Built-In Lubrication on Cotton Fabrics[1]

RUTH R. BENERITO, JOHN B. McKELVEY and RALPH J. BERNI,
Southern Regional Research Laboratory,[2] New Orleans, Louisiana 70119

ABSTRACT

Partial cotton esters of long chain fatty acids of low degrees of substitution (D.S.<0.20) have been prepared by a variety of methods. In particular, the effects of the introduction of a stearoyl or an oleoyl group into the cellulose matrix on fabric properties, such as softness of hand and wrinkle recovery, have been studied. Attempts have been made to compare fabric properties of partial esters of like D.S. prepared by various methods of esterification and effect of a chemically attached alkanoyl group with effect of the same group deposited or adsorbed on the surface of the cotton fabric. Consideration has been given to the size of the alkyl group, its orientation on the surface of the fiber and its hydrophobicity. Data indicate that resistance to abrasion of cottons chemically modified with long chain alkyl groups is reduced whenever the finished fabric has high dry wrinkle recovery. High dry wrinkle recovery is obtained after esterification of cotton in nonaqueous media. Improvement in resistance to abrasion is pronounced when the alkyl group has not been chemically combined with the cellulose matrix in the absence of water, and usually is obtained when the finished cottons possess only high wet wrinkle recovery.

INTRODUCTION

Throughout the history of the textile industry, lubricants have been used during processing, finishing and laundering of textile products. Naturally occurring lubricants of native cotton or those added to cotton textiles often possess a long chain alkyl group. Cationic reagents, such as quaternary ammonium salts in which at least one of the alkyl groups is a long chain group, have been used to advantage in the cotton industry. The efficiency of such cationic reagents has been attributed to the fact that initially the positively charged quaternary ions, by a process of ion exchange, are located at the sites of carboxylate groups in cotton (1,2). As a secondary step, amounts of the reagent larger than that predicted by the ion exchange capacity of the cotton are adsorbed by a process of ion pairing. Usually, the amount of cationic reagent adsorbed by cotton goes through a maximum, which depends to some extent on the concentration of the cationic reagent being used and the relation of this concentration to the critical micelle concentration of the reagent. Nevertheless, the amount of cationic reagent containing a quaternary ammonium ion with a long chain alkyl group, such as a cetyl or octadecyl group, required to give a cotton fabric a soft and pliable hand, is very small. Usually less than 0.3% of weight of the fabric is required. Another advantage of cationic softeners or lubricants for cotton is that, because of the strong electrostatic or ionic bonds between cotton and the quaternary groups, the softeners are not removed by physical means and are rather difficult to remove by chemical means. Cotton adsorbs anionic and nonionic lubricants or softeners, all of which possess long chain groups, to a lesser extent (3,4). What is to be emphasized in this study is the effect of attaching a long chain alkyl group to cotton by a relatively stable bond and a comparison of the effects of such a group chemically attached to cotton with effects of the presence of the same group simply deposited on the surface of cotton or attached to cotton by bonds less stable than covalent bonds.

Unfortunately, when cotton fabric is finished with conventional polyfunctional reagents, such as the N-methylolated urea derivatives to impart high wrinkle recovery in the dry state, the resultant fabrics are not as resistant to abrasion as is the untreated cotton control. Therefore, cottons finished for easy care or wrinkle free properties are also treated with various lubricants or softeners. When it was reported (5,6) that cotton could be given wrinkle recovery in the dry as well as wet states by its partial esterification with long chain monobasic acid chlorides in dimethylformamide (DMF), it was suggested (7) that such cottons might exhibit interesting properties of lubricity and have resistance to flex abrasion. Such cottons with chemically attached long chain groups, and possessing wrinkle resistant properties, would be of great value to the cotton industry.

With cellulose partial esters of long chain monobasic acids of degrees of substitution (D.S.)<0.20 prepared by the acid chloride-DMF method, high dry wrinkle recovery was attained, but resistance to abrasion was considerably lowered (8). By this method, the partial cellulose esters of those long chain monobasic acids having unsaturation, an aromatic group, or an hydroxyl group in the chain had higher dry recovery than did the cellulose ester of like D.S. of the corresponding saturated acid (8). For example, the partial cellulose esters of oleic, phenyl stearic, or 12-hydroxystearic were more wrinkle resistant than the ester of stearic acid at like D.S. Usually, cellulose esters of unsaturated acids had higher moisture contents and higher wet recovery as well as higher dry recovery than the cellulose esters of the corresponding unsubstituted saturated acid. Chipalkatti (9-11) ostensibly showed that "built-in" lubrication may be produced in cotton fabrics as a result to their reaction with the stearic acid ester of 1,3-dichloro-2-propanol in the presence of strong aqueous NaOH. Improvements in Stoll flex abrasion values of several thousand per cent were realized, but the fabrics showed no improvement in dry wrinkle recovery. More recently, a comparison of cellulose esters of like D.S. prepared by a variety of methods of esterification showed that the method of esterification is a controlling factor in resultant fabric properties of a given cellulose ester (12).

