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The Effect of Crosslinking on the Swelling of Cotton in Solutions of Sodium Hydroxide and Cadoxen

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Synopsis

This paper describes the effects of prior crosslinking in dimethylol ethyleneurea (DMEU) on the swelling of cotton fiber in aqueous solutions of sodium hydroxide and in cadoxen solutions (solutions of cadmium oxide in mixtures of ethylenediamine and water). The degree of swelling in the weaker swelling solutions is markedly reduced by the crosslinking, but in the stronger solutions (particularly in concentrated sodium hydroxide) the effect of prior crosslinking is only small; this is accounted for in terms of a fibril-tearing mechanism in these stronger solutions. Crosslinking cotton reduces the mercerizing effect of strong alkali solutions (i.e., the disordering and the cellulose I → II lattice change), and also reduces the solubility of the fiber in solutions of cadoxen and cuprammonium hydroxide.

INTRODUCTION

Microscopic investigations have shown that the crosslinking of cotton fibers reduces the degree of swelling and dissolution of these fibers in swelling agents and solvents.[1,2] This reduction is very large if the degree of crosslinking is sufficiently high. In this paper, investigations of the effects of prior crosslinking treatments on (a) the swelling behavior of cotton in alkali solutions of mercerizing strength and in solutions of cadoxen (as characterized by measurements of absorption of swelling agent and increases in fiber width), and (b) the structural changes produced in the cotton by these swelling treatments, are described. The swelling of uncrosslinked cotton in mercerizing solutions, and the structural changes produced, have been studied in detail by a large number of workers.[3] An investigation of the cotton–cadoxen swelling system has recently been made in these laboratories.[4]

There has been some technical interest in the "postmercerization" of crosslinked cotton fabrics; it has been shown,[5,6] for instance, that the postmercerization leads to an increase in strength and loss in dry crease recovery. A subsidiary aim of the work described in this paper was to throw light on the fine structural modifications causing these changes in mechanical properties.

EXPERIMENTAL

Cotton. A scoured cotton fiber (Acala 4-42) was studied in most of this work. In one series of experiments, the swelling of methylated cotton was examined. For convenience, the cotton was methylated in the fabric form with dimethyl sulfate in dimethyl sulfoxide, after pretreatment in 2*N* sodium hydroxide.[6] Samples of degrees of substitution of 0.18, 0.66, and 1.33 were prepared in this way. The substituted fabrics were then pulled apart to threads to remove tensions present in the fabric structure.

Crosslinking Treatment. The crosslinking agent chosen was dimethylol ethyleneurea (referred to below as DMEU). This crosslink is thought to be stable in concentrated alkali solutions under the present conditions of treatment. The cotton was immersed in DMEU solution (4, 8, or 12% by weight DMEU in water) containing magnesium chloride catalyst (0.32, 0.64, and 0.96% by weight, respectively) for 30 min at room temperature. Excess solution was removed from the fiber by pressing, to give an uptake of 70% by weight. The fiber was then baked at 155°C for 6 min and then washed in an aqueous solution of 0.25% by weight soda ash, 0.5% by weight Lissapol N, at 70°C. The nitrogen contents of crosslinked fibers were determined by a Kjeldahl method.

Swelling Treatments. Samples of cotton were swollen in the slack condition for 1 hr at 25°C in aqueous solutions of sodium hydroxide or in cadoxen solutions (solutions of cadmium oxide in mixtures of ethylenediamine and water). The total amount of swelling agent absorbed was measured by weighing the samples, excess swelling agent being removed by a centrifuging technique.[4] The separate uptakes of the various components of the swelling solutions were determined by extracting the swollen fibers in water, followed by standard analysis of the extract.[4] The water-washed samples were dried in air at room temperature.

The widths of some of the swollen cotton fibers were measured by a standard microscopic technique. The solubility of various samples of cotton fiber in a cadoxen solution (4.99% by weight cadmium, 28.3% by weight ethylenediamine) and in a cuprammonium hydroxide solution (15 g/l. Cu, 200 g/l. ammonia) was determined by a simple weight loss method.

