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Liquid Ammonia Mercerisation of Cotton.

Part V: The Influence of Anhydrous Liquid Ammonia on Certain Chemical Properties of Cotton

by

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LIQUID AMMONIA MERCERISATION OF COTTON. PART V: THE INFLUENCE OF ANHYDROUS LIQUID AMMONIA ON CERTAIN CHEMICAL PROPERTIES OF COTTON

by F.A. BARKHUYSEN

ABSTRACT

It was found that the fluidity of the cotton was not significantly affected by either liquid ammonia or sodium hydroxide mercerisation. Neither of these treatments, however, effected complete mercerisation, as judged by the barium activity numbers. The fabrics had a slightly better affinity for dyestuffs after mercerisation and a greater depth of shade was observed on mercerised fabrics.

INTRODUCTION

Previous reports in this series have shown that liquid ammonia mercerisation has a beneficial effect on certain *physical* properties of cotton fabrics[1,2,3]. The influence of liquid ammonia mercerisation on the *chemical* properties of these fabrics was, however, another aspect which had to be considered.

Chemically cotton comprises almost pure cellulose, which is composed of polymeric molecules of about one thousand repeating units of cellobiose. X-ray photographs of cotton fibres have shown that these long molecules are arranged as a network of more or less parallel chains with bundles of these parallel chains forming crystalline micelles which are surrounded by amorphous regions[4].

It is generally agreed that the crystalline regions are less accessible to chemical reagents than the amorphous regions. The accessibility of the cotton fibre can be increased by changing the internal structure of the fibre. Treatment of the cotton fibre with swelling or mercerising agents results in structural changes such as swelling, deconvolution, shrinkage and a change in cross-sectional shape. Internally the swelling results in a separation of the molecular chains and an accompanying rearrangement that affords increased reactivity. This change may be attributed to an increase in the number of available hydroxyl groups in the cellulose chains. The amorphous regions of native cotton may possess two accessible hydroxyl groups per glucose unit, while the crystalline regions are believed to contain no free hydroxyl groups[4]. On treatment with a swelling agent, however, some of the crystalline regions are transformed into semi-crystalline regions which have one free hydroxyl group per glucose unit. Mercerisation therefore changes the cellulose lattice, thereby increasing the number of accessible hydroxyl groups. Apart from changing the internal structure of the fibre, mercerising agents also change the flat ribbon-like cotton fibre into a smooth cylindrical rod, resulting in an increase in fibre lustre.

The purpose of this study was to investigate the effect of liquid ammonia as a swelling agent on the reactivity of cotton and to establish the degree of mercerisation imparted to cotton fabrics by different processing parameters. Another objective was to establish whether liquid ammonia mercerisation would influence the fluidity of the cotton.

EXPERIMENTAL

Materials:

The machine, materials and processing parameters used were the same as those described previously[1,5].

Cuprammonium Fluidity of Cotton:

To determine whether liquid ammonia mercerisation will degrade cotton under these conditions of treatment, the fluidity values of the samples were determined. The fluidity is the reciprocal of the viscosity (expressed in poises) of a 0,5 *per cent* solution of cotton in a standard cuprammonium hydroxide solvent. The fluidity values were calculated from the formula:

$F = {}^{c}/_{t}$, where c is a constant for the Shirley X type viscometer as given on the calibration certificate and t is the time taken for the meniscus of the solvent to fall from the first timing mark B to the third timing mark D as shown on the viscometer. All the above determinations were carried out at a temperature of 25°C.

Degree of Mercerisation:

The degree of mercerisation (given by the barium activity number) was determined according to the AATCC Test Method 89 — 1971. This test is based on the fact that mercerised cellulosic material absorbs more alkali (barium hydroxide) than unmercerised material. The ratio of barium hydroxide absorbed by the mercerised sample to that absorbed by the unmercerised sample multiplied by 100, gives the barium activity number. Barium numbers varying between 150 and 160 represent a complete mercerisation action whereas values between 100 and 105 indicate no mercerisation.

