

Certain Fine Structure and Thermal Properties of Benzhydrylated Cotton Cellulose

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Synopsis

The present paper describes the results of a preliminary study of certain physical and thermal properties of benzhydrylated cotton yarns. The 200-yd. lengths of 7/2 yarn consisting of purified mercerized cellulose were reacted in a special reactor to various degrees of substitution from DS 0.31 to DS 1.22 with benzhydryl bromide in a mixture of equal volumes of 2,6-lutidine and dimethylformamide. The products were examined for tensile strength at break, which decreased only slightly with substitution; ultimate elongation, which was relatively uniform at 60–70% of the control yarn; and tenacity, which decreased with substitution largely due to added weight. The energy of rupture remained relatively constant at about 50% above the control. Tensile stiffness decreased progressively with substitution to about 25% of the control. Density decreased 10–11% with substitution. Crystallinity of the cellulose largely disappeared with substitutions above DS 1, and the lattice of benzhydryl cellulose began to appear. Stiffness, elastic recovery and work recovery were measured on 5-in. specimens of the yarn in an oven while they were subjected to repeated extension to about 1–2% and relaxed as the temperature was raised twice to 200°C. and lowered. During the heating phase of the first cycle the yarn underwent considerable heat adaptation. However, during the cooling phase and during both heating and cooling phases of the second cycle, the yarns showed generally favorable behavior. Attempts are made to interpret the results in terms of molecular modifications.

INTRODUCTION

Benzhydryl cellulose is a relatively new member of the cellulose ether family. It was first prepared¹ in 1960 by reacting cotton cellulose with benzhydryl (diphenylmethyl) bromide in 2,6-lutidine. Although cotton yarns were modified in that work, the structural and mechanical properties of the benzhydrylated yarns were not discussed.

More recently² an improved method, employing dimethylformamide as a diluent, was used in the production of benzhydrylated cotton. The prepared yarns were examined by differential thermal analysis (DTA) and by thermogravimetric analysis (TGA).²

The same yarns which were used in the DTA and TGA studies have been examined for certain changes in mechanical and structural properties caused by progressive benzhydrylation. The results are reported in the present paper.

MATERIALS AND METHODS

The yarn samples investigated in the present study have already been briefly described.² The treated yarns had degrees of substitution (DS) ranging from 0.31 to 1.22 with respect to benzhydryl groups. Yarn properties are reported for the untreated original 7/2 commercially mercerized cotton yarn; and for a portion of it which had been put through the entire process with all reagents present except the benzhydryl bromide.

Chemical Modification of the Yarns

Since the detailed conditions of preparation may be more important in a study of structural and mechanical properties than in the previous study² some additional information is furnished.

A 40-g. portion of commercially mercerized, nominally 7/2 (167 tex) cotton yarn (0.25 mole cellulose), wrapped on the yarn holder of the reactor described by Stanonis et al.³ was activated with 17.5% sodium hydroxide solution. The yarn, still on the holder, was then washed successively with water, 5% acetic acid, water, pyridine, and finally lutidine. To the lutidine-washed yarn was added a solution made by mixing 184 ml. of 2,6-lutidine, 184 ml. of *N,N*-dimethylformamide and 317 g. (1.2 mole) of benzhydryl bromide. The reactions were carried out in the reactor for various lengths of time at 120°C. At the end of the preselected period the reaction was terminated and the samples washed successively with pyridine, methanol, and water. The results are given in Table I. The kinetics of the reaction approximated that expected on the basis of a Sakurada plot.⁴

The test methods have been previously described,⁴ except for certain modifications that were introduced in a few cases.

The x-ray diffractograms were prepared as described before,⁵ except that instead of using the tracings, the number of seconds required for a count of 2000 was automatically printed out for each 0.25° 2θ over the

TABLE I
Conditions and Details of Yarn Preparation

Type of sample	Medium used	Length of treatment, min.	Yarn number, tex	Degree of substitution DS
Original	None	0	200.2	0
Control	Lutidine, <i>N,N</i> -dimethylformamide	80	197.0	0
Reacted	Lutidine, <i>N,N</i> -dimethylformamide, benzhydryl bromide	20	231.6	0.31
Reacted	"	45	268.4	0.46
Reacted	"	90	378.6	0.87
Reacted	"	210	418.8	1.12
Reacted	"	150	391.0	1.13
Reacted	"	160	431.0	1.22

range $2\theta = 5\text{--}30^\circ$ and the reciprocal used as a measure of intensity. The precision in terms of standard deviation of any point on the curves was, therefore, equal to about 2.2%. Crystallinity was also determined by the Wakelin correlation method⁶ by use of a computer program for the range $2\theta = 10\text{--}30^\circ$.