Structural Investigations. The dried samples were studied with the infrared-deuteration technique to provide information on the fractions of hydrogen bond ordered and hydrogen bond disordered cellulose, and on the nature of the hydrogen bond ordered material. The basic nature of this technique has been described previously.[7–9] The cotton fibers were formed into a disc, suitable for infrared studies, by a technique[4,10,11] similar to one employed previously: they were cut into short lengths (about 1 mm), ground in a vibratory ball mill for 20 sec, sieved onto the bottom plate of a die, and pressed. With these crosslinked fibers it was, however, necessary to increase the pressure on the die somewhat and also to increase the duration of pressing (16 hr at 170,000 psi, compared with 20 min at 145,000 psi for uncrosslinked fibers).

Some of the fiber samples, after being swollen and washed in water, were solvent exchanged in this washed, never-dried condition to pyridine and then acetylated in this solvent (for 24 hr at 25°C in a 50/50 v/v mixture of acetic anhydride and pyridine). The extent of acetylation (determined by a modified Eberstadt procedure) is thought to be a semiquantitative measure of the total "surface area" of the original swollen fiber, i.e., of the degree of interfibrillar opening and separation produced by the swelling (plus the external surface area of the fiber).[3]

RESULTS AND DISCUSSION

Treatment in Aqueous Solutions of Sodium Hydroxide

Figures 1 and 2 show the effect of the prior crosslinking of cotton fiber on the swelling of the fiber in aqueous solutions of caustic soda. The

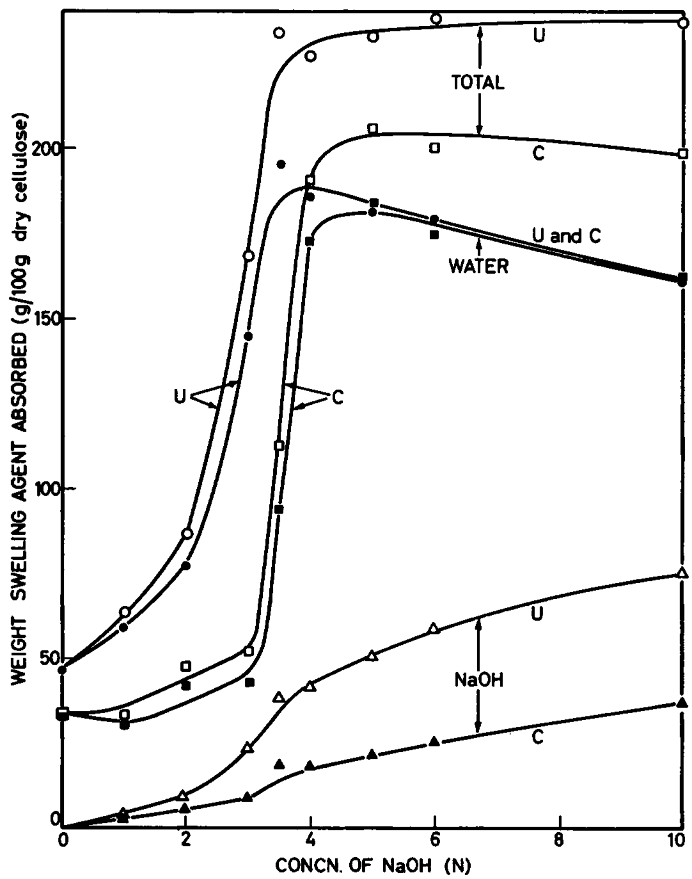

Fig. 1. Effect of crosslinking in DMEU on the absorption from aqueous solutions of sodium hydroxide: (U) uncrosslinked cotton; (C) crosslinked cotton (nitrogen content 0.88%).

