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Some Chemical Properties and the Response to Liquid Ammonia and Sodium Hydroxide of Various South African Cotton Cultivars

by

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SOME CHEMICAL PROPERTIES AND THE RESPONSE TO LIQUID AMMONIA AND SODIUM HYDROXIDE OF VARIOUS SOUTH AFRICAN COTTON CULTIVARS

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ABSTRACT

Some chemical properties of various South African cotton cultivars, and their response to mercerising treatments were determined. The iodine sorption value and accessibility to moisture of the various cultivars did not differ significantly. Furthermore, maturity was negatively correlated with the Alkali Centrifuge Value (ACV). The cultivars did not seem to differ in terms of the exhaustion and fixation of certain reactive dyes. The treatment of cotton fibres in a slack state with liquid ammonia or sodium hydroxide increased the iodine sorption value, accessibility to moisture and exhaustion of dyes, and decreased the ACV but these changes appeared to be similar for the various cultivars.

INTRODUCTION

The cotton plant, Gossypium, is a genus belonging to the Mallow family or Malvaceae. There are a number of different species of Gossypium from which many hybrids and varieties have been developed. Among the various species only four, namely *G. arboreum, G. herbaceum, G. hirsutum* and *G. barbadense,* account for all the cultivated varieties of cotton. The first two species, known as Old World Cottons, are diploid in nature having 13 pairs of chromosomes, while the latter two species are tetraploid with 26 pairs of chromosomes[1]. In South Africa cultivars from mainly the *G. hirsutum* species are grown.

Although they all belong to the same genus, it is well known that different cotton varieties can differ widely. Differences have been observed in the fibre structure as well as in the physical and chemical properties. Furthermore, there are large differences within a single variety, mainly due to environmental factors. The most common variations are associated with the morphology of the fibres (especially fineness, length, circularity, cell wall thickness and maturity) as well as with the fine structure (crystallinity and orientation).

De Boer[2] showed that there are distinct structural differences between the fibres of *G. barbadense* and *G. hirsutum.* The former generally has a greater fibre length and a lower number of convolutions per unit length than the latter. Furthermore, the bundle breaking strength and elongation at break of fibres of *G. hirsutum* are lower than that of fibres of *G. barbadense.* It is interesting to note that these differences are still present even after mercerising and resin treatment. Datar *et al* [3] studied *G. hirsutum* and *G. herbaceum* cottons and concluded that the latter has a cell wall with smaller micropores, more disordered regions and smaller crystallites than the former, even though the total volume of the void space of the fibres do not differ significantly.

Pai and Panda[4,5] studied the crystallite orientation angles of different cottons from *G. hirsutum* and *G. barbadense* and found values ranging from a low 28° to as high as 43°. The orientation angles of the samples were correlated with their tensile strength. Dobb *et al* [6] conducted a study to determine whether differences in properties between different cotton varieties can be attributed to differences in the fibre structure. They found that there were no obvious differences in the nature of the crystallographic units or the supramolecular crystalline aggregates between cotton varieties such as St Vincent Sea Island, Acala, Menoufi etc. and they concluded that the observed differences in mechanical properties must have been due to the arrangement of these units (e.g. orientation) or to differences at higher levels of structural organisation.

The response of different cotton varieties to mercerisation and chemical treatment is well documented. Rebenfeld[7], for example, studied the response of 12 widely different cottons to mercerisation in fibre form and found that the breaking stress increased by 1% for certain varieties and by more than 70% for others. Similarly, the reduction in breaking elongation varied from 5% to 45%. In some further studies[8] he found that when different cottons were mercerised in yarn form, the cottons also responded differently. Rebenfeld[9-11] also studied the effect of various other chemical treatments, including crease resist finishing, on different cotton varieties and found that the cottons responded differently to the chemical treatments. He concluded that it is important to consider different cottons as unique fibre types, each possessing different mechanical and chemical properties.

Raes *et al* [12-14] carried out a series of investigations on the response of different cottons to chemical treatments and also found that the different varieties responded differently. In some further studies[15] these workers investigated the influence of cotton variety and growth location on the chemical response of the cotton. Six different cotton varieties which were grown in Greece and in Uganda were tested and the authors concluded that the chemical response of the cotton has to be considered a varietal characteristic. Furthermore, the influence of growth conditions upon the chemical response appeared to be relatively small.

