FINAL REPORT

MICROBIAL DAMAGE TO COTTON – II

(A JOINT PROJECT)

PROJECT UNS2C

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1. Aims

- To evaluate treatments that inhibit or restrict microbial degradation to cotton when the seed cotton harvest is delayed by wet weather.
- To ensure that such treatments do not affect subsequent processing and dye uptake.
- To develop dyeing formulations that minimize the effects that microbial damage has on the dyeing of cotton blends.

2. Industry Significance

Microbial degradation of mature cotton fibre has previously been identified as a potentially significant problem in Australian cotton. Studies completed as part of CRDC funded project UN1C have confirmed that the problem is mainly associated with exposure of mature seed cotton to periods of wet weather prior to harvest.

These studies also showed that fibre degradation could continue in the module after harvest. Treatments which arrest fibre degradation are required to prevent further deterioration of fibre quality between picking and processing.

3. Collaboration

During the three-year term of this project Professor Mike Pailthorpe made four trips to visit Dr Stephen Allen (ACRI Narrabri) for project discussions. These visits were as follows:

- 16 October 1996 Prof. Mike Pailthorpe
- 29 May 1997 Prof. Mike Pailthorpe and Dr Jackie Cai
- 25 February 1998 Prof. Mike Pailthorpe
- 29 April 1998 Prof. Mike Pailthorpe and Ms Karen Taylor

4. Methods

4.1. Cotton Samples from ACRI (Narrabri)

Cotton was grown and defoliated as for normal commercial production however harvest was delayed until after the open bolls had been exposed to several periods of wet weather. If wet weather was not forthcoming then water was applied through overhead sprinklers early in the morning and/or late in the afternoon to encourage microbial activity. An area of seed cotton was covered with a temporary rain-out shelter to ensure a supply of 'undamaged' lint. The development of microbial damage was monitored by microscopic observation of cotton fibres mounted in 18% sodium hydroxide.

In addition, we also prepared degraded cotton fabrics by laboratory incubation using selected microorganisms.

4.2. Fabric Sample Preparation

The ginned cotton fibres supplied from Narrabri were then processed into clean fibre webs, yarn and knitted fabric in the textile laboratories at UNSW. The yarn count obtained was about 74 tex. Fabrics were prepared in two fabric weights.

4.3. Scouring, Bleaching and Dyeing

Scouring and bleaching was carried using conventional recipes. Dyeings were carried out with selected reactive dyes (e.g. Procion Navy HE-R and Drimarene Brilliant Red K-4BL) using the conditions recommended by the dye manufacturers. 2.0-2.5% owf dyestuff and liquor ratios (LR) of 20:1 and 25:1 were used in this investigation.

4.4. Field Experiments

Microbial damage to the cotton fibre usually occurs under field conditions following exposure to wet weather and the consequent delayed harvest. Mr David Moore of Colly Farms was interested in establishing a large scale experiment to evaluate the potential of applying treatments by air prior to harvest in an attempt to prevent the development of microbial damage in the field. Treatments included and untreated control, acetic acid (Farmoz 'Spraybuff' buffering agent containing 500g/l acetic acid and alkali salts of acetic acid) and 'Sporekill' (a quaternary ammonium compound). Treatments were applied by air in March 1999 and the crop was harvested and classed as for commercial cotton. Samples were also collected for pH determination and microscopic examination in 18% sodium hydroxide. Unfortunately the experiment received several rainfall events and harvest was delayed considerably. There was no opportunity to repeat the experiments.

Despite the development of microbial damage in the field prior to harvest damage can further develop during storage in the module and even in the bale. All commercial cotton pickers include a water supply system which sprays water onto moisture pads that wipe over the spindles in the picking head and aid the picking process. Two biocidal additives to the picker water (Borax with sodium dodecyl sulphate and 'Sporekill' which is a quaternary ammonium compound) were evaluated under field conditions while harvesting microbially damaged cotton during the 1997/98 and 1998/99 seasons. The effectiveness of these treatments was determined by counting the number of viable fungal propagules per gram of lint for each of the treatments with water as the untreated control. Counts were obtained using a dilution plate method with Potato Dextrose Agar with added streptomycin sulphate as the isolation medium.

