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Pretreatment of Cotton Fibres with Alcohols to Optimize Dye Uptake

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ABSTRACT

Cotton fibres were subjected to cleaning process and then characterized for maturity. Decrystallisation and swelling processes with caustic soda, ethanol, propan-2-ol and Trichloroethene on the native fibres were carried out. The effects of these on the strength and moisture regain were investigated. The activation energies of the dyeings were also analysed with Durazol Scarlet Red 4 BAS. The results indicated that unlike the traditional scouring/bleaching processes the use of these reagents did not lead to adverse loss in strength. The moisture regain values also appreciated above the control indicating swelling, which might have resulted from decrystallization. The reduction of the activation energy as a result of the pretreatments confirmed the assertion. The performance of propan-2-ol was phenomenal. It suffices to say that propan-2-ol could replace the caustic soda kiering process with its attendant environmental hazards and often-difficult recycling procedure.

Key Words: Activation Energy, Decrystallization, , Diffusion, Swelling agents

INTRODUCTION

Scouring and bleaching chemical agents, in addition to imparting the desired degree of whiteness also remove material from cell wall and leave behind voids. The presence of these voids has been demonstrated by many methods. The most popular being nitrogen gas absorption which has been of considerable value in the elucidation of the internal structures of many inorganic D`Silva *et al*. (2000) and many organic materials, Everett and Stone (1958). Porter and Rollins (1972) used the method to investigate the changes in the internal morphology of lint cotton during scouring in 5M NaOH. They compared the surface area and pore size distribution with changes in crystallinity and fibrillar aggregation and found that the large changes in the fibres' internal structures were accompanied by changes in the crystal structures. Rowland and Bertoniere (1985), used reverse gel to follow the pore structure of cotton through three pre-treatments that commonly precede chemical modification for imparting easy-care properties e.g. scouring/bleaching, caustic mercerizing, and liquid ammonia treatments. The water-soluble solutes were a series of oligomeric sugars, ethylene glycol and glymers with molecular dimensions in the range of conventional finishing agents for cotton. Their results showed large pores in NaOH-treated cottons that resulted in the greatest dye yield; whereas the loss of large pores in ammonia treated cotton was balanced in part by an increase in small pores with significant decrease in the total pore volume. This resulted in an increase in the internal association of the microfibrillar units, leading to an enhanced degree of resilience. The effect of swelling treatments on pore structure was confirmed by Bertoniere and King (D'Silva *et al*. 2000a). They found an increase in effective pore volume on swelling with mercerization using caustic soda and liquid ammonia. There was substantial increase in micropore volume (pore diameter <1nm) with the elimination of the macropores of diameter 6nm. In an earlier work by Warwicker *et al*. (1966), it was reported that the increase in accessibility following mercerization and ammonia treatments was more related to the reduction in crystallite size rather than to the change in the total crystallinity. D'Silva *et*

al. (2000a) used a differential dye absorption method to indicate the formation of voids in cotton following chemical treatment e.g. during scouring and bleaching operations as well as those due to physical treatments such as submitting the bleached cotton to alcohol boiling. Much earlier, Daruwalla and D'Silva (1963) used dye sorption method.

The retention of an internal surface of water-swollen cellulose by gradual exchange of water by non-polar solvents was first noticed by Kistler, (D'Silva *et al.* 2000b) in his research on cellophane . He obtained a fully expanded aerogel by the gradual replacement of water firstly with ether followed by the replacement of ether with propane and then removal of the propane above its critical temperature. The thermokinetics of the action of water, methanol, ethanol, propan-1-ol, butan-1-ol, acetic acid, concentrated aqueous solutions of sodium hydroxide and ethylene diamine on native mercerized and regenerated cellulose were investigated by Balcerzyk *et al.*(1969) using a microcalometric method . They found that the penetration rate depended on the structure of the accessible regions and the dimensions of the penetrant molecule and that the accessible phase in cellulose has a discontinuous structure within the spacing of structural elements in the intermicrofibrillar and intermolecular regions. The intermolecular distances in the accessible regions of the microfibrils in cotton appeared to be of the same order of diameter as that of the ethanol molecule (0.57nm). Past research work carried out on fabrics indicated that carboxymethylation significantly increased the absorbency of cotton fabrics, D'Silva *et*

al. (2000b). During the carboxymethylation in propan-2-ol solutions, it was noticed that the absorption of cotton continued to rise despite decreasing the concentrations of the chemical reactants to near zero, indicating that propan-2-ol was probably the main factor for increased absorbency. D'Silva *et al.* (2000b) investigated the effect of polar solvents on the absorption characteristics of bleached cotton of various micronaire values; the polar solvents used were linear alcohols of increasing chain length. Ethane-1, 2-diol and cyclohexanol were included to investigate the effect of much higher boiling temperatures. The results obtained from the research showed that the limiting pore diameter for penetration solvents appears to be 0.169nm as noted from the absorption results of propan-1-ol and propan -2-ol.