In this investigation the warp and weft threads were separated and the barium activity numbers of both threads were determined separately.

Dyeing Characteristics of Unmercerised and Mercerised Cotton Fabrics:

(a) **Dyes:** Reactive and direct cotton dyes were selected to establish the influence of liquid ammonia mercerisation on the dyeing behaviour of cotton fabrics. The dyeing trials were carried out in a Linitest laboratory dyeing apparatus and were performed according to the manufacturer's specifications.

(b) **Determination of Dyebath Exhaustion:** To determine the amount of dye absorbed by the cotton, the absorbance of the exhausted dye liquor was measured using a Zeiss PM 2 DL Spectrophotometer. The wavelength of maximum absorbance was first determined in a Beckman DB-GT spectrophotometer by scanning a standard solution of the dye (10 mg/ℓ). The Zeiss spectrophotometer was then calibrated using the same standard solution, allowing the concentration of the unknown sample to be read off directly.

(c) **Determination of the Colour Difference Values of Dyed Fabrics:** The colour value of the dyed samples was determined on a Harrison Shirley Digital Colorimeter. The tristimulis values X, Y and Z were determined, from which the Colour Difference (ΔE) between the unmercerised and mercerised samples was determined by the ANLAB 42 method[6]. The tristimulis values were obtained after the dyed samples had been soaped to remove unfixed dye which could have influenced the values.

RESULTS AND DISCUSSION

1. Cuprammonium Fluidity of Cotton

Cellulose is a polymer comprising anhydro-D-glucose units. To determine whether liquid ammonia would have any effect on the degree of polymerisation of cellulose, the solubility of samples in a standard cuprammonium hydroxide solvent was determined. If the degree of polymerisation of the cellulose was reduced by liquid ammonia mercerisation, this would show up in the fluidity values of the cotton. Normally, the cuprammonium hydroxide fluidity value increases as the degree of polymerisation decreases. Fluidity values from 1 to 5 usually indicate a mild scouring treatment, values from 5 to 10 indicate a normal scouring and bleaching treatment, values from 10 to 20 indicate some loss of strength of the fibre and values from 30 to 40 indicate a significant degradation of the fibre structure.

Samples were selected from those treated fabrics where the highest degree of fibre degradation was anticipated. These treatments comprised the conditions where the fabrics were in contact with the liquid ammonia for the longest time, while being stretched to the highest degree.

It was found that the fluidity values of cotton were not affected by liquid ammonia mercerisation under the conditions of treatment used in this investigation. The untreated control fabric had a fluidity value of 6,7 whereas an average value of 7,3 was obtained in the case of the mercerised fabrics.

2. Barium Activity Number of Cotton

To determine the degree of mercerisation of cotton treated with liquid ammonia under different processing conditions, the barium activity numbers were determined. It was found that the only parameter which influenced the degree of mercerisation was the degree of stretch applied to the fabric. Other parameters, such as contact time and the removal of ammonia from the fabric by heat, cold water or hot water had no significant effect on the barium activity number. Only the average values of the results obtained with the different contact times and methods of ammonia removal were therefore considered. Figure 1 shows the effect of the degree of stretch applied to the different fabrics on the barium activity numbers of the warp and weft yarns. It is obvious that different effects were obtained on the different fabrics. The barium numbers of the warp and weft yarns of the lightweight plain fabric first decreased and then increased as the degree of stretch was increased. In the case of the heavyweight plain and twill fabrics the barium numbers of the warp and weft yarns decreased as the degree of stretch applied was increased. Furthermore, the warp yarns had lower barium numbers than the weft yarns for the lightweight plain fabric, whereas the reverse was found for the heavyweight plain and twill fabrics. It is interesting to note that the degree of mercerisation of the weft yarns followed the same trend as the warp yarns, although no stretch was applied in this direction.

No explanation can at this stage be offered for the observed differences between the lightweight fabric and the two heavyweight fabrics. All the barium activity number results were subjected to a statistical analysis (quadratic regression analysis).

