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Swelling of Cotton in Alkalis and Acids

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Synopsis

A study of the swelling of Acala 4-42 cotton in aqueous alkalis and acids has been carried out. The degree of swelling of the cotton in the reagents has been indicated by measurement of the variations in width of the cotton at its widest point. The nature of the swelling process whether interfibrillar or intrafibrillar has been deduced from microscopical and x-ray evidence. It has been shown that a similarity of shape of the swelling curves, i.e., an equal degree of swelling in the same or other reagents, does not imply the same mechanism of swelling. The results are more readily explained in terms of the crystalline-fibril theory than by the fringe-micellar theory, especially when high degrees of swelling have been achieved.

INTRODUCTION

The literature on the swelling of cotton with alkalis and acids has been recently reviewed by Warwicker et al.[1] It was found that the information with regard to the action of caustic soda on cotton is extensive, but much less is known about the action of other alkaline and of acidic swelling agents. A systematic study of the action of swelling agents on the fine structure of cotton was, therefore, undertaken to compare the action of caustic soda on fine structure of cotton with that of other swelling agents.

In this study a measure of the extent of swelling in the different reagents was required. Owing to the complex physical form, morphology, and fine structure of cotton it is difficult to make an unequivocal measurement of the degree of swelling, and all methods so far devised are imperfect. Swelling would be best recorded as a volumetric change, and attempts to do this with cotton have been made,[2] but it is generally experimentally impractical. Length changes[3,4] have been studied but are considered unsatisfactory.[3] The most studied dimensional changes indicative of swelling are width or cross-sectional area changes.[5] Width changes can take place without corresponding swelling effects,[6] and even when swelling takes place a width measurement may not represent the complete swelling change.[7] Cross-sectional area measurements on cotton are complicated in many swelling agents by the so-called "mushroom-head" phenomenon and cannot always be accurately measured.[5,8,9] It was therefore decided to use the width measurement at the widest point of the cotton hair[7,10] as an indication of the swelling, since this measurement is simple to carry out and is the least open to objection. It is realized that it does not give an absolute measure of swelling, but it does adequately indicate the general swelling behavior of cotton in the different reagents.

Microscopical examination of the cotton hairs in the swelling agents was included in this study because it sometimes reveals morphological changes brought about by swelling. Such morphological changes can cause important modifications in the properties of cotton.

There is often confusion in the literature[1] as to whether swelling agents penetrate the crystalline fibrils of native fibers and bring about lattice changes. This confusion often arises because different swelling conditions are compared by different authors. It was therefore thought important to check the possible formation of complexes by a systematic x-ray study of cotton in the presence of the swelling agent and also after its removal.

Further detailed work on the fine structural changes brought about by swelling treatments is to be subsequently published.

EXPERIMENTAL

The cotton used was mature Acala 4-42 cotton from the San Joaquin Valley, U.S.A.

Swelling Agents and Conditions of Swelling

Sodium Hydroxide. The sodium hydroxide solutions were made up and standardized at room temperature, and the concentrations quoted are those at room temperature. Swelling was carried out for 30 min in the required solution before slides were prepared for the measurements of width.

Iron Tartrate Solutions (EWNN). The maximum solubility of cellulose in iron tartrate solutions (EWNN) was found by Jayme and Bergmann[11] to be in a solution of composition: 390 g/l. iron tartrate complex (EWN), $2N$ free sodium hydroxide, 30 g/l. free sodium tartrate. Swelling was therefore carried out in solutions of the same composition of free sodium hydroxide and free sodium hydroxide and free sodium tartrate, but with varying EWN content. The preparation of these solutions was by the methods given by Jayme and Bergmann.[12]

Since the age of solution had some effect on swelling, only freshly made solutions were used. Swelling was for $^1/_2$ hr unless stated otherwise.

Sulfuric, Phosphoric, Nitric, and Perchloric Acids. The solutions were made up by weight and checked by measurement of the specific gravity.

Swelling treatments were for 30 min in sulfuric and phosphoric acids, but a 5 min swelling treatment in nitric and perchloric acid was found sufficient.

