SAWTRI TECHNICAL REPORT

No. 550

Some Sorption and X-Ray Characteristics of Cotton Fibres Treated in Yarn Form with Anhydrous and Aqueous Liquid Ammonia

by
F A Barkhuysen and N J J van Rensburg

SOUTH AFRICAN
WOOL AND TEXTILE RESEARCH
INSTITUTE OF THE CSIR

P.O. BOX 1124
PORT ELIZABETH
REPUBLIC OF SOUTH AFRICA

ISBN 0 7988 2908 7

SOME SORPTION AND X-RAY CHARACTERISTICS OF COTTON FIBRES TREATED IN YARN FORM WITH ANHYDROUS AND AQUEOUS LIQUID AMMONIA

by F A. BARKHUYSEN and N J.J VAN RENSBURG

ABSTRACT

The modification of the structure of bleached cotton treated in yarn form with anhydrous liquid ammonia and liquid ammonia containing as much as 15% water was determined with the aid of iodine and moisture absorption tests, X-ray diffraction studies, and surface area determinations. Treatments with anhydrous liquid ammonia resulted in a significant increase in the iodine sorption values of cotton, especially when the ammonia was removed by heat. The addition of water to the liquid ammonia, however, reduced this effect. The moisture sorption of the cotton was increased by anhydrous liquid ammonia, while the addition of water to the liquid ammonia increased it even further. It was found that different treatments differed in their effects on the surface area of the cotton. Increasing concentrations of water in liquid ammonia increased the surface area of the cotton when treated under tension while a treatment in a slack state reduced the surface area. The degree of decrystallisation of cotton by anhydrous and aqueous liquid ammonia was verified by X-ray diffraction studies.

INTRODUCTION

The physical and chemical properties of cotton are determined by its structure. It is well known that the cotton fibre comprises crystalline and amorphous regions and that most chemical reactions involve the hydroxyl groups of the cellulose. The availability of the hydroxyl groups to chemical reagents is therefore very important and determines several properties of the cotton fibre including its response to dyeing and resin finishing. The hydroxyl groups in the crystalline fractions are relatively inaccessible to chemical reagents, due to the high order and extensive hydrogen bonding in the structure, whereas the opposite is true for the amorphous fractions[1,2]. It has been stated[3] that the accessibility of the hydroxyl groups in the crystalline regions is such that small reagent molecules can reach only 10 to 15% of these groups, compared with 85 to 95% in the amorphous regions. In order to modify the cellulosic structure so that the availability of hydroxyl groups is increased, a strong swelling or decrystallizing agent is required. Numerous agents such as sodium hydroxide, liquid ammonia, cuprammonium hydroxide, copper ethylenediamine, sulphuric acid, phosphoric acid and quaternary ammonium bases, have been studied[4].

Tests

The iodine sorption value (mg I_2/g sample) of untreated and treated cotton was calculated according to the method described by Hessler and Power[17]. The moisture sorption [moles H_2O/anhydroglucose unit (AGU)] of the cellulose was determined according to the method of Pandey and Nair[18]. The surface area of the fibres was determined as follows: samples (0,5g) were analysed by means of a Micromeritics Orr surface area-pore volume analyser with Krypton as adsorbate at the temperature of liquid nitrogen according to the BET method[19]. The samples were degassed at 50°C for two hours prior to testing.

Debye Scherrer (X-ray) diagrams were obtained as follows: a 2 cm long bleached cotton yarn segment was dipped in ®Damar gum. After drying, it was mounted with beeswax in a copper holder. The holder was then placed into a 57,3 mm diameter Debye Scherrer camera loaded with a Kodak Medical X-ray film. The camera was placed into an X-ray apparatus in such a way that the sample was perpendicular to the X-ray beam. The sample was bombarded with X-rays for 20 minutes at a voltage of 40 kV and filament current of 20 mA. The different planes of the cellulose crystal lattice deflected the X-rays and a diffraction diagram was obtained on the film. The film was subsequently developed with ®Solidex for 3,5 minutes at 24°C and fixed with ®Amfix for at least 10 minutes followed by rinsing and drying. Positive prints were produced from these negatives.

