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SORPTION AND X-RAY DIFFRACTION STUDIES ON COTTON FABRICS TREATED IN ANHYDROUS AND AQUEOUS LIQUID AMMONIA

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ABSTRACT

The effect of anhydrous and aqueous liquid ammonia as well as sodium hydroxide on the sorption of moisture, iodine and barium hydroxide by cotton was investigated. Furthermore, the effect of these swelling agents on the fine structure of cotton was investigated by means of X-ray diffraction studies.

A significant increase in the sorption of moisture, iodine and barium hydroxide by cotton was found after it had been treated in anhydrous liquid ammonia or sodium hydroxide. When increasing amounts of water were added to the liquid ammonia, the sorption of the chemicals by the cotton progressively decreased. Cotton treated in liquid ammonia containing as much as 10% water, however, still showed higher sorption values than cotton treated in sodium hydroxide.

The removal of the ammonia from cotton by heat or air drying produced considerably larger increases in the sorption values of cotton than did the removal of the ammonia by steam. The various chemical sorption tests used in this study to measure changes in the fibre accessibility differed somewhat in their response to variations in the conditions of treatment which were investigated. In general, however, the conclusions drawn from the sorption test results were verified by the X-ray studies.

INTRODUCTION

The chemical and physical properties of the cotton fibre have been studied in great detail over the past century[1]. The structure of cotton cellulose is quite complex and it has been stated that each individual fibre is composed of approximately 40×10^{10} cellulose molecules[2]. Basically cellulose is a polymer of β-D-glucose units linked through 1-4 glucosidic linkages. The cellulose polymers are organised into crystalline (ordered) and amorphous (disordered) regions in the fibre. The cotton fibre, however, cannot be considered as a simple two phase system containing only "perfectly crystalline" and "perfectly amorphous" material[3-4]. It actually comprises different regions varying in their degree of crystallinity. It is accepted generally that there is a relationship between the structure of the cotton fibre and its properties. In general, the crystallinity determines the physical properties of the fibre while the amor-

phous regions are of importance to the accessibility (internal volume accessible to a given reagent) i.e. to the chemical properties of the fibre[4].

The morphology and the fine structure of cotton can be modified by various treatments, and thus the physical and chemical properties of the fibre can be changed. For example, native (crystalline) cellulose can be converted to at least three different polymorphic structures by appropriate treatments, namely cellulose I, II and III. These structures differ only in the crystalline packing of the chains because all the polymorphs show the same cellobiose repeat unit of approximately 1,03 nm[5]. The cellulose I lattice exists in a variety of native celluloses obtained from plant, bacterial and algal origins[6]. Cellulose II is found in all regenerated celluloses such as cuprammonium and viscose rayon[7]. The industrial mercerisation of cotton with sodium hydroxide also results in the formation of cellulose II. The treatment of cotton with liquid ammonia, on the other hand, results in the formation of cellulose III. Two different cellulose III structures can be obtained, depending on the starting material. When cellulose I is treated with liquid ammonia, the so-called cellulose III_I is formed, whereas the treatment of cellulose II produces cellulose III_{II}[8]. Both structures were found to be less stable than cellulose I and II[9].

The effect of anhydrous liquid ammonia on the physical and chemical properties of the cotton fibre has been studied in great detail by a large number of research workers[10]. It is accepted that anhydrous liquid ammonia increases fibre tenacity, accessibility as measured by moisture regain and iodine sorption, while it decreases crystallinity as determined by X-ray diffraction. Despite the fact that anhydrous liquid ammonia increases the accessibility of the fibre, attempts to dye cotton in a liquid ammonia medium generally have been unsuccessful[11]. Recently it was shown, however, that liquid ammonia could be used as a solvent for dyeing cotton, provided that a cosolvent such as water is present in the system[12]. In contrast to the unlevel dyeings obtained in anhydrous liquid ammonia, level dyeings were obtained when the liquid ammonia contained some water.

Little is known, however, about the effect of liquid ammonia containing water on the structure of the cotton fibre. Anhydrous liquid ammonia has the ability to penetrate the intracrystalline fractions of the cellulosic structure where it breaks hydrogen bonds and decrystallises the structure. Water, on the other hand, only penetrates the amorphous regions. Various workers have shown, with the aid of X-ray analysis, that the intramolecular spacing of the crystalline regions remains unaltered during swelling with water[13,14]. It is possible, therefore, that the addition of water to the liquid ammonia could reduce or nullify the decrystallising effect of liquid ammonia. Obviously it was very important to study the effect of *aqueous* liquid ammonia on the structure of the cotton fibre, because if no decrystallisation occurred under these conditions, there was little merit in using liquid ammonia as a medium for dyeing.

It was decided therefore, to investigate the effect of anhydrous and

aqueous liquid ammonia on the structure of cotton. Different conditions of treatment were studied, i.e. cotton fabrics were treated in a slack state or under tension and the ammonia was removed from the fabrics by air drying, heating or steaming. In some cases the effect of liquid ammonia on the cotton fibre was compared with that of sodium hydroxide, the traditional swelling agent for cotton. The modification of the fibre structure by the different treatments was monitored with the aid of various tests such as moisture, iodine and barium hydroxide sorption as well as X-ray diffraction.

EXPERIMENTAL

Fabric

A scoured and bleached lightweight plain weave cotton fabric (128 g/m^2) comprising 29 ends and 34 picks/cm with yarn linear densities of 19 tex and 25 tex for warp and weft, respectively, was used in this study.