This report summarizes the effects of introducing a stearoyl or an oleoyl group into cotton by the following methods of esterification: acid chloride-DMF (6), trifluoroacetic acid anhydride (TFAA)-acid-benzene (12), cotton in aqueous NaOH-acid chloride in CCl$_4$ (classical Karrer method) (13), and acid chloride-sodium cellulosate-DMF (14).

The present study also offers an explanation of the high values of abrasion resistance values reported by Chipalkatti (9,10).

EXPERIMENTAL PROCEDURE

Preparation of Cellulose Esters

An 80 x 80 cotton print cloth (3.1 oz/yd^2) which had been desized, scoured and bleached was used in all

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experiments. After esterification, all fabrics were washed in excess solvent and hot methanol, neutralized and washed in distilled water before being ironed dry. All fabrics were air equilibrated for 24 hr before being analyzed and tested for fabric properties.

DMF-Acid Chloride Method. The acid chloride (0.06 mole) and 180 ml of DMF were mixed in a 250 ml glass-stoppered cylinder and heated to 105 C; the pyridine (20 ml) was brought to reaction temperature in a separate flask and mixed with the DMF solution just prior to immersion of a rolled fabric sample (10 g) which had been predried for 45 min at 105 C. As indicated, some experiments were for longer intervals at lower temperatures.

TFAA-Acid-Benzene Method. An air-equilibrated fabric (5 g) was rolled and placed in a graduated cylinder containing 12.6 g (0.06 mole) of TFAA and the acid (0.03 mole) in 100 ml (total volume) of benzene. Reaction mixtures were shaken for various times at room temperature.

Karrer-Acid Chloride-CCl₄-Aqueous NaOH. Fabric samples (5 g) were twice padded to 100% wet pickup with aqueous 23% NaOH, rolled and placed in stoppered graduated cylinders containing the acid chloride (0.03 mole) in 100 ml (total volume) of CCl_4 at 35 C.

Acid Chloride-Sodium Cellulosate-DMF. Sodium cellulosates were prepared by reacting cotton with methanolic solutions of sodium methoxide under an atmosphere of dry nitrogen (15,16). A 10 g fabric sample was placed for 24 hr in an enclosed reaction chamber containing dry DMF, solvent exchanged three times with absolute methanol under dry nitrogen and then reacted in 1.0 M sodium methoxide in methanol for various times. The resulting sodium cellulosate was washed in *t*-butanol and then reacted in an inclosed vessel containing the acid chloride (0.06 mole) in 100 ml of DMF at either 105 C for short intervals or at 25 C for longer times.

ANALYSES OF FABRICS

Fabric Testing

Physical tests were performed according to standard ASTM procedures (17) and included measurements of breaking strength and elongation at break as determined on strips raveled to 1 in. (17a), Stoll flex abrasion (17b) and moisture regains (17c). Conditioned wrinkle recovery angles were determined on the Monsanto tester with a 500 g weight (17d) and wet wrinkle recovery angles by the Lawrence modification (18).

Measurements of immediate and delayed recoveries were made on an Instron Tensile Tester. Fabric strips were 1½ in. wide. A 5 in. gauge length and a chart speed of 10 in./min were used. Fabrics were successively extended to 3, 6, 10, 15, 20 and 30 lb loads, with 1 min at each extension and 1 hr between extensions.

Degree of Esterification

Extent of reaction was determined by weight gains and saponification equivalents obtained by conventional methods with alcoholic NaOH (6). At the low degrees of substitution, D.S.<0.2, absorptivities of the IR band characteristic of the cellulose ester varied linearly with saponification equivalents and were used to determine extent of esterification (6). In addition, the partial esters were saponified with methanolic solution of tetramethylammonium hydroxide and the hydrolysates were directly chromatographed as the methyl esters (19). Fabrics of like D.S. were selected and used for a comparison of fabric properties obtained by various methods of esterification.

Microscopical Evaluation

Techniques of light and electron microscopy were used to detect effects of esterification of cotton (20). Uniformity of esterification in each method was followed by dyeing techniques and by observing the effects of 0.5 M cupriethylenediaminehydroxide (cuene) on whole fibers of the cellulose esters during 30 min of immersion. Surfaces of the fibers before and after esterification were examined by use of the two-stage polystyrene-carbon replica techniques.