RESULTS AND DISCUSSION

The Effect of Anhydrous Liquid Ammonia on the Iodine and Moisture Sorption of Cotton

The effect of liquid ammonia on the iodine sorption of cotton yarn treated for various periods either in a slack state or under tension is shown in Table I. This table also shows the effect of the method by which the ammonia was removed from the cotton, namely dry heat or steam, on the iodine sorption value. The treatment of cotton yarns in a slack state in liquid ammonia resulted on average, in marginally higher iodine sorption values than the treatments carried out under tension. The state of the yarn during the treatment (slack or under tension) in general seemed to have had little effect on the decrystallisation or swelling of the cellulosic structure by the liquid ammonia. Similarly, the time of immersion in the liquid ammonia generally had little effect. On the other hand, the method by which the ammonia was removed from the cotton had a pronounced effect on the iodine sorption value. Table I shows that the removal of the ammonia from the yarns by dry heat resulted in significantly higher iodine sorption values than the removal by steam. In other words, the former treatment

produced a much greater decrystallisation of the cotton structure than the latter.

These results are in agreement with those obtained when *fabrics* were treated with liquid ammonia[14]. Furthermore, similar observations were made by other research workers. Jung *et al* [20] postulated that the method of ammonia removal would determine whether hydrogen bond cleavage by the ammonia would cause only a temporary shift in the positions of the cellulosic chains or a

TABLE I

IODINE SORPTION OF COTTON YARN TREATED SLACK AND UNDER TENSION IN LIQUID AMMONIA FOR VARIOUS TIMES

Immersion Time	IODINE SORPTION (mg I_2/g sample)			
	Treated in a Slack State		Treated under Tension	
	NH_3 Removed by Dry Heat	NH_3 Removed by Steam	NH_3 Removed by Dry Heat	NH_3 Removed by Steam
10 s	265,8	156,5	276,5	119,9
30 s	261,7	114,4	247,7	106,9
60 s	269,1	137,4	265,0	132,1
5 min.	264,2	118,1	268,3	146,1

Untreated Control: 102,5

shift in the relative positions of the chains themselves so that a new crystalline structure is formed. Calamari *et al*[21] stated that if the ammonia is removed from cellulose by evaporation, the crystalline lattice of native cellulose (Cellulose I) is changed to Cellulose III. When the ammonia/cellulose complex is quenched with water, however, Cellulose I is regenerated.

The decrystallising effect of liquid ammonia is lower for cotton treated in yarn form than cotton treated in the form of loose fibres. For example, it was found that the iodine sorption value of similar cotton treated as loose fibres was about 330 after a liquid ammonia/heat treatment, compared with about 268 when the cotton was treated in yarn form[11]. This difference can most likely be ascribed to the fact that the swelling and deconvolution of the fibres in the yarn were partially inhibited by the twist in the yarn.

Table II shows the moisture sorption values of yarns treated in liquid ammonia under various conditions. In general, the liquid ammonia treatments