Tensile stiffness and elastic and work recovery were determined simultaneously at temperatures from 25 to 200°C. on 5-in. specimens in an insulated oven mounted on the Instron crosshead.⁴ Previous studies² showed that no detectable degradation occurred at 225°C.

The overall dimensional change in the stainless steel rods on which the specimens were mounted was determined for the same temperature range by means of 5-in. lengths of copper wire and quartz thread of known linear expansion. Corrections were determined and subtracted from the observed extensions in all cases. During a series of thermal observations a stream of nitrogen was bubbled through a standard saturated salt mixture (NH_4Cl and KNO_3 mixture giving 69–71% R.H. at room temperature), and then through the oven at a rate of 100–125 cm.³/min. The crosshead of the Instron was set to move at a rate of 0.2 in./min. both up and down. Readings of temperature, maximum load, and integrator areas were made at intervals of 5 min. as the temperature was raised at a rate of approximately 2°C./min.

RESULTS

Tensile Properties

The tensile properties of the different samples are recorded in Table II, according to degree of substitution. It will be noted that the breaking strength remained relatively constant, but decreased somewhat at substitutions above DS = 1. Elongation at break increased to nearly double the untreated control (to 10–11%) except for the treated control for which

TABLE II
Tensile Properties of Benzhydrylated Yarns

DS	Breaking strength, g./tex. ^a	Elongation, %	Tenacity, g./tex.	Energy of rupture, g./tex.	Tensile stiffness, g./tex.	Density, g./cc.
0 ^b	25.1	6.3	25.1	0.79	397	1.536
0 ^c	26.4	18.6	26.4	2.45	142	1.531
0.31	25.3	10.5	21.5	1.33	205	1.433
0.46	27.1	11.8	19.9	1.59	169	1.400
0.87	24.8	10.7	12.9	1.33	120	1.375
1.12	21.6	11.5	10.2	1.25	88	1.359
1.13	21.5	11.3	10.8	1.21	96	1.362
1.22	22.8	10.9	10.4	1.24	96	1.363

^a Breaking strength, based on tex. of control.

^b Untreated original, commercially mercerized yarn.

^c Control treated for 80 min. at 120°C. with all reagents except benzhydryl bromide.

it increased nearly threefold. To what extent this increase is due to contraction in the process is not known. The small change in yarn number (Table I) speaks for very little contraction, but the uniformity of the yarn itself may not be high enough to justify this conclusion.

Tenacity, reflecting as it does the weight increase due to combined substituent, decreased regularly to about 40% of the control at a substitution of $DS = 1$. The energy of rupture (area under the tenacity-elongation curve), being highly dependent on the elongation, is greatly increased for the treated control and remained relatively constant at about 50% above the control with increasing substitution. Tensile stiffness shows a somewhat irregular decrease with substitution to a minimum of about 25% of the control at substitutions above $DS = 1$. In general, the yarns were all of textile quality.

Density

The density of the cellulose and cellulose derivatives of the yarns is presented in Table II and is plotted against DS in Figure 1. It will be observed that the density first decreases rapidly with increasing substitution, eventually reaching an approximately constant value 11% below its initial value.

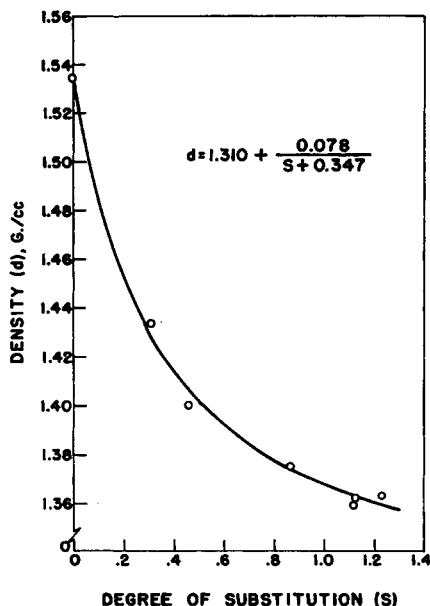


Fig. 1. Change of density d of cotton cellulose with degree of benzhydryl substitution S .