Treatments

Fabric samples (30x30 cm^2) were immersed for 60 seconds in anhydrous liquid ammonia either in a slack state or under tension by mounting them on a pinframe thus holding the samples to their original dimensions in both the warp and weft directions. The samples were subsequently squeezed through Benz padding rollers to remove excess liquid ammonia. Various methods were then employed to remove the residual ammonia from the samples. Firstly, some of the samples were steamed immediately with dry saturated steam at 100°C for 5 minutes. Secondly, samples were heated in a Benz laboratory oven for 5 minutes at 100°C. Thirdly, the ammonia was removed from some other samples by air drying at room temperature.

A set of cotton fabrics was also treated in liquid ammonia containing from 1 to 15% (v/v) water, in a manner similar to that described for the anhydrous liquid ammonia treatments.

Finally, some fabrics were treated in a slack state, and also under tension, in a solution containing 19% (m/v) sodium hydroxide and 0,5 g/ℓ ®Leophen BN wetting agent for 60 seconds at room temperature. The samples were then thoroughly washed, neutralised (1% acetic acid), rinsed and dried.

Tests

Moisture sorption of cotton, i.e. number of moles of water per anhydroglucose unit (AGU) was determined according to the method described by Pandey and Nair[15]. The iodine sorption value (mg I_2/g sample) was determined according to the method described by Hessler and Power[16]. The barium hydroxide sorption of cotton fabrics was determined according to AATCC Test Method No. 89-1971.

The X-ray diffraction diagrams (diffractograms) of cotton fabrics were obtained on a Phillips Diffractometer. A disc, 20 mm in diameter, was cut

from the fabric and embedded with 1 mℓ Damar gum in a stainless steel holder which had a diameter of 20 mm and a depth of 0,6 mm . (Xylene was used to clean the holder prior to embedding the sample.) X-rays were generated from a cobalt source. An iron filter was used to produce a monochromatic beam of X-rays. The apparatus was operated at a voltage of 40 kV and a filament current of 30 mA . The X-rays were emitted at a take-off angle of 6° and directed through a divergent and anti-scatter slit of 2° and a receiving slit of 0,1 mm . Each sample was scanned at a speed of 1° 2θ/min. The sample was spun in a horizontal plane to counteract preferred orientation of the cellulose structure. The diffractograms were recorded at a chart speed of 5 mm/min, a time constant of 1 second and at a detection voltage of 1 750.

RESULTS AND DISCUSSION

The Effect of Anhydrous and Aqueous Liquid Ammonia on the Sorption of Moisture, Iodine and Barium Hydroxide by Cotton

It was decided to study the sorption characteristics of cotton treated in anhydrous liquid ammonia and liquid ammonia containing various percentages of water. The percentage increase in the moisture sorption (moles H_2O/anhydroglucose unit), iodine sorption (mg I_2/g cotton) and barium hydroxide sorption values (based on that of an untreated control fabric) of cotton fabrics treated in liquid ammonia containing from 0 to 15% (v/v) water, followed by the removal of the solvent under various conditions, are given in Table I.

It is clear from Table I that the sorption characteristics of cotton were affected considerably by treatment in anhydrous liquid ammonia or liquid ammonia containing various percentages of water. A multiple regression analysis was carried out on the results in Table I with the dependent variables, moisture sorption (Y_1), iodine sorption (Y_2) and barium hydroxide sorption (Y_3).

The independent variables were:

X_1 = % water (0, 1, 5, 10, 15%)
X_2 = slack or treated under tension
X_3 and X_4 = method of ammonia removal (heat/steam/air drying).

The analysis yielded the following "best fit" equations:

Moisture Sorption (Y_1)

$$Y_1 = -0{,}0905\, X_1^2 X_2 X_4 + 9{,}09\, X_4 + 40{,}4 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$n = 30$
(% Fit : 28,5)

TABLE I

THE PERCENTAGE INCREASE IN THE MOISTURE, IODINE AND BARIUM HYDROXIDE SORPTION OF COTTON FABRICS TREATED SLACK AND UNDER TENSION IN LIQUID AMMONIA CONTAINING VARIOUS AMOUNTS OF WATER

% Water in NH_3 (v/v)	PERCENTAGE INCREASE IN																	
	Moisture Sorption						Iodine Sorption						Barium Hydroxide Sorption					
	Slack			Tension			Slack			Tension			Slack			Tension		
	Heat	Steam	Air Dry	Heat	Steam	Air Dry	Heat	Steam	Air Dry	Heat	Steam	Air Dry	Heat	Steam	Air Dry	Heat	Steam	Air Dry
0	56,4	47,3	41,8	60,0	43,6	47,3	405,5	191,6	349,0	431,4	134,2	369,4	104,3	42,9	102,9	97,2	15,7	61,4
1	40,0	49,1	47,3	49,1	38,2	32,7	408,3	184,2	357,4	412,0	190,7	376,8	104,3	41,4	105,7	100,0	41,4	104,4
5	54,5	27,3	58,2	60,0	30,9	47,3	301,8	123,1	347,2	298,1	79,6	254,6	64,3	15,7	74,3	85,7	30,0	78,6
10	61,8	34,5	47,3	34,5	41,8	47,3	267,6	143,5	281,4	247,2	112,0	186,9	31,4	34,3	55,7	38,6	32,9	30,0
15	21,8	47,3	61,8	21,8	43,6	34,5	187,9	112,0	214,8	133,3	80,5	190,7	32,9	11,4	34,3	28,6	5,7	18,6
NaOH (19%)	43,6			47,3			156,4			123,1			21,4			17,2		

Iodine Sorption (Y_2)

$$Y_2 = 244\,X_4 - 12\,X_1X_4 - 4{,}5\,X_1X_2 + 145{,}5 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

n = 30

(% Fit : 91,7)

Barium Hydroxide Sorption (Y_3)

$$Y_3 = 71{,}6X_4 - 5{,}02\,X_1X_4 + 27{,}1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

n = 30

(% Fit : 84,7)

The treatment of cotton with anhydrous liquid ammonia generally resulted in the largest increases in the moisture, iodine and barium hydroxide sorption values. The addition of increasing amounts of water to the liquid ammonia, however, progressively reduced the sorption of moisture, iodine or barium hydroxide by the cotton, compared with the treatment in anhydrous liquid ammonia. Despite this reduction, however, all the treatments studied (up to liquid ammonia containing 15% (v/v) water) still produced cotton samples having higher sorption values than the untreated fabrics.

