The Role of Crosslinking in Enhancing Wet Crease Recovery of Cellulosic Fabrics

GIULANA C. TESORO

J. P. Stevens & Co., Inc., Central Research Laboratory, Garfield, New Jersey

1. INTRODUCTION AND SCOPE OF THE INVESTIGATION

In the course of the last decade, many investigations have been reported which were designed to lead to an understanding of the mechanism by which the dry crease recovery of cellulosic fabrics is enhanced when the fabrics are treated with polyfunctional reagents capable of reacting with more than one hydroxyl group in the cellulose. Although it has not been possible to obtain direct proof of the hypothesis that crosslinking of cellulose chains is essential to the achievement of high crease recovery values (50% or more higher than that of the untreated fabrics), the indirect experimental evidence reported has been, almost without exception, consistent with this hypothesis. Thus, the role of crosslinking in enhancing dry crease recovery of cellulosic fabrics is generally recognized, even while researchers continue to strive in order to achieve a deeper understanding of the fundamental relationships between the number, location, and structure of the crosslinks on one hand and the fiber and fabric properties on the other.

More recently, the wet crease recovery of cellulosic fabrics has been studied, and the significance of the dry/wet crease recovery relationship in the overall wash-wear behavior of cellulosic fabrics has been discussed by several authors. Steele[1] has presented a clear analysis of this particular relationship for cotton and regenerated celluloses, and the work of Reeves, Perkins, and Chance[2] has established that the dry/wet crease recovery ratio can be varied by crosslinking cotton fabric with acid-catalyzed formaldehyde at various degrees of fiber swelling.

The actual role of crosslinking in enhancing wet crease recovery has not been studied experimentally, however. It is known that wet crease recovery can be greatly increased by carrying out a crosslinking reaction while the fibers are in a swollen state,[2,3] but it has also been proposed that the wet crease recovery of cellulosic fabrics can be substantially increased in the total absence of crosslinking.

Wet crease recovery can be increased by surface deposition of resin. This phenomenon has been analyzed by Steele[1] and explained as a macroscopic crosslinking effect, or spot welding of fibers inside the yarns. This method of fabric treatment alters the physicomechanical elements of the fabric structure without necessarily involving chemical modification of the fiber molecule. For this reason, it does not bear a direct relationship to the work reported in this paper in which the effect of molecular substituents on fabric properties has been studied.

The moderate increase in wet crease recovery which is noted when regenerated cellulosic fabrics are treated with caustic solutions may be related to physical changes within the fiber or possibly to a partial dissolution of the cellulose during the caustic treatment, resulting in precipitation of an amorphous cellulose "film" on the fiber surface when the caustic solvent is neutralized or otherwise removed.

The partial phosphonomethylation of cotton fabric was stated to produce high wet crease recovery, although no actual measurements were reported in the initial study.[4,5] A recent publication,[6] in which the crease recovery properties of cotton partially phosphonomethylated with and without prior crosslinking are described in some detail, indicates that the increase in wet crease recovery due to phosphonomethylation alone is actually smaller than obtained with the sodium hydroxide solution employed as reaction medium. Thus, the observed changes in the wet properties of the phosphonomethylated fabrics probably result from physical changes within the fiber structure and not, as had been postulated earlier.[4,5]

from the effect of the substituent introduced. Similar considerations may apply in the case of methylated cotton which has been stated to exhibit increased wet crease recovery. No data have been reported for "methylated" cellulosic fabrics, and the conditions employed for the methylation reaction are not known. However, earlier studies of the methylation of cotton yarn[7] have indicated that an extensive disorganization of the original crystallite structure takes place during the methylation reaction, particularly in the case of methylation with dimethyl sulfate in presence of aqueous alkali.

The high wet crease recovery which is obtained on cotton by treatment of alkali swollen fabric with dichloropropanol[8] and with diepoxides[9] has often been attributed to the presence of monomeric and polymeric side chains and of cyclic (intramolecular) substitution products rather than to the formation of intermolecular crosslinks. Since polyfunctional reagents were employed for these reactions, the formation of crosslinks cannot be excluded. While the ratio of crosslinked products to simple substitution products is undoubtedly lower when a reaction with polyfunctional reagents is carried out on highly swollen fibers (due to the effect of dilution), and the formation of graft polymers is certainly significant in these particular systems, it is still probable that the high wet crease recovery observed in the reaction products be

due entirely or in part to the presence of covalent crosslinks.

No experimental evidence is available which offers satisfactory proof that high wet crease recovery can be achieved in cellulosic fabrics by the introduction of simple substituents only; in the known instances in which high wet crease recovery was obtained in the absence of extensive changes in fiber structure, either surface deposition of amorphous polymer on the fibers or the formation of covalent crosslinks or both factors could play a role in addition to the substitution reaction. In this paper, we will present experimental evidence indicating that monofunctional substituents of unequivocal functionality are not effective in enhancing the wet crease recovery of cellulosic fabrics, while a comparable extent of modification with bifunctional reagents results in greatly increased wet crease recovery.

In order to achieve a comparison of the effects of simple substituents and crosslinks on the wet crease recovery of cellulosic fabrics, we attempted to design a reaction system in which the following requirements would be fulfilled.

(1) The reaction of monofunctional and bifunctional reagents of identical size and unequivocal functionality is carried out under comparable reaction conditions.

(2) The reactions are carried out in presence of a swelling medium, allowing significant increases in

TABLE I

Reagent no.	Formula	Functionality	Physical form	Reference	Equiv. wt.[a]		Cl, %	
					Calcd.	Found	Calcd.	Found
	Monosulfones							
I	CH₃CH₂SO₂CH₂CH₂NC₅H₅ ⎮ Cl	1	White crystals	—	235	230	15.2	15.7
II	C₅H₅NCH₂CH₂SO₂CH₂CH₂NC₅H₅ ⎮ ⎮ Cl Cl	2	White crystals	13 b	175 (184)	— 183	20.3 (19.3)	— 19.4
III	CH₃CH₂SO₂CH₂CH₂SSO₃Na	1	White crystals[c]	—	256	256	—	—
IV	NaO₃SSCH₂CH₂SO₂CH₂CH₂SSO₃Na	2	White crystals	13	195	196	—	—
	Disulfones							
V	CH₃CH₂SO₂CH₂CH₂SO₂CH₂CH₂NC₅H₅ ⎮ Cl	1	White crystals	—	328	328	10.8	10.7
VI	C₅H₅NCH₂CH₂SO₂CH₂CH₂SO₂CH₂CH₂NC₅H₅ ⎮ ⎮ Cl Cl	2	Tan powder	—	221	223	16.2	15.6
VII	CH₃CH₂SO₂CH₂CH₂SO₂CH₂CH₂OSO₃NH₄	1	Tan powder[d]	—	327	361	—	—
VIII	H₄NO₃SOCH₂CH₂SO₂CH₂CH₂SO₂CH₂CH₂OSO₃NH₄	2	White crystals	—	220	—	—	—

[a] Equivalent weight determined by electrometric titration with standard NaOH.
[b] Monohydrate.
[c] M.p. 103–105°C.
[d] M.p. 175–118°C.

wet crease recovery even at low degrees of substitution.

(3) The reactions are carried out under conditions which eliminate or minimize the possibility of partial dissolution of the fiber and of extensive physical changes within the fiber structure.