5. Results

5.1 Inhibition of Microbial Growth on Cotton

Microbial degradation of cotton has been previously identified as a potentially significant problem for Australian cotton, which is intensified in wet weather conditions. The microbial attack often results in detrimental effects on cotton quality and subsequent processing, for example increased difficulty in spinning and unlevel dyeing behavior. The microorganisms that

are responsible for this damage can be fungi and bacteria from the soil. Fungi play a key role in this microbiological process.

In our previous studies, selected commercial biocides and acetic acid were employed to protect the cotton. These results are summarized in Table 1.

Table 1

Microbial Damage after Six Weeks Incubation

SAMPLE	pH (±0.1)	DNS (±0.1)
Control	7.2	0.6
Incubated	7.5	0.1
Dodigen 3519	7.9	0.3
Diquat NF	6.4	0.3
Acticide 50XA	6.2	0.4
Acticide SPX	6.1	0.7
Acticide OTW	5.8	0.3
Ca Propionate	8.1	0.5

On the basis of the combination of the pH and DNS results, Acticide SPX provided the best protection against microbiological attack of the six commercial products examined.

Attempts to evaluate the use of aerially applied biocides in the field prior to harvest were unsuccessful as a result of extended wet weather at the end of the season. There were no treatment differences detected during classing, pH determination or microscopic observation of the fibres.

During 1998 Dr Jackie Cai was employed to continue work on the evaluation of antimicrobial agents for their ability to prevent microbial damage to cotton. Using cotton samples provided by Dr Stephen Allen (ACRI) from the 1996/97 harvest, several antimicrobial agents (selected from commercially available sources) together with other simple and safe chemicals (e.g. sodium dodecyl sulphate and borax) were studied. It was found that a combination of sodium dodecyl sulphate (SDS) and borax was very effective.

The evaluation of the SDS/borax treatment was persued using samples of microorganisms from Sydney garden soil and *Aspergillus niger* supplied by Dr Stephen Allen. These organisms were used to inoculate both Agar plates and bleached cotton fabric, which were then treated with the various antimicrobial agents. These results confirmed that SDS has a good ability to inhibit fungal growth, being superior to borax and the proprietary cationic agents.

The combination of SDS and Borax is even more effective than SDS alone, indicating a synergistic effect. The results of this work were included in our paper presented at the 9th Australian Cotton Conference [1].

The addition of Borax with SDS to the picker water during harvest under field conditions reduced the number of fungal propagules by 72.2% from 576,800 to 160,400 per gram of lint. The use of 'Sporekill' in the picker water reduced the number of fungal propagules per gram of lint by 36.7%.

5.2. Strategies at the Dyehouse

5.2.1. Dyeing of the Undamaged and Damaged Cotton Pairs

As shown in Table 2, the undamaged and damaged cotton samples exhibit an obvious difference in their initial colour. Undamaged cotton has a higher lightness (L*) than the damaged cotton with a total colour difference (ΔE) between the two samples of 1.89. A ΔE value of 1.89 represents 6 "just noticeable differences" for the average observer.

Table 2

Colour Parameters of the Initial and Bleached Cotton Samples

Samples	Parameter	Undamaged	Damaged	Difference	ΔE
Initial samples	L*	87.48	86.24	-1.24	1.89
	a*	0.65	0.57	-0.08	
	b*	10.67	9.27	-1.40	
	WIE	22.41	26.41	4.00	
Hypochlorite bleached	L*	93.44	92.17	-1.27	1.53
	a*	-0.73	-0.53	0.20	
	b*	3.33	4.14	0.81	
	WIE	66.48	59.96	-6.52	

The results for the dyeing behavior of the two samples are given in Table 3. In the individual dyeing experiments, the undamaged cotton is dyed deeper in shade with a higher dye exhaustion (E%= 91% and 89% for the undamaged and damaged cotton, respectively), compared with the damaged cotton.

In the case of union dyeing, the colour difference between the two cotton samples becomes more obvious than for the individual dyeing conditions. The ΔE value of the dyed samples is about 2.0 for a 2% owf dyeing. Hence microbial attack generally leads to a lower dyeability of cotton fibres with reactive dyes.

5.2.2. Effect of Bleaching Treatment

From the results provided in Table 2 it can be seen that the undamaged cotton is bleached to a much brighter and whiter colour than is damaged cotton under the same conditions (union bleaching). The ΔE value between the bleached cotton pair is still high (ΔE = 1.53). Therefore

bleaching does not significantly reduce the initial colour difference of the between two samples.