It is also interesting to note that there was not a marked difference between the sorption characteristics of cotton fabrics treated in a slack state and those of samples treated under tension. If anything, the fabrics treated under tension had slightly lower sorption values than those treated in a slack state. It is clear also that the method used to remove the ammonia from the fabric after the treatment, had a much more pronounced effect on the sorption characteristics of the cotton than the state of the cotton during the liquid ammonia treatment, i.e. slack or under tension. In general, the removal of the ammonia by heat increased the sorption values most, followed by air-drying, while steaming had the least effect.

It is interesting that the three different sorption tests which were used to detect differences in the fibre structure, differed significantly in their relative assessment of the degree of modification of the fibre structure as a result of the liquid ammonia treatments. The iodine sorption test was the most sensitive followed by the barium hydroxide and moisture sorption tests. These differences are probably due to the fact that the three reagents involved, namely iodine, barium hydroxide and water vapour have different molecular masses and sizes. Furthermore, the first two tests are performed on wet swollen fibres whereas the last test is carried out on unswollen conditioned fibres.

A Comparison between Moisture, Iodine and Barium Hydroxide Sorption Values of Cotton Pretreated in Liquid Ammonia and Sodium Hydroxide

Table I gives the sorption characteristics of cotton treated in liquid ammonia as well as the values obtained when cotton was treated in 19% (v/v)

sodium hydroxide. Although treatment with sodium hydroxide resulted in a significant percentage increase in the sorption of moisture, iodine and barium hydroxide, this increase was not as pronounced as that obtained with a liquid ammonia treatment. This was especially the case with the iodine and barium hydroxide sorption values and it applied to fabrics treated in a slack state, as well as under tension. Although adding increasing amounts of water to the liquid ammonia progressively reduced the sorption values of the samples, it is clear that treatment with liquid ammonia containing up to 10% water, generally produced cotton with significantly higher sorption values than treatment with sodium hydroxide.

X-Ray Diffraction Studies on Cotton Fabrics Treated in Liquid Ammonia and Sodium Hydroxide

In some further studies, X-ray diffraction diagrams of fabrics treated under various conditions with liquid ammonia or sodium hydroxide were determined. These diagrams are shown in Figures 1 to 7.

Figure 1 shows the X-ray diffractogram of the untreated control fabric, and reveals a well-defined crystalline structure with prominent 002, 101 and $10\bar{1}$ crystalline peaks. The X-ray diffractograms of cotton treated in a slack state in anhydrous liquid ammonia, followed by the removal of the ammonia by heating, steaming or air drying are shown in Figures 2, 3 and 4, respectively. It is clear that anhydrous liquid ammonia treatment followed by the removal of the ammonia by heat or air drying resulted in diffractograms showing not such well-defined peaks, thus depicting a highly decrystallised cellulose structure. The ill-defined patterns obtained are probably the result of a mixed lattice of Cellulose I and Cellulose III. The removal of the ammonia by steam (Fig 3) resulted in a diagram similar to that of the untreated control fabric (Fig 1). This indicates that the Cellulose III which was formed during the liquid ammonia treatment was converted almost completely to Cellulose I, the cellulose polymorph of native cotton, by steaming. The amorphous content of the cotton, however, was increased to some extent by the treatment. This can be seen in the greater peak widths.

The effect of the presence of water in the liquid ammonia on the X-ray diffraction diagram of cotton was then investigated. The treatment of cotton in liquid ammonia containing 10% water, followed by the removal of the ammonia from the cotton by heat, produced an X-ray diffractogram shown in Figure 5. This is similar to that of cotton treated in anhydrous liquid ammonia (Fig 2), followed by the removal of the liquid ammonia with heat. This indicates that the presence of water in the liquid ammonia did not have a pronounced effect on the final structure of the cellulose.

The effect of the state of the cotton during the liquid ammonia treatment (i.e. slack or under tension) on its X-ray diffractogram was then studied. Fig 6 shows the X-ray diffractogram of cotton treated under tension in anhydrous

liquid ammonia, followed by the removal of the ammonia by heat, whereas Figure 2 shows the diffractogram of cotton treated in a slack state. It is clear that the treatment under tension yielded slightly better defined crystalline peaks, i.e. cotton with a slightly more crystalline structure than cotton treated in a slack state.

The fabric treated with sodium hydroxide (Figure 7) gave an X-ray diffractogram depicting a highly crystalline character. This indicates that sodium hydroxide did not decrystallise the cellulosic structure to the same degree as the liquid ammonia treatments especially when the ammonia was removed from the cotton by heat or air-drying (Figs 2 and 4).

The crystallinity indices of the samples were then calculated from the X-ray diffraction diagrams. The method suggested by Segal *et al*[17] was followed, and the "crystallinity index" was calculated from the ratio of the maximum intensity of the 002 reflection to the minimum intensity at $2\theta = 18°$. In this study the minimum intensity was measured at $2\theta = 21°$ because the emission of X-rays from a cobalt source caused a shift of 3° in the diffraction meter angle. The crystallinity indices of the various cotton samples are given in Table II.