Fabric samples were also mounted on the specimen studs of the Steroscon Cambridge scanning electron microscope and vacuum-coated with a thin layer of gold. Observations were made with the specimen tilted at 45° to the reflecting beam. Photographs of several fibers of each specimen were taken to record surfaces typical of the various esterified cottons.

Preparation of 1,3-Dichloroisopropyl Stearate (the Stearic Acid Ester of 1,3-Dichloro-2-Propanol)

The 1,3-dichloroisopropyl stearate was prepared by the second of Whitby's two methods (21). Stearoyl chloride and a 10% mole excess of dichloropropanol were heated at 100 C for 2 hr. A solid, precipitated out on cooling, was recrystallized from ethanol (mp 41 C; Whitby, 39.5 C; % Cl: found 18.00; theory, 17.96).

The 2-alkanoyl-1,3-dichloropropanes were also prepared by a modification of Whitby's other method (21) which calls for the heating of the fatty acid chloride with epichlorohydrin in sealed tubes. In the modified method, acid chloride and epichlorohydrin at a 5% mole excess were heated at 125 C for at least 4 hr. Usually, the solid esters crystallized out within 7 hr.

Preparation of 2-Pyran Ether (Ketal) of 1,3-Dichloro-2-Propanol

The 2-pyran ether of 1,3-dichloro-2-propanol was prepared by the Paul Reaction (22). Equimolar quantities of dihydropyran and 1,3-dichloro-2-propanol were mixed at room temperature and reaction started by the addition of one drop of concentrated HCl. After standing overnight in a closed vessel at room temperature, the reaction mixture was fractionally distilled through a Vigreux column. The colorless liquid (157 g) (bp 86 C, 1.0 mm) represented a 74% yield based on one mole of reactant. (Found: C, 45.07; H, 6.50; Cl, 33.30; theory $(C_8H_{14}O_2Cl_2)$: C, 45.50; H. 6.82; Cl, 32.20.)

Application of 2-Alkanoyloxy-1,3-Dichloropropane and of 2-Pyran Ether of 1,3-Dichloro-2-Propanol

Fabric was padded to a 135% wet pickup with a 20% solution of the dichloropropanol derivative in CCl_4, dried at room temperature and then immersed in 20% aqueous NaOH for 24 hr at room temperature. Finished fabrics were washed in benzene, soured in 2% acetic, rinsed in water and line dried. In experiments where indicated, fabrics were initially washed in hot ethanol rather than benzene.

RESULTS AND DISCUSSION

Effects of Method of Esterification on Fabric Properties

Cottons esterified to the same low D.S. of a stearoyl group by the TFAA or by the Karrer method showed no significant improvement in conditioned wrinkle recovery but some increase in wet wrinkle recovery as shown by typical data in Table I. However, esterification to the same D.S. of stearoyl groups by the acid chloride in DMF with either cotton or sodium cellulosate as the starting fabric resulted ·in fabrics with some improvement in wet wrinkle

TABLE I

Partial Cellulose Stearates and Oleates

Method of esterification[a]	DS[b]	Recovery angles		Breaking strength, % retained	Elongation at break, %	Abrasion resistance, % retained
		Dry	Wet			
DMF-RCOCL	0.05	235	190	85	8.5	---
	0.12	245	190	75	12.5	85
	0.16	250	200	75	12.5	90
DMF, R'COCl	0.07	225	187	98	10.3	---
	0.14	258	234	86	12.7	---
	0.16	275	247	60	13.0	90
	0.18	276	247	62	14.5	90
TFAA, RCOOH, C_6H_6	0.04	184	180	78	11.7	100
	0.12	220	193	78	17.2	100
	0.16	205	207	78	---	40
	0.19	215	207	78	23.7	40
TFAA, R'COOH, C_6H_6	0.08	251	217	70	8.4	40
	0.11	260	240			20
	0.16	285	270	60	16.6	20
	0.20	285	270	55	16.6	20
Aq. NaOH, RCOCl, CCL_4[c]	0.16	200	210	---	---	150
	0.18	148	167	---	---	200
Aq. NaOH, R'COCl, CCl_4[c]	0.15	160	231	---	---	200
CellŌ Na+, DMF, RCOCl	0.08	210	201	90	---	170
	0.10	248	198	70	---	106
	0.15	250	200	70	---	100
CellŌ Na+, DMF, R'COCl	0.04	220	204	90		---
	0.12	260	211	77		92
	0.15	260	215	70		90
Control	---	190	155	(45 lb)	7.0	(1420 cycles)

[a]R = $CH_3(CH_2)_{16}$; R' = $CH_3(CH_2)_7CH = CH(CH_2)_7$.