Crystallinity

The crystallinity of the cellulose of the different samples is indicated by the diffractograms of Figure 2. It will be observed that the diffractogram

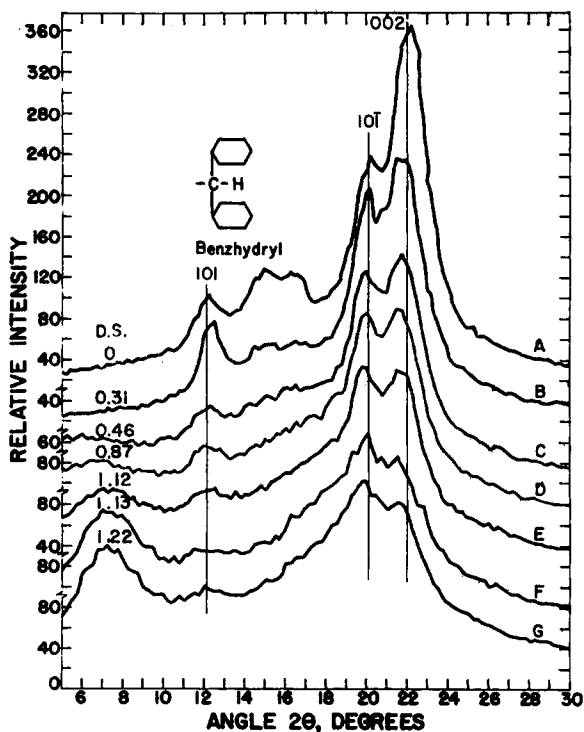


Fig. 2. Diffractograms of benzhydrylated cotton cellulose of different degrees of substitution.

of the untreated control (curve *A*) is that of relatively crystalline mercerized cellulose, but that it still shows evidence of the native cellulose pattern at $2\theta = 14.7^\circ$, 16.3° , and 22.6° . By the Wakelin correlation method⁶ this sample had an estimated degree of crystallinity of 65%. However, before reaction with benzhydryl bromide it was further reacted with 17.5% sodium hydroxide which would have removed most of the residual native cellulose pattern. After exposure to the reaction media and temperature for 80 min., the crystallinity of the treated control was estimated to be 70%.

The introduction of a small number of benzhydryl groups, (curve *B*) occurs largely at the expense of the native crystalline component, leaving a sharp hydrate crystal pattern. Further introduction of benzhydryl groups (curves *C* and *D*) takes place at the hydrate crystalline regions, gradually reducing them to an essentially amorphous state (curves *F*, *G*). The peaks of the latter at $2\theta = 7-8^\circ$ are due to subsequent ordering of the benzhydryl cellulose formed.

After four of the 5-in. specimens of the more highly substituted (DS = 1.12-1.22) yarns had been subjected to two cycles of heating at 22°C . and cooling to room temperature in the tensile studies they were cut and examined by x-ray diffraction. Comparison of the resulting tracings with the

curves before heat treatment showed that any changes in x-ray pattern were negligible. Thus, no additional crystallization occurred.⁴

Stiffness

The tensile stiffness of benzhydrated yarns of different degrees of substitution are shown in Figure 3. Each yarn specimen was carried through two cycles of heating to 200°C. or slightly above and cooling. The changes of stiffness with temperature during the heating phase of the first cycle are indicated by dashed curves in the left-hand portion of the chart and identified by DS numbers. It will be observed that in almost all cases the stiffness values, as indicated in dynes per square centimeter by the grid lines and numbers, are considerably below those of the corresponding smooth curves representing the heating phase of the second cycle. Thus, an important change in tensile stiffness is imparted to the yarn by the stressing and relaxation during the heating phase of the first cycle.