The objective of the present work is to study the effect of some of these solvents on the activation energy of dye adsorption.

MATERIALS AND METHODS
Fibre Parameter Determination

1kg of the cotton sample was passed through the Shirley Analyzer MK2 at the Institute for Agricultural Research, Samaru Zaria. The fibre maturity was analysed by the Fibro Sampler Model 192.

Scouring

10g of the cotton fibres were subjected to scouring treatment using 4% owf NaOH with a liquor ratio of 10:1 at the boil for 1hr. This was followed by a thorough rinse with warm water and then with cold water and oven dried at 90°C overnight. The extent of

Table 1. The Maturity of the Cotton Samples

Sample number	Sample Size (Amount of Fibers)	Fiber Span length (mm) 50%	Fiber Span length (mm) 2.50%	Beard Weight (mg)	Maturity%
1	868	10.9	24.4	0.151	
2	843	10.6	23.2	0.155	
3	795	10.4	23.4	0.151	
4	895	11.5	24.2	0.158	
5	795	10.4	22.8	0.160	
6	805	10.1	23.0	0.148	
7	667	10.2	22.8	0.123	
8	641	10.3	23.2	0.131	
9	667	10.6	23.4	0.128	
10	836	10.4	22.9	0.158	
Average	781.2	10.54	23.33	0.1463	94.30%

Table 2. The Micronaire Readings of the Samples.

1st Parking	2nd Parking	3rd Parking	4th Parking	5th Parking
3.50	3.50	3.48	3.46	3.46
3.42	3.46	3.46	3.40	3.42
			Average	3.45

Table 3. Percentage loss in weight, increase in moisture regain and bundle strength due to the pretreatments.

Treatment	% Loss in weight	% Increase in Moisture regain over control	Bundle strength (g/tex)
Ethanol	**1.998**	**50**	**14.87**
Propan-2-ol	2.50	155	14.49
2%NaOH	2.48	100	14.57
Trichloroethene	2.23	92	15.85
Control			15.90

cleaning was calculated as the percentage loss in weight compared to the 90°C oven dried control.

Fibre Treatment with some selected Alcohols

10g samples untreated (control) fibres, were each refluxed in 200cm^3 ethanol, propan-2-ol and Trichloroethene for thirty minutes. This was followed with a thorough rinse with cold water and then dried in the oven as above.

Determination of moisture regain

All the treated samples above were conditioned for 24hrs to constant weight and then placed inside an oven at 100°C for 24hrs. The regain was then calculated.

Determination of the Strengths of the Samples

The strengths of the treated samples were carried out using Stelometer Model 154M.

Four different determinations were made in each case.

Determination of the Wavelength of Maximum Absorption of the Dye Solution

A solution of the dye was made in 10% Pyridine diluted with 50cm^3 distilled water and scanned in the Visible Spectrum with a Unicam UV-Visible Spectrometer equipped with a V 1.21 Vision Software. The wavelength of maximum absorption was then read off.

Determination of the Kinetics of Dyeing

Dyeing was carried out with the dye; Durazol Fast Scarlet using 10% owf at a liquor ratio of 100:1 with the assistance of 1% NaCl. The dyeing was done at the temperatures indicated in Table 4 for 2, 5, 10, 15min and 1hr respectively.

At the end of the prescribed periods, the samples were removed and quickly rinsed in cold water. The dyed samples were then stripped in 10cm^3 of 10% Pyridine solutions

Table 4. Diffusion coefficient and activation energy.

Treatment	Diffusion Coefficient (Sec^{-2})		Activation energy (kJ mol^{-1})
Ethanol	3.467×10^{-5} (70°C)	5.018×10^{-5} (80°C)	37.2
Propan-2-ol	5.664×10^{-5} (70°C)	6.421×10^{-5} (80°C)	12.6
2%NaOH	5.532×10^{-5} (58°C)	7.453×10^{-5} (70°C)	21.8
Trichloroethene	3.519×10^{-5} (58°C)	6.210×10^{-5} (80°C)	25.1
Control	2.161×10^{-5} (70°C)	4.351×10^{-5} (80°C)	70.5

at the boil for 20min. The extracted solutions were diluted to 50cm^3 with water and then scanned with a Colorimeter at the wavelength of maximum absorption of the dye.