The analysis showed that the decrease in barium number of the warp and weft yarns of the heavyweight plain and twill fabrics, with an increase in the degree of stretch, was statistically significant at the 95 *per cent* confidence level. The only exception was that no significant change in barium number was found for the heavyweight warp and twill weft yarns when the degree of stretch was increased from 0 to 4 *per cent*. In the case of

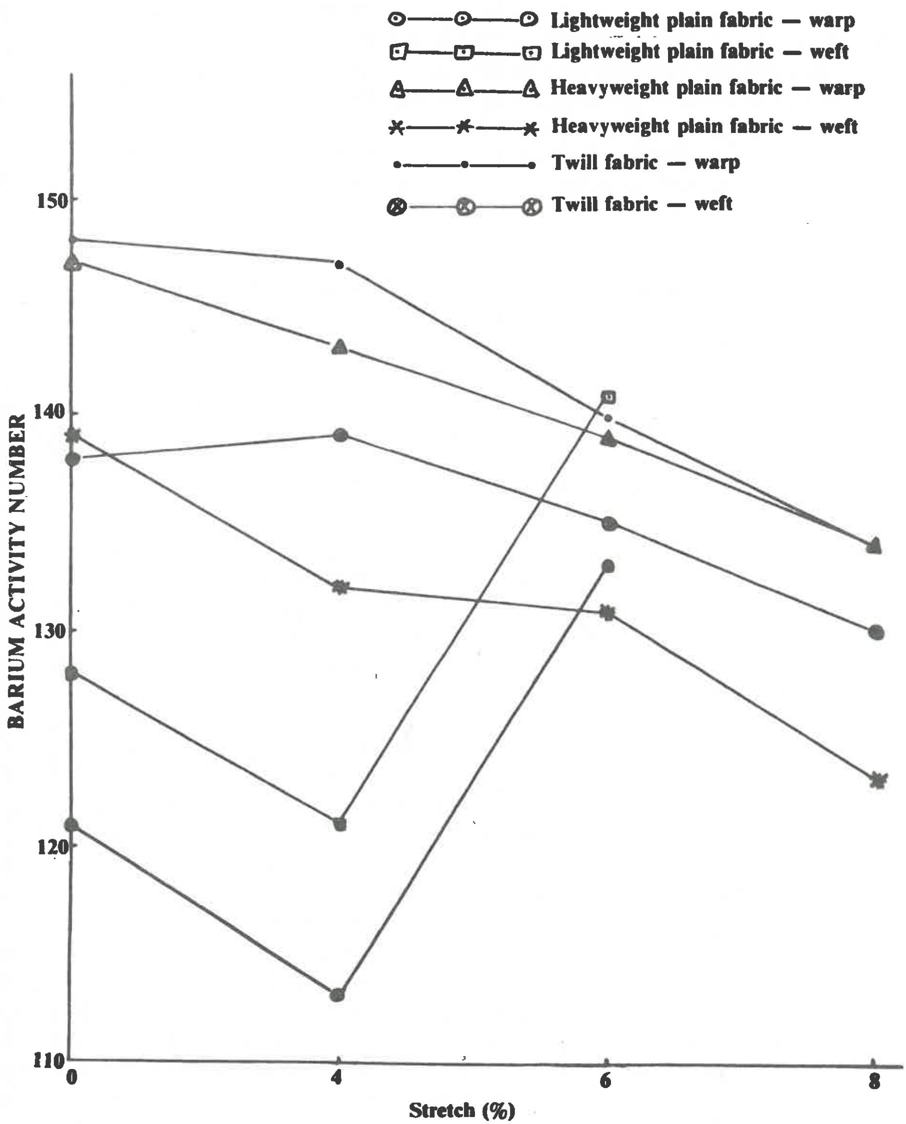

Figure 1 The effect of stretch applied to the fabrics on the degree of mercerisation in the warp and weft directions of the fabrics.

the lightweight plain fabric, the decrease in barium number of the warp yarn from 0 to 4 *per cent* stretch, and the increase from 4 to 6 *per cent* stretch, was statistically significant. The decrease in barium number of the weft yarns from 0 to 4 *per cent* stretch was not statistically significant, but the increase from 4 to 6 *per cent* was significant.