(4) The structure of the reagents is such that the formation of graft polymers and resin is minimized.
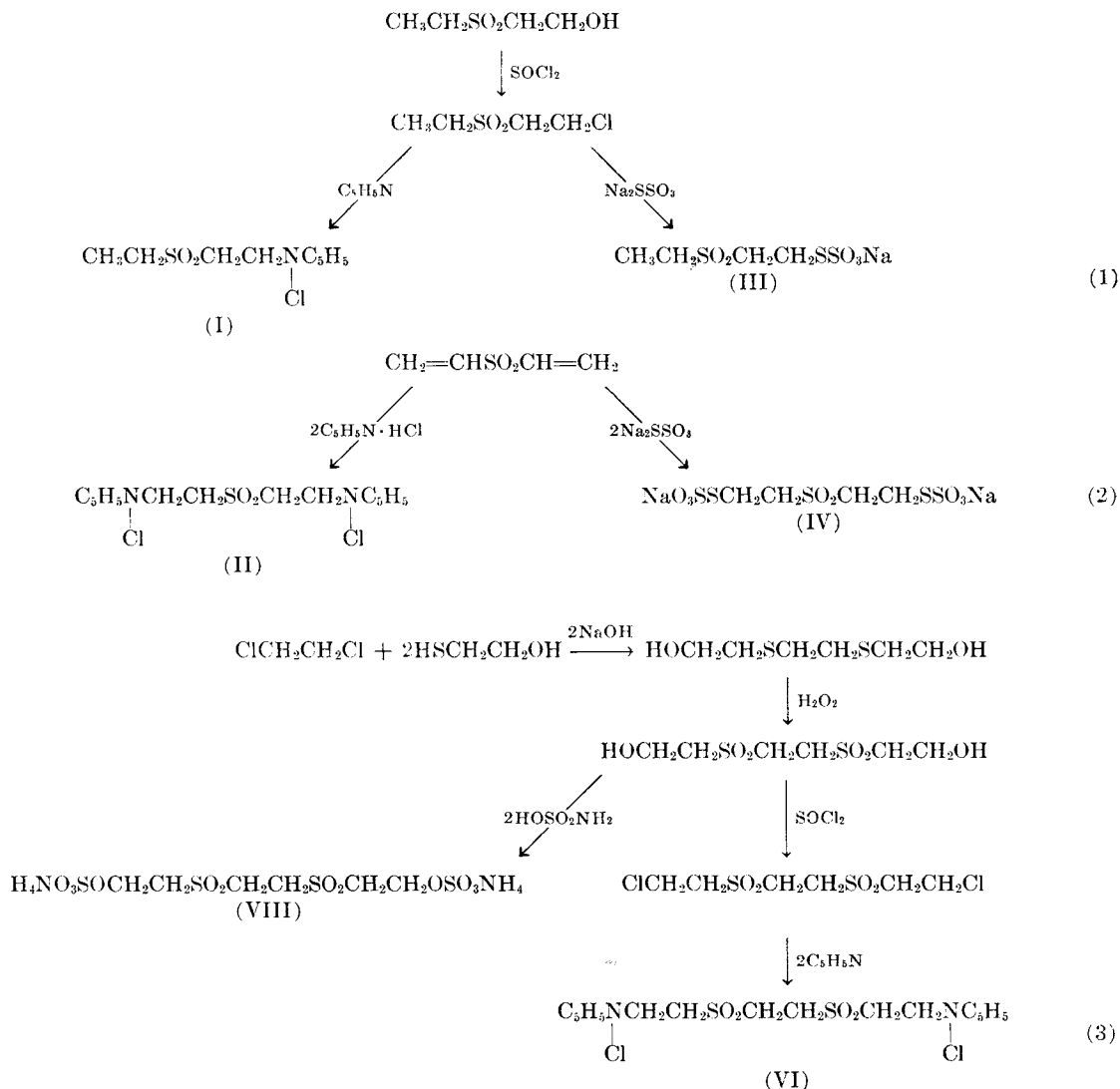
The reaction of cotton, viscose rayon, and a polynosic fiber, Zantrel (a product of Hartford Fibers, Inc.), with the reagents shown in Table I, was studied. Vinyl sulfone derivatives of this type are known to react readily with cellulose,[10] and the compounds listed in Table I appeared to fulfill the requirements listed above. In addition, it was hoped that the effects of reagents of different size could be compared by employing monosulfones (compounds I to IV in Table I) and di-

sulfones (compounds V to VIII in Table I). Actually, the choice of the γ-disulfones proved to be unfortunate, since these compounds might decompose under the conditions used for the reaction with cellulose, yielding divinyl sulfone derivatives among the decomposition products. Thus, a comparison of the effects of substituents of different size on fabric properties could not be achieved.

2. SYNTHESIS OF REAGENTS

All reagents were prepared in our laboratory. The synthesis of the monosulfones (I to IV) shown in the upper part of Table I, was carried out from known intermediates [eqs. (1) and (2)].

The synthesis of the disulfones (V to VIII) shown in the lower part of Table I, and particularly of the monofunctional compounds V and VII presented some difficulty, and several approaches

$$CH_3CH_2SO_2CH_2CH_2OH$$
$$\downarrow SOCl_2$$
$$CH_3CH_2SO_2CH_2CH_2Cl$$

C_5H_5N ↙   ↘ Na_2SSO_3

$CH_3CH_2SO_2CH_2CH_2\overset{|}{\underset{Cl}{N}}C_5H_5$ $CH_3CH_2SO_2CH_2CH_2SSO_3Na$ (III)   (1)

(I)

$$CH_2{=}CHSO_2CH{=}CH_2$$

$2C_5H_5N\cdot HCl$ ↙   ↘ $2Na_2SSO_3$

$C_5H_5\overset{|}{\underset{Cl}{N}}CH_2CH_2SO_2CH_2CH_2\overset{|}{\underset{Cl}{N}}C_5H_5$ $NaO_3SSCH_2CH_2SO_2CH_2CH_2SSO_3Na$ (IV)   (2)

(II)

$$ClCH_2CH_2Cl + 2HSCH_2CH_2OH \xrightarrow{2NaOH} HOCH_2CH_2SCH_2CH_2SCH_2CH_2OH$$
$$\downarrow H_2O_2$$
$$HOCH_2CH_2SO_2CH_2CH_2SO_2CH_2CH_2OH$$

$2HOSO_2NH_2$ ↙   ↓ $SOCl_2$

$H_4NO_3SOCH_2CH_2SO_2CH_2CH_2SO_2CH_2CH_2OSO_3NH_4$ $ClCH_2CH_2SO_2CH_2CH_2SO_2CH_2CH_2Cl$
(VIII)

$\downarrow 2C_5H_5N$

$C_5H_5\overset{|}{\underset{Cl}{N}}CH_2CH_2SO_2CH_2CH_2SO_2CH_2CH_2\overset{|}{\underset{Cl}{N}}C_5H_5$ (3)
(VI)

were tried unsuccessfully before finding satisfactory synthetic routes. The preparation of the bifunctional compounds VI and VIII was carried out as shown in eqs. (3).