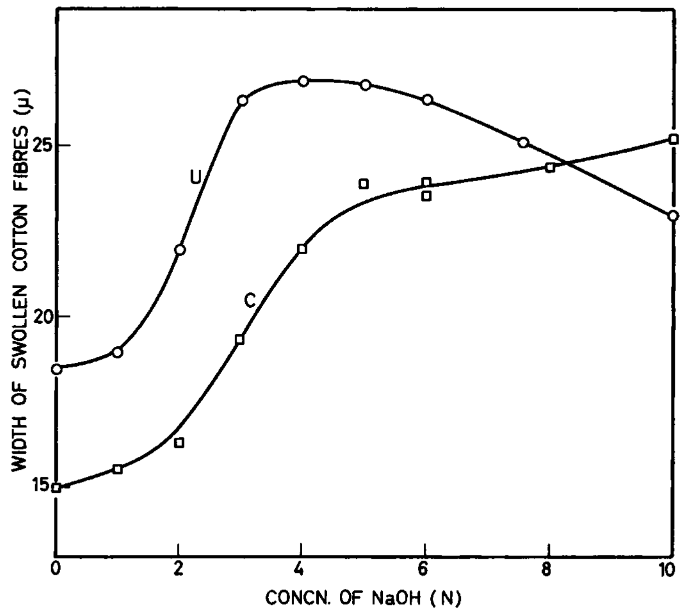

Fig. 2. Effect of crosslinking in DMEU on the width of cotton fibers swollen in aqueous solutions of sodium hydroxide: (U) uncrosslinked cotton; (C) crosslinked cotton (nitrogen content 0.88%).

crosslinking markedly reduces the swelling at the lower concentrations of alkali. At concentrations greater than 4*N*, however, the overall degree of swelling is only slightly less with the crosslinked fiber than with the uncrosslinked fiber; this is thought to be the result of a "fibril tearing" mechanism, as discussed below. The absorption of water from these concentrated solutions is almost the same for both types of fiber (Fig. 1). The absorption of sodium hydroxide is, however, less for the crosslinked material at all concentrations of alkali. This difference between the absorptions of water and alkali is discussed later.

Figure 3 illustrates that prior crosslinking with DMEU reduces the "mercerizing" effect of alkali treatment; the extent of lattice conversion from cellulose I to cellulose II is markedly diminished compared with uncrosslinked cotton, the effect becoming greater as the level of crosslinking is increased (low degrees of crosslinking have a negligible effect). Increasing the concentration of sodium hydroxide increases the degree of lattice conversion at a particular level of crosslinking, but the "mercerization transition range" becomes much less pronounced and abrupt as the concentration of resin in the fiber increases. The effect of crosslinking on the disordering effect of strong alkali solutions is, however, at most slight: the percentage hydrogen bond disorder in the most highly crosslinked samples, after treatment in 6*N* and 10*N* alkali, was 66%–70%, similar within experimental error to the disorder in the uncrosslinked fiber after the corresponding alkali treatments. These effects of crosslinking on the structural

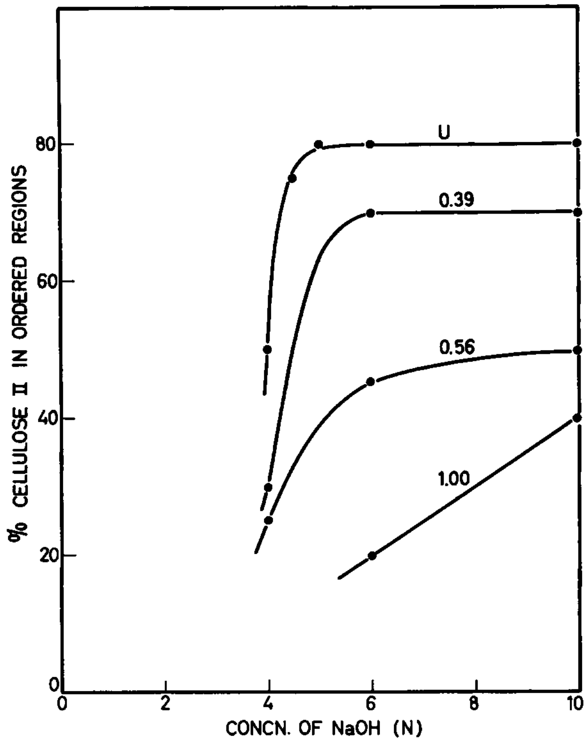

Fig. 3. Effect of crosslinking in DMEU on cellulose I → II lattice change produced by alkali treatment. Nitrogen content as shown on the curves; (U) uncrosslinked cotton.

changes taking place during mercerization (the marked reduction in lattice change and the at most slight reduction in disordering) are qualitatively similar to the effects of tension on the mercerization behavior of the cotton.[11]