Measurement of Hair Width

The cotton hairs were first treated in the required liquid for a given time at a given temperature. A drop of this liquid was placed on a microscope slide, a few prepared hairs transferred to it, and a cover slip placed over the hairs in the liquid and sealed to the microscope slide with wax. The prepared slide was then placed on a heated stage of a projection microscope kept at the experimental temperature. Measurement of the projected image was made by a projected eyepiece-scale previously calibrated against a standard stage micrometer. Two hundred measurements of the widest point of the cotton hairs were made on a series of prepared slides, and the final value quoted is that of the mean of the 200 readings.[13]

In a test experiment of the method on another sample of cotton, the standard deviation σ about the mean of 21.1 μ for 200 individual readings was 3.28 μ. The standard error of the mean defined as $\sigma/\sqrt{n} = 0.23\ \mu$ and the 95% confidence limits defined as $\pm$ 2 S.E. = $\pm 0.46\ \mu$. A similar test carried out with 100 individual readings gave a standard deviation σ of 3.46 μ about a mean of 21.38 μ. The standard error of the mean was, therefore, 0.35 μ and the 95% confidence limits $\pm$ 0.7 μ.

It is clear from these values that a tolerable accuracy can be obtained from 100 readings but a significant increase in accuracy is obtained by 200 readings, and this number was adopted as standard.

Further errors, however, are inherent in the method due to the personal error of the different observers. To minimize this error, the control value used was that observed during the measurement of widths for the particular set of swelling experiments.

Finally, to make all experiments comparable with each other, the degree of swelling is quoted in relation to the swelling of cotton hairs in water under the experimental conditions.

Microscopical Examination

Examination by phase-contrast microscopy with hairs mounted as described for the width measurements was also carried out to see whether any visible changes in the cotton hairs could be detected when swollen in alkali or acid.

X-Ray Examination

Qualitative x-ray examination of the samples from particular swelling conditions was carried out. In one set of results the samples were examined in the presence of the swelling agents, and also wet after washing-out the reagents; the experimental details for carrying out such experiments have already been described.[14] In the other set of results, the x-ray diagram of a standard parallel bundle of fibers prepared from the samples treated in the reagent, washed, and dried, was examined. This method is essentially that described for azimuthal scans.[15]

The x-ray photographs were taken with nickel-filtered copper Kα radiation on a cylindrical camera of radius 3 cm.

DISCUSSION OF RESULTS

Width Swelling of Cotton Hairs

The influence of the different aspects of morphology on the width swelling can be seen by the use of cotton at different stages of processing. Raw cotton in 5N sodium hydroxide achieves a degree of swelling (DS_w) of 1.25 relative to that in water; if the cotton is solvent extracted to remove the fats and waxes the DS_w is 1.30; and when scoured cotton is used on which there is no pectinous layer, the DS_w is 1.45. Mercerized cotton in 5N sodium hydroxide attains a DS_w of 1.66, but the final width is the same as that of scoured cotton swollen in the same solution. The difference of $DS_w = 1.66$ for mercerized cotton in 5N sodium hydroxide and $DS_w = 1.45$ for scoured cotton in the same solution lies in the fact that the width of mercerized cotton in water is less than the widest part of scoured cotton in water. This difference of width in water is largely due to different cross-sectional shapes, since mercerized cotton has an elliptical, almost round, cross section, and scoured cotton is "ear-shaped" and approximates a flat ribbon at the point of measurement. These measurements emphasize the difficulties associated with the measurement of width as an indication of swelling. The fact that the mercerized cotton and scoured cotton have the same width in 5N sodium hydroxide suggests that the swelling of mercerized cotton is a reversible phenomenon. All subsequent work was carried out with scoured cotton, since this is almost pure α-cellulose.

