If you are participating in the presentations this year, please provide a written report and a copy of your final report presentation by 31 October. If not, please provide a written report by 30 September.

Part 1 - Summary Details

Please use your TAB key to complete Parts 1 & 2.

CRDC Project Number: TFT 0904

Project Title: Preliminary Investigation into the effects of Quarantine Treatments

Project Commencement Date: 01/07/2008  Project Completion Date: 30/06/2010

CRDC Program: Value Chain

Part 2 – Contact Details

Administrator: Jo Cain, Administration Manager, Cotton Management & Improvement
Organisation: CPI
Postal Address: Locked Bag 59, Narrabri, NSW 2390
Ph: 02 6799 1513  Fax: 02 6793 1186  E-mail: jo.cai@csiro.au

Principal Researcher: René van der Sluijs, Textile Technologist
Organisation: CMSE
Postal Address: Henry Street, Belmont, Victoria 3216
Ph: 03 5246 4000  Fax: 03 5246 4057  E-mail: rene.vandersluijs@csiro.au

Supervisor: Stuart Gordon, Project Leader
Organisation: CMSE
Postal Address: Henry Street, Belmont, Victoria 3216
Ph: 03 5246 4000  Fax: 03 5246 4057  E-mail: stuart.gordon@csiro.au

Signature of Research Provider Representative: ________________________________
Part 3 – Final Report Guide

(The points below are to be used as a guideline when completing your final report.)

Background

1. Outline the background to the project.

Due to Australia’s age, extreme variable weather patterns and long-term geographic isolation, much of the country’s fauna and flora is unique and diverse. This isolation is rapidly changing as the barriers of time and distance become less relevant and international travel and trade increase. With this comes the risk of exotic pests and diseases entering Australia that can seriously affect their unique environment, native flora and fauna, tourism and lifestyle.

The Australian Quarantine Inspection Service (AQIS) plays a critical role in ensuring that Australia remains free from many serious pests, weeds and diseases present in other parts of the world. Australia places great importance on quarantine and has among the strongest quarantine measures of any country in the world. These measures are undertaken by AQIS who inspect all animal and plant products imported into Australia. Aside from inspections, import permits and treatments are used to control the danger posed by the large and diverse number of plant and animal-based commodities imported into Australia each year.

Whilst a permit is not necessarily required to import cotton lint, all imported cotton lint into Australia needs to be treated (sanitized) to ensure the consignment is free of live insects, soil and other debris (faeces, animal materials etc) or verified that any quarantine risk material present will be dealt with during processing. The quarantine treatments used can be chemical (fumigation) or by radiation (normally gamma irradiation) based. Gamma irradiation is the preferred process by the United Nations Food and Agriculture Organisation (FAO) as the treatment has high penetration and is lethal to insects at any age and leaves no residue. Dosages between 300 and 1000 Gray (Gy) are thought to take care of most insects (Fields et al 2002), although AQIS prescribe 25 kGy or 50 kGy. Whilst this level is efficient at controlling stowaway pests, the treatment can also damage important chemical structural bonds in plant and animal materials.
Fumigation processes can leave poisonous residues and the main chemical used for fumigation methyl bromide, although very efficient, depletes ozone in the atmosphere and is slowly being phased out (Fields et al 2002).

AQIS currently prescribe either gamma irradiation at either 25 or 50 kGray (kGy) or fumigation using ethylene oxide or methyl bromide to treat and sanitize imported raw commodities.

Australia exports up to 98% of its cotton for high quality end use in mills mainly in South East Asia. It is currently the sixth largest exporter after the USA, India, Uzbekistan, Brazil and West Africa. Despite being a large exporter of raw cotton, a large number of cotton samples are still imported into Australia on a yearly basis. These samples are used to calibrate and evaluate fibre testing instruments that are used to benchmark Australian cotton to other growths. An amount of cotton is also imported for commercial processing. These samples are subject to one of the sanitizing treatments mentioned, which creates problems in terms of gamma radiation effects and residues from fumigation.