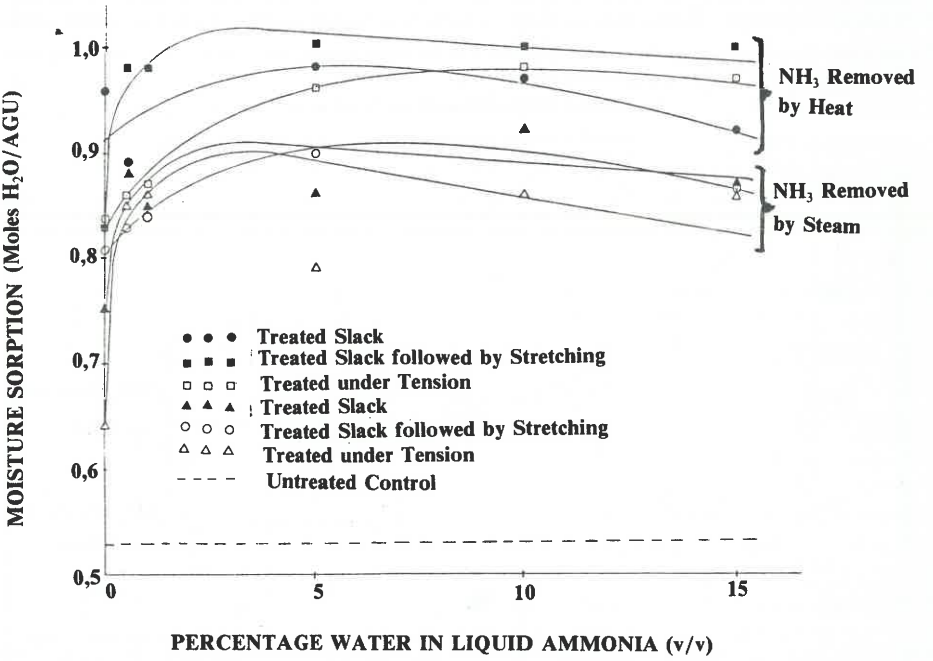


Fig. 2 – Moisture sorption of cotton yarn treated under different conditions in liquid ammonia containing various percentages of water.

had a significant effect on the iodine sorption value of the cotton. In general, the iodine sorption decreased rapidly when the water content of the ammonia increased, up to a level of about 5% (v/v), after which further increases in the water content had little effect. The results obtained on yarns treated under different conditions, i.e. slack, or slack followed by stretching or under tension, did not seem to differ significantly. On the other hand, the method by which the ammonia was removed from the cotton had a significant effect. Steaming generally produced samples with slightly lower iodine sorption than that of the untreated control yarn, whereas the samples treated with dry heat had higher values. In general, it appears that the presence of water in the liquid ammonia had an adverse effect on the decrystallisation or opening up of the fibre structure by the liquid ammonia. In fact, the results indicate that the presence of water in the liquid ammonia could lead to a re-arrangement of the cellulose into a structure which is less accessible to iodine than the original untreated cotton.

It has already been shown that the sorption of moisture by the cotton was increased by an anhydrous liquid ammonia treatment. Figure 2 shows that the moisture sorption increased even further when water was added to the liquid ammonia, up to a level of 5% (v/v) water, whereafter little further change was noticed. The method of treatment in liquid ammonia (i.e. slack, tension, etc.) did not have a clear or consistent effect on the moisture sorption values. In general the removal of the ammonia by heat resulted in cotton with higher moisture sorption values than the removal by steam.

The reasons for the observed increase in moisture sorption after treatment with liquid ammonia containing water are not yet clear. The water molecule can only penetrate the amorphous regions of the fibre and it does not affect the intramolecular spacings of the crystalline regions. When cotton is treated with liquid ammonia, however, the presence of water possibly enhances the intracrystalline swelling properties of the liquid ammonia, thereby increasing the accessibility of the fibre to moisture.

In further studies the effect of the different liquid ammonia treatments on the surface area of the fibre, using the Krypton gas adsorption technique, was evaluated. This technique gives a measure of the total surface area (internal and external) of the cotton. Figure 3 shows the effect of varying percentages of water in the liquid ammonia on the total surface area of the cotton. It is clear that the liquid ammonia treatments reduced the surface area of the cotton considerably, compared with the untreated control yarn. An increase in the amount of water in the liquid ammonia increased the surface area of the cotton very slightly. Furthermore, the removal of the ammonia from the cotton by heat produced yarns with a slightly lower surface area than removal by steam. The surface area of the yarns treated under tension was higher than that of the untreated control, while that of the yarn treated in a slack state was lower.