Width swelling of cotton hairs in sodium hydroxide has been studied many times[5,7,13] for different purposes. The results shown in Figure 1 are included here for comparison with the results for other swelling agents with the same cotton. They do, however, show some additional features not previously remarked upon. The swelling curve at 100°C is closely similar to that at 25°C, except that the DS_w is smaller throughout. Since at 25°C the swelling is approaching the limit set by the restrictive primary wall, the

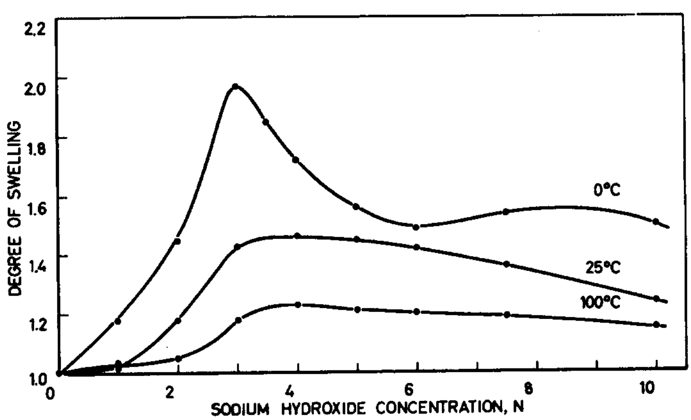

Fig. 1. Degree of swelling of scoured Acala 4-42 cotton in solutions of sodium hydroxide at different temperatures.

shape of the swelling curve might be expected to be modified accordingly, but this would not be expected at 100°C. The somewhat sharp maximum in the curve for 0°C is due to the primary wall bursting and has been noted previously.[13]

It will be seen from the swelling curve at 25°C that the DS_w for scoured cotton in 2N sodium hydroxide is 1.18, but it is known from other data that no lattice change has taken place during the swelling so this must represent interfibrillar swelling. It is also important to note this value in considering the results of swelling in EWNN, which are given as degrees of swelling related to the swelling in water similarly to the results for sodium hydroxide. Here (Fig. 2) the DS_w for 20 g/l. EWN is 1.16 within the experimental error of DS_w, 1.18 for 2N sodium hydroxide alone, so the presence of 20 g/l. EWN and free sodium tartrate has no measurable effect. However on the increase in the EWN content the DS_w increases linearly with the EWN concentration up to a concentration of 100 g/l. EWN.

In 100 g/l. EWN solution the DS_w is 1.58, greater than that found in any solution of sodium hydroxide at 25°C, but this is probably due to the balloon swelling observed with cotton hairs in this solution (Table I). However, x-ray examination of the fibers surrounded by EWNN, or after washing in sodium hydroxide containing sodium tartrate to remove EWN, or after complete washing and drying, failed to show any evidence of lattice change. It can only be concluded that the swelling in solutions of EWNN up to a concentration of 100 g/l. EWN is entirely interfibrillar. Microscopical examination also revealed that in contrast with its disappearance in solutions of sodium hydroxide that produce the maximum swelling (mercerization), the lumen of the cotton is still distinct and distended in a 100 g/l. EWN solution. High swelling of cotton commensurate with or greater

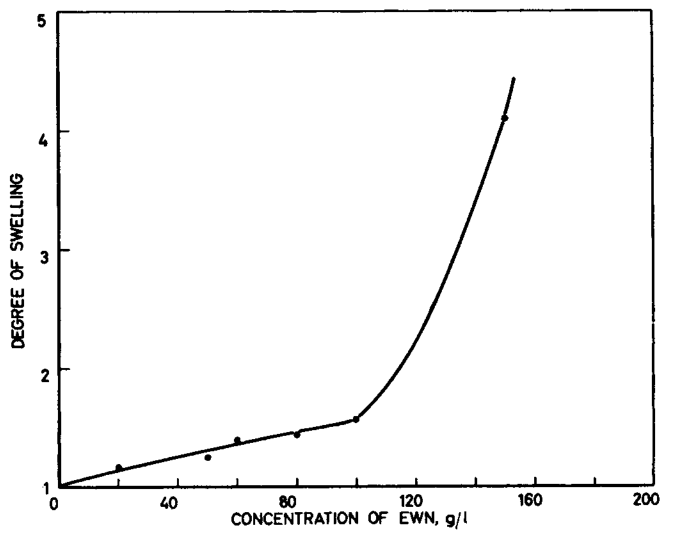

Fig. 2. Degree of swelling of scoured Acala 4-42 cotton in solutions of EWNN at 25°C.