The effect of radiation on cellulose has been investigated by several authors over the last 50 years (Blouin, Demint, Teszler and Winogradoff). However all these studies were conducted using high dosages of irradiation > 4000 kGy and are thus not relevant to the treatments applied by AQIS (Foldvary et al 2003 and Takacs et al 1999). Anecdotal evidence from the cotton industry indicates the AQIS prescribed levels of irradiation affect the quality of the cotton, particularly fibre bundle strength, although there is little direct scientific information available on the extent of the effect on the quality of cotton.

**Objectives**

The aims of the project are to determine if damage is caused to cotton fibre properties by current quarantine treatments and if so to what extent.

**Methods**

In order to determine the affect of the various quarantine treatments on the physical properties of cotton lint in general it was decided to collect not only normal standard Upland cotton but also Long Staple Upland cotton as well as Extra Long Staple cotton.
At the time, bales of commercially grown Australian Upland saw ginned (Sicala V2R) and Long Staple Upland (Sicala 350B) cotton as well as Extra Long Staple roller ginned (Pima A8) cotton were being processed through the cotton mill situated at CSIRO Materials Science and Engineering (CMSE). These bales were grown during the 2006/07 season under commercial growing conditions and machine harvested. The Sicala V2R cotton was grown at Trangie in the Macintyre Valley of New South Wales (NSW); the Sicala 350B was grown at Narrabri in the Namoi Valley of NSW and the Pima A8 was grown at Moree in the Gwydir Valley of NSW. Samples were gathered from different areas of the three bales and sent for fibre testing.

**Fibre Testing**

Bale (raw fibre) samples were conditioned under standard conditions of 20°C +/-2°C and 65% +/-3% relative humidity for 24 hours as per ISO 139. The samples were then tested on an Uster Technologies 1000 High Volume Instrument (HVI), as per ASTM D5867, for Micronaire, staple length, length uniformity, staple strength and elongation were measured (Table 1).

Fibre fineness was determined using the CSIRO Cottonscan instrument, which determines fibre fineness (linear density) by measuring the length of fibre in an accurately weighed specimen of fibre snippets. Combined with an independently measured Micronaire value from the HVI, the average fibre maturity was also calculated using Lord’s empirical relationship between Micronaire, maturity ratio and fineness (Table 2).

Bale samples were also tested for nep, seed-coat neps (SCN) and short fibre content (SFC) by an Uster Technologies Advanced Fibre Information System (AFIS PRO) testing 5 replicates per sample (Table 3).

**Table 1 - Fibre results by the HVI 1000**

<table>
<thead>
<tr>
<th>Variety</th>
<th>Tenacity cN/tex</th>
<th>Elongation %</th>
<th>Length inch</th>
<th>SFI %</th>
<th>UI</th>
<th>Micronaire µg/inch</th>
<th>Colour Rd</th>
<th>Colour +b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sicala V2R</td>
<td>29.8</td>
<td>6.1</td>
<td>1.161</td>
<td>9.1</td>
<td>82</td>
<td>4.08</td>
<td>80.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Sicala 350B</td>
<td>31.5</td>
<td>5.2</td>
<td>1.289</td>
<td>7.7</td>
<td>84</td>
<td>4.37</td>
<td>79.0</td>
<td>9.1</td>
</tr>
<tr>
<td>Pima A8</td>
<td>44.5</td>
<td>6.4</td>
<td>1.358</td>
<td>5.9</td>
<td>86</td>
<td>4.01</td>
<td>73.7</td>
<td>11.8</td>
</tr>
</tbody>
</table>

*Calibrated using HVI ICC Upland and Pima Calibration Cottons *Average of 10 tests
Table 2 - Fineness\(^2\) by Cottonscan and calculated maturity results

<table>
<thead>
<tr>
<th>Variety</th>
<th>Fineness (mtex)</th>
<th>Maturity Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sicala V2R</td>
<td>187</td>
<td>0.71</td>
</tr>
<tr>
<td>Sicala 350B</td>
<td>200</td>
<td>0.70</td>
</tr>
<tr>
<td>Pima A8</td>
<td>167</td>
<td>0.75</td>
</tr>
</tbody>
</table>