Table 3

Dyeing Behavior of the Undamaged and Damaged Cotton

Conditions	Parameters	Undamaged	Damaged	Difference	Δ E
Individual Drimarene Br. Red	L*	44.64	43.9	-0.74	1.41
	a*	57.73	56.67	-1.06	
	b*	-2.41	-2.98	-0.57	
Union Drimarene Br. Red	L*	42.97	44.61	1.65	1.96
	a*	58.05	57.50	-0.55	
	b*	-1.22	-2.06	-0.85	
Union Procion Navy	L*	27.52	29.43	1.91	1.95
	a*	-3.88	-4.18	-0.30	
	b*	-18.62	-18.86	-0.24	

5.2.3. Application of Surfactants

A variety of surfactants and commercial products were selected for the evaluation of their potential to assist in the scouring and dyeing of microbially damaged cotton. These products are listed in Table 4.

Table 4

Surfactants and Commercial Products Used in this Work

Product Name	Chemical specifications	Supplier
Albatex Pon. Conc.	Polyglycol ether derivative of a sulfonated alkyl benzimidazole, anionic	Ciba-Geigy
Albegal A	Amphoteric, anionic	Ciba-Geigy
Albegal B	Amphoteric	Ciba-Geigy
Invadine LU	Alkyl aryl sulphonates, anionic	Ciba-Geigy
Invadine 4382	Alkyl alcohol ethoxylates and alkyl sulfonates, anionic	Ciba-Geigy
Tinovetin JU high Conc.	Alkyl aryl polyglycol ether, nonionic	Ciba-Geigy
Polyethylene glycol	Nonionic	BDH
Teric 16A22	Nonionic	ORICA
Lissopol TN 450	Nonionic	ORICA
SDS or SLS	Sodium Dodecyl sulphate or sodium lauryl sulphate	AJAX

The results given in Table 5 indicate that the incorporation of these products in dyeing recipes is not effective in achieving acceptable dyeing levelness of the microbially damaged cotton. However slight improvements were observed with some products.

Table 5

Effect of Surfactants on the Colour Difference between Undamaged and Damaged Cotton Dyed with Procion Navy HE-R.

PRODUCT	ΔE Unbleached	ΔE Sodium hypochorite bleached	ΔE Reductive bleached
Albegal A	1.82	1.74	1.80
Albatex PON.	1.36	1.28	
Invadine 4382	1.78	1.57	
Tinovetin JU	1.96	1.7	
Albegal B	2.07		

Scouring with the surfactants only has marginal influence on the subsequent dyeing levelness. The ΔE values of the scoured and dyed cotton pairs varied from 1.20 to 2.10.

5.2.4. Pretreatment with Cationic Polymers

Pretreatment of the microbially damaged cotton samples with a suitable cationic substance was considered to be a possible treatment to minimize or eliminate the difference in dyeing behavior of the cotton samples. The following cationic products were evaluated: Polymer PL, Chitosan, Basolan MW and Basolan SW.

The results given in Table 6 show that Basolan MW and SW provided only a slight improvement. Chitosan provided a significant improvement in reducing the unevenness of the microbially damaged cotton dyeings, however the colour difference of the resultant dyeings is still noticeable. Clearly, the best results were obtained using the Polymer PL pretreatment. The ΔE value was reduced to less than 0.2, which is commercially acceptable.

Table 6

Effect of Cationic Polymers on the Colour Difference of Undamaged and Damaged Cotton Dyed with Procion Navy HE-R and Drimarene Br. Red K-4BL

Pretreatment	L*,a*,b*	Undamaged	Damaged		E
Control	L*	27.52	29.42	1.90	1.95
	a*	-3.88	-4.17	-0.29	
	b*	-18.62	-18.85	-0.23	
Polymer PL	L*	28.41	28.23	-0.18	0.18
	a*	-3.77	-3.81	-0.04	
	b*	-18.03	-18.04	-0.01	
Basolan MW	L*	28.09	29.49	1.40	1.45
	a*	-3.64	-3.99	-0.35	
	B*	-18.67	-18.79	-0.12	
Basolan SW	L*	28.47	30.01	1.54	1.57
	a*	-3.76	-4.09	-0.33	
	b*	-19.66	-19.66	0.00	
Chitosan	L*	44.05	44.14	0.09	0.59
	a*	56.53	56.12	-0.41	
	b*	-2.34	-2.76	-0.42	

Many other chemical treatments were examined to achieve a level dyeing effect, however no significant improvements were obtained.