The results show that a change in the surface area of the cotton is not

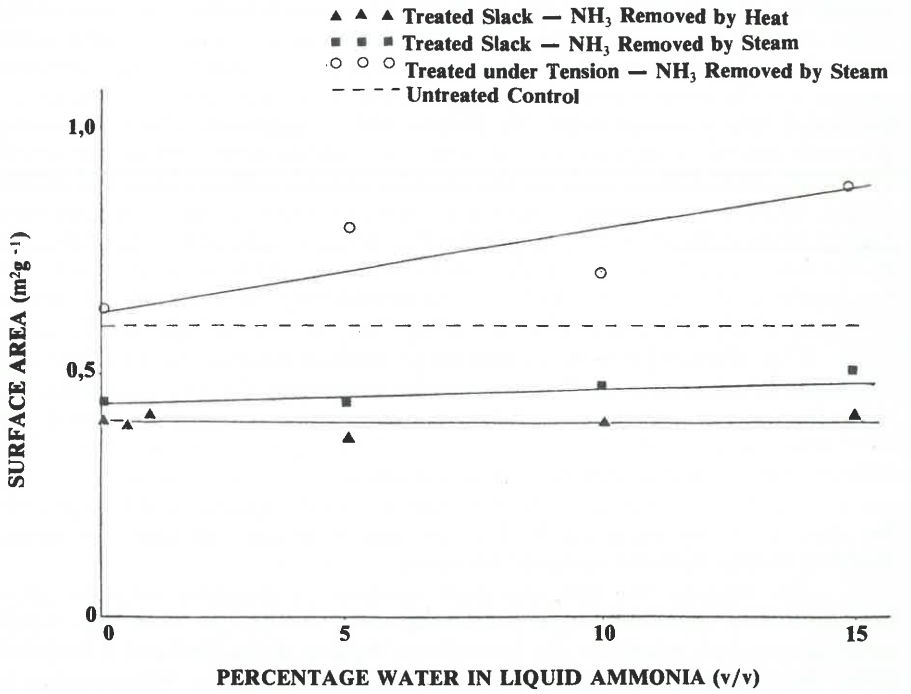


Fig. 3 – The surface area of cotton treated slack and under tension in liquid ammonia containing various percentages of water.

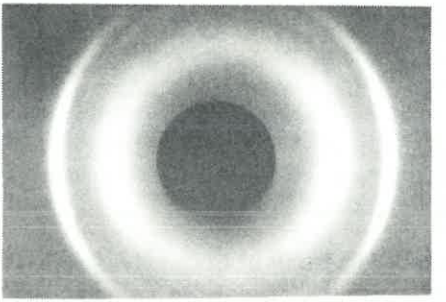
necessarily correlated with a change in the moisture and iodine sorption characteristics or the accessibility of the fibre to chemicals. This is in agreement with the observations made by Rousselle *et al*[9] and confirm the views of Jeffries *et al*[22] on this matter. Furthermore, the surface area results found during the present study are in close agreement with those of Rowen and Blaine[23] who found a value of 0,72 m^2/g of sample using nitrogen at -195° C. They stated that this value probably represents the true surface area and that it is not correlated with moisture sorption values.

X-ray (Debye Scherrer) Diagrams of Cotton Treated with Liquid Ammonia and Sodium Hydroxide

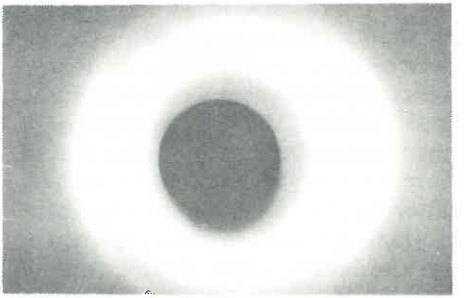
In some further studies the X-ray diagrams of cotton treated with liquid ammonia and sodium hydroxide under various conditions were determined and are shown in Figures 4 and 5. All the samples were treated for 60 seconds in either liquid ammonia or sodium hydroxide. The X-ray diagram of an untreated control yarn is shown in Figure 4(a). The high degree of order or crystallinity of the untreated cotton fibres is quite obvious from the well-defined X-ray reflection patterns.