[b]DS, degree of substitution.

[c]Karrer method.

recovery, and a moderate degree of dry wrinkle recovery.

Similar data for cellulose oleates prepared by the four methods of esterification are also shown in Table I.

With the Karrer method, improved dry recovery angles were never realized, regardless of chain length of acid or of degree of unsaturation of the acid. Also, with this method, the increase in wet wrinkle recovery was small enough to be attributed to the pretreatment with aqueous 23% NaOH before its immersion in CCl_4 solution of the acid chloride. Always, the Karrer method improved abrasion resistance of cotton; usually greatest improvement was at very low D.S. values of the stearates. Unfortunately, this method of esterification never improved dry recovery values. Methods of esterification which did not adversely affect resistance to abrasion were the sodium cellulosate-DMF-acid chloride method and the DMF-acid chloride method on cotton provided enough pyridine was present to act as basic scavanger for the liberated acid.

Conventional difunctional reagents used to give cotton improved recovery in the dry state usually reduce the permanent set (PS) of the fabric by increasing the immediate recovery (IR) and not greatly affecting the delayed recovery (DR). A typical example is that of a cotton given easy care properties with dimethylol-di-hydroxyethyleneurea or a dibasic acid. Differences in recovery properties of a fabric treated with a difunctional reagent glutaroyl dichloride, in DMF (Fig. 1b) are contrasted with those of an unmodified cotton (Fig. 1a) in the quadratic graphs shown in Figure 1. Cottons possessing high dry recovery angles because of their partial esterification with a long chain monobasic acid chloride by the DMF method also show a decrease in PS, but the decrease is due to an improvement in the DR rather than the IR as shown by the quadratic graph for the oleate (Fig. 1c). The cellulose oleates prepared by the TFAA method also showed increase in total recovery due to increases in DR rather than IR. It has been said (23) that a softener or lubricant, if effective by its proper orientation with respect to the surface of the substrate, simply reduces friction by having contact between sliding surfaces and hydrophobic tails of the lubricant. In such instances, the stress-strain properties of the polymer are not changed. Only in the case of penetration of the polymer are the stress-strain properties changed. It has been shown experimentally (19) that the rates of reaction of the acid chlorides of monobasic acids with cotton via the DMF method to form esters of low D.S. are independent of chain length. For example, equimolar quantities of acetyl, octanoyl and stearoyl chlorides were reacted with cotton in DMF. Analyses of the resultant product by gas liquid chromatography showed equimolar quantities of the cellulose acetate, octanoate and stearate. The data would indicate a surface reaction only. With the cellulose esters of long chain acids, stress-strain properties of yarns as well as of fabrics are changed, and finished fabrics showed some reduction in resistance to abrasion inspite of their soft hand and drapeability. It is known (24,25) that in esterification, the long chain groups are perpendicular to the fiber axis. The spacings along the cellulose chains do not change, but the distances between chains increase with the number of carbon atoms in the side chains which are perpendicular to the direction of fiber axis. With the partial oleates and stearates, of chain length 20-30A, changes in x-ray diffractograms can be observed at a D.S. as low as 0.12.

TABLE II

Esterification of DEAE-Cottons[a]

Reactants	Add-on wt %	Recovery angles		Elongation, %	Abrasion resistance % retained
		Dry	Wet		
1. Epichlorohydrin	10	285	265	---	50
2. Epichlorohydrin + oleoyl chloride	17[b]	285	175	32	80
3. Epichlorohydrin + stearoyl chloride	22	221	150	28	140
4. Oleoyl chloride in dimethylforamide	10-20	230	200	---	85
5. Stearoyl chloride in dimethylforamide	10-20	225	205	---	---
6. Oleoyl chloride in dimethylforamide	3	221	180	---	140
7. Fabric (6) + epichlorohydrin	7	275	250	---	80
8. DEAE-cotton	---	200	190	---	120
9. Cotton	---	190	150	---	100

[a]Diethylaminoethyl (DEAE) cotton containing 1 MEq/g of tertiary amine groups reacted at 25 C with oleoyl or stearoyl chloride in indicated solvents.

[b]Presence of ester determined by IR and saponifications.