TABLE II

CRYSTALLINITY INDICES OF COTTON FABRICS TREATED IN LIQUID AMMONIA AND SODIUM HYDROXIDE CALCULATED FROM X-RAY DIFFRACTOGRAMS INTENSITIES

Treatment			Crystallinity Index
Medium	Condition	NH_3 removed by	
NH_3	Slack	Heat	28,2
NH_3	Slack	Steam	59,2
NH_3	Slack	Air Drying	28,4
$NH_3 + 10\%\ H_2O$	Slack	Heat	29,1
NH_3	Tension	Heat	40,5
NaOH	Slack	—	49,0
Untreated Control	—	—	70,3

The decrystallisation of the cotton structure by swelling agents such as liquid ammonia or sodium hydroxide is clearly illustrated in Table II. It is obvious that liquid ammonia is generally a more effective swelling or decrystallising agent than sodium hydroxide. It can also be seen that, in the case of the

liquid ammonia treatments, the method used to remove the ammonia from the cotton had a larger effect on the crystallinity index than the state of the cotton during treatment (i.e. slack or under tension), or the presence of water in the liquid ammonia. These results are in general agreement with those previously obtained with the various sorption studies.

SUMMARY AND CONCLUSIONS

The effect of anhydrous and aqueous liquid ammonia as well as sodium hydroxide on the structure of the cotton fibre was investigated. Changes in the fibre structure were monitored with the aid of various tests such as moisture, iodine and barium hydroxide sorption as well as X-ray diffraction.

It was found that the treatment of cotton with anhydrous liquid ammonia resulted in the largest increase of moisture, iodine and barium hydroxide sorption. Although the addition of increasing amounts of water to the liquid ammonia progressively reduced the sorption of these reagents, liquid ammonia containing 15% (v/v) water still produced cotton with higher sorption values than the untreated fabric.

The method used to remove the ammonia from the fabric had a much larger effect on the sorption characteristics of the cotton than the state of the cotton during treatment i.e. slack or under tension. In general, the removal of the ammonia by heat increased the sorption values of the cotton most, followed by air drying, while steaming had the least effect.

Sodium hydroxide also resulted in a significant increase in the moisture, iodine and barium hydroxide sorption values of the cotton. This increase, however, was not as pronounced as that obtained with anhydrous liquid ammonia, and, in fact, it was also lower than that of cotton treated in liquid ammonia cointaining as high as 10% (v/v) water.

The decrystallisation of the cotton structure by the different swelling treatments was clearly illustrated by X-ray diffraction studies. The untreated cotton revealed well-defined 002, 101 and $10\bar{1}$ crystalline peaks. The X-ray diffractogram of cotton treated in liquid ammonia followed by the removal of the ammonia by steam was similar to that of the untreated control fabric. This indicates that the Cellulose III lattice which formed during the liquid ammonia treatment was converted to Cellulose I, the polymorph of native or untreated cotton, by steaming. Cotton treated in anhydrous liquid ammonia or liquid ammonia containing 10% (v/v) water, however, revealed not such well-defined diffractogram peaks indicating a highly decrystallised structure. This is probably the result of a mixed lattice of Cellulose I and III, and indicates that the presence of water did not have a pronounced influence on the decrystallising effect of liquid ammonia.

Finally, a comparison of the diffractograms of cotton treated in liquid ammonia and sodium hydroxide indicated that liquid ammonia is a more

effective swelling or decrystallising agent than sodium hydroxide. This was also borne out by the crystallinity indices of the samples which were calculated from the X-ray diffraction diagrams.

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THE USE OF PROPRIETARY NAMES

The fact that products with proprietary names have been used in this report does not imply that SAWTRI recommends them or that there are not substitutes which may be of equal or even better value.