The barium numbers of the fabrics mercerised under industrial conditions with sodium hydroxide were as follows for the warp and weft yarns, respectively:

Lightweight plain fabric	141 and 154
Heavyweight plain fabric	120 and 125
Twill fabric	144 and 130

It is clear, therefore, that neither the sodium hydroxide nor the liquid ammonia treatment resulted in a complete mercerisation of the fabrics.

3. Dyeing Behaviour of Mercerised Cotton Fabrics

One of the most important advantages of mercerisation is the improved lustre obtained on mercerised cotton. To investigate the effect of liquid ammonia mercerisation on the dyeing behaviour of cotton, unmercerised and mercerised samples were dyed with several direct and reactive cotton dyes. The percentage dye exhausted onto the various samples of the lightweight plain fabric, heavyweight plain and twill fabric, together with the corresponding colour difference values are given in Tables I, II and III, respectively. These results were analysed statistically and the analysis is given in Table IV. The analysis took the form of a two factorial (6 x 5) analysis of variance and the main effects, significant at a 95 *per cent* confidence level, were judged against the interaction term. From Table IV, it is clear that mercerisation with either liquid ammonia or sodium hydroxide generally resulted in a slight increase in dye exhaustion. The effects were significant in many cases especially for the heavyweight plain and the twill fabrics. It was found that, on average, mercerisation increased the dye exhaustion by about 3 *per cent*. It is furthermore clear that liquid ammonia and sodium hydroxide mercerisation treatments generally resulted in practically the same dye exhaustion on the fabrics. It is also clear that cold or hot water removal of ammonia resulted in better dye exhaustion than heat removal of ammonia, especially on the heavyweight plain and the twill fabrics.

Differences were also found in the colour difference values of the different samples. According to Anderson[7] colour difference values correspond to the following Grey scale ratings:

Colour Difference Values (ΔE)	Grey Scale Ratings
0	5
1,5	4
3	3
6	2
12	1

The rating system is based upon a geometrical progression of colour difference so that differences between a rating of 1 and 2 are much bigger than those between a rating of 4 and 5. It is obvious that the larger the colour difference value of a sample, the greater the difference in colour between that sample and the control sample.

The results on the colour difference values were also analysed statistically (Table IV). It is clear that mercerisation resulted in a significant increase in the colour difference value (depth of shade) of the fabrics. It is clear also that, as observed from Tables I, II and III, water removal of ammonia resulted in a greater depth of shade of the fabrics than heat removal of ammonia. Cold and hot water removal of ammonia resulted in about the same depth of shade. For the lightweight plain fabric, the depth of shade of fabrics mercerised with sodium hydroxide was significantly greater than that of those treated in liquid ammonia. Although the analysis shows no statistical significant difference in the case of the other two fabrics, there was a trend, however, for sodium hydroxide mercerisation to result in a slightly greater depth of shade.

It is well-known that mercerisation results in a big improvement in fibre lustre and recently it has been stated that mercerisation is carried out for the sole purpose of increasing fibre lustre[8]. The greater depth of shade observed on mercerised fabrics can probably be attributed to the amount and quality of light which is reflected from the fibre surface. Mercerisation yields a fibre with a more smooth and almost circular cross-section and which has a much thicker fibre wall due to the swelling. The effect of mercerisation is to reduce the ratio of major to minor fibre cross-sections which will result in an increase in the intensity of light reflected from the fibre, i.e. the lustre[9]. According to Heap the quality of light reflected from the inside of an unmercerised and mercerised fibre also is different. Due to the thicker fibre wall after mercerisation, the path length of the light through the fibre is increased with the result that a deeper shade is observed. Unmercerised fibres will appear paler in shade due to the shorter path length of the light through the flat fibres.