Grant *et al* [16] processed three different cottons into different fabrics, which were then mercerised and resin treated. They found that the fabrics which were made from the different cottons differed in their crease recovery angles, resistance to abrasion and wear during laundering. It is interesting to note, however, that Weiss *et al* [17] found that the differences due to fibre characteristics gradually became less as different cottons were processed from fibres into yarns.

The effect of fibre maturity on the properties and chemical behaviour of cotton has been studied in great detail in the past and a lot of information is available on this topic. Fibre maturity is an important characteristic of cotton and it gives a measure of the extent of cell wall development of the fibres. In many cases research workers have studied the effect of maturity *per se* on the physical and chemical properties of the cotton fibre, without specifically paying attention to any possible effect of the cotton variety and from the results published in the literature it is not always possible to separate the effect of maturity from that of variety. It is generally accepted, however, that cottons varying in maturity respond differently to mercerisation treatments as well as crease resist finishing. The changes in tenacity and extension, however, do not appear to have any significant dependence on maturity or orientation[18,19]. In a recent more specific investigation Lawson *et al*[20] studied the relation between cotton fibre maturity and strength uniformity to changes in tenacity after mercerisation. They used eight different cultivars of *G. hirsutum* collected from bolls picked 26, 32, 38 and 44 days after flowering. They found that there was a high correlation between fibre maturity and tenacity within a cultivar and a fair correlation when the results of all the cultivars were combined. Chauhan *et al*[21] studied the morphological and mechanical properties of raw and swollen cotton fibres of 14 samples belonging to four different species, picked at different periods of growth. They concluded that there is a good linear correlation between percentage fibre maturity and the ratio of cell wall thickness to fibre diameter. Kulshreshtha *et al*[22] studied cotton picked from bolls after various periods of growth and concluded that the mechanical properties are related to the maturity of the fibres.

In a study specifically planned to allow for the effect of fibre maturity, Akcetin and Verschraege[23] studied the chemical response of four different Turkish cottons of the *G. hirsutum* type having the same maturity as well as identical fibre perimeter. This means that the interference of wall thickness on the results could be neglected. They evaluated the effect of bleaching and γ-irradiation on the degree of polymerisation, breaking strength and elongation of the four varieties and in general could not observe any differences between the behaviour of the varieties.

Reference should at this stage also be made to the effect of fibre morphology on dyeing behaviour. It is well known that variations in fibre maturity have a pronounced effect on dyeing behaviour. For example, fibre maturity can be determined by the use of certain dyes. One of the best known tests for maturity was developed by Goldthwait, Smith and Barnett[24]. This test is based on the use of a mixture of two different dyes, namely C.I. Direct Red 82 and C.I. Direct Green 26. The former dye has an affinity for mature fibres and the latter for immature or dead fibres. Apart from the test mentioned above there are tests for determining fibre maturity using a single dye[25]. Furvik[26] studied the dyeing behaviour of immature and mature cotton using six different dyes and concluded that maturity did not affect the amount of dye absorbed at equilibrium, but rather the absorption and desorption rates. These rates were higher for immature fibres than for mature fibres. Mercerisation of the fibres prior to dyeing did not greatly affect the differences between mature and immature fibres.

The cotton cultivars grown commercially in South Africa are from the *G. hirsutum* species and according to statistics published by the Cotton Board[27] the main cultivars grown are the following:

Cultivar	% of Production
Acala	52
Albacala	13
Albar	9
SJI	7
Deltapine	10
CS2	4
Clarcot Coker	4
Others	1

Relatively little is known about the chemical response of these different cultivars and consequently a study was initiated to investigate this matter in more detail. Apart from evaluating some chemical properties of the different cottons, the dyeing behaviour as well as the response to mercerisation with liquid ammonia and sodium hydroxide were evaluated.

EXPERIMENTAL

Raw Fibre

Six South African cotton cultivars were used in this study. Some fibre characteristics of the samples are given in Table I.

Treatments

Residual fats and waxes were removed from the cotton by scouring in a solution containing 4% (o.m.f.) sodium carbonate and 0,5 g/ℓ ®Nonidet P40 for 60 min at 100°C in a liquor to goods ratio of 20:1. This was followed by hot (60°C) and cold rinsing and drying at 50°C.