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FIGURE 1

X-Ray Diffractogram of an Untreated Control Cotton Fabric

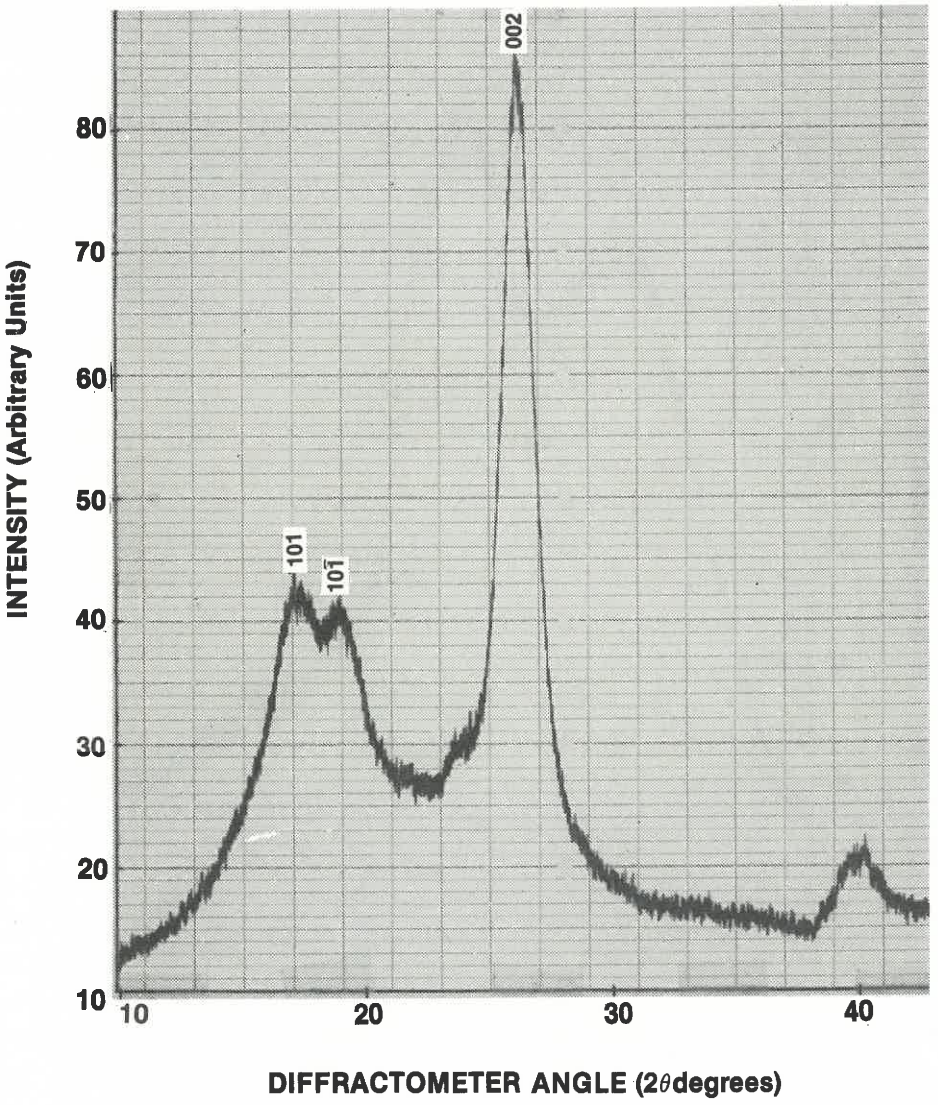


FIGURE 2

X-Ray Diffractogram of a Cotton Fabric Treated Slack in Anhydrous Liquid Ammonia followed by the Removal of the Ammonia by Heat

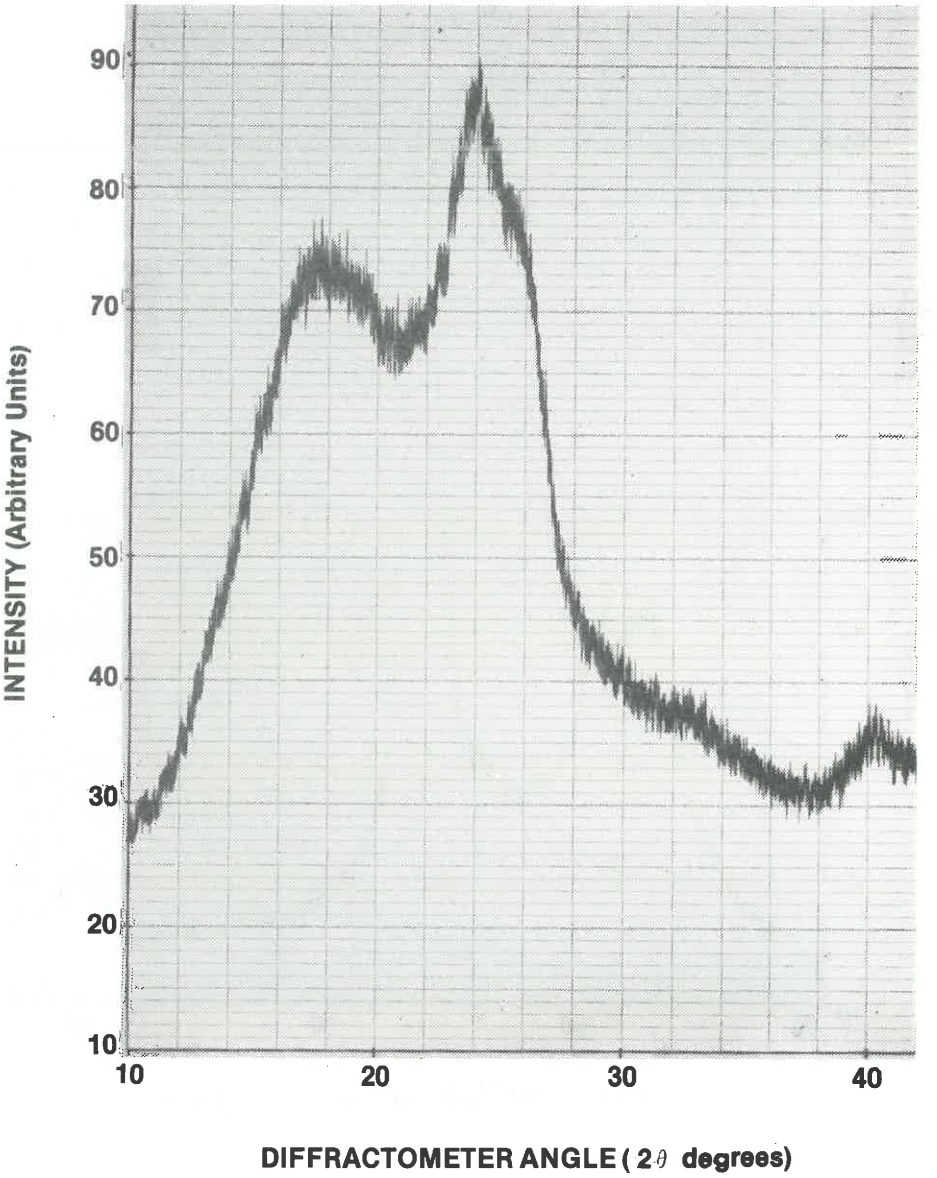


FIGURE 3

X-Ray Diffractogram of a Cotton Fabric Treated Slack in Anhydrous Liquid Ammonia followed by the Removal of the Ammonia by Steam