During the cooling phase of the first cycle, the yarn displays a tensile

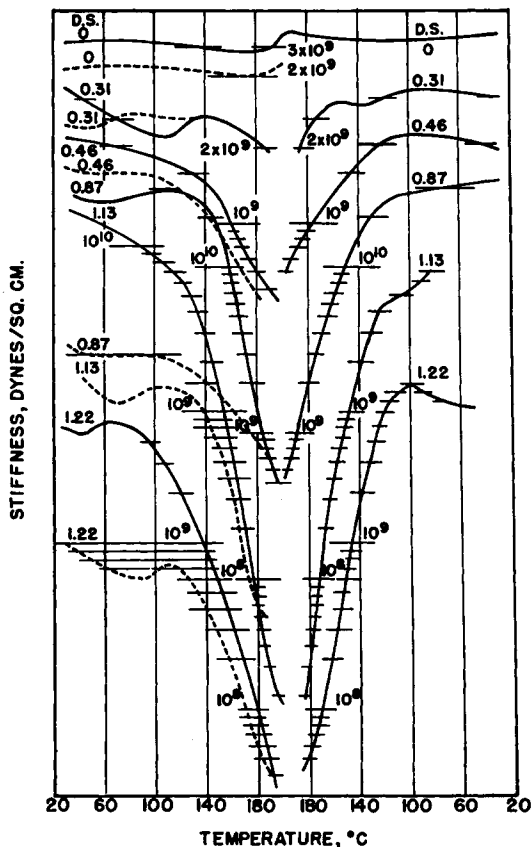


Fig. 3. Stiffness of cotton yarns of different degrees of substitution at different temperatures and cycles of treatment: (---) first cycle; (—) second cycle.

stiffness which is almost identical with that followed during both the heating and cooling phases of the second cycle. In fact, the tensile stiffness curves during the cooling phases of the first and second cycle were so nearly identical that they could be represented by single stiffness curves, and no dashed curves are shown. As is evident, the tensile stiffness undergoes a very large change with temperature, in some cases approximately three decades. Due to beginning thermoplastic flow in samples with the higher substitutions it was not possible to work at temperatures much above 200°C., although in a few cases temperatures were raised to 220°C. As pointed out above, under discussion of the x-ray diffractograms, there was little, if any, change in the x-ray pattern as a result of heat treatment.

Elastic Recovery

The elastic recovery from deformation at different substitutions and temperatures is shown in Figures 4 and 5. Figure 4 shows the thermal behavior during the first cycle of heating and cooling. During the heating phase of the cycle, it is evident that, with increasing temperature, recovery is generally decreased below that of the control even at the lowest degree of substitution ($DS = 0.31$) and that the loss becomes quite large at substitutions of $DS = 0.87$ and above. There appears to be a minimum in the recovery curves at 120–180°C., indicative of second-order transition behavior. However, the elastic recovery fails to show these minima during

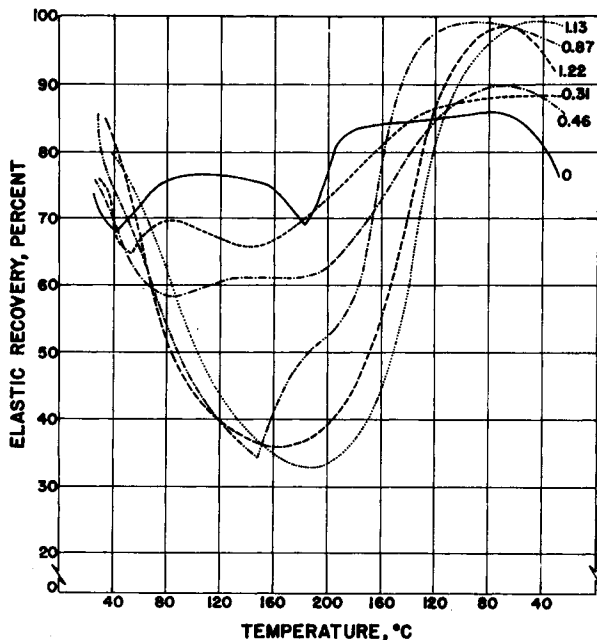


Fig. 4. Elastic recovery of benzhydrylated cotton yarns of different degrees of substitution during the first cycle of heating and cooling.