Figures 4 (b) and (c) show the X-ray diagrams of cotton treated in a slack state in anhydrous liquid ammonia followed by the removal of the ammonia by dry heat and steam, respectively. It is clear that treatment in anhydrous liquid ammonia produced a cellulose structure which caused a very diffuse scattering of X-rays. Although X-rays can only resolve crystallites above a certain size, the diffraction patterns suggest that these samples contained a large percentage of amorphous material. Their crystallinity was therefore much lower than that of the untreated control sample. Secondly, the removal of the ammonia by dry heat [Figure 4 (b)] resulted in a more diffuse scattering of X-rays than the removal of the ammonia by steam [Figure 4(c)]. The former treatment therefore resulted in a less crystalline cellulose structure than the latter. These findings are in agreement with the X-ray diffraction results obtained by other research workers[9, 20, 21].

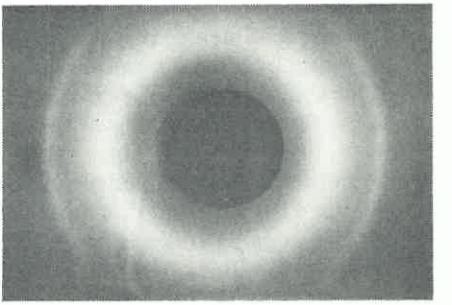
The addition of water to the liquid ammonia was found to have a marked effect on the structure of the cellulose. Figure 5 shows the X-ray diagrams of cotton treated for 60 seconds in a slack state or under tension in anhydrous liquid ammonia and in liquid ammonia containing 5% (v/v) water followed by the removal of the ammonia by steam. It is clear that a treatment of cotton in a slack state in anhydrous liquid ammonia resulted in a structure giving a diffuse scattering of X-rays. A similar diagram was obtained when the yarns were treated under tension. When the yarns were treated in liquid ammonia containing 5% water, however, both treatments (slack or under tension) produced samples which had a higher crystallinity than those samples treated in anhydrous liquid ammonia.



(a) Untreated Control



(b) NH_3 followed by dry heat



(c) NH_3 followed by steam

Fig. 4 – X-Ray (Debye Scherrer) diagrams of some cotton yarns treated in liquid ammonia.