The preparation of the monofunctional compounds V and VII was carried out as follows [eqs. (4)].

solids which liberate vinyl groups in the presence of hydroxyl ion in the manner shown by Stahmann[13] for derivatives of divinyl sulfone. The reaction of these compounds with cellulose was expected to follow the general course discussed in a previous publication[10] for derivatives of divinyl sulfone (compounds II and IV in Table I).

$$CH_3CH_2SO_2CH_2CH_2OH \xrightarrow{SOCl_2} CH_3CH_2SO_2CH_2CH_2Cl$$

$$\downarrow NaOH + HSCH_2CH_2OH$$

$$CH_3CH_2SO_2CH_2CH_2SCH_2CH_2OH$$

$$\downarrow H_2O_2$$

$$CH_3CH_2SO_2CH_2CH_2SO_2CH_2CH_2OSO_3NH_4 \xleftarrow{HOSO_2NH_2} CH_3CH_2SO_2CH_2CH_2SO_2CH_2CH_2OH$$

$$\downarrow SOCl_2$$

$$CH_3CH_2SO_2CH_2CH_2SO_2CH_2CH_2Cl$$

$$\downarrow C_5H_5N$$

$$CH_3CH_2SO_2CH_2CH_2SO_2CH_2CH_2NC_5H_5$$
$$\underset{Cl}{|}$$

$$(V) \hspace{8cm} (4)$$

A summary of the physical properties and analytical data for the intermediates prepared in the course of this work is given in Table II. The yields were generally good, although greatly dependent on the reaction conditions employed and on the specific techniques selected for the isolation of the desired reaction products.

All the products used for reaction with cellulose and shown in Table I are water-soluble, odorless

3. REACTION WITH CELLULOSE

a. Materials and Methods

The following fabrics were used in the study of the reaction with the compounds shown in Table I: cotton, 80 × 80 print cloth, bleached and desized, not mercerized; viscose rayon challis, desized and scoured, not dyed; Zantrel challis, desized and scoured, not dyed.

TABLE II

Compound	M.p. (or b.p.), °C.	Sulfur, %		Chloride, %		Reference
		Calcd.	Found	Calcd.	Found	
$CH_3CH_2SO_2CH_2CH_2Cl$	(110–112/2 mm.) 27	—	—	22.8	23.0	11
$CH_3CH_2SO_2CH_2CH_2SCH_2CH_2OH$	[a]	16.3[b]	16.7	—	—	—
$CH_3CH_2SO_2CH_2CH_2SO_2CH_2CH_2OH$	93	27.8	27.0	—	—	—
$CH_3CH_2SO_2CH_2CH_2SO_2CH_2CH_2Cl$	172–173	—	—	14.4	14.4	—
$HOCH_2CH_2SCH_2CH_2SCH_2CH_2OH$	58–60	35.0	37.2	—	—	12
$HOCH_2CH_2SO_2CH_2CH_2SO_2CH_2CH_2OH$	115–116	25.8	25.9	—	—	12
$ClCH_2CH_2SO_2CH_2CH_2SO_2CH_2CH_2Cl$	200–203	—	—	25.2	22.4	12

[a] Liquid; not distilled.
[b] As sulfide.

All fabrics were used without preparation or pretreatment. Fabric samples weighing 10–30 g. were conditioned at 65% R.H., 70°F., weighed on an analytical balance to the nearest milligram, padded with the aqueous reagent solution, framed to the original dimensions, and dried at 160–170°F. They were then padded with a sodium hydroxide solution so as to yield 1.25 equivalents (±0.25) of sodium hydroxide for each equivalent of reagent present on the fabric, rolled smoothly on rubber cores, and allowed to react wet at room temperature for 30 min.

The samples were then neutralized in cold 3% acetic acid, washed at 110–120°F. with a solution of nonionic detergent, framed to the original dimensions, dried at 200–220°F., and conditioned for analytical weighing. The moisture regain of treated samples at 65% R.H. was determined, and the actual weight gain was calculated by correcting the observed weight increase according to the differences in moisture regain between the treated sample and the untreated control fabric. A number of treated samples were analyzed for sulfur content in order to confirm the accuracy of the weight gain results, and the values obtained for sulfur content were generally in excellent agreement with those calculated from the weight gains. Some examples of such data are shown in Table III for cotton samples treated with various reagents.

Control samples were padded with water only and with varying concentrations of sodium hydroxide within the range employed for the reactions with the sulfones, neutralized, washed, and dried exactly as for the treated samples. The properties of these control samples were tested in order to establish the effect of the alkaline reaction medium on fabric properties.

b. Reactivity and Yields

It is apparent from the equivalent weight of the reagents employed (see Table I) that different concentrations of sodium hydroxide are required in order to maintain the same equivalent ratio of alkali for a given weight of reagent. Furthermore, it was found that under comparable reaction conditions, the yields obtained with bifunctional compounds are consistently higher than those obtained with monofunctional compounds of comparable structure. A summary of the yields obtained in the reaction of the sulfones with cellulosic fabrics is presented in Table IV; the maximum and minimum concentrations of reagent applied, the corresponding maximum and minimum concentrations of NaOH employed in the second step, and

TABLE III

Reagent (Table I)	Observed wt. increase, %	Corrected wt. gain, %	S, % Calcd. from corrected wt. gain	Found
I	3.7	3.7	1.0	1.0
I	2.4	2.4	0.65	0.74
I	4.7	4.7	1.27	1.26
II	5.0	3.5	0.95	0.98
II	5.1	3.6	0.98	0.99
II	2.8	2.0	0.54	0.58
II	2.3	2.0	0.54	0.59
III	4.6	4.6	1.24	1.32
III	7.8	7.8	2.1	1.73
VI	5.8	4.3	1.30	1.21
VI	4.1	3.0	0.93	0.93
VI	2.1	1.6	0.49	0.42

TABLE IV
Yields in Reaction with Cellulose: Summary

Fabric	Reagent (Table I)	% Reagent OWF[a] Max.	% Reagent OWF[a] Min.	% NaOH OWB[b] Max.	% NaOH OWB[b] Min.	Yield, % of theory[c] Max.	Yield, % of theory[c] Min.
Cotton							
	I	38	13	13.0	2.6	26	15
	II	29	16	10.0	4.5	70	50
	III	42	18	12.5	5.2	37	19
	IV	31	10	10.0	2.6	100	96
	V	21	10	4.0	1.6	27	13
	VI	27	10	7.5	2.5	33	21
	VII	30	10	11.0	3.0[d]	33	25
	VIII	27	10	16.0	5.0[d]	54	45
Rayon							
	I	21	13	6.0	2.2	43	23
	II	30	8	6.0	2.0	80	70
	III	39	20	7.2	4.2	48	36
	IV	29	10	7.5	2.6	100	83
	V	22	10	4.0	1.6	40	22
	VI	28	9	6.0	1.9	67	42
Zantrel							
	I	33	11	5.0	1.7	36	23
	II	31	8	7.5	2.0	73	57
	III	40	20	7.2	5.2	43	31
	IV	32	10	7.5	2.6	80	73
	V	22	10	3.5	1.6	30	23
	VI	27	9	6.0	1.9	63	33

[a] OWF = on weight of fabric.

[b] % NaOH OWB (on weight of solution) to give 1.25 (±0.25) equivalents NaOH on fabric.

[c] Reaction time: 30 min. at room temperature (wet).