5.2.5. Work of Ms Karen Taylor

In the 1998 calendar year, Ms Karen Taylor, a 4th year honors student, was assigned to the project. Karen conducted a literature survey on the availability of proprietary leveling agents for the reactive dyeing of cotton and found that two new products had been released, namely:

- Levegal RL (Bayer Australia Limited), and,
- Drimagen ER Liquid (Clariant Australia Pty Ltd).

Ms Karen Taylor and Professor Mike Pailthorpe visited Dr Stephen Allen at the ACRI on 29 April 1998 for project review and discussions. As a result of this meeting it was agreed that Karen would also investigate the role of enzyme pre-treatments on the dyeing performance of microbially damaged cotton. The enzyme treatment selected for evaluation was:

- Cellusoft™ L (Novo Nordisk Bioindustrial Pty Ltd).

Dr Stephen Allen (ACRI) provided samples of undamaged and microbially damaged cotton from the 1997/98 season. This cotton was ginned at the ACRI before shipment to UNSW. The cotton samples were carded at UNSW to remove vegetable fault and to thoroughly blend the lots.

Random samples were selected from the bulk lots, scoured in 1g/l Lissapol TN450 (ORICA) and 2g/l sodium carbonate at 60°C for 25 minutes, rinsed and then dyed. The dyeing recipes employed were those recommended by the dyestuff and leveling agent manufacturers. All dyeings were conducted in quadruplicate and repeated four times to provide sufficient data for statistical analysis. Colour measurements were made using a Pacific Scientific Spectrogard Colour Computer System. The results for the total colour difference (ΔE) between damaged and undamaged cotton, for 2% owf dyeings, are given in Table 7.

Table 7

Total Colour Difference (ΔE) between Damaged and Undamaged Cotton

Conditions	Harcofix Black VB	Evercion Blue HEGN
Control	3.94 ± 0.03	3.07 ± 0.36
Drimagen ER (1g/l)	1.65 ± 0.20	**4.55 ± 0.11**
Drimagen ER (2/g/l)	**4.25 ± 0.05**	1.68 ± 0.18
Levegal RL (1%)	0.97 ± 0.07	2.16 ± 0.14
Levegal RL (2%)	2.48 ± 0.25	2.39 ± 0.21
Cellusoft (1%)	1.37 ± 0.05	2.19 ± 0.15
Cellusoft (2%)	2.97 ± 0.08	1.81 ± 0.22

A ΔE of 0.30 is a just noticeable colour difference for the average observer. A close colour match, eg. Where garment panels are to be sewn together, requires a ΔE of ≤ 1.0; whereas batch to batch colour differences of 3.0 are acceptable in other applications.

The control results confirm our earlier findings that large colour differences between identical dyeings do occur between undamaged and microbially damaged cotton. The microbially damaged cotton always dyes lighter than the undamaged cotton.

With the exception of two cases (marked in bold), the results provided in Table 7 show that the levelling agents Drimagen ER Liquid and Levegal RL, as well as the enzyme pretreatment Cellusoft L, reduce the differential dye uptake to a small, but significant degree. However, the reduction in the ΔE values is not large enough to be commercially significant.

6. Conclusions

Whilst microbial damage to cotton does not cause significant changes in the HVI results, the effects do manifest themselves "downstream" particularly at the dyeing stage.

We have shown that microbial damage to cotton can be minimized by the application of selected chemicals, e.g. acetic acid, Acticide SPX, SDS/borax, to the affected seed cotton by either a spray technique or by addition to the "picker" water. However, the successful use of a biocide during harvest does not remedy the microbial damage that has already occurred prior to harvest and there are problems and perceptions associated with the use of aerial sprays on

open cotton bowls prior to harvest. Problems caused by microbial damage must be addressed during the spinning and dyeing procedures.

We have evaluated a wide range of dyeing assistants for their ability to minimize the colour difference that develops between undamaged and microbiologically damaged cotton in conventional dyeing recipes. Whilst many of the dyeing assistants have a small beneficial effect, only Polymer PL and Chitosan are worthy of future investigation.

7. Publications

1. Allen, S.J. and Pailthorpe, M.T., Managing Weather Damaged Cotton in the Field and in the Gin, Proc. 9th Australian Cotton Conference, 643-650 (August, 1998).

2. Taylor, K., The Evaluation of Leveling Agents for the Dyeing of Microbially Damaged Cotton, UNSW, Honors Thesis, November, 1998.