TABLE I
Microscopical Examination of Scoured Acala 4-42 Cotton in EWNN

Concn. EWN, g/l.	Time, hr	Observation
50	48	Convolutions removed, expanded wall and distended lumen
100	48	Balloon swelling
150	48	Extensive balloon swelling Fibrillar appearance "Mushroom-head" at ends Some evidence for partial solution
100	1.5	Balloon swelling on some fibers Some fibers uniformly swollen Some with distended lumens "Mushroom-head" at ends
150	$^1/_6$–8	Balloon swelling as well as uniformly swollen fibers with distended lumens and walls; as time progressed the swelling became greater but its character stayed the same

than that found when cotton is mercerized can thus be produced in EWNN by interfibrillar swelling alone without any evidence for intrafibrillar swelling.

Above 100 g/l. EWN, the swelling phenomena change and depend on the time of swelling. Thus in 30 min high swelling that can be measured can be seen in a 150 g/l. EWN solution, but when the cotton was left 24 hr in this solution there was evidence for partial solution. In 200 g/l. EWN the cotton completely dissolved in 24 hr. These changes in the swelling behavior are clearly shown by the swelling curve that no longer is linear but rises rapidly (Fig. 2) above 100 g/l. EWN, and a DS_w of 4.1 is recorded in 150 g/l. EWN solution. It became experimentally impossible to measure DS_w values for cotton hairs in 200 g/l. EWN solution, however. Even with these high degrees of swelling, the lumen did not seem to be eliminated as it is in mercerizing solutions of sodium hydroxide. The x-ray evidence was difficult to obtain in the presence of EWNN because iron compounds fluoresce in copper $K\alpha$ radiation, and in consequence, x-ray diagrams become obscured. However, if the EWN was washed out by sodium hydroxide containing sodium tartrate and then by water, the water-wet sample previously swollen in 150 g/l. EWN solution showed a mixed diagram of those of cellulose I and water–cellulose. On drying the sample, a mixed x-ray diagram of those of cellulose I and cellulose II was produced. It seems reasonable to deduce from this evidence that some intrafibrillar swelling must have taken place during the treatment, but whether a definite EWN–cellulose complex was involved could not be ascertained. It is, however, interesting to note that, despite the high degree of swelling, complete conversion to cellulose II had not been achieved; the majority of the swelling must thus be still interfibrillar in character. At such high degrees of swelling between fibrils it would seem plausible that fibrillation of cellulose in these solutions might be easily accomplished by beating or other techniques. The evidence is also in full support of the modern views on the cotton structure, since such high degrees of swelling without lattice change can be more easily visualized on a crystalline-fibril theory[13] than with the older fringe-micellar theory.

When acid solutions are used as swelling agents there are features in common with swelling in alkaline solutions, but other complexities arise. Swelling in sulfuric acid (Fig. 3) in which swelling was allowed to take place for 30 min resembles the swelling of cotton in EWNN. No evidence for any marked changes in a smooth swelling behavior has ever been found in sulfuric acid concentrations below 60%, and after a few preliminary tests to check this, no width-swelling measurements were made in these solutions. There is thus an implied linear swelling increase with increase in the concentration of sulfuric acid. The interest, however, arises in the swelling of cotton in 60–63% sulfuric acid. Above 63% H_2SO_4, solution of cotton in the sulfuric acid rapidly takes place, and width measurements could not be carried out. Brief swelling treatments of cotton in concentrations of sulfuric acid from 63 to 74% can be carried out, but the effect of such treatments has been studied by other techniques and will be reported elsewhere.

The degree of swelling in 60% sulfuric acid was 1.25, commensurate with that in a 50 g/l. EWN solution and with that for swelling in sodium hydroxide solutions before intrafibrillar swelling takes place. No lattice changes could be detected by x-ray methods, and the microscopical examination