Partial Esterification and Partial Etherification

It had been suggested (7) that the process of partial esterification of cotton with a long chain monobasic acid chloride in DMF should not only provide a degree of permanent lubrication due to the reaction of the acid chloride on fiber surfaces only, but that the tensile strength of such wrinkle resistant fabrics should be higher than those fabrics finished with conventional crosslinking reagents because of the absence of strength reducing crosslinks in the partial esters. It was also suggested that combining the partial esterification method with a treatment capable of providing wet recovery only might produce an ideal fabric. The conventional theory states that wet wrinkle recovery is usually imparted in swollen fibers by reagents which increase the hydrophilicity of the fabric. Usually, fabrics with high wet recovery only do not suffer a reduction in resistance to abrasion.

Since partial cellulose oleates of low D.S. usually have high dry wrinkle recovery and only moderate degrees of wet recovery, attempts were made to esterify cottons pretreated with a reagent capable of imparting only a high degree of wet recovery. For example, cotton can be reacted with epichlorohydrin such that wet recovery angles as high as 300 (W +,F)· can be imparted without loss in abrasion resistance at relatively small add-ons (<10%). Subsequent treatment of such etherified cottons by the oleoyl chloride-DMF method to a D.S. ≤0.2, resulted in cottons still possessing high wet recovery, but only a moderate degree (maximum of 240°) of dry recovery, and resistance to abrasion less than control values, Similar results were obtained with premercerized fabrics, which have moderate dry and wet recovery angles and show no decreases in resistance to abrasion. Esterification of premercerized fabrics by the DMF-acid chloride method required a higher D.S. than did an unmercerized fabric to attain the same level of dry recovery. Use was also made of cotton containing tertiary amine groups as are found in diethyl-aminoethyl (DEAE) celluloses. Epichlorohydrin reacts with a DEAE cotton <1% nitrogen to give a fabric of high wet and high dry wrinkle recovery, but possessing poor resistance to abrasion. Data in Table II are typical for fabrics esterified to a low D.S. in the absence or presence of epichlorohydrin as indicated. Only esterification with the stearoyl chloride improved resistance to abrasion, but this improvement was accompanied by a decrease in recovery angles.

Attempts to quaternize DEAE cotton in fabric form with a stearyl halide or with an oleyl halide by methods used to quaternize DEAE with methyl or ethyl halides were unsuccessful. Also, a variety of efforts to etherify cottons via cellulose-epoxide reactions with epoxy compounds

containing stearyl or oleyl groups met with little success. Reacting cotton with chloromethylethers of stearyl alcohol resulted in cottons of high recovery values, low abrasion resistance and containing only formaldehyde but no stearyl groups.

All data studied thus far indicate that the resistance to abrasion of cottons chemically modified with long chain alkyl groups is reduced whenever the finished fabric has high dry wrinkle recovery. High dry wrinkle recovery usually results after esterification in nonaqueous media. Improvement in resistance to abrasion is pronounced only when the long chain alkyl group has not been chemically combined with the cellulose matrix in the absence of water and usually when the finished cottons possess only high wet wrinkle recovery.

Chipalkatti Method

Initially, we were able to reproduce Chipalkatti's experiments insofar as we were able to improve the Stoll flex abrasion values manyfold over that of the control fabrics. It was noted, however, that in the Chipalkatti method (9)
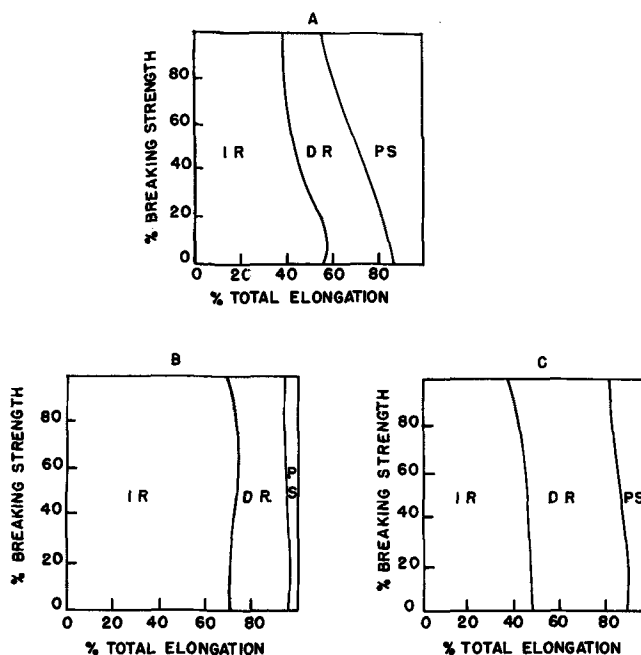

FIG. 1. Conditioned recovery behavior of cotton (A), cotton esterified in dimethylformamide (DMF) with glutaroyl dichloride (B) and oleoyl chloride (C). DS of esters 0.10; immediate recovery, IR; delayed recovery, DR, and permanent set, PS.