Measurements of the acetylation in pyridine of the crosslinked fibers after being swollen in water (or in dilute alkali solution followed by washing in water) and then solvent exchanged to pyridine indicate (Table I) that the internal surface of these swollen crosslinked fibers (i.e., the microfibrillar surface made available by the "opening up" action of the swelling agent) is considerably less than that of the correspondingly treated uncrosslinked material. Acetylation of cotton fibers solvent exchanged after a swelling treatment in the more concentrated alkali solutions, however, gives acetyl values that are similar for both uncrosslinked and crosslinked cotton (Table I). This result, at first surprising, becomes readily explicable when the swelling behavior of the two types of fiber is considered (Figs. 1 and 2). The acetylation results are, in fact, a simple reflection of the degrees of swelling of the fibers in the various alkali solutions. In the more dilute alkali solutions, where the swelling is reduced by crosslinking, the

TABLE I
Effect of Alkali Treatment of DMEU-Crosslinked Cotton on Subsequent Acetylation

Concn. of NaOH, N	Nitrogen content, %	Acetyl value[a]
0	0	7.5
0	0.65	4.45
2	0	8.0
2	0.65	5.05
6	0	17.0
6	1.0	17.5
10	0	18.2
10	1.0	18.9

[a] After standard acetylation treatment given to solvent-exchanged fiber.

acetylation is also reduced. In the stronger alkali solutions both the swelling and surface area are relatively unaffected by prior crosslinking.

The large effect of crosslinking in the more dilute alkali solutions clearly suggests that many of the crosslinks are interfibrillar, thus preventing high degrees of interfibrillar swelling and separation. The more concentrated alkali solutions must, in some way, remove these interfibrillar linkages. It is thought[6] that these concentrated solutions do not disrupt the DMEU crosslinks themselves but, as a result of the high swelling pressures involved, destroy the interfibrillar cohesion by causing microfibrils to "tear off" the surfaces of adjacent microfibrils. Thus interfibrillar swelling is now able to take place and the marked increase in the swelling of the crosslinked fiber occurring between $3N$ and $4N$ alkali (Figs. 1 and 2) and in the internal surface area of the swollen fiber (Table I) is presumably a consequence of this.

It is now possible to consider reasons why the uptake of sodium hydroxide by the crosslinked fiber does not show any marked increase at alkali concentrations greater than $3N$, corresponding to the sudden and marked increase in the absorption of water. This low alkali uptake over the whole concentration range must mean that soda cellulose is not being formed readily or completely and explains the low degree of lattice change in the washed and dried fibers (Fig. 3). If the restriction on uptake of sodium hydroxide is simply a result of tensions in the structure caused by the interfibrillar linking, then this would obviously be expected to disappear when the "surface tearing" mechanism operates (at $4N$ and above). The low alkali uptake over the whole range of concentration may, therefore, mean that some of the crosslinks are within the fibrils themselves, in some way tending to prevent access of swelling agent and to restrict molecular rearrangements, thus preventing the satisfactory formation of soda cellulose. It is certainly not possible to explain the low alkali uptake in terms of removal of hydroxyl groups by the crosslinking molecules. At the highest degrees of crosslinking studied, there is on the average only about one crosslink for every 60 hydroxyl groups.

Treatment in Cadoxen Solutions

Table II illustrates that the swelling of cotton fiber in cadoxen solutions can be very markedly reduced by prior crosslinking with DMEU. The magnitude of the effect increases as the degree of crosslinking is increased, as would be expected. With the higher degree of crosslinking (nitrogen content 1.31%), the reduction in swelling is very large indeed. With these crosslinked fibers, the curves relating swelling agent absorbed to concentration of cadmium in the cadoxen do not, in general, have any clearly defined maxima of the type shown by the uncrosslinked samples.[4] Balloon swelling was, as expected, largely absent in the crosslinked fibers.

The very low degrees of swelling of the more strongly crosslinked fibers (nitrogen content 1.31%) shows that no "fibril tearing" takes place in these swollen fibers. This is perhaps surprising in view of the very high levels of swelling attainable with uncrosslinked fibers in these solutions (Table II). However, with the less highly crosslinked samples (nitrogen content 0.65%), some of the more powerfully swelling cadoxen solutions