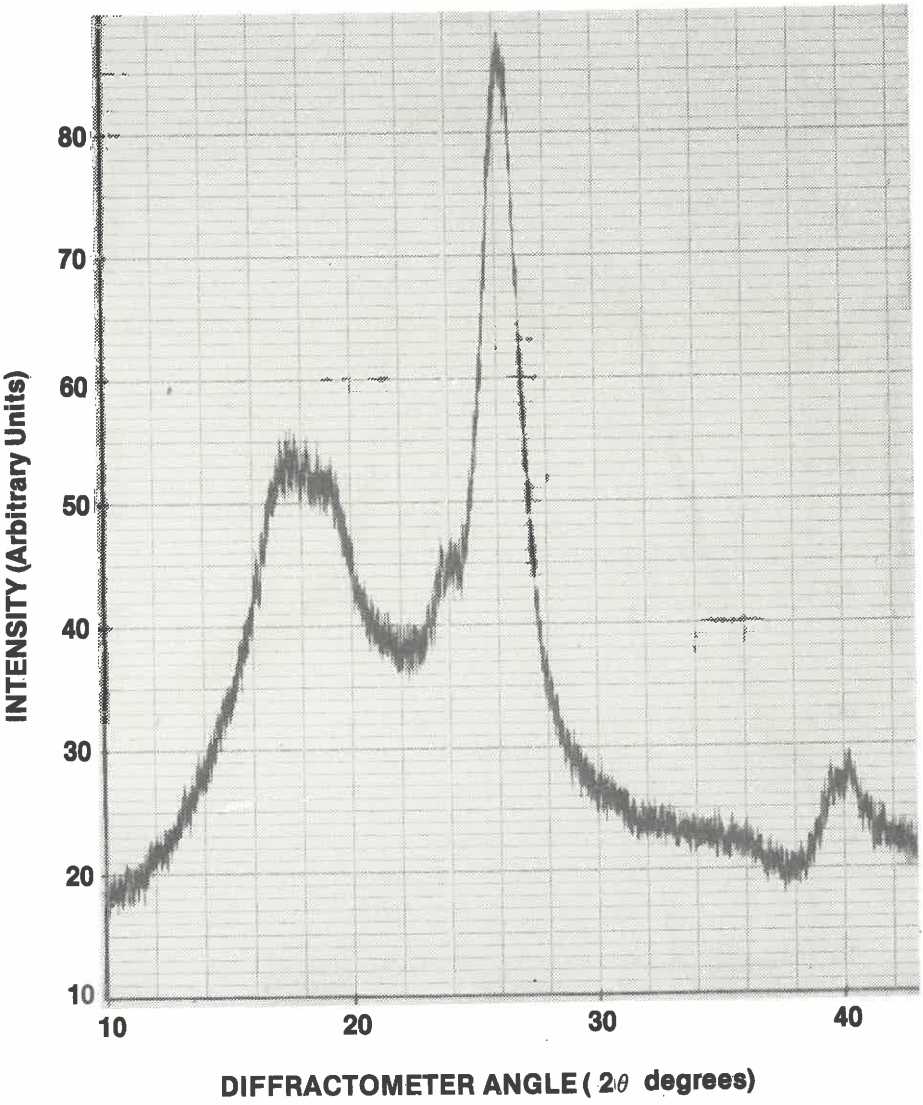


FIGURE 4

X-Ray Diffractogram of a Cotton Fabric Treated Slack in Anhydrous Liquid Ammonia, followed by the Removal of the Ammonia by Air Drying