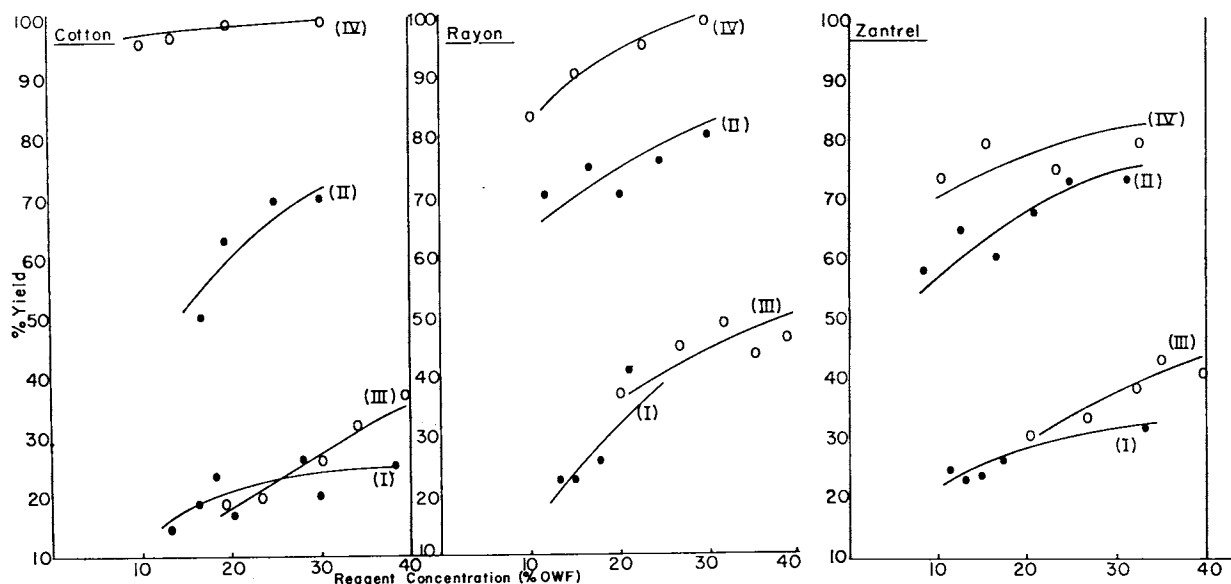[d] Requires double amount of NaOH to displace ammonia.

Fig. 1. Reaction yields with monosulfones: (I), (II), (III), (IV) as in Table I.

the maximum and minimum yields (determined from the corrected weight gain and/or sulfur analysis) are shown in this table. For mono-sulfones (compounds I to IV), the yields obtained with bifunctional reagents are higher than those obtained with the corresponding monofunctional compounds by a factor of 2 to 3. For disulfones (compounds V to VIII), the difference in the yields obtained with mono and bifunctional reagents is smaller, due to the fact that bifunctional disulfones give somewhat lower yields than the bifunctional monosulfones.

The relationship between reaction yield and reagent concentration is shown graphically in Figure 1 for the monosulfone reactions on cotton, rayon, and Zantrel. For the four reagents, the yield tends to increase with increasing reagent concentration (and therefore increasing concentration of the sodium hydroxide solution), but the effect of reagent functionality on yield is far more profound. In terms of our investigation, the immediate consequence of these large differences in yield observed in the reaction of cellulose with mono- and bifunctional compounds was that higher concentrations of reagent (and therefore of sodium hydroxide) were required in order to achieve a comparable weight increase with the monofunctional reagents. Strictly speaking then, a direct comparison of the properties of fabrics reacted to comparable extent with mono- and bifunctional compounds is truly valid only for those properties which are not affected significantly by treatment with sodium hydroxide only. This obstacle could not be completely overcome simply by evaluating the properties of control samples treated with sodium hydroxide only, since in presence of the reagent, the sodium hydroxide participates in the reaction and de-

TABLE V

Reagent (Table I)	Reagent		Substituent grouping[a]	
	Functionality	Code name	Formula	M.W.
I	1	Monofunctional P/salt	$CH_3CH_2SO_2CH_2CH_2-$	121
II	2	Bifunctional P/salt	$-CH_2CH_2SO_2CH_2CH_2-$	120
III	1	Monofunctional B/salt	$CH_3CH_2SO_2CH_2CH_2-$	121
IV	2	Bifunctional B/salt	$-CH_2CH_2SO_2CH_2CH_2-$	120
V	1	Monofunctional P/salt	$CH_3CH_2SO_2CH_2CH_2SO_2CH_2CH_2-$	213
VI	2	Bifunctional P/salt	$-CH_2CH_2SO_2CH_2CH_2SO_2CH_2CH_2-$	212
VII	1	Monofunctional sulfate	$CH_3CH_2SO_2CH_2CH_2SO_2CH_2CH_2-$	213
VIII	2	Bifunctional sulfate	$-CH_2CH_2SO_2CH_2CH_2SO_2CH_2CH_2-$	212

[a] Assuming no side reactions.

creases in concentration as the reaction proceeds, with the formation of byproduct salts.

In the discussion of the effect of substituents and crosslinks on fabric properties, this unavoidable failure to separate the effect of the sodium hydroxide concentration from that of other variables must be borne in mind, particularly in the case of regenerated cellulose. For cotton, the effect of caustic solutions within the range of concentrations and conditions used for the reactions is essentially nil, and the effect of the crosslinks and simple substituents on fabric properties can thus be assessed more accurately on a comparative basis.

The substituent groupings introduced by the reactions described above are shown in Table V without indicating side reactions. Among the possible side reactions, one which is common to all reagents results from the addition of water to the vinyl sulfone grouping:

$$-SO_2CH=CH_2 + H_2O \rightarrow -SO_2CH_2CH_2OH$$
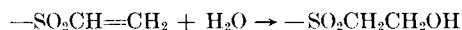
and the subsequent addition of the vinyl sulfone grouping to the hydroxyethyl sulfone compound thus formed:

$$-SO_2CH_2CH_2OH + -SO_2CH=CH_2 \rightarrow$$
$$-SO_2CH_2CH_2OCH_2CH_2SO_2-$$
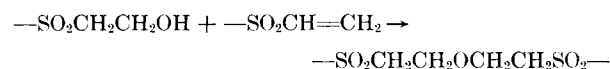
Under the conditions employed for the reaction with cellulose, this side reaction could lead to the formation of polymeric crosslinks and side chains in the reaction of cellulose with bifunctional compounds. In the case of monofunctional compounds, the products resulting from this side reaction would be a hydroxyethyl sulfone compound, $RSO_2CH_2CH_2OH$, and its unreactive "dimer" ether, $RSO_2CH_2CH_2OCH_2CH_2SO_2R$, both of which would be inert under the conditions employed. It is tempting to attribute the difference in the apparent yields obtained with mono- and bifunctional compounds to the formation of byproducts which are not capable of reaction with cellulose in the former case (monofunctional) but do react with cellulose in the latter (bifunctional).

Side reactions which are specific to the disulfones will be discussed in detail later.

4. PROPERTIES OF MODIFIED FABRICS

a. Test Methods

The moisture regain was determined by equilibrating the fabric samples from the dry state at 65% R.H. and 70°F., weighing, drying for 4 hr. at 220°F., cooling in a desiccator, and weighing immediately.