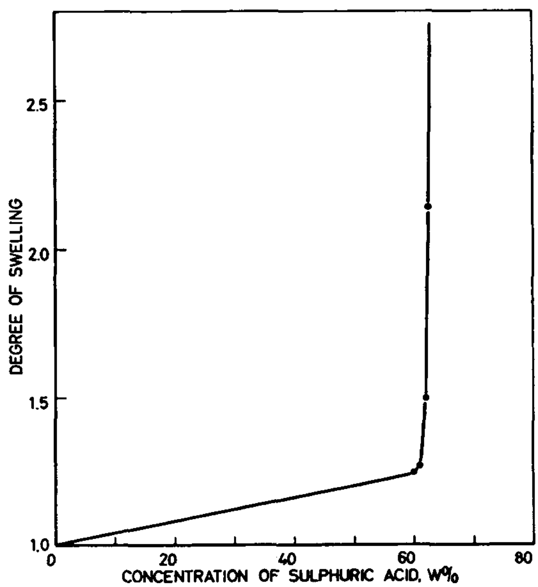

Fig. 3. Degree of swelling of scoured Acala 4-42 cotton in sulfuric acid at 25°C.

TABLE II
Microscopical Examination of Scoured Acala 4-42 Cotton Treated with Sulfuric Acid (30 min) 25°C[a]

Acid concn, wt-%	Observation
0	Typical cotton; convoluted
61	Distended lumen; increase in wall thickness; a few convolutions
62	Distended lumen; increase in wall thickness; no convolutions
62.5	Similar to 62.0% but with greater swelling.
63	Similar to 62.0 and 62.5% but with the greatest swelling of all; swollen walls but distinct swollen lumen
	In the 62.5 and 63.0% acid fibrillation is quite clear

[a] Observations in the presence of acid.

revealed that the cotton was little different from that in water. Cotton in sulfuric acid solutions above 60% rapidly swells and achieves a measurable DS_w of 2.14 in 62.5% sulfuric acid; measurement became impossible in 63% sulfuric acid, and solution occurred. Despite the high swelling achieved no evidence could be found by x-ray methods for any lattice change, either in the presence of the acid or when washed and left wet in water, or when washed and dried. The conclusion is that the swelling was interfibrillar in solutions of sulfuric acid up to a 62.5% concentration. However, the microscopical evidence (Table II) shows that the lumen distends at the same time as the cellulose walls of the cotton swell, and in the higher concentrations of acid fibrillation is evident. It is suggested that the solution mechanism is one of degradation and solution of smaller fragments rather than of separation and solvation of chains as is probable in viscosity solvents such as EWNN. The high swelling in sulfuric acid appears to be completely interfibrillar and different from the high swelling in EWNN that includes some intrafibrillar swelling.

The degree of swelling achieved is greater than that found in sodium hydroxide, even at 0°C when there was evidence of burst primary wall, and this raises the question why balloon swelling was never observed in these solutions of sulfuric acid. It was suspected that the high degree of swelling could only be achieved by the dissolution of the primary wall, and later electronmicroscope evidence (reported elsewhere) confirmed this.

Phosphoric acid can dissolve cotton only when two specific concentration ranges are used: 82–85% and above 95%, at all other concentrations swelling only takes place. A further complication arises in that Danilov and Gintse[16] found that presoaking the cotton in water promotes greater swelling than found with dry fibers and can facilitate solution in concentrations of phosphoric acid that would otherwise only swell cotton. This observation was tested with cotton in concentrations up to 80% and found to be correct (Fig. 4). It was found particularly difficult to work with fibers immersed in phosphoric acid of concentrations above 82%, so that it was impossible to be sure whether in concentrations between 82 and 85% solution did take place or only such high swelling that gel formation occurred: in concentrations above 95% solution genuinely took place.

It will be seen (Fig. 4) that up to a concentration of 70% very little swelling takes place with dry fibers (DS_w = 1.09), but this is improved by presoaking of the fibers in water (DS_w = 1.18). Even in 75% acid the DS_w is 1.14 (dry fiber) or 1.26 (wet fiber), but after this a rapid increase in swelling takes place with increase in phosphoric acid concentration, and the highest measured DS_w was 2.42 in 81% phosphoric acid.

Microscopical evidence showed balloon swelling in 81% acid (Table III), but distended walls and lumens were present. However, despite the high swelling, x-ray diagrams of the products after swelling and washing out the acid failed to give evidence for lattice changes. It is therefore highly probable that the swelling in this first range of concentrations is only interfibrillar. The high swelling is achieved clearly by the rupture of the primary wall of the cotton.