TABLE I

THE PERCENTAGE DYE EXHAUSTED ONTO, AND COLOUR DIFFERENCE VALUES OF, LIGHTWEIGHT PLAIN COTTON SAMPLES DYED WITH DIRECT AND REACTIVE DYES AFTER MERCERISATION WITH LIQUID AMMONIA AND SODIUM HYDROXIDE

Treatment	DYES											
	C.I. Direct Green 26		C.I. Direct Red 81		C.I. Reactive Red 2		C.I. Reactive Red 11		C.I. Reactive Red 43		C.I. Reactive Red 58	
	Exhaustion (%)	Δ E	Exhaustion (%)	Δ E	Exhaustion (%)	Δ E	Exhaustion (%)	Δ E	Exhaustion (%)	Δ E	Exhaustion (%)	Δ E
Untreated Control	89,6		85,1		85,1		80,2		84,3		81,3	
NH_3 + * Heat Removal of Ammonia	88,3	1,11	91,5	3,83	82,1	2,09	81,3	2,43	82,9	1,76	86,4	6,83
NH_3 + * Cold Water Removal of Ammonia	90,7	4,11	86,7	5,14	85,1	3,80	85,1	4,14	85,1	2,42	84,8	5,69
NH_3 + * Hot Water Removal of Ammonia	—	—	—	—	84,0	4,94	85,1	4,66	84,8	3,82	-	-
NaOH Mercerised	95,2	5,34	85,1	8,17	86,4	7,12	87,5	7,99	84,3	8,42	86,9	9,54

* 6 *per cent* stretch applied to the fabrics at a speed of 3 m/min (i.e. 5 seconds contact time in liquid ammonia)

TABLE II

THE PERCENTAGE DYE EXHAUSTED ONTO, AND COLOUR DIFFERENCE VALUES OF, HEAVYWEIGHT PLAIN COTTON SAMPLES DYED WITH DIRECT AND REACTIVE DYES AFTER MERCERISATION WITH LIQUID AMMONIA AND SODIUM HYDROXIDE

Treatment	DYES											
	C.I. Direct Green 26		C.I. Direct Red 81		C.I. Reactive Red 2		C.I. Reactive Red 11		C.I. Reactive Red 43		C.I. Reactive Red 58	
	Exhaustion (%)	Δ E	Exhaustion (%)	Δ E	Exhaustion (%)	Δ E	Exhaustion (%)	Δ E	Exhaustion (%)	Δ E	Exhaustion (%)	Δ E
Untreated Control	90,9		83,7		84,3		80,5		80,2		82,1	
NH_3 + * Heat Removal of Ammonia	93,3	3,07	84,3	3,57	82,9	1,59	80,0	3,93	81,8	3,05	82,1	2,86
NH_3 + * Cold Water Removal of Ammonia	92,8	4,15	86,4	6,63	85,8	4,33	86,4	6,63	85,1	7,02	85,6	6,04
NH_3 + * *Hot Water* Removal of Ammonia	93,1	2,42	86,9	6,14	84,8	3,98	84,0	6,13	83,4	5,62	84,5	6,29
NaOH Mercerised	93,9	4,34	83,4	4,74	85,6	6,50	85,1	7,52	83,7	6,53	86,1	8,00

* 8 *per cent* stretch applied to the fabrics at a speed of 3 m/min (i.e. 5 seconds contact time in liquid ammonia)

TABLE III

THE PERCENTAGE DYE EXHAUSTED ONTO, AND COLOUR DIFFERENCE VALUES OF, TWILL COTTON SAMPLES DYED WITH DIRECT AND REACTIVE DYES AFTER MERCERISATION WITH LIQUID AMMONIA AND SODIUM HYDROXIDE