Dry crease recovery angle was measured by the Monsanto method, A.S.T.M. D-1295-60T. Wet crease recovery angle was also measured by the Monsanto method, the sample being immersed in water and blotted before measurement. Tensile strength was tested by the ravel strip method, A.S.T.M.-D-39-59, and tear strength by the Elmendorf method, A.S.T.M.-D-1424-59. Water imbibition was determined by the procedure of Daul and Drake.[14]

b. Moisture Regain

The effect of substituents on moisture regain is shown in Figures 2, 3, and 4 for cotton, rayon, and Zantrel fabrics, respectively. In these graphs, the observed weight increase (uncorrected) is plotted against the experimental moisture regain. The portion of the graphs which is on the left of the vertical line shows the moisture regain of control samples treated with varying concentrations of sodium hydroxide, washed and dried as for the sulfone treated fabrics. In each graph, the upper curves (A) show results obtained on samples treated with mono- and bifunctional monosulfones
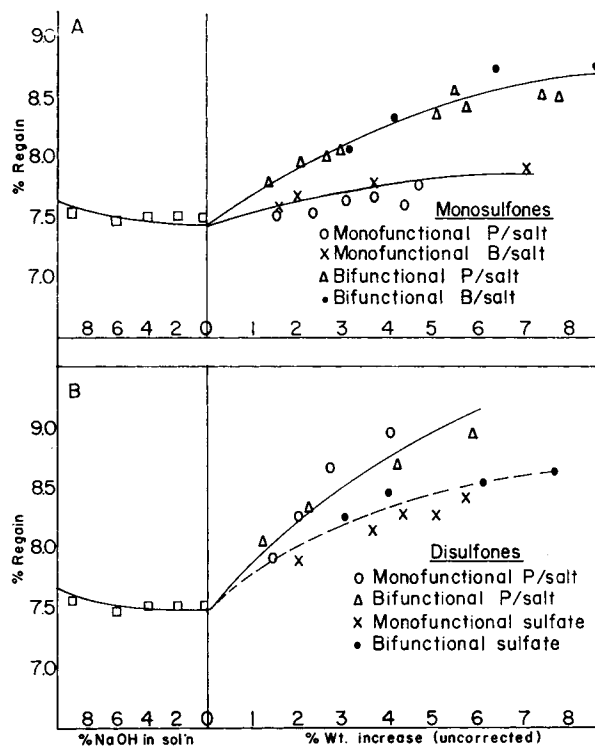

Fig. 2. Effect of substituents on moisture regain of cotton (80 × 80) at 65% R.H., 70°F.
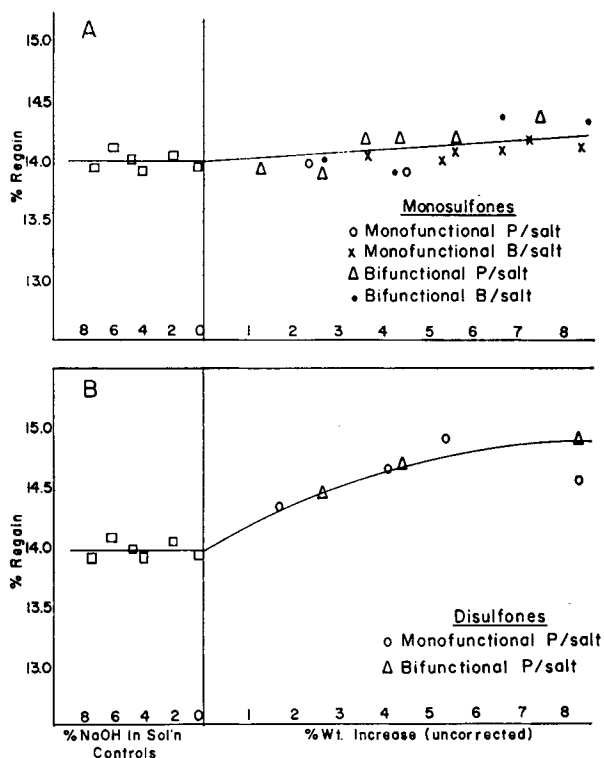
Fig. 3. Effect of substituents on moisture regain of rayon challis at 65% R.H., 70°F.
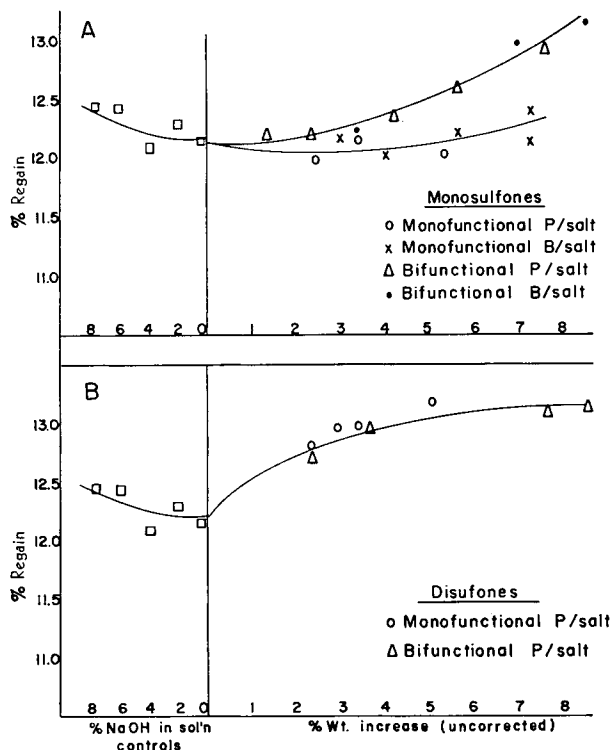

Fig. 4. Effect of substituents on moisture regain of Zantrel challis at 65% R.H., 70°F.

and the lower curves (B) show results obtained on samples treated with mono- and bifunctional disulfones.

For cotton treated with bifunctional monosulfones (Fig. 2A), the moisture regain increases with increasing extent of reaction, but a comparable extent of monofunctional substitution does not have any significant effect on the moisture regain of the treated fabric. This can be explained by assuming that the crosslinks formed in the reaction with bifunctional compounds can "freeze" the disorder produced by the swelling medium, while the monofunctional substituents do not efficiently prevent the "reorganization" of the disordered regions during drying. This difference between the effects of mono- and bifunctional compounds is not apparent in cotton fabrics treated with disulfones (Fig. 2B). In this case, the increase in regain seems independent of the functionality of the disulfone used, although possibly somewhat dependent on the nature of the solubilizing group present in the reagent.

For rayon, reaction with mono- and bifunctional monosulfones (Fig. 3A) does not have an appreciable effect on the regain, while reaction with the disulfones (Fig. 3B) increases the regain significantly, and to the same extent for mono- and bifunctional reagents.

For Zantrel, as for cotton, reaction with bifunctional monosulfones increases the regain, while reaction with monofunctional monosulfones does not (Fig. 4A). The shape of the former curve is different than for cotton, but this may be due to the difference in response of the two fibers to the caustic solution. The increase in regain which results from treatment with disulfones (Fig. 4B) appears independent of functionality for Zantrel also, as for cotton and rayon.