Cotton treated in 90% phosphoric acid (a concentration in the second swelling region) and then washed and dried gave an x-ray diagram of cellulose II. This clearly shows that the swelling is intrafibrillar as well as interfibrillar in this concentration of acid. Whether a phosphoric acid–cellulose complex was formed during swelling could not be established, but the fact that the lattice was penetrated suggests the possibility of such a complex.

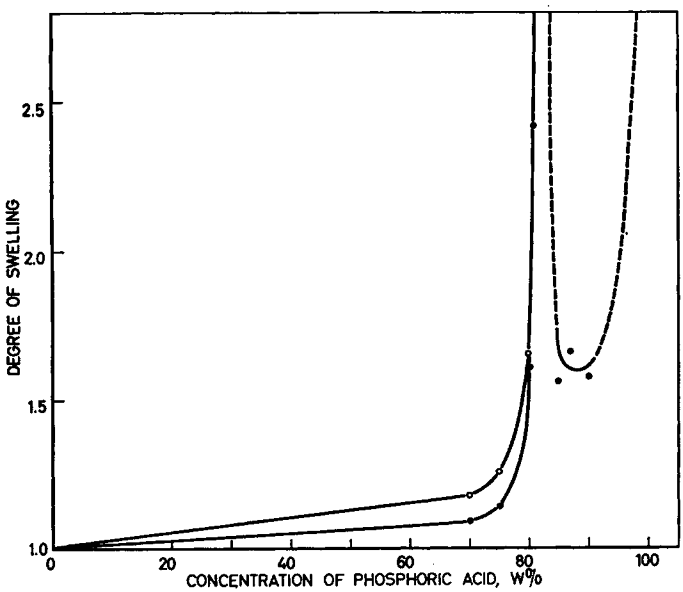

Fig. 4. Degree of swelling of scoured Acala 4-42 cotton in phosphoric acid at 25°C: (○) dry fiber; (●) prewetted fiber (first branch only).

TABLE III
Scoured Acala 4-42 Cotton Treated with Phosphoric Acid 25°C; Microscopical Examination

H_3PO_4, %	Observation
75	Convolutions absent lumen wider, some wall swelling
80	Similar
81	Balloon swelling; wide lumen, wide walls; fibrils evident.
82	Greater swelling of wall and lumen; fibrillar appearance well marked.
90	Similar to 75%; no convolutions, some wall swelling
95	Wall appears to be disintegrating into fibrillar pieces

Microscopically, however, the cotton in 90% acid appeared very similar to cotton in solutions of the first swelling range (Table III), but further work with cross sections might be useful to permit differentiation of the samples from each range. Cotton, therefore, in this second swelling range of concentrations behaves similarly in many respects to samples in mercerizing solutions of sodium hydroxide. It should be noted that the degree of swelling in 90% acid is 1.58, similar to that in 80% acid (DS_w = 1.61), but the products from the two solutions are quite different.

Nitric acid provides an even more complex system than phosphoric acid. Very little change is found up to a concentration of 61.2% acid, where the degree of swelling is 1.13 (Fig. 5). However, there is a peak in the swelling curve at 65% acid, where the DS_w is 1.26. Cotton swollen in nitric acid of concentration around this peak value still retains a few convolutions, and a

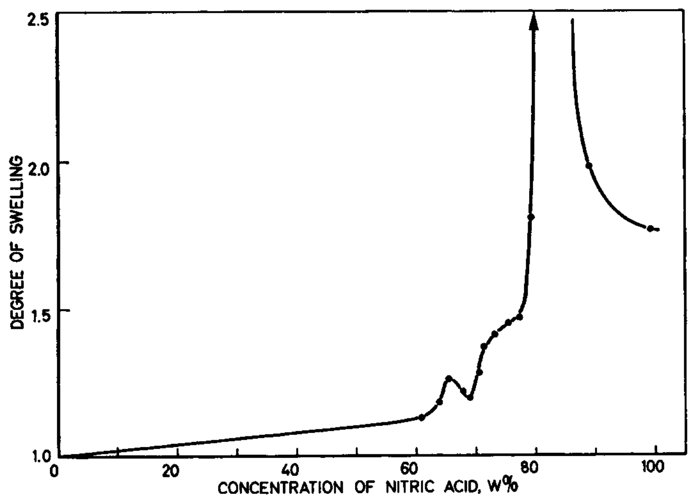

Fig. 5. Degree of swelling of scoured Acala 4-42 cotton in nitric acid at 25°C.