Part of the scoured cotton was bleached in a solution containing 2,8 mℓ/ℓ H_2O_2, 2 g/ℓ ®Prestogen PC and 0,6 g/ℓ NaOH for 90 min at 100° C. This was followed by an aftertreatment with 0,5 g/ℓ sodium dithionite for 20 min at 60° C followed by hot and cold rinsing.

The bleached cotton fibres were treated in a slack state with sodium hydroxide and liquid ammonia according to procedures described previously[28].

Samples of the different cottons were dyed with some reactive dyes according to the recommendation of the manufacturers.

TABLE I

RAW FIBRE CHARACTERISTICS

CULTIVAR	2,5% Span Length (mm)	Fibre Linear Density (mtex)	O-Gauge Tenacity (cN/Tex)	Uniformity Ratio	Micronaire	Maturity Ratio
Clarcot CS 2	27,6	173	39,9	47	4,1	0,86
Deltapine RSA	27,8	183	37,4	44	4,2	0,87
Acala 1517/70	31,1	136	43,7	46	3,4	0,87
Acala SJ 141	28,5	158	43,7	44	4,0	0,94
Deltapine 5826	27,5	179	38,9	46	4,5	0,98
Albar	27,7	142	39,4	46	3,2	0,78

Tests

The Alkali Centrifuge Value (ACV) of the cotton was determined according to the method described by Honold and Grant[29]. The iodine sorption value (ISV) of the cotton was carried out using a method proposed by Hessler and Power[30]. The moisture regain, number of moles of water per anhydroglucose unit (AGU) and accessibility of the cellulose structure to moisture was determined according to the method of Pandy and Nair[31]. The fluidity of the various cotton fibres was determined according to a standard procedure[32].

RESULTS AND DISCUSSION

A number of physical properties of the different cultivars used in this investigation are given in Table I. It is clear that, with a few exceptions, the different samples were reasonably well matched as far as most of the properties were concerned. The maturity of cotton is a very important fibre characteristic and is an index of the extent of cell wall development. It is known that the primary wall of an immature cotton fibre has not developed to the same extent as that of a mature fibre. There is general agreement that the primary wall of a cotton fibre determines the extent of swelling i.e. the degree to which the fibre can absorb chemicals, for example sodium hydroxide. This has lead to the development of the ACV test (alkali sorption or alkali centrifuge value) for determining the maturity of cotton[33]. In fact, various authors[34,35] have found an excellent correlation between ACV and percentage maturity, provided that there is no microbiological damage of the fibre.

It was decided, therefore, to determine the alkali centrifuge value of three of the cotton cultivars having similar maturity ratios. The alkali centrifuge and fluidity values are given in Table II. It is clear that the various cotton cultivars having similar maturity ratios also had fairly similar alkali centrifuge values, indicating that the primary wall of the three specific samples studied, was developed to the same extent. The fluidity of the different cultivars was about the same, with the exception of the Deltapine cultivar which had a slightly higher fluidity.

The effect of mercerising treatments using sodium hydroxide or liquid ammonia on the alkali centrifuge values of various cotton cultivars is shown in Table III. The alkali centrifuge values of the untreated cotton samples generally seemed to decrease with an increase in maturity ratio, which is in agreement with the findings of other research workers[36]. Lawson *et al* [20] stated that a mature fibre has a wall thickness two or three times that of an immature fibre, which has less material in the cell wall and a larger lumen than the former. Outward swelling is restricted by the primary wall and consequently there is more space for swelling to occur and for the fibrils to move to relieve strains in immature fibres than in mature fibres.

TABLE II

ALKALI CENTRIFUGE AND FLUIDITY VALUES OF VARIOUS COTTON CULTIVARS HAVING SIMILAR MATURITY RATIOS

Cultivar	Maturity Ratio	ACV	Fluidity
Acala 1517/70	0,87	240	3,3
Clarcot CS2	0,84	230	3,1
Deltapine RSA	0,87	244	5,1

Table III shows that the ACV of the samples generally decreased after mercerising treatments with NaOH or liquid ammonia. Obviously the fibres were modified by the mercerising treatments and their swelling capacity reduced. The highest degree of fibre modification was obtained by the sodium hydroxide treatment, followed by a slightly smaller effect by the liquid ammonia/heat treatment. When the ammonia was removed by water, the effect, if any, was fairly smal'.