Thus, we can conclude that reaction with bifunctional monosulfones (crosslinking) increases the moisture regain of cotton and Zantrel, but not of rayon. Reaction with monofunctional monosulfones does not increase the regain of any of the three fibers studied significantly. Reaction with the disulfones increases the regain of the three fibers, independently of the apparent functionality of the reagent employed. The probable course of this reaction with disulfones will be discussed later.

c. Crease Recovery

The effect of the substituents on wet crease recovery is illustrated in Figures 5, 6, and 7 for cotton,
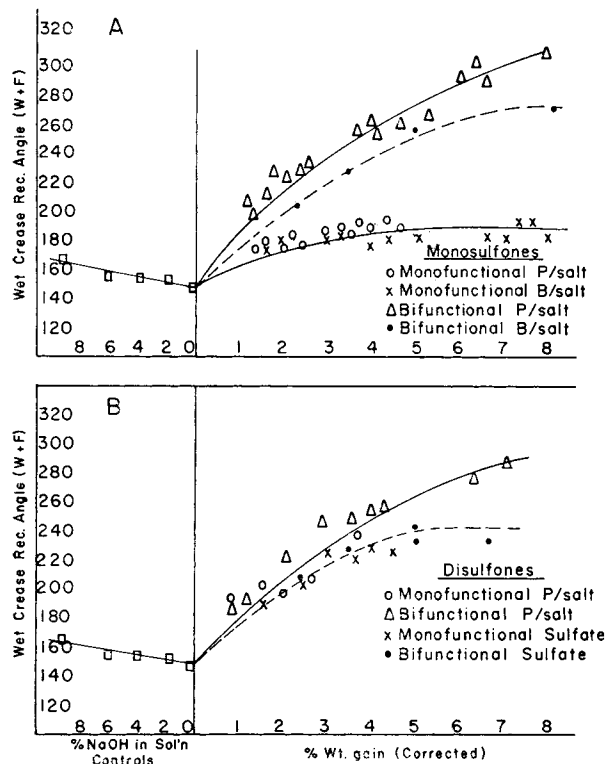
Fig. 5. Effect of substituents on wet crease recovery of cotton (80 × 80).
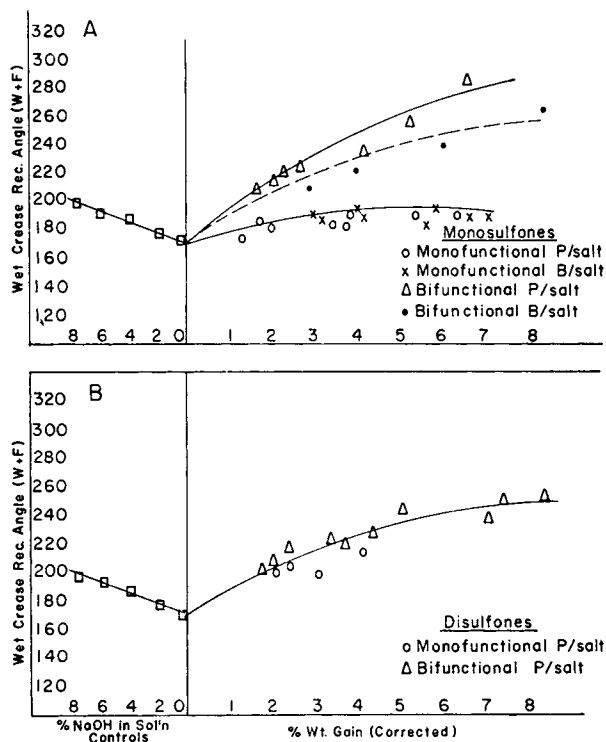
Fig. 7. Effect of substituents on wet crease recovery of Zantrel challis.

rayon, and Zantrel fabrics, respectively. In these graphs, the actual weight increase (corrected for differences in moisture regain) due to reaction is plotted against the wet crease recovery angle (W + F), the results obtained with monosulfones (upper graph A) and disulfones (lower graph B) again being separated, and the effect of sodium hydroxide solutions being shown to the left of the vertical line.

The wet crease recovery changes are essentially parallel to the regain changes in the case of cotton (Fig. 5). For rayon (Fig. 6), the wet crease recovery increases sharply as a result of the treatment with bifunctional monosulfones; this has no significant effect on moisture regain. The wet crease recovery changes produced by all reagents are of the same order of magnitude and follow the same general pattern for cotton (Fig. 5), rayon (Fig. 6), and Zantrel (Fig. 7).

Thus we can conclude that the wet crease recovery of the fabrics studied is increased by reaction with bifunctional monosulfones and reaction with disulfones. It is not increased significantly by a comparable or even greater extent of reaction with monofunctional monosulfones.

The changes in dry crease recovery which ac-

Fig. 6. Effect of substituents on wet crease recovery of rayon challis.
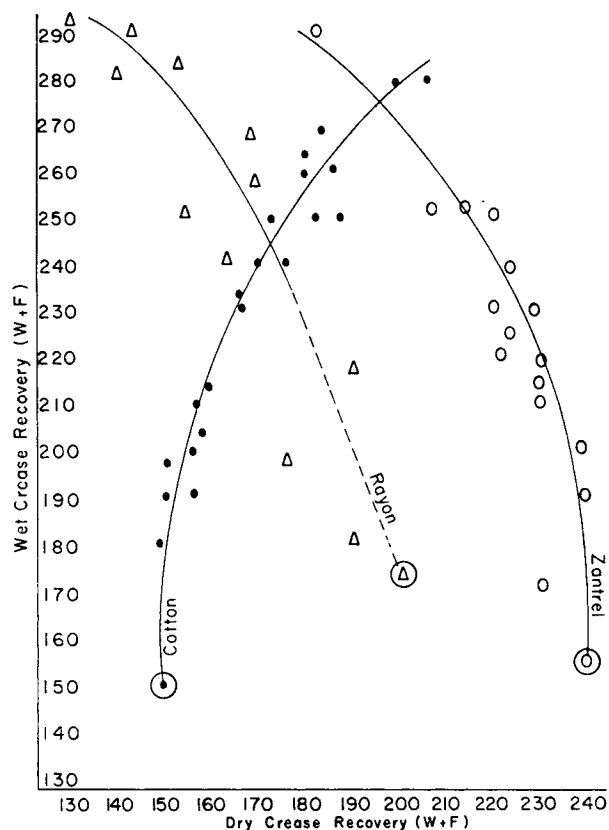
Fig. 8. Wet crease recovery and dry crease recovery for:
(●) cotton; (△) rayon; (○) Zantrel.

company the wet crease recovery increases are shown in Figure 8, in which the experimental points were taken at random for fabrics treated with various reagents. For cotton, the dry crease recovery increases moderately but consistently with increasing wet crease recovery. For rayon, the reproducibility of the dry crease recovery values is poor, but the dry crease recovery decreases sharply with increasing wet crease recovery. For Zantrel, the dry crease recovery decreases only slightly with increasing wet crease recovery values until high wet crease recovery values (250°) are reached, and then decreases rapidly.

d. Tensile and Tear Strength

The reaction with bifunctional reagents (which increase wet crease recovery) produces the expected decrease in tensile and tear strength. This decrease is generally attributed to crosslinking. The reaction with monofunctional disulfones, which increases wet crease recovery, also decreases tensile and tear strength to a comparable extent. As will be seen later, it is probable that this effect

actually results from a side reaction which makes crosslinking possible with the monofunctional disulfones. Reaction with monofunctional monosulfones, which does not increase wet crease recovery, has no effect on the tensile and tear strength of cotton fabrics. A quantitative correlation of wet crease recovery with strength is not possible for the regenerated cellulose fabrics and particularly for rayon, for which a decrease in strength results from the treatment with the caustic solution
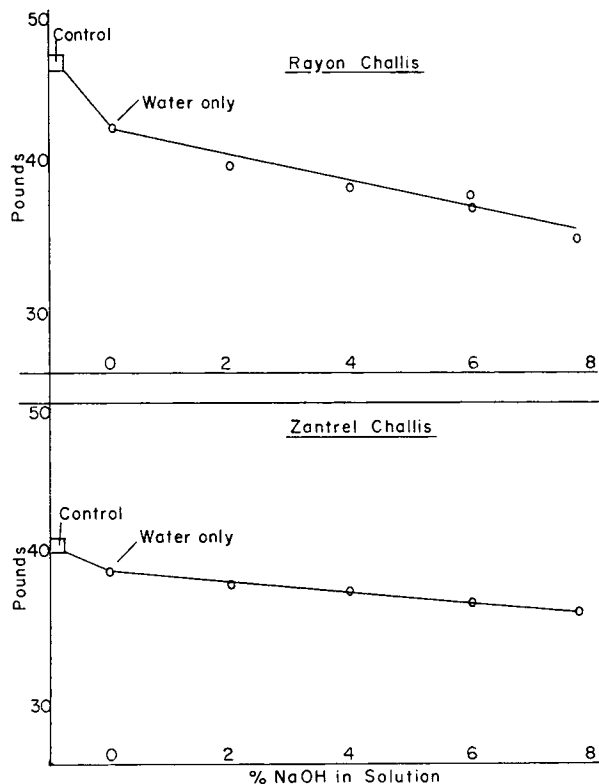
Fig. 9. Effect of NaOH on warp tensile strength of rayon challis and Zantrel challis.

only (Fig. 9), but the relationship observed for cotton can be considered significant, since the tensile and tear strength of the control samples treated with sodium hydroxide only do not differ from those of the untreated fabric.