TABLE IV
Scoured Acala 4-42 Cotton Treated with Nitric Acid, 25°C: X-Ray Diagrams of Samples in Presence of Acid

Acid concn, wt-%	Observation
61.2	Oriented cellulose I diagram.
65.4	Powder pattern of cellulose I with a diffuse inner ring probably originating from the Knecht compound
68.8	Powder pattern of the Knecht compound
71.1	Powder pattern of the Knecht compound on a diffuse pattern possibly arising from a nitrated fraction

distinct lumen is seen under the microscope. The x-ray observations in the presence of the acid (Table IV) reveal that the main pattern is that of cellulose I. The fact that a powder pattern is produced is attributed to the high crimping of the fibers in this acid concentration and the lack of tension on the bundle enclosed in the Pantak tube. There is, however, an inner ring on the x-ray pattern that is highly diffuse but of the correct spacing for one of the main reflections of the Knecht compound,[17] so that this gives some evidence for intrafibrillar swelling. Nevertheless the main swelling phenomenon in this acid concentration is interfibrillar.

At the minimum swelling ($DS_w = 1.20$) in 68.8% acid, before the rapid rise in swelling with increasing acid concentration, the X-ray diagram of the swollen product reveals a conversion to the Knecht compound,[17] so intrafibrillar swelling has taken place as well as interfibrillar swelling. The maximum at 65% acid is thus probably the point at which inter- and intrafibrillar swelling processes balance. It is visualized that as intrafibrillar swelling takes place, the increase in size of the fibrils occurs at the expense of the space between the fibrils, resulting in less total swelling than if only interfibrillar swelling had taken place. It should also be remembered that the morphology of the cotton may also be a factor in the process, especially if the outer primary wall is acting as a restricting layer forcing the increase in diameter of the fibrils to occupy the available space in the lumen as well as between the fibrils. Microscopy, however, shows that the lumen is still present in the concentration of acid (Table V). There is no x-ray evidence for any nitration to have taken place for cotton in 68.8% acid.

In 70.2% acid, $DS_w = 1.28$, very close to that of the cotton in 65% acid, but the swelling process now clearly involves intra as well as interfibrillar swelling. The x-ray diagram of cotton in the presence of 71.1% acid has an underlying diffuse pattern that could be interpreted as the onset of nitration so that it is suspected that as the high swelling is achieved in the higher concentrations of acid, nitration must accompany the inter- and intra-

TABLE V
Microscopical Examination of Scoured Acala 4-42 Cotton Treated with Nitric Acid

Acid concn, wt-%	Observation
61.2	Some convolutions present; slight swelling, distinct lumen
67.7	Few convolutions; distinct lumen, some swelling
70.2	No convolutions; distinct swelling, distinct lumen
73.2	Cellulose wall swollen, lumen apparent
75.3	Highly swollen wall, lumen distinguished some twisting of fiber
77.2	Highly swollen wall; lumen not seen on all fibers; signs of disintegration on outer edges
79.4	Highly swollen fibrillar structure; lumen not easily seen, some signs of disintegration
88.9	Highly swollen fibrillar structure; evidence for the lumen confused by the other details
99.4	Less swollen than in 88.9% acid; some fibers are highly twisted and some have an outer crinkled appearance with an inner swollen layer; the possibility of the outer layer being nitrated and gelatinous cannot be eliminated

fibrillar swelling processes. Dissolution of cotton in nitric acid solutions of concentrations between 80 and 85% corresponds to a probable action of nitric acid monohydrate[18] that can completely penetrate the cellulose structure. This fact raises the important question of the function of the structure of the solutions as well as that of the substrates in swelling.

Swelling without solution can again be observed in high concentrations of nitric acid but the degree of swelling now falls as the concentration is raised. Indications from the microscopical examination of the fibers in these acid concentrations suggest that rapid nitration is taking place simultaneously with swelling. Owing to experimental difficulties in the use of fuming nitric acid, x-ray diagrams of samples immersed in these high acid concentrations were not attempted.