TABLE II
The Absorption of Cadoxen Solutions by Crosslinked Cotton Fibers

Swelling solution			Absorption of swelling agent[a]	Swelling solution			Absorption of swelling agent[a]
Cd, wt-%	EDA, wt-%	Nitrogen content		Cd, wt-%	EDA, wt-%	Nitrogen content	
4.35	28.0	1.31	27	3.1	36.4	1.31	31
		0.51	170[b]			0.51	440[b]
		0	750			0	635
3.05	28.0	0.65	30	3.30	38.4	0.65	300[b]
		0	140			0	380
2.06	28.0	0.65	26	2.80	38.4	0.65	350[b]
		0	80			0	470
0	28.0	0.65	40	2.50	38.4	0.65	48
		0	55			0	460
4.35	34.9	1.31	27	2.00	38.4	0.65	43
		0.65	530[b]			0	295
		0	580	3.4	40.9	1.31	16
3.65	34.9	1.31	17			0	325
		0.65	320[b]				
		0	900				
3.25	34.9	1.31	16				
		0.65	205[b]				
		0	800				
3.18	34.9	0.65	420[b]				
		0	760				
2.84	34.9	0.65	70				
		0	200				
1.36	34.9	0.65	25				
		0	75				

[a] In g/100 g cellulose.
[b] Fibril tearing probably present.

(marked with superscripts b in Table II) did produce high degrees of swelling. This suggests that a "fibril tearing" mechanism can take place in this system, as in caustic soda solutions.

The large reduction in the degree of swelling caused by crosslinking is obviously associated with a large reduction in the absorption by the fiber of all three components, cadmium, ethylenediamine, and water. The results suffer from too much experimental scatter for any detailed analysis to be useful (because of the very low overall degrees of swelling), but it may be generally concluded that the ratio of cadmium to EDA–water in the absorbed solution is greater with these crosslinked samples than with uncrosslinked cotton swollen in the same cadoxen solutions.

Infrared deuteration measurements on crosslinked fibers, after being subsequently treated in cadoxen solutions, washed and dried, showed that the crosslinking in general prevented the cellulose I to cellulose II lattice change and increase in disorder observed with uncrosslinked fibers treated in the stronger cadoxen solutions.[4] The great restrictions placed upon the swelling and expansion of the cotton structure by the crosslinks are obviously sufficient to prevent any marked molecular rearrangements during the swelling, washing, and drying processes.

The Swelling of Methylated Cotton in Cadoxen and Sodium Hydroxide Solutions

It is thought that the large reduction in swelling caused by crosslinking is the result of mechanical restrictions imposed by the holding together of the fibrils by the crosslinks. These restrictions hinder the access of swelling agent to parts of the fibrillar surfaces and prevent the separation of the fibrils necessary to achieve the higher degrees of interfibrillar swelling. It is, however, just possible that the mere reduction in the number of hydroxyls in the crosslinked cotton, and their replacement by the DMEU, could affect the swelling independently of any crosslinking action: the formation of complexes between the swelling agent and the cellulose may well be sensitive to slight changes in the chemistry of the cellulose. The effect of methylation on the degree of swelling was, therefore, studied in an attempt to obtain some indication of any such "chemical" effect of the crosslinks.

The results (Table III) show clearly that the degree of swelling is reduced by the presence of large numbers of methyl groups in the cellulose. At smaller degrees of substitution, however, the swelling appears to be increased over the values observed with the unsubstituted cotton. The methylation appears, therefore, to have two opposing effects on swelling. One of these, apparently the more important at the higher degrees of substitution, is a reduction in the ability of the cellulose to form swelling complexes with the caustic alkali or cadoxen, as a result of the replacement of hydroxyl groups with "inert" methoxyl groups. The second effect of methylation, showing itself at the lower degrees of substitution, is to reduce

TABLE III
Absorption of Swelling Solutions by Methylated Cotton

Swelling solution	Degree of substitution	Absorption of swelling solution[a]
	0	225
	0.18	310
NaOH, 6N	0.66	245
	1.33	23
Cadoxen	0	1200
(4.3 wt-% Cd,	0.18	1850
28.3 wt-% EDA)	0.66	1100
	1.33	35
Cadoxen	0	235
(1.9 wt-% Cd,	0.18	390
50.9 wt-% EDA)	0.66	320
	1.33	36

[a] In g/100 g cellulose.

the interfibrillar hydrogen bonding and cohesion, thus promoting interfibrillar separation and swelling (the methoxyl groups, in effect, "prop open" parts of the fibrillar structure).