TABLE III

THE ALKALI CENTRIFUGE VALUE OF VARIOUS SOUTH AFRICAN COTTON CULTIVARS

CULTIVARS	**Maturity Ratio**	**ALKALI CENTRIFUGE VALUES**			
		Untreated Control	**Liquid Ammonia (Heat Removed)**	**Liquid Ammonia (Water Removed)**	**Sodium Hydroxide**
Acala 1517/70	0,87	240,4	217,6	241,2	214,3
Acala SJ 141	0,94	234,7	208,1	220,5	195,1
Deltapine 5826	0,98	218,1	191,7	205,9	186,5
Clarcot CS 2	0,89	230,0	222,1	234,5	212,8
Albar	0,78	249,0	211,5	236,5	220,7

It is interesting to compare the response to mercerising (as depicted by the actual change in the ACV) of cotton from two different cultivars having approximately the same maturity ratio, namely Acala 1517/70 and Clarcot CS 2. An analyses of the results given in Table III showed that there was no significant difference between the two cottons in this respect.

The accessibility of the cotton fibre to chemical reagents, and the effect of mercerising or swelling treatments on accessibility, are important aspects which were dealt with in some further studies. The iodine and moisture sorption values of the different cotton cultivars as well as the accessibility (calculated from the moisture sorption value) are given in Table IV. A statistical analysis of the iodine sorption values revealed that the amount of iodine adsorbed was not dependent on the cultivar. The same applies for the moisture sorption values and the accessibility to moisture of the various cottons. Table IV also shows that a treatment with liquid ammonia or sodium hydroxide increased the iodine and moisture sorption values and the accessibility of the cotton considerably, but

TABLE IV

THE IODINE SORPTION, MOISTURE SORPTION AND ACCESSIBILITY VALUES OF VARIOUS COTTON CULTIVARS

CULTIVAR	UNTREATED CONTROL			LIQUID AMMONIA — HEAT REMOVED			LIQUID AMMONIA — WATER REMOVED			SODIUM HYDROXIDE		
	ISV* (mg I/g sample)	MSV** (moles H_2O/ AGU)	Accessibility (%)	ISV (mg I/g sample)	MSV (moles H_2O/ AGU)	Accessibility (%)	ISV (mg I/g sample)	MSV (moles H_2O/ AGU)	Accessibility (%)	ISV (mg I/g sample)	MSV (moles H_2O/ AGU)	Accessibility (%)
Acala 1517/70	80,0	0,54	35,3	301,0	0,74	48,2	164,0	0,73	47,7	191,60	0,94	61,4
Acala SJ 141	96,7	0,63	40,9	321,9	0,82	53,5	168,1	0,72	47,1	178,22	0,94	61,3
Deltapine 5826	85,6	0,59	38,9	299,2	0,81	53,1	151,9	0,73	47,8	181,69	0,91	59,5
Clarcot CS 2	89,3	0,63	41,4	307,7	0,80	52,3	166,2	0,66	43,2	189,03	0,85	55,7
Albar	101,4	0,61	39,8	302,5	0,84	55,1	167,8	0,73	47,9	168,26	0,96	62,8