In Figure 10 the wet crease recovery of cotton treated with mono- and bifunctional reagents is plotted against the warp tensile strength. It is apparent that all the experimental points fall on a single curve, independently of the reagent used to modify the fabric. The relationship between the wet crease recovery and warp tear strength of the treated cotton samples is essentially the same.
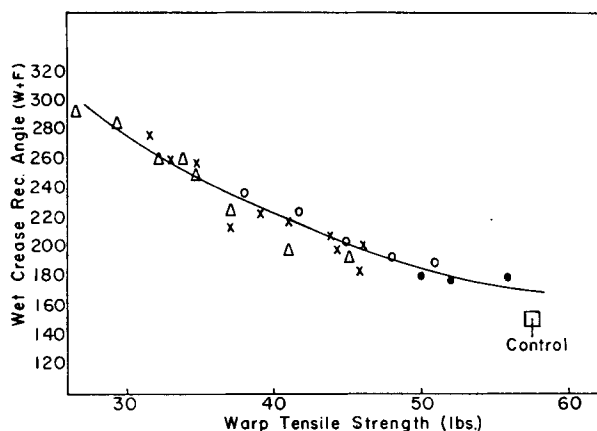
Fig. 10. Wet crease recovery vs. warp tensile strength for cotton (80 × 80) with monosulfones: (●) monofunctional P/salt, (×) bifunctional P/salt; and with disulfones: (△) bifunctional P/salt; (○) monofunctional P/salt.

e. Water Imbibition

An attempt was made to correlate the extent of reaction (weight gain) with the values obtained for water imbibition on treated rayon and Zantrel samples. The results obtained are shown in Figure 11. The reactions generally increase the imbibition value slightly. While the increase appears to be greater for monofunctional reagents than for bifunctional reagents, this is probably due to the higher reagent concentration and alkali concentration required to obtain comparable weight gains with the monofunctional compounds (due to the lower yields).

Reeves and co-workers have shown[2] that for cotton crosslinked with formaldehyde at various degrees of fiber swelling, the state of swelling during reaction has a greater effect on the water imbibition than the extent of reaction. Since in our work the state of swelling during reaction could not be kept constant for varying concentrations of the reagents used, it is not possible to interpret the experimental results shown in Figure 11 in terms of the effect of specific substituents on imbibition value.

5. DISCUSSION

The results obtained with the monosulfones show that the wet crease recovery of cellulosic fabrics cannot be increased significantly by introducing a moderate number of simple substituents into the cellulose molecule. On the other hand, a comparable extent of reaction achieved under similar conditions with bifunctional compounds of identical size and structure increases the wet crease recovery greatly. This finding suggests that crosslinking does indeed take place with the bifunctional monosulfones, although the relative amounts of crosslinking, monosubstitution, and cyclization products formed in the reaction of the swollen cellulose with the bifunctional reagents cannot be estimated.

The results obtained with the disulfones, taken at face value, are inconsistent with the conclusion that monofunctional substituents do not enhance the wet crease recovery of cellulosic fabrics, since reaction with disulfones increases wet crease recovery significantly in the case of monofunctional and bifunctional compounds as well. We believe, however, that these results are probably due to a hydrolytic decomposition of the γ-disulfones even

Fig. 11. Effect of substituents on imbibition value (*WI*).

under the mild conditions (30 min. at room temperature) employed for the reaction with cellulose. The formation of unsaturated compounds and sulfinic acids from dialkyl sulfones (monosulfones) generally takes place with fused potash at 200°C.,[15] but γ-disulfones have been reported[16] to undergo this cleavage under far milder conditions.

The alkaline cleavage of the γ-disulfones used in our work could result in the formation of divinyl sulfone from the monofunctional compounds:

$$C_2H_5SO_2CH_2CH_2SO_2CH_2CH_2\overset{|}{\underset{Cl}{N}}C_5H_5 \xrightarrow{2NaOH}$$

$$C_2H_5SO_2Na + NaCl + C_5H_5N$$
$$+ CH_2\!=\!CHSO_2-CH\!=\!CH_2\!= + 2H_2O$$

and from the bifunctional compounds as well:

$$C_5H_5\overset{|}{\underset{Cl}{N}}CH_2CH_2SO_2CH_2CH_2SO_2CH_2CH_2\overset{|}{\underset{Cl}{N}}-C_5H_5 \xrightarrow{2NaOH}$$

$$CH_2\!=\!CH_2 + SO_2 + 2NaCl + 2C_5H_5N$$
$$+ CH_2\!=\!CHSO_2CH\!=\!CH_2 + 2H_2O$$

The effective reactant in the cellulose modification would then be divinylsulfone and the changes in fabric properties resulting from the reaction with mono- and bifunc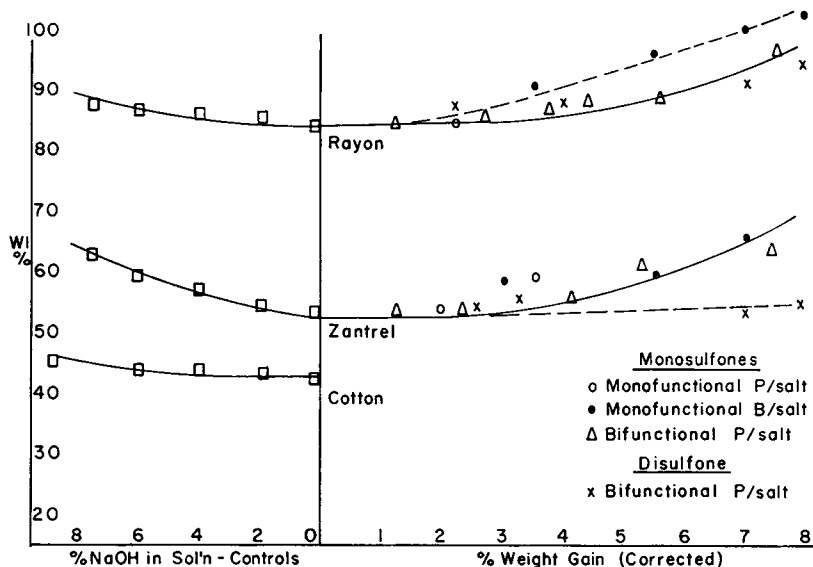tional disulfones would be due to crosslinking of the swollen fiber essentially as obtained with bifunctional monosulfones. Our attempts to confirm experimentally that this postulated cleavage of the disulfones takes place more rapidly than their reaction with cellulose were unsuccessful. Unfortunately, we were unable to isolate the by-products by extraction of the fabric after reaction, possibly due to the lack of chemical stability of the sulfinic acid[17] and to the reaction of the divinylsulfone with the cellulose.