The final acid to be investigated was perchloric acid. In 58% acid the DS_w was 1.09, so that little swelling is produced over that in water. In acid of concentration 60% the DS_w is 1.14 and in 67% acid the DS_w is 1.11, so that a small maximum swelling occurs in 60% acid. In 64% acid there were signs of the cotton disintegrating so that further measurements in higher concentrations were not attempted.

In 60 and 62% perchloric acid, microscopical evidence showed that the walls and the lumen of the cotton were distended, and evidence of some fibrillar structure was shown. The x-ray evidence in presence of the acid was obscured by the x-ray absorption by perchloric acid, but a faint pattern was detected that showed differences from the x-ray pattern of cellulose I. It was difficult to identify this pattern, and to help in its identification, ramie was used in the presence of 62% perchloric acid at 0°C; when the x-ray diagram of this preparation was taken at room temperature an x-ray diagram of the complex as described by Andress and Reinhardt[19] was obtained. Ramie in 62% perchloric acid at 25°C however gave variable results; on one occasion a sharp x-ray diagram was given different from that of Andress and Reinhardt, but this could not be repeated and in general a faint diagram of a complex, probably the same as that of Andress and Reinhardt, was given. Comparison of the x-ray diagrams produced from cotton and ramie at 25°C suggests that at least partial conversion to a perchloric acid–cellulose complex is attained in the cotton. On washing out the perchloric acid and taking an x-ray diagram while the cotton was still wet with water, a mixed diagram of those of water cellulose and cellulose I was given, and the x-ray diagram of the dried sample was a mixture of those of cellulose I and cellulose II. It seems fairly certain, therefore, that a complex is partially formed in 60–62% perchloric acid at 25°C and hence intra- as well as interfibrillar swelling has taken place. The few experiments with ramie also indicate that swelling with perchloric acid is probably greater at 0° than at 25°C.

These experiments clearly demonstrate that a measurement of swelling alone is not sufficient to indicate the nature of the alteration of the fine structure of cotton in the presence of swelling agents. Equal degrees of swelling, even with the same reagent, can be brought about by two different mechanisms. However, by a combination of swelling measurements, microscopical examination, and x-ray analysis it is possible to gain a more detailed insight into the swelling process. The effects that have been observed are more comprehensible in terms of the crystalline-fibril theory of fine structure than by reference to the fringe-micellar structure, especially when high degrees of swelling are achieved. Thus on the crystalline-fibril theory the high lateral swelling achieved without a commensurate shrinkage can be imagined to be attained by cleavage and lateral displacement of fibrils, whereas a network as envisaged by the fringe-micellar structure might be expected to exert a limit to the lateral swelling. The nature of the ionic species present in the swelling agent and their variable hydration is an important factor in the swelling mechanism and deserves investigation if suitable and reliable methods can be devised for this purpose.

Summary and Conclusions

An investigation into the swelling of Acala 4-42 cotton has been carried out in sodium hydroxide, EWNN, and sulfuric, phosphoric, nitric, and perchloric acid solutions.

The degree of swelling has been determined by a measurement of the widest part of the cotton hair immersed in the swelling solutions.

The nature of the swelling process, whether interfibrillar or intrafibrillar, has been determined by microscopical and x-ray methods.

It has been shown that the same degree of swelling can be achieved even in the same reagent by two different mechanisms, one by interfibrillar swelling alone, and the other by a combination of interfibrillar and intrafibrillar swelling.

The occurrence of similar types of swelling curves with increase of concentration of different swelling reagents does not imply that the swelling mechanism is the same for the different reagents.

It has been confirmed with nitric and perchloric acids that acid-cellulose complexes can be formed during the swelling process.

Other complications can occur with acids, such as degradation of the cellulose by sulfuric acid or nitration by nitric acid, but there are regions of swelling with these acids in which these effects are either small or absent.

The nature of the ionic species in the swelling solutions and their possible hydrate formation is important, but is not investigated here.

It is thought that the effects observed, especially when high degrees of swelling are found, can best be interpreted in terms of the crystalline-fibril theory and not by the fringe-micellar theory.

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