and cotton has been investigated. A new chemical analytical method for the elucidation of the chemical structure of resin-treated cotton has been developed. Data are presented for the degree of substitution of cellulose by trimethylolmelamine., and for the distribution of these substituents between the various hydroxyl groups of the anhydroglucose unit under various curing conditions. It has been shown by an investigation of weathered resin-treated cotton samples that periodate oxidation can be used as a sensitive index of the structural changes occurring during resin degradation. Microscopy and solubility studies in the in the cellulose solvent cadoxen, in connection with Smith degradations, have been found to provide a method for assessing any cellulose chemical treatment for uniformity and effectiveness of covalent cross-linking. Preliminary results are presented on the distribution of resin substituents along the cellulose chain, and considerable nonuniformity of resin substitution is indicated.

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Cotton textiles	9		9			
Chromatographic analysis	10					
Microanalysis	10					
Prevention			8			
Deterioration			8,9			
Impregnation			10			