TABLE III

Effects of Depositing Reagent on Fabric[a]

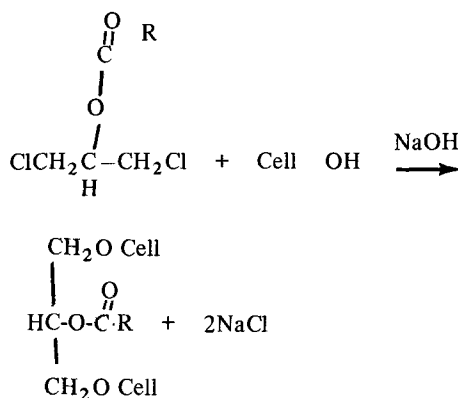| Reagent	Extraction solvent	Add-ons, wt %	Abrasion resistance, % retained	Recovery angles	
				Dry	Wet
Monostearin	Benzene	0	90	190	146
Monostearin	Benzene, ethanol	0	80	183	142
Distearin	Benzene	0	75	182	137
Distearin	Benzene, ethanol	0	90	177	145
Tristearin	Benzene	0	70	175	165
Tristearin	Benzene, ethanol	0	80	165	145
SED[b]	Benzene	0	117	184	196
SED	Benzene, ethanol	1.0	62	180	147
Stearic acid	---	27.5	141	162	133
Oleic acid	---	31.3	227	184	143
Stearic acid	Benzene	0.8	120	180	156
Oleic acid	Benzene	0.5	306	149	149
Stearic acid	Benzene, ethanol	1.1	135	171	138
Oleic acid	Benzene, ethanol	0.5	225	146	162
Stearic acid, NaOH[c]	Benzene	2.0	185	187	199
Oleic acid, NaOH[c]	Benzene	2.0	398	180	194
Stearic acid, NaOH[c]	Benzene, ethanol	1.4	202	170	189
Oleic acid, NaOH[c]	Benzene, ethanol	1.5	191	136	176
Control	---	---	(1348 cycles)	165	145

[a]Fabrics padded with monoglyceride in hot $CHCl_3$ or with di- or triglycerides in hot petroleum ether; with all other reagents, fabrics padded with 15% reagent in CCl_4 or $CHCl_3$; fabrics air-dried and then extracted with indicated solvents.

[b]2-Stearoyl ester of 1,3-dichloropropanol.

[c]Air-dried fabric treated with aqueous 23% NaOH and redried before extractions.

benzene was used as solvent to wash the treated fabrics. Admittedly, benzene dissolves the reagent ester. However, if hot anhydrous ethanol is substituted for benzene as washing solvent for the fabrics finished by Chipalkatti's method, the abrasion resistance values are not at all spectacular. In fact, abrasion resistance values of fabrics washed in ethanol were no better than that of the controls, and indicated that little if any improvements were really built-in or chemically attached to the cottons.

Chipalkatti assumed that the following reaction occurs:

$$ClCH_2\overset{\displaystyle \overset{O}{\underset{\displaystyle |}{\overset{\displaystyle ||}{C}}}\ R}{\underset{\displaystyle |}{\underset{\displaystyle H}{C}}}-CH_2Cl \ + \ Cell \ \ OH \ \xrightarrow{\ NaOH\ }$$

$$\begin{array}{l} CH_2O\ Cell \\ \ | \quad \overset{O}{\overset{||}{}} \\ HC\text{-}O\text{-}C\cdot R \ + \ 2NaCl \\ \ | \\ CH_2O\ Cell \end{array}$$

Apparently, the above reaction was just assumed to occur in early experiments in which the short chain β-esters of 1,3-dichloropropanol were reacted with cotton and ester linkages were detected in the finished fabric. The short chain esters produced improvements in wet wrinkle recovery, but no improvement in abrasion resistance or lubricity. In that report, however, only ester content was reported. Proof is not forthcoming from the work as to the site of attachment of the ester group, or, indeed, if attachment really occurred. Acyl migration (26) was not considered.

A known method for preparation of epoxides (27) is to contact a gem chloro-ester with KOH. It might be assumed that a gem chloro-stearate, such as that used by Chipalkatti, would be somewhat more difficult to saponify and de-hydrohalogenate because of the imiscibility of the reagents used. Nevertheless, we have obtained both sodium chloride and sodium stearate as a result of the reaction. From the reaction medium in which cotton was treated with the stearic acid ester of 1,3-dichloro-2-propanol according to the prescribed method of Chipalkatti, we have isolated the unreacted reagent, sodium stearate, and another crystalline solid (mp 68.5 C; C, 74.9%; H, 12.50%; Cl, 0.00%). This analysis shows that the byproduct is not a partial chloro derivative of the starting reagent nor is it β-stearin (mp 74.0 C; C, 70.40%; H, 11.70%). The analysis corresponds to that of a distearin (C, 74.86%; H, 12.31%). Also, chloride ions were present in the caustic steeping liquor which was originally free of ionic chlorine.