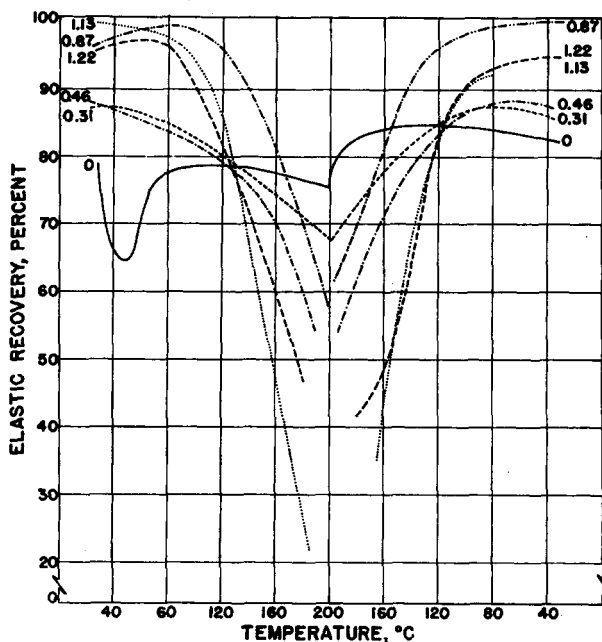


Fig. 5. Elastic recovery of benzhydrylated cotton yarns of different degrees of substitution during the second cycle of heating and cooling.

the cooling phase of the cycle where recovery is rapid. The very large elastic recovery at temperatures below 120°C ., especially for the three higher substitutions, is especially noteworthy.

Figure 5 shows the change of elastic recovery with temperature during the heating and cooling phases of the second cycle. It will be noted that, with the exception of the control sample, the curves are quite symmetrical with respect to temperature. They essentially duplicate those of the cooling phase of the first cycle. Also, it will be noted that all substituted samples, especially the three most highly substituted ones at temperatures of 120°C . or lower, have considerably improved elastic recoveries as compared with that of the control sample. Above 120°C . the recoveries are inferior to that of the control sample. No minima indicative of second-order transitions are to be seen.

Work Recovery

The work recovery at different substitutions and temperatures is shown for the first and second cycles of heating and cooling in Figures 6 and 7, respectively. Figure 6 for the first cycle shows relatively low recoveries during the heating phase, the recovery being less than that for the control at all temperatures above 80°C .. There are very distinct evidences of second-order transition phenomena at about 140°C .. This is further supported by several of the curves (see $\text{DS} = 1.13$ and 1.22) during the cooling phase of this cycle. During cooling the work recovery at temperatures

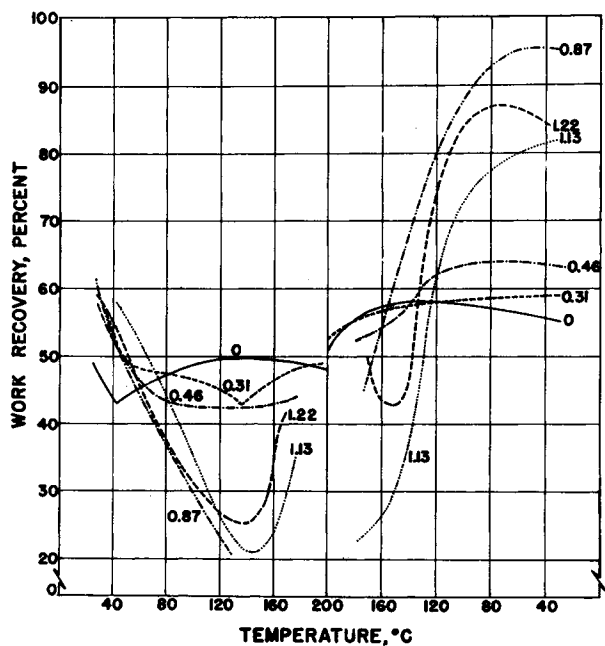


Fig. 6. Work recovery of benzhydrilated cotton yarns of different degrees of substitution during the first cycle of heating and cooling.