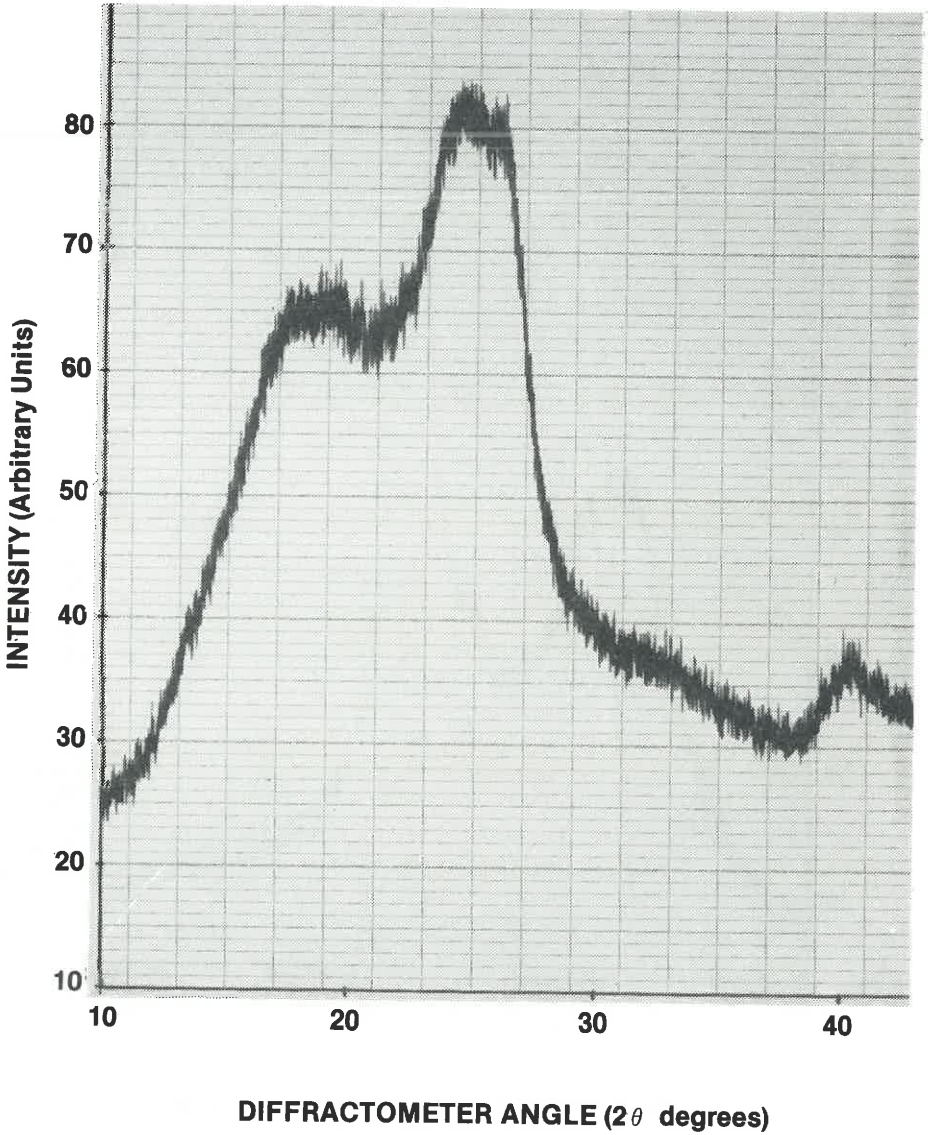


FIGURE 5

X-Ray Diffractogram of a Cotton Fabric Treated Slack in Liquid Ammonia containing 10% Water followed by the Removal of the Ammonia by Heat

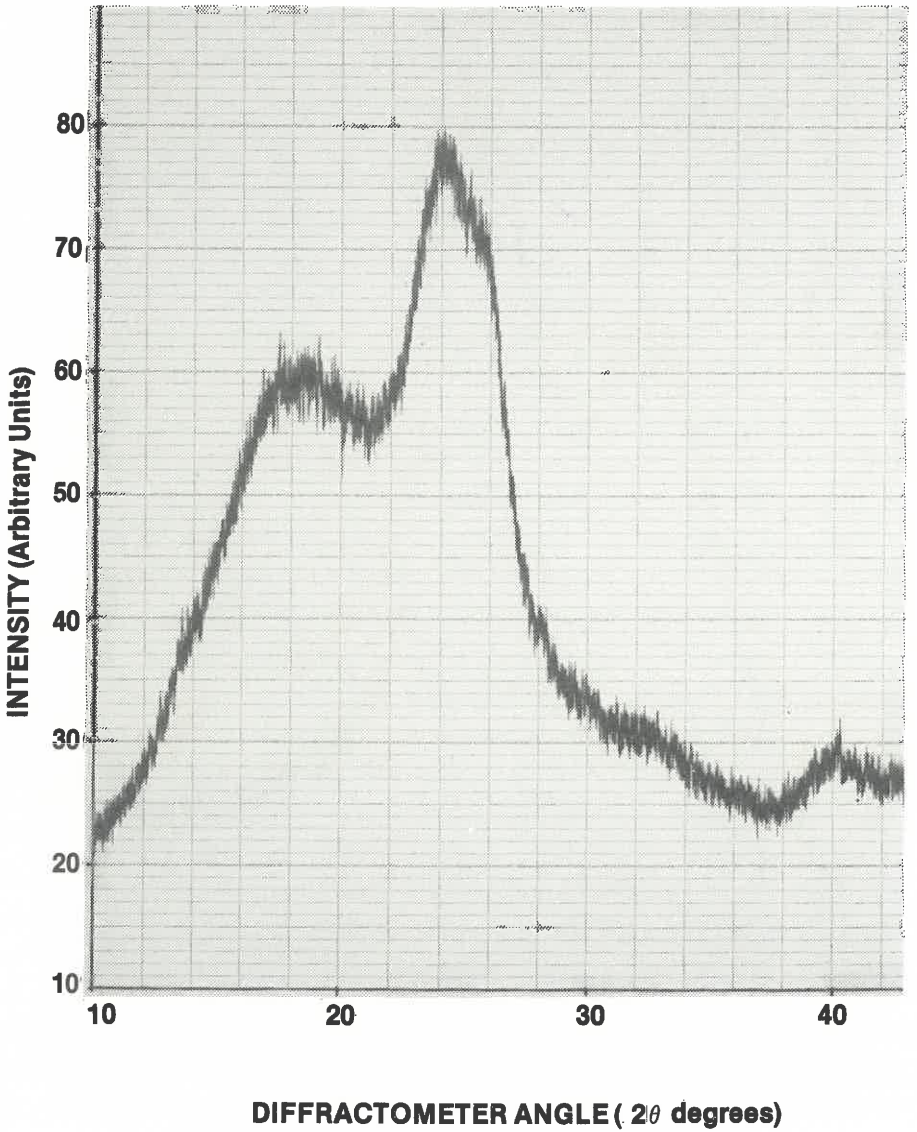


FIGURE 6

X-Ray Diffractogram of a Cotton Fabric Treated under Tension in Anhydrous Liquid Ammonia followed by the Removal of the Ammonia by Heat