Furthermore, cotton was treated with the 2-pyran ether of 1,3-dichloro-2-propanol rather than with the stearoyl ester of 1,3-dichloro-2-propanol according to the Chipalkatti method. This compound was selected because of the stability of the 2-pyran ether group to NaOH (28). The absence of reaction of cotton with the pyran ether indicates that the reaction of cotton with the ester reagent occurs via a saponification and dehalogenation step rather than as suggested in Equation 1. The stability of the 2-pyran ether of 1,3-dichloro-2-propanol in aqueous base and also its inertness with soda cellulosate in nonaqueous media are evidence that the mechanism depicted in Equation 1 does not occur. Reaction of cotton with a 1,3-dichloro-2-propanol derivative in basic media occurs only when the 2-hydroxy group is present.

We believe that Chipalkatti's excellent abrasive resistant fabrics resulted from residual stearates deposited in the fabric. In fact, fabrics treated by his method have solid deposits which can be observed easily during rough handling and some treated samples before washing in

benzene had add-ons approximating 40 wt.% of the treated cotton. Chipalkatti's papers attribute the built-in lubrication to the proper orientation of the pendant long chain alkyl groups on the cross-linker, 2-alkanoyloxy-1,3-dichloropropane. Others (23) have discussed the possible significance of oriented adsorption as the lubricating mechanism of yarn softeners. A reduction of the frictional coefficient was considered to result from the long hydrophobic chain pointing away from the fiber surface while the polar or ionic head of the adsorbed group was attracted to the polar groups on the fiber's surface. Such adsorption of long chain stearates as a vertically oriented monolayer on the fiber surface would be similar to that discussed recently by Ottewill (29) in his report of the adsorption of long chain fatty acids on rutile from n-heptane.

Application of Stearoyl or Oleoyl Groups Chemically Attached

Data in Table III are given to illustrate the fact that a mono-, di-, or tristearin simply deposited on cotton can be extracted with benzene and ethanol such that the resultant fabric has essentially the same recovery angles as the control and has lost only a small percentage of its resistance to abrasion. Data in Table III also show typical recovery angles and percentages of abrasion resistance retained for cotton treated with the stearic ester of 1,3-dichloro-2-propanol (SED) or with stearic or oleic acid and then extracted. In every instance, except when SED was extracted with ethanol as well as benzene, abrasion resistance was higher than that of the control cotton.

A typical cotton fabric treated with SED according to the Chipalkatti method had a 40 wt.% add-on before being washed in excess benzene. After several extractions in benzene, the fabric had only a 0.5% weight gain, but its resistance to Stoll flex abrasion was always double that of the untreated control. Extraction of the treated fabric with hot ethanol, in which stearic acid dissolves better than in benzene, resulted in fabrics with 0.3% weight gain but the resistance to Stoll flex abrasion was only half that of the untreated control, or one fourth that of the sample extracted with benzene only.

Microscopical Evaluation

An interesting study of the influence of application conditions on softener efficiency for cottons was reported recently (23). This study included stearyltrimethylammonium chloride as one of the cationic softeners applied throughout the fiber by an exhaustive process from aqueous solvents, on the periphery of the fibers by an aqueous pad technique and on the surface only by a solvent application. Cottons by all three methods had a soft hand and drapeability. Attempts to differentiate relative efficiencies of the three methods of application by use of microscopical staining techniques were not successful.

Cellulose esters of this study were subjected to various light and electron microscopical techniques described previously (20). Electron micrographs of surface replicas of an unmodified cotton fiber and of fibers removed from the variously esterified cotton fabrics were examined. Rugosities in the surface of the unmodified cotton and fibrillar texture of cotton were lost on its esterification to a low D.S. in nonaqueous media. The smooth surface was typical of the partial cellulose oleates and stearates prepared by all except the Karrer method. With the latter, the surface was smoother than that of the control cotton, but not as smooth as that obtained by the other three methods of esterification. Attempts to correlate the surface appearance of the modified cotton fibers with resistance to flex abrasion values of the finished fabrics were unsuccessful.