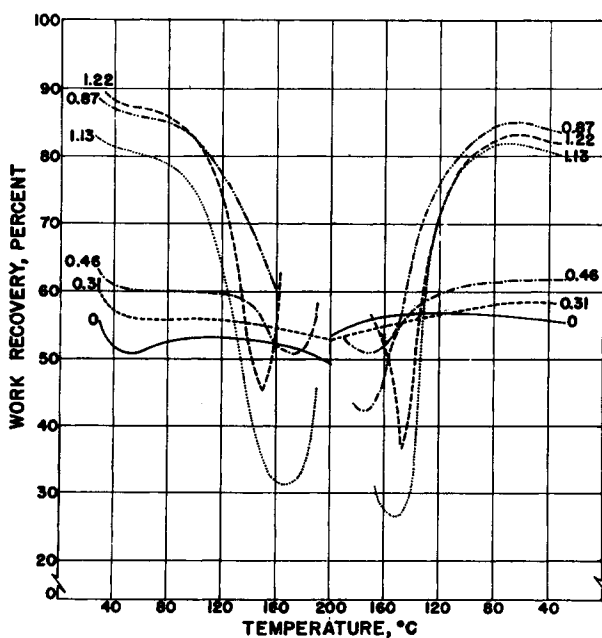


Fig. 7. Work recovery of benzhydrilated cotton yarns of different degrees of substitution during the second cycle of heating and cooling.

below 120°C. is improved relative to the control, especially at substitutions of DS = 0.87 and above.

The work recovery curves for the second heating and cooling cycle (Fig. 7) are quite symmetrical and similar to those for the cooling phase of the first cycle. Now, at temperatures below 120°C. curves for all substitutions show superior recovery as compared with the control. Well-characterized second-order transition phenomena are indicated. It appears that an important limit occurs in the DS range 0.46–0.87 at which the degree of substitution contributes to optimum recovery behavior.

DISCUSSION

The present study shows that the cellulose in cotton yarns can be benzhydrylated to about 40% of its total hydroxyl groups without loss of textile properties and with a number of interesting changes in physical properties.

Relatively little of the original breaking strength is lost. Thus, it appears that side bonding contributes in a relatively minor way toward the original strength. If an appreciable proportion of the original strength were due to side bonds, it would be expected that the introduction of the bulky benzhydryl groups would result in a much greater loss of strength as substitution increases. Energy of rupture, on the basis of the untreated control is considerably increased at all substitutions while tensile stiffness decreased noticeably (76%).

The decrease in density (11%) is associated with the changes in the crystal lattice shown in Table III.

TABLE III

	<i>a</i> , A.	<i>b</i> , A.	<i>c</i> , A.	β , deg.
Cellulose II	8.14	10.3	9.14	62
Benzhydryl cellulose	12.90	10.3	12.40	41

From the increase in unit cell dimensions a 60% increase in volume can be computed. However, on the basis of four anhydroglucose units included in the volume and a molecular weight of 167 for each benzhydryl group a much larger percentage increase would be computed for the weight at DS 1.22. This would lead to an *increase* of density rather than a decrease. Presumably, the decrease is associated with the noncrystalline components of the cellulose. It appears from this as well as from the fact that the x-ray diffractograms show much loss of crystallinity that a good deal of loosening of the cellulose structure occurs. Some of this may have been brought about by the alkaline reactivation step in the process but much of it results, no doubt, from the introduction of the bulky diphenylmethyl groups into the cellulose chains.

The results of the present study resemble in a number of ways those of previous studies.^{4,7} The density invariably decreases and the stiffness

usually decreases. Also, during mechanical working at elevated temperatures the stiffness and elastic and work recovery curves during the heating phase of the first cycle differ quite impressively from those of the cooling phase and both heating and cooling phases of the second cycle. Presumably, considerable movement and accommodation of the cellulose molecules occurs during the first phase of this process.

Unlike the results of earlier studies,^{4,5,8} there was little crystallization of the disorganized cellulose. This should have been indicated by the x-ray diffractograms made on the 5-in. specimens remaining from the thermal studies and probably would have shown up in the DTA curves.² This failure may again be associated with the bulky nature of the benzhydryl groups which in the cellulose chain cannot accommodate themselves appreciably to the requirements of the crystalline lattice. This failure may have an element of benefit in it in contributing to the favorable toughness or energy to rupture.

The authors wish to thank the Textile Testing Investigations for physical tests on the yarns. They also wish to thank Verne W. Tripp for the diffractograms and for computing the lattice dimensions of the reacted samples.