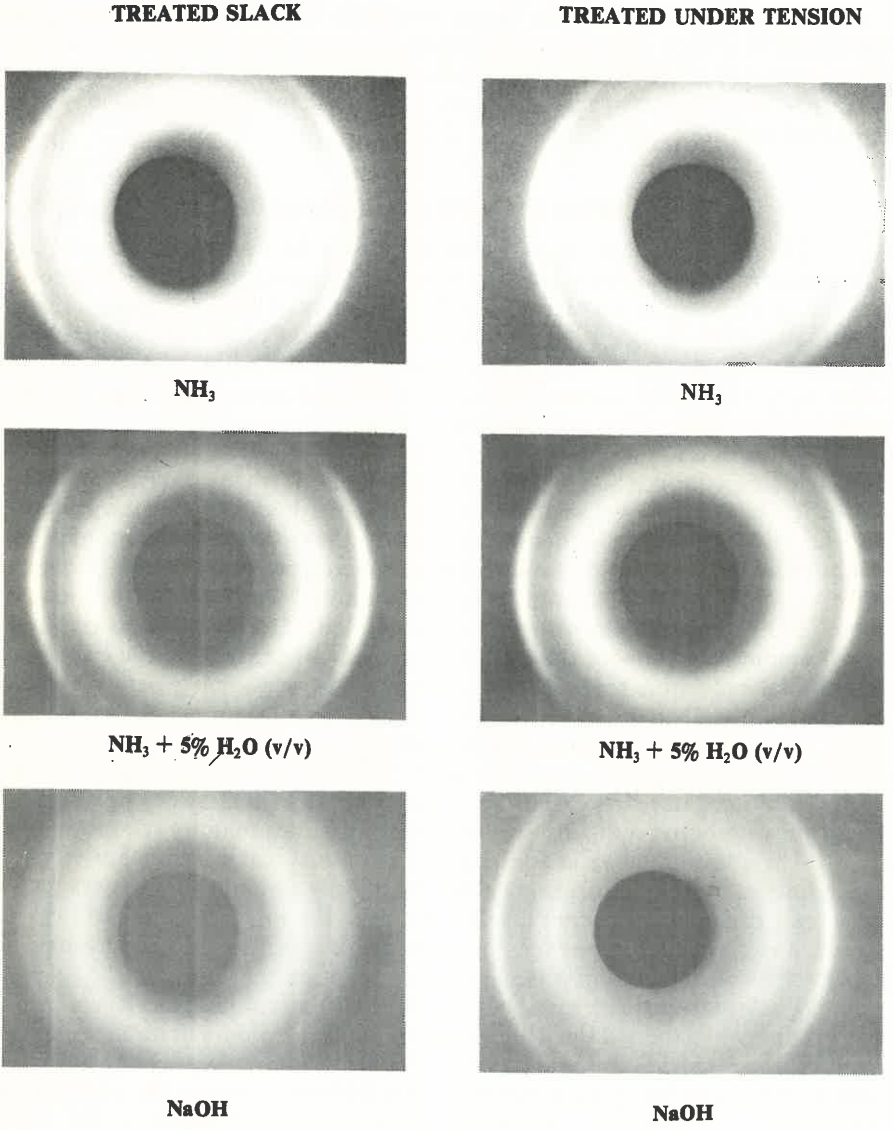


Fig. 5 – Debye Scherrer diagrams of cotton yarns treated slack and under tension in sodium hydroxide and in liquid ammonia containing various quantities of water.

Figure 5 also shows the X-ray diagrams of yarn treated with sodium hydroxide in a slack state and under tension, respectively. The yarn treated in a slack state gave an X-ray diagram similar to the liquid ammonia treated yarns. The yarns treated under tension, however, gave a diagram similar to that of the untreated control yarn, but less well defined.

SUMMARY AND CONCLUSIONS

The effect of anhydrous liquid ammonia as well as liquid ammonia containing various concentrations of water on the structure of bleached cotton treated in yarn form was studied with the aid of iodine sorption moisture sorption, surface area and X-ray diffraction studies. Cotton yarns were treated in a slack state, or under tension or in a slack state followed by stretching. The yarns were treated for various periods in the liquid ammonia, which was then removed from the cotton by steaming or heating in an oven.

Variations in the conditions of the liquid ammonia treatment, such as the immersion time, or method of treatment (slack or under tension) had little effect on the iodine sorption value of the cotton. The method by which the ammonia was removed, however, had a pronounced effect. When the ammonia was removed by dry heat the iodine sorption was increased by about 300%, whereas there was only a slight increase when the ammonia was removed by steam.

The sorption of moisture by the cotton seemed to be more sensitive to the liquid ammonia treatment than iodine sorption. In general, all the treatments increased the moisture sorption of the cotton. Slack treatment generally resulted in yarn with higher moisture sorption values than treatment under tension. There was a rapid initial increase in the moisture sorption value when the cotton was immersed in liquid ammonia with, if anything, a decrease when the immersion times were increased. The removal of ammonia by dry heat resulted in cotton with better moisture sorption characteristics than by steam removal.

The addition of water to the liquid ammonia had a significant effect on the iodine and moisture sorption values. Increasing amounts of water resulted in a decrease of the iodine sorption value. As far as the sorption of moisture by the cotton was concerned, however, the addition of water to the liquid ammonia generally resulted in an increased moisture sorption.

The total surface area of the cotton (determined by Krypton gas adsorption) when treated slack in anhydrous liquid ammonia or liquid ammonia containing up to 15% water was, on average, lower than that of the untreated cotton. When the yarns were treated under tension, however, the surface area was higher. Furthermore, increasing concentrations of water in the liquid ammonia generally increased the surface area of the cotton.