Fabric surfaces of cellulose oleates and stearates of
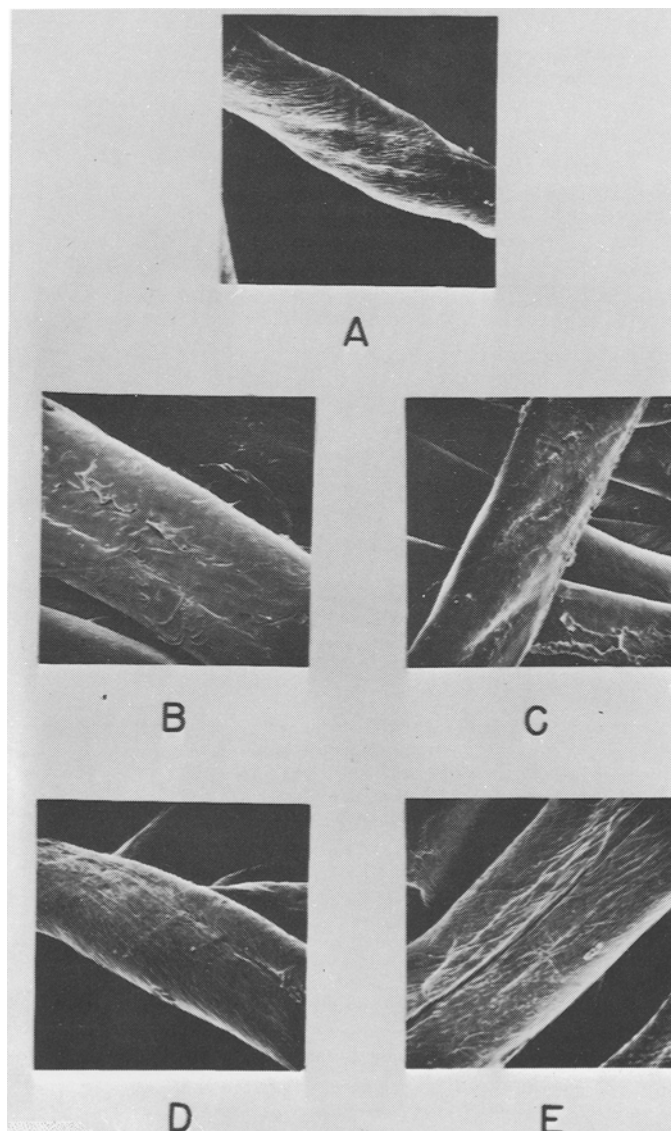

FIG. 2. Surface views of control cotton fabric (a); partial cellulose stearate (b) and partial oleate (c) prepared by reacting cotton with the alkanoyl chloride in DMF; partial cellulose stearate (d) and partial oleate (e) prepared by pretreating cotton with aqueous NaOH and then reacting with the alkanoyl chloride in CCl_4. (DS of all esters = 0.10; magnification of each micrograph 2000X.)

various D.S. values prepared by the four methods were examined on the scanning electron microscope. Fibers of all partial esters had surfaces smoother than that of the untreated cotton. Those prepared by the Karrer method were not as smooth as those prepared in nonaqueous media. In Figure 2a are shown surface characteristics of an untreated cotton control fabric. The smooth surfaces of fabrics resulting from their partial esterifications in nonaqueous media are illustrated in Figure 2b and c, which are typical of the partial stearate and oleate, respectively. The surface characteristics obtained with the cellulose stearate or oleate prepared by the Karrer method are illustrated in Figure 2d and e, respectively. Some of the fibers subjected to the TFAA-acid-benzene method showed occasional damage to the primary wall of cotton. The DMF-acid chloride method applied to sodium cellulosates rather than to cotton resulted in the most homogeneous treatment as judged by examination of fiber surfaces on the electron microscope.

Fibers removed from the partial oleates and stearates prepared from acid chlorides in DMF were also insoluble

after 30 min immersion in 0.5 M cuene. These findings indicate that such esters prepared in nonaqueous media prevent the basic cuene solution from saponifying the ester linkages very readily. This hydrophobic property of partial cellulose esters of long chain monobasic acids prepared in DMF has been used most recently by Deanin (30) to prepare breathable, permanent water repellent cottons suitable for rainwear. Although the groups are hydrophobic, we have found that the partial cellulose oleates possessing high dry recovery have moisture regain values of approximately 6%. The moisture regain values of the oleates prepared by the DMF-acid chloride method do not vary with D.S. from 0.05 to 0.20. However, the corresponding cellulose stearates, which have less dry recovery, have moisture regain values of about 4.0% at a D.S. - 0.05 and only about 3.% at a D.S. = 0.15 as compared to a value of 6.0% for an untreated cotton fabric.

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