Treatment	DYES											
	C.I. Direct Green 26		C.I. Direct Red 81		C.I. Reactive Red 2		C.I. Reactive Red 11		C.I. Reactive Red 43		C.I. Reactive Red 58	
	Exhaustion (%)	Δ E	Exhaustion (%)	Δ E	Exhaustion (%)	Δ E	Exhaustion (%)	Δ E	Exhaustion (%)	Δ E	Exhaustion (%)	Δ E
Untreated Control	89,6		84,8		83,4		81,1		82,6		80,0	
NH_3 + * Heat Removal of Ammonia	85,6	1,41	85,6	5,65	82,6	1,15	80,0	2,87	82,4	3,67	81,1	3,10
NH_3 + * Cold Water Removal of Ammonia	92,5	3,35	86,7	8,44	86,1	5,94	86,4	4,58	85,8	7,56	84,3	6,88
NH_3 + * Hot Water Removal of Ammonia	89,6	8,47	86,7	7,25	85,1	5,40	87,2	4,08	84,8	5,85	82,4	6,14
NaOH Mercerised	93,1	3,31	86,4	10,06	84,3	7,51	85,8	8,60	83,4	8,13	83,4	7,86

* 8 *per cent* stretch applied to the fabrics at a speed of 3 m/min (i.e. 5 seconds contact time in liquid ammonia)

TABLE IV

MEAN VALUES OF DYE EXHAUSTION AND COLOUR DIFFERENCE VALUES OF FABRICS MERCERISED WITH LIQUID AMMONIA AND SODIUM HYDROXIDE

TREATMENT	DYE EXHAUSTION			COLOUR DIFFERENCE (ΔE)		
	Lightweight Plain Fabric	Heavyweight Plain Fabric	Twill Fabric	Lightweight Plain Fabric	Heavyweight Plain Fabric	Twill Fabric
Untreated Control	84,3	83,6	83,6	Nil	Nil	Nil
NH_3 + Heat Removal of Ammonia	85,4	84,1	82,9	3,0	3,0	3,0
NH_3 + Cold Water Removal of Ammonia	86,3	87,0	87,0	4,2	5,8	6,1
NH_3 + Hot Water Removal of Ammonia	86,2	86,1	86,0	5,1	5,1	6,2
NaOH Mercerised	87,6	86,3	86,1	7,8	6,3	7,6
$\tilde{x}$	2,5	1,4	1,6	1,5	1,2	1,7

$\tilde{x}$ is the minimum difference required between any two mean values for those mean values to be judged as different at the 95% confidence level.

The relative contributions of the increased dye absorption, lustre and possibly shrinkage of the fabrics on the increased depth of shade after mercerisation at this stage is not yet clear and some further investigations have to be carried out in this respect.

SUMMARY AND CONCLUSIONS

Some chemical properties, such as the fluidity, the barium activity number and the dye affinity of unmercerised and mercerised cotton fabrics were investigated.

It was found that none of the different processing parameters used during liquid ammonia mercerisation had any effect on the fluidity values of the cotton. The same was found for sodium hydroxide mercerisation.

As far as the degree of mercerisation was concerned, it was found that neither liquid ammonia nor sodium hydroxide mercerisation treatments gave a complete mercerisation action, as indicated by the barium activity numbers.

It was also found that mercerised fabrics had an increased affinity for dyestuffs but this effect, however, was relatively small. Water removal of ammonia generally seemed to result in fabrics with a higher dye affinity than fabrics where the ammonia was removed by heat. The dye exhaustion of fabrics mercerised with sodium hydroxide and liquid ammonia was found to be the same.

After dyeing mercerised fabrics also showed a greater depth of shade than the dyed control fabric. A greater depth of shade was observed on fabrics where the ammonia was removed by either cold or hot water than on fabrics where the ammonia was removed by heat. Although the difference in depth of shade on fabrics mercerised with liquid ammonia and sodium hydroxide was found to be statistically insignificant, except for the lightweight plain fabric, sodium hydroxide mercerised fabrics appear to have a greater depth of shade.

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THE USE OF PROPRIETARY NAMES

The fact that proprietary names have been used in this report in no way implies that there are not substitutes which may be of equal or even better value.

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