The sulfur content of the treated fabrics could not reflect the side reaction, since it differs only slightly for the desired reaction of the disulfones (30% of the actual weight gain) and for the reaction of the divinyl sulfone postulated as by-product (27% of the actual weight gain).

The presence (or absence) of crosslinks in the treated fabrics could not be established by determining solubility in cupriethylenediamine: a 1M solution of cupriethylenediamine dissolved all treated fabrics after 20 hr. at room temperature. Since the β-sulfonylethyl ether grouping (—OCH₂-CH₂SO₂—) present in the modified fabrics is not completely stable to alkaline hydrolysis, existing crosslinks were undoubtedly severed by the test solution.

Although experimental proof of the disulfone breakdown is lacking, cleavage to divinyl sulfone is probable, and we must conclude that the γ-disul-

fones do not fulfill the requirement of unequivocal functionality which is apparently fulfilled in the case of monosulfones.

The changes in dry crease recovery which accompany the increases in wet crease recovery exhibited by the treated fabrics differ widely for the three fibers studied. The decrease in dry crease recovery observed for regenerated cellulose might be due to crosslinking of the swollen disordered structure produced by the alkaline reaction medium as postulated by Steele.[1] Since the effect of alkaline solutions in the concentration range employed as far less profound on cotton than on rayon, the moderate increase in dry crease recovery observed for the crosslinked cotton fabrics is not inconsistent with this hypothesis. It is interesting to note that the wet/dry crease recovery ratio obtained for cotton fabrics crosslinked with bifunctional monosulfones (in systems containing 50 to 60% water) is 1.35 (see Fig. 8): this value agrees well with the ratio of 1.4 reported for cotton crosslinked with 0.8% combined formaldehyde in a system containing 50–55% water.[2]

In summary, there are apparently two distinct mechanisms by which high wet crease recovery can be achieved in the absence of deep structural changes within the fiber. These are in principle independent of each other, but they probably play simultaneous roles in many known reactions and finishing processes. They are: (1) surface deposition of polymer, which has been described by Steele as a "macroscopic crosslinking" of fibers within yarns, and (2) formation of covalent crosslinks while the fiber is in a swollen state.

The experimental evidence reported in this paper suggests that side chains are ineffective in enhancing wet crease recovery. Cyclization products can be assumed to be equivalent to side chains, and also ineffective. The increase in wet crease recovery resulting from the reaction of swollen cellulose with polyfunctional reagents must therefore be attributed to the formation of covalent crosslinks.

Thus, the mechanism by which wet crease recovery is increased would not differ in principle from that by which dry crease recovery is increased, although the ratio of crosslinks to cyclic and side chain substituents and the location of the groupings introduced within the fiber undoubtedly depend on the degree of fiber swelling which prevails during the crosslinking reaction.

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Synopsis

Considerable experimental evidence has been reported in recent years in support of the theory that covalent crosslinkages between cellulose chains are essential to impart dry crease recovery to cellulosic fabrics. It has been proposed also that wet crease recovery can be increased by simple substitution in the total absence of crosslinking. It is the purpose of this paper to report a direct comparison of the effects of monofunctional and bifunctional reagents of identical size and unequivocal functionality on the wet crease recovery and other properties of cotton, rayon and other regenerated cellulose fabrics. The compounds employed are derivatives of vinyl sulfones. The synthesis of these products is briefly described, with some emphasis on the new compounds and intermediates prepared. The procedure selected for reacting the sulfones with cellulosic fabrics is described, and the differences observed in the chemical behavior of the mono- and bifunctional compounds are discussed. A comparison of the physical properties, and particularly of the wet crease recovery of fabrics modified to the same extent with mono- and bifunctional reagents, suggests that side chains are ineffective in enhancing wet crease recovery of cellulosic fabrics. The increase in wet crease recovery resulting from the reaction of swollen cellulose with polyfunctional reagents must therefore be attributed to the formation of covalent crosslinks.

Résumé

Les résultats d'un grand nombre d'expériences publiés pendant les dernières années donnent l'indication que des pontages covalents entre les chaînes de cellulose sont essentiels à la récuperation du froissement à sec des tissus cellulosiques. La proposition a été faite également que la récuperation au froissement à l'état humide peut être augmentée par une simple substitution, sans le moindre pontage. Il est l'objet de cet article de faire une comparaison directe entre les effets des réagents mono- et bifonctionnels de grandeur identique et de fonctionnalité inéquivoque sur la récuperation du froissement à l'état humide et sur d'autres propriétés du coton, de la rayonne et d'autres tissus de cellulose régénérés. Les composés utilisés sont des dérivés des sulfones de vinyle. Une description brève de la synthèse de ces produits donne quelque importance aux composés nouveaux et aux intermédiares qui ont été préparés. Il y a aussi une description du procédé choisi pour faire réagir les sulfones avec les tissus cellulosiques autant q'une discussion des différences observées dans l'action chimique des composés mono- et bifonctionnels. Une comparaison des propriétés physiques des tissus, et particulièrement de la récuperation au froissement à l'état humide, modifiées à un certain degré par l'emploi des réagents mono- et bifonctionnels, suggère que les chaînes latérales n'ont point l'effet d'améliorer la récuperation du froissement à l'état humide des tissus cellulosiques. L'augmentation de cette récuperation, qui est le résultat de la réaction de la cellulose gonflée avec les réagents polyfonctionnels, doit, par conséquant, être attribuée à la formation des pontages covalents.

Zusammenfassung

In den letzten Jahren wurde aine grosse Anzahl experimenteller Arbeiten veröffentlicht, die alle dafür sprechen, dass für die Trockenknitterfestigkeit von Cellulosegeweben kovalente Vernetzungsstellen zwischen den Celluloseketten wesentlich sind. Weiters wurde angenommen, dass die Nassknitterfestigkeit auch bei völliger Abwesenheit von Vernetzungsstellen durch einfache Substitution verbessert werden kann. In der vorleigenden Arbeit wird ein direkter Vergleich der Einflüsse von mono- und bifunktionellen Regagenzien gleicher Grösse und eindeutiger Wertigkeit auf die Nassknitterfestigkeit und auf andere Eigenschaften von Baumwolle, Rayon und anderen regenerierten Cellulosegeweben durchgeführt. Als Reagenzien wurden Derivate von Vinylsulfonen verwendet. Die Synthese dieser Verbindungen wird kurz beschrieben, wobei besonders auf die neu dargestellten Verbindungen und Zwischenstufen hingewiesen wird. Das für die Reaktion der Sulfone mit den Cellulosegewegen gewählte Verfahren wird beschrieben und die im chemischen Verhalten zwischen mono- und bifunktionellen Verbindungen beobachteten Unterschiede werden diskutiert. Ein Vergleich der physikalischen Eigenschaften, besonders der Nassknitterfestigkeit, von Geweben, die im gleichen Ausmass mit mono- und bifunktionellen Reagenzien behandelt wurden, weist darauf hin, dass Seitenketten die Nassknitterfestigkeit von Cellulosegeweben nicht verbessern. Das Ansteigen der Nassknitterfestigkeit, das bei der Reaktion von gequollener Cellulose mit polyfunktionellen Reagenzien eintritt, muss daher der Bildung kovalenter Vernetzungsstellen zugeschrieben werden.