The changes in the fibre structure were monitored by iodine and moisture sorption and X-ray diffraction studies. The results showed that the liquid

ammonia treatments generally reduced the crystallinity of the cotton. The removal of the ammonia by heat produced a less crystalline structure than did removal by steam. The addition of water to the liquid ammonia generally reduced its decrystallizing effect.

ACKNOWLEDGEMENTS

The assistance of Mr J W Stander of the Chemical Engineering Research Group (CSIR) and SASOL I for putting their X-ray apparatus at the disposal of the authors, is gratefully acknowledged. The authors also wish to thank Mrs C Dorfling and Mrs S Buchanan for valuable technical assistance.

USE OF PROPRIETARY NAMES

The names of proprietary products where they appear in this report are mentioned for information only. This does not imply that SAWTRI recommends them to the exclusion of other similar products.

REFERENCES

1. Anon., Text. Ind., **132** (12), 146 (1968).
2. Scallan, A.M., Text. Res. J., **41** (8), 649 (1971).
3. Bose, J.L., Roberts, E.J. and Rowland, S.P., J. Appl. Polym. Sci., **15**, 2999 (1971).
4. Warwicker, J.O. Jeffries, R., Colbran, R.L. and Robinson, R.N., Shirley Inst. Pamphlet No. 93, The Cotton, Silk and Man-Made Fibres Research Assoc. Shirley Institute, Manchester (Dec., 1966).
5. Bredereck, K. and Heap, S.A., Textilveredl., **9**, 251 (1974).
6. Heuser, E. and Bartunek, R., Cellulosechem., **6**, 19 (1925).
7. Heap, S.A., J. Soc. Dyers and Colour., **47**, 2 (1975).
8. Lewin, M. and Roldan, L.G., J. Polym. Sci., Part C, (36), 203 (1971).
9. Rousselle, M-A, Nelson, M.L., Hassenboehler, C.B., Jr. and Legendre, D.C., Text. Res. J., **46** (4), 306 (1976).
10. Nelson, M.L., Hassenboehler, C.B., Jr., Andrews, F.R. and Markezich, A.R., Text. Res. J., **46** (12), 872 (1976).
11. Barkhuysen, F.A., Ph.D. Thesis, University of Port Elizabeth (Dec. 1979).
12. Hermans, P.H. and Weidinger, A., J. Polym. Sci., **4**, 135 (1949).
13. Valentine, L., J. Polym Sci., **27**, 213 (1958).
14. Barkhuysen, F.A. and Van Rensburg, N.J.J., SAWTRI Techn. Rep. No. 478 (Aug. 1981).
15. Gailey, R.M., Textilveredl., **7**, 789 (1972).
16. Van Rensburg, N.J.J. and Barkhuysen, F.A., Proceedings, Symposium on New Technologies for Cotton, Port Elizabeth, RSA (July, 1982).
17. Hessler, L.E. and Power, R.E., Text. Res. J., **24** (9), 822 (1954).

18. Pandey, S.N. and Nair, P., Text. Res. J., **44** (12), 928 (1974).
19. Brunauer, S., Emmett, P.H. and Teller, E., J. Am. Chem. Soc., **16**, 309 (1938).
20. Jung, H.Z., Berni, R.J., Benerito, R.R. and Carra, J.H., Text. Res. J., **45** (9), 682 (1975).
21. Calamari, T.A. Jr., Schreiber, S.P., Cooper, A.S. Jr. and Reeves, W.A., Text. Chem. Color., **3**, (10), 61 (1971).
22. Jeffries, R., Jones, D.M., Roberts, J.G., Selby, K., Simmens, S.L. and Warwicker, J.O., Cellulose Chem. Technol., **3**, 2, 55 (1969).
23. Rowen, J.W. and Blaine, R.L., Industr. Eng. Chem., **39**, 1659 (1947).

ISBN 0 7988 2908 7

Published by
The South African Wool and Textile Research Institute
P.O. Box 1124, Port Elizabeth, South Africa
and printed in the Republic of South Africa
by P U D Repro (Pty) Ltd., P.O. Box 44, Despatch