* Iodine Sorption Value

** Moisture Sorption Value

TABLE V

EXHAUSTION AND FIXATION VALUES OF DIFFERENT COTTON CULTIVARS DYED WITH VARIOUS COTTON REACTIVE DYES

CULTIVAR	PROCION RED MX-5B								PROCION BLUE H-B							
	Untreated Control		NH_3/Heat		NH_3/Steam		NaOH		Untreated Control		NH_3/Heat		NH_3/Steam		NaOH	
	Exh. (%)	Fix. (%)	Exh. (%)	Fix. (%)	Exh. (%)	Fix. (%)	Exh. (%)	Fix. (%)	Exh. (%)	Fix. (%)	Exh. (%)	Fix. (%)	Exh. (%)	Fix. (%)	Exh. (%)	Fix. (%)
Acala 1517/70	68,5	55,5	77,2	63,1	76,8	65,2	77,1	66,1	55,5	34,0	62,0	39,2	57,7	39,2	65,5	50,2
Albar	68,1	54,5	74,4	61,0	75,0	64,2	76,5	64,9	55,6	35,0	61,0	41,5	56,7	38,2	65,0	49,9
Clarcot CS2	66,5	53,1	74,6	60,1	73,2	61,8	76,1	64,4	52,8	32,3	60,4	40,1	57,2	38,0	64,8	49,7
Deltapine 5826	66,3	62,8	71,6	57,9	75,1	63,9	73,9	62,4	52,8	32,7	59,5	39,8	58,2	39,4	63,4	48,7
Acala SJ 141	65,7	52,4	73,2	59,2	76,4	65,2	74,5	62,8	53,0	32,6	59,5	39,0	56,8	38,4	64,0	49,2

CULTIVAR	PROCION YELLOW MX-6G								CIBACRON YELLOW F3R							
	Untreated Control		NH_3/Heat		NH_3/Steam		NaOH		Untreated Control		NH_3/Heat		NH_3/Steam		NaOH	
	Exh. (%)	Fix. (%)	Exh. (%)	Fix. (%)	Exh. (%)	Fix. (%)	Exh. (%)	Fix. (%)	Exh. (%)	Fix. (%)	Exh. (%)	Fix. (%)	Exh. (%)	Fix. (%)	Exh. (%)	Fix. (%)
Acala 1517/70	26,6	18,8	28,3	21,4	33,7	25,3	27,2	18,8	56,75	39,69	67,89	48,25	65,91	48,40	76,25	60,40
Albar	28,4	20,6	29,1	22,2	36,2	28,0	32,3	24,0	61,25	43,61	68,16	47,33	67,63	49,05	77,51	60,25
Clarcot CS2	23,3	15,6	26,4	19,4	29,2	21,5	29,3	21,1	58,87	42,21	66,83	47,85	66,17	48,92	77,57	60,99
Deltapine 5826	23,5	15,8	24,6	17,6	28,7	20,6	24,3	16,4	57,81	41,49	64,97	45,20	67,89	49,72	76,65	60,87
Acala SJ 141	25,8	18,0	26,3	19,4	30,4	22,5	26,5	18,6	57,55	40,04	66,31	47,40	67,09	49,64	75,85	60,06

once again a statistical analysis of the results showed that the increase was independent of the cultivar and maturity.

In an attempt to establish whether the exhaustion and fixation of dye depended on the different cultivars, and on the various swelling or mercerising treatments, the samples were dyed with various reactive cotton dyes. From the results, given in Table V, it is clear that there was practically no difference between the various cultivars as far as dye exhaustion and fixation were concerned. The pretreatment of the cotton with liquid ammonia or sodium hydroxide resulted in an increase in the exhaustion and fixation values of the cotton but this increase was similar for the various cultivars. On average the sodium hydroxide treatment increased the dye exhaustion by 10%, while the liquid ammonia/heat treatment increased dye exhaustion by 6% and the liquid ammonia/steam treatment increased it, by 7%. It is interesting to note that the different dyes did seem to differ somewhat in their response to the mercerising treatments.

SUMMARY AND CONCLUSION

A number of chemical properties and the response to mercerising treatments of different cotton cultivars grown in South Africa were determined.

It was found that cotton cultivars having the same maturity ratio gave similar alkali centrifuge values (ACV). Furthermore, the treatment of cotton with swelling agents such as liquid ammonia or sodium hydroxide generally decreased the ACV. Sodium hydroxide generally had a larger effect than liquid ammonia. It was also found that the different cotton cultivars studied did not respond differently to these swelling agents.

In further studies the various samples were subjected to a number of sorption tests. Although the various cultivars differed in certain fibre characteristics (fibre linear density, micronaire, maturity etc.) and despite the fact that their alkali centrifuge values differed, no difference was found between the various samples in the adsorption of iodine as well as the accessibility to moisture. Furthermore, the different cultivars did not differ significantly as far as the exhaustion and fixation of certain reactive dyes were concerned. Finally, it was found that the treatment of the samples with liquid ammonia and sodium hydroxide resulted in an increase in the adsorption of iodine, moisture and dye molecules by the cotton, but the increase seemed to be similar for the various cultivars.

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