Crosslinking with DMEU to a nitrogen content of 1.31% corresponds to a degree of substitution of only about 0.1. For such a low degree of substitution of methoxyl groups, the degree of swelling in cadoxen or caustic soda solutions would, if anything, be *increased.* Allowing, therefore, for the possible differences between methoxyl groups and DMEU crosslinks in their effects on the formation of swelling complexes, it seems safe to conclude that the very large reduction in swelling caused by the crosslinking is, in fact, almost entirely a mechanical restriction effect.

The Swelling and Solubility of Alkali-Treated Crosslinked Cotton in Cadoxen and Cuprammonium Hydroxide Solutions

The purpose of these experiments was to obtain more information on the "fibril tearing" that takes place in crosslinked cotton in strong alkali solutions. These alkali-treated crosslinked fibers should, as a result of the fibril tearing, swell more than the crosslinked fibers before treatment in alkali and also might be expected to dissolve more readily in solvents for cellulose. Samples of fiber, crosslinked with DMEU to nitrogen contents of 0.51 and 1.31% were treated in 6N sodium hydroxide for 2 hr at 25°C, washed in water, and dried. Values for the swelling and solubility of these fibers and of the untreated crosslinked fibers in cadoxen and cuprammonium hydroxide solutions are listed in Table IV.

The results show that the alkali treatment increases markedly the swelling of crosslinked cotton in cadoxen solutions, though not to the level of the uncrosslinked fiber. The increase is particularly large with the more

TABLE IV
Swelling and Solubility of Crosslinked Cotton in Cadoxen and Cuprammonium Hydroxide Solution

Swelling solution	Nitrogen content	Alkali-treated prior to swelling	Absorption of swelling agent[a]	% by wt dissolved
Cadoxen	0	no	c. 2000	50–60
(4.99 wt-%	0.51	yes	550	0
Cd, 28.3	0.51	no	340	5
wt-% EDA)	1.31	yes	340	0
	1.31	no	28	2
Cuprammonium	0	no	—	100
hydroxide	0.51	yes	—	27
15 g/l.	0.51	no	—	21
Cu, 200 g/l.	1.31	yes	—	7
ammonia)	1.31	no	—	9

[a] In g/100 g undissolved cellulose.

highly crosslinked fiber and confirms the presence of a fibril-tearing mechanism during the alkali treatment.

Crosslinking reduces the solubility of cotton in cadoxen and cuprammonium hydroxide solutions, as expected[12] (Table IV). The alkali-treated samples are, however, little different in this respect from the untreated crosslinked fibers. Thus fibril tearing does not seem to free the cellulose structure sufficiently to allow any significant increase in solubility.

SUMMARY

This paper describes the effects of prior crosslinking with DMEU on the swelling of cotton fiber in aqueous solutions of sodium hydroxide and in cadoxen solutions. In the weaker swelling solutions, the absorption of swelling agent and the increase in the fiber width are markedly reduced by the prior crosslinking; for example, the absorption of dilute alkali solutions is reduced by as much as 50% by crosslinking to a nitrogen content of 0.88% and the absorption of certain cadoxen solutions can be reduced by more than 70%. In stronger swelling solutions the effect of prior crosslinking is, however, smaller; in 4–10*N* solutions of sodium hydroxide the reduction in the absorption of swelling agent is only about 15%, this being largely accounted for by a reduction in alkali uptake, the absorption of water being about the same in crosslinked cotton as in uncrosslinked cotton. This low effect of crosslinking on the swelling of cotton in strong swelling solutions is thought to be the result of a "fibril tearing" mechanism: the swelling stresses do not break the interfibrillar crosslinks themselves but instead cause the fibrils to tear off the surfaces of the adjacent fibrils, thus allowing a high degree of interfibrillar expansion and swelling. The prior crosslinking of cotton also reduces the cellulose I → II lattice change in alkali solutions of "mercerizing" strength, the effect becoming

greater as the level of crosslinking is increased. The effect of crosslinking on the disordering effect of strong alkali solutions is, however, at most slight.

The effect of crosslinking in reducing swelling is thought to be almost entirely the result of physical restrictions on the expansion of the cellulose structure. Any "chemical" effect of the crosslinks in reducing swelling is thought to be at most small; this conclusion is supported by measurements of the absorption of alkali solutions and cadoxen solutions by methylated cotton.

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