Graphs of M_t/M_o against time were then plotted from the slopes of which, the diffusion coefficients and then activation energies were calculated from the slopes of the Arrhenius plots according to the equations below.

M_t is the absorbance at time t.

M_o is the absorbance at infinity (1hr).

$$D_T = \frac{(slope)^2 \Pi}{4} \qquad (1)$$

$$\ln D_T = \ln D_{o} - E_{/RT} \qquad (2)$$
E is the activation energy.

The activation energy of diffusion (E) may be obtained directly from the slope of the plot of $\ln D_T$ against $1/T$.

R being the gas constant.

RESULTS AND DISCUSSIONS
Fiber Parameter Detemination

The fibre maturity was analysed by the Fibro Sampler Model 192 and the micronaire readings are given in Tables 1 and 2.

Effect of prrtretment on strength of fibres

From Table 3 it could be seen that the pretreatments were not destructive to the fibres. The control had a bundle strength of 15.90 g/tex, whereas the least in the group was that due to the propan-2-ol pretreatment which recorded 14.49 g/tex. Of course, Trichloroethene pretreatment was the safest as far as degradation is concerned; it recorded a bundle strength of 15.85 g/tex.

Effects of moisture absorption on the samples

The percentage loss in weight after the pretreatments shown in Table 3 indicated the extent of cleaning that had taken place in consequence. Propan-2-ol in this respect had given the highest reduction in the weight of the samples. Raw cotton fibres contained natural fats, oils waxes pectins and other Proteinous admixtures. The removal of these substances is the major objective of scouring. It is of note that some correlation exists between the extents of removal of these substances with the boiling points of the solvents used in this study with the exception of the caustic soda solution. The boiling points of

the solvents are: Propan-2-ol (81°C), ethanol (78.4^{o}C) and Trichloroethene (87°C). As reported by D'Silva *et al.* (2000b), the time of sinking of a bleached, untreated sample was 4.78s, that of ethanol was 2.25s, butan-1-ol ; 1.78s, and prapan-2-ol; 1.94s. The extents of natural admixture removal recorded in this report correlated very strongly with the time of sinking mentioned above. As could also be seen from the percentage increase in moisture regains there is some form of correlation between their findings with this report. The molecular diameter of ethanol is 0.504nm and that of Propan-2-ol is 0.619nm it did appear that the propan-2-ol with the higher molecular diameter recorded the biggest removal of the admixtures. This is in agreement with the findings of Balcerzyk *et al.*(1969), they reported about the thermokinetics of cellulose fibre penetration by liquids into accessible regions of cellulose. They described the accessible region as consisting of discontinuous structures within which are intermicrofibrilar and intermolecular regions. They found that the intermolecular distances between these accessible regions are of the same order as the ethanol molecule.

However, D'Silva *et al.* (2000b) discovered that this limiting diameter is the order of propan-2-ol diameter being 0.619nm. But we here want to state that the diameter of a liquid solvent changes with temperature, at the point of penetration (since the pretreatments were carried out at the boiling points of the solvents) the molecular diameter would have actually expanded above its nominal value at room temperature. Therefore, the limiting diameter could be a value much bigger than 0.619nm. It however is yet to be confirmed beyond reasonable doubt that actually, the property that governs penetration of the solvents into the accessible regions of the polymer is the diameter of the solvents. It does seem that boiling points of the solvents and such other physico-chemical properties as cellulose-admixture solubility etc may play more dominant roles.

Activation Energy

From Table 4 the effect of the pretreatment on the activation energy of dye diffusion is reported. It is seen that all the pretreatments lead to a drastic reduction in the activation energies of dyeing. The activation energy of the control is 70,462.81 J/mol. Incidentally,