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Résumé

On décrit dans cet article les résultats d'une étude préliminaire de certaines propriétés physiques et thermiques de fils de coton benzhydratés. On a fait réagir dans un réacteur spécial en présence de bromure de benzhydryle dans un mélange composé à part égale de 2,6-lutidine et de diméthylformamide, des fils de 7/2 de cellulose mercerisée, purifiée d'une longueur de 200 yards. Les degrés de substitution obtenus (DS) varient de 0.31 à 1.22. On a examiné quelques propriétés physiques de ces produits telle que la résistance à la tension, qui ne diminue que légèrement avec la substitution. L'élongation à la rupture, qui reste sensiblement constante et garde une valeur comprise entre 60 et 70% dans le fil initial; et la tenacité, qui décroît dans des proportions très grandes, ceci en raison du poids additionné. L'énergie de rupture reste sensiblement stable et a une valeur d'environ 50% plus élevée que le fil de contrôle. La raideur en tension diminue progressivement avec la substitution et atteint une valeur égale à 25% de la valeur trouvée pour le fil de contrôle. La densité diminue de 10-11% avec la substitution. La cristallinité de la cellulose disparaît très fortement avec la substitution, lorsque le degré de substitution (DS) dépasse l'unité, et le réseau de cellulose benzhydratée apparaît progressivement. On détermine la raideur, le recouvrement élastique, le travail de recouvrement sur des échantillons de cinq pouces, de fil. Ces mesures ont été effectuées dans une étude,

les fils étant soumis à des extensions répétées de 1-2% et relaxées ensuite, et la température étant élevée par deux fois jusqu'à 200°C et abaissées. Pendant la phase d'élévation de température du premier cycle, on a constaté que le fil subissait une transformation considérable sous l'influence de la chaleur. Cependant, durant la phase de refroidissement et durant la phase de chauffage et de refroidissement du second cycle, on a constaté que le fil avait un comportement généralement plus favorable. On a tenté d'interpréter ce résultat par des modifications moléculaires.

Zusammenfassung

Die vorliegende Mitteilung befasst sich mit den Ergebnissen einer vorläufigen Untersuchung gewisser physikalischer und thermischer Eigenschaften benzhydrierter Baumwollgarne. 200 Yard Länge eines 7/2-Garns aus gereinigter mercerisierter Cellulose wurde in einem Spezialreaktor mit Benzhydriylbromid in einem Gemisch gleicher Volumina von 2,6-Lutidin und Dimethylformamid bis zu verschiedenen Substitutionsgeraden von DS = 0,31 bis 1,22 in Reaktion gebracht. Die Produkte wurden auf ihre Zugfestigkeit beim Bruch, welche mit der Substitution nur schwach abnahm, auf ihre Reissdehnung welche ziemlich einheitlich bei 60-70% von derjenigen des Kontrollgarns lag, und auf ihre Zähigkeit, welche grossenteils infolge der Gewichtszunahme mit der Substitution abnahm untersucht. Die Bruchenergie blieb verhältnismässig konstant auf etwa 50% oberhalb des Kontrollwertes. Die Zugsteifigkeit nahm mit der Substitution stetig bis auf etwa 25% des Kontrollwertes ab. Die Dichte fiel mit der Substitution um 10-11% ab. Die Kristallinität der Cellulose verschwand grossenteils bei Substitution oberhalb DS = 1 und das Gitter der Benzhydriylcellulose trat in Erscheinung. Steifigkeit, Elastizität und Arbeitsfähigkeit wurden an 5-in Proben des Garns in einem Heizschrank während wiederholter Dehnung um etwa 1-2% und Relaxation durch zweimalige Temperaturerhöhung auf 200°C und darauffolgende Erniedrigung gemessen. Während der Erhitzungsphase des ersten Cyclus zeigte das Garn eine beträchtliche Wärmeadaptation. Während der Abkühlphase und während Erhitzungs- und Abkühlungsphase des zweiten Cyclus zeigten die Garne jedoch im allgemeinen ein günstiges Verhalten. Es wird versucht, die Ergebnisse durch die Annahme von Molekülmodifikationen zu deuten.

Received August 9, 1966
Prod. No. 1478