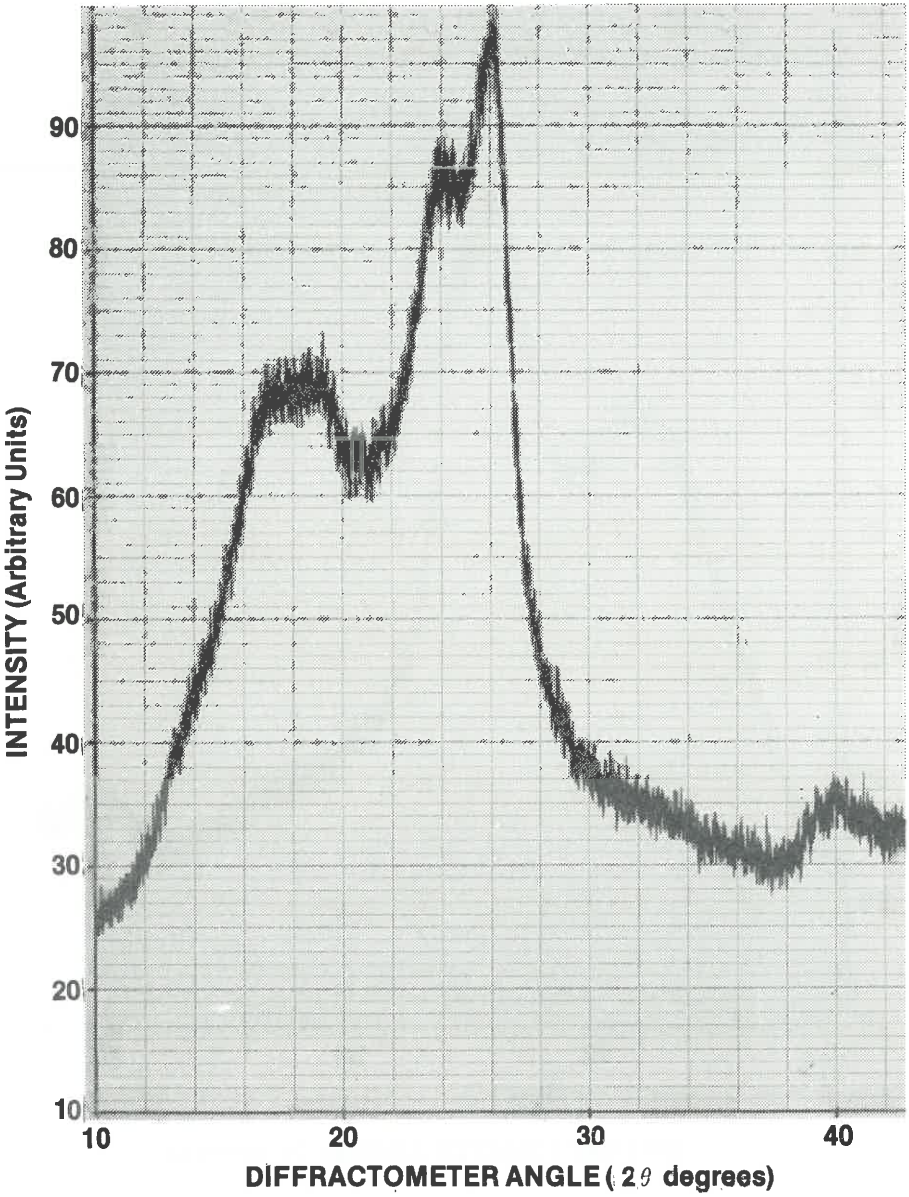
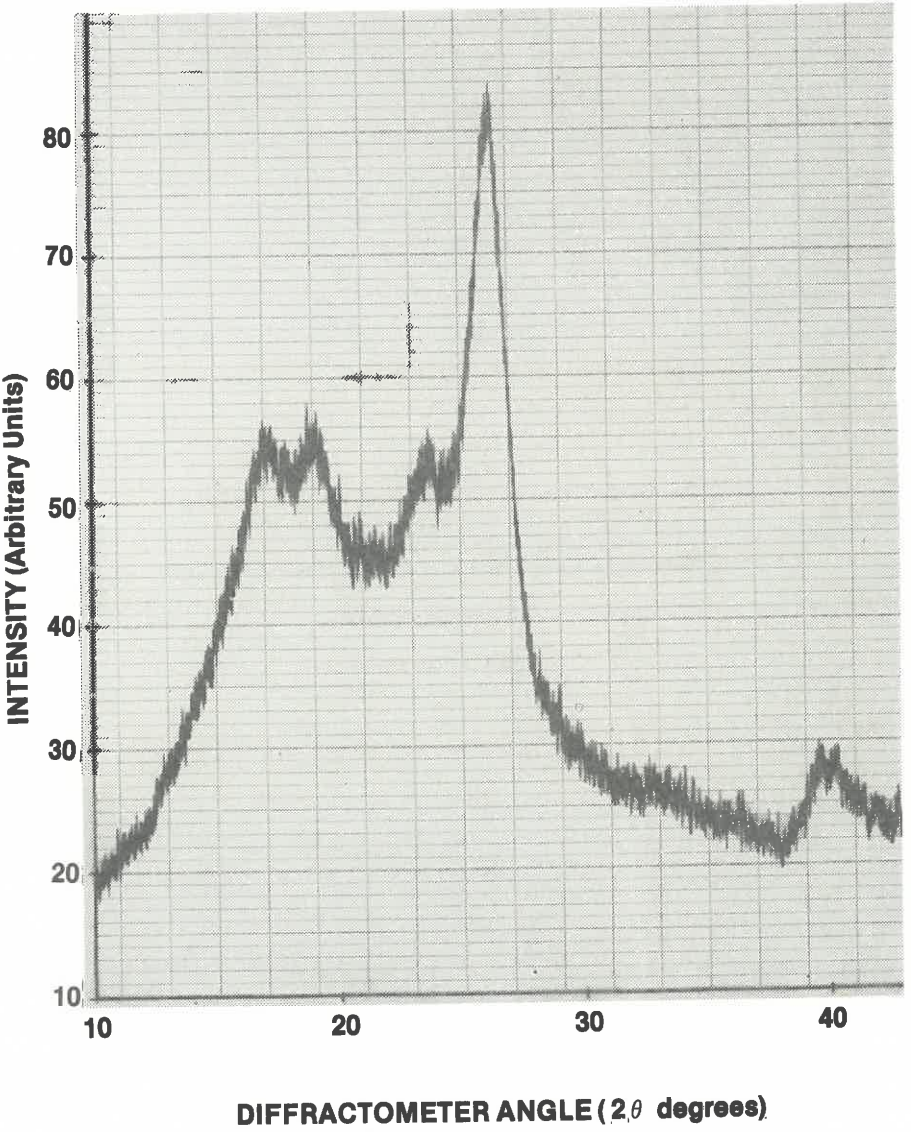


FIGURE 7

X-Ray Diffractogram of a Cotton Fabric Treated Slack in 19% Sodium Hydroxide



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