propan-2-ol recorded the least activation energy of 12,623.15 J/mol ethanol (37,211 J/mol), NaOH(21,784 J/mol) and Trichloroethene (25,076 J/mol). The activation energy of diffusion is related to the energy necessary to disrupt the intermolecular forces in the internal structure of the fibre/ polymer to bring about dye penetration. It gives an assessment of the forces necessary to overcome during dyeing. The effect of pretreatment as investigated in this study with respect to the activation energy has revealed the extent of the modifications that had occurred in the internal regions of the fibre. The higher the activation energy, the more rigid the structure making up the fibres/polymer and the more the energy needed to push the molecules of the dyes into the accessible regions of the fibres. It had been found by Lemin and Vickerstaff (1947) that direct correlation exists between the number of cross links and activation energy. In other words, an increase in the number of cross-links decreases the dye diffusion. Pretreatments of the fibre, which leads to break up of cross-links, have been found to increase the rate of dyeing and hence reduce the activation energy. According to Sivaraja Iyer (1974), the increase in activation energy because of cross-linking is attributable to the reduction in the accessibility and average pore size of the pretreated fibres. A very important finding was due to Tsuruta and Koshimo (1965) and Koshimo and Kakishita (1965) who discovered that the activation energy for steam-set nylon fibres was lower than untreated fibres but that the dry heat –set material gave activation energy that was higher than the control. They ascribed this difference to the changes in the molecular parking in the amorphous regions, which were partly broken by steam-setting, leading to greater mobility of molecular chains and a more open structure, which facilitated dye diffusion. As already seen in Table3, the loss in weight followed similar trend to the percentage increase in moisture regain, similarly the activation energy of diffusion also followed the same order. It could be agued from the aforementioned that some form of opening-up in the cellulose structure had taken place because of the cleaning of the natural admixtures (scouring) on the material. The extents of scouring is evident by the decrease in the weights compared to the control, the opening-up is predicated on the increase in the moisture absorption and on the decrease in the activation energy compared to the control.

CONCLUSION

This work has indicated that there is a strong correlation between the extent of scouring with the increase in moisture regain and the decrease in activation energy of dye diffusion when the cellulosic fibres were pretreated with some solvents. The power of a solvent/swelling agent to bring about decrystallization is related to its scouring ability. Factors that increase this ability such as solubility of the cellulose admixtures in the solvents, boiling points of the solvents and temperature of pretreatment etc could explicate the best mechanism for this interaction.

REFERENCES

Balcerzyk, E., Kazlowski, W. and Wlodarski, G. (1969) Thermokinetics of Cellulose Fiber Penetration by Physically and Chemically Reactive Liquids and Structure of Accessible Regions. *Text.Res. J.,* **39,** 666-667

D'Silva, A.P., Harrison G., Harrocs, A.R. and Rhodes, D. (2000a) Investigation into Cotton Fibre Morphology Part II: Effect of Scouring and Bleaching Treatments on Absorption. *J. Text.Inst.* **91,** 107-122

D'Silva, A.P., Harrison, G., Harrocs, A.R. and Rhodes, D. (2000b) Investigation into Cotton Fibre Morphology Part III: Effect of Alcohol Treatment on Water Absorption. *J. Text.Inst.* **91,** 123-131

Daruwalla E. H and D'Silva A. P (1963) Heats of Dyeing of Direct Cotton Dyes on Cellulose a new Thermodynamic Approach to the Determination of Activity of Direct Dyes in Cellulose. *Text. Res. J.* **33** , 40-51

Everett, D. H. and Stone, F. S. (1958) The structure and properties of porous materials, Butterworths, London, UK. pp. 23-87

Koshimo, A. and Kakishita, T. (1965) Steam and Heat Setting of Nylon 6 Fiber X. Effect of Heat Setting on Diffusion of Dyestuff into Nylon 6 fiber. *J. Appl. Polym.Sci.* **9,** 91

Lemin, D. R. and Vickerstaff, T. (1947) The Measurement of the Affinity of Monobasic Acid Dyes for Wool. *J.Soc. Dyers and Col.* **63,** 405

Porter, B. R. and Rollins, M. L. (1972) Changes in Porosity of Treated Lint Cotton Fibers

I. Purification and Swelling Treatments. *J. Appl.Polym.Sci.* **16,** 217-236

Rowland, S. P. and Bertoniere, N. R. (1985) Chemical methods of studying supramolecular structure in cellulose chemistry and its application. Ellis Harwood, Chichester, West Sussex, UK pp 112-137

Sivaraja Iyer S. R. (1974) Physical Chemistry of Dyeing: Kinetics, Equilibrium, Dye-Fiber Affinity and Mechanism. *The Chemistry of Synthetic Dyes* (ed. by Venkataraman K.) Vol.Vii, pp 115-191 Academic Press. New York, Sanfrancisco, London

Tsurata, M. and Koshimo, A. (1965) Steam and Heat Setting of Nylon 6 Fiber I. Effect of Dry Heat Setting and Steam Setting on Young's Modulus and Specific Gravity of Nylon 6 Fiber. *J. Appl. Polym. Sci.* **9,** 3

Warwicker J. O, Jeffries R, Colbran R.L and Robinson, R. N (1966) A Review of the Literature on the Effect of Caustic Soda and other Swelling Agents on the Fine Structure of Cotton (Shirley Institute Pamphlet No. 93) Shirley Institute, Manchester, U.K