\(^2\)Average of 5 tests

Table 3 - Nep, Seed-Coat Nep and SFC results by the AFIS PRO\(^3\)

<table>
<thead>
<tr>
<th>Variety</th>
<th>Neps/gram</th>
<th>SCN/gram</th>
<th>SFC(w) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sicala V2R</td>
<td>326</td>
<td>21</td>
<td>8.9</td>
</tr>
<tr>
<td>Sicala 350B</td>
<td>256</td>
<td>21</td>
<td>7.1</td>
</tr>
<tr>
<td>Pima A8</td>
<td>167</td>
<td>10</td>
<td>2.9</td>
</tr>
</tbody>
</table>

\(^3\)Average of 5 tests

Quarantine Treatments

In order to determine the affects of the various quarantine treatments on the physical fibre properties of the cotton fibre, samples of cotton fibre weighing around 1.5 kgs were packed into cardboard boxes and forwarded to the Steritech Pty Ltd plant in Melbourne, for gamma irradiation and fumigation by ethylene oxide. The samples were irradiated as per the standard methods prescribed by AQIS at various dosage levels (Table 4) using the radioactive isotope Cobalt 60. Cobalt 60 is one of the most common sources of gamma rays and is specifically manufactured for the gamma irradiation process. As gamma irradiation is known as a ‘cold process’ packaging around the sample remains intact as the temperature of the processed product does not significantly increase. To ensure even exposure to Gamma rays products are rotated. Further samples were subject to fumigation by ethylene oxide under an initial minimum vacuum of 50 kilopascals at 1200 g/m\(^3\) for 5 hours at 50°C.

The use of methyl bromide as a quarantine method is currently under investigation with its general use prohibited in Australia. Samples of cotton fibre weighting around 50 kgs were packed into woolpacks and forwarded to ISS Australia in Sydney for fumigation with methyl bromide at a rate of 32g/m\(^3\) for 24 hours at 21°C.
Table 4 - Dosages of gamma irradiation

<table>
<thead>
<tr>
<th>Cotton Type</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sicala V2R</td>
<td>19.2 kGy</td>
</tr>
<tr>
<td>Sicala V2R</td>
<td>20.8 kGy</td>
</tr>
<tr>
<td>Sicala V2R</td>
<td>28.6 kGy</td>
</tr>
<tr>
<td>Sicala V2R</td>
<td>56.9 kGy</td>
</tr>
<tr>
<td>Sicala V2R</td>
<td>74.2 kGy</td>
</tr>
<tr>
<td>Sicala 350B</td>
<td>19.2 kGy</td>
</tr>
<tr>
<td>Sicala 350B</td>
<td>20.8 kGy</td>
</tr>
<tr>
<td>Sicala 350B</td>
<td>28.6 kGy</td>
</tr>
<tr>
<td>Sicala 350B</td>
<td>56.9 kGy</td>
</tr>
<tr>
<td>Pima A8</td>
<td>19.2 kGy</td>
</tr>
<tr>
<td>Pima A8</td>
<td>20.8 kGy</td>
</tr>
<tr>
<td>Pima A8</td>
<td>28.6 kGy</td>
</tr>
<tr>
<td>Pima A8</td>
<td>56.9 kGy</td>
</tr>
<tr>
<td>Pima A8</td>
<td>74.2 kGy</td>
</tr>
</tbody>
</table>

**Fibre testing**
After treatment all the samples were retested on the same instruments under the same conditions as described earlier in the methodology section.

**Further analyses**
In order to determine the reason for any potential changes in the physical fibre properties samples were analysed by Scanning Electron Microscope (SEM), x-ray diffraction microanalysis, Fourier Transform Infrared Spectrometry (FTIR) and Infrared Analysis.

Chemical analysis was also conducted. The cotton samples were prepared for molecular weight determination of cellulose as described by Evtuguin et al., (2003). Samples (1 g) of cotton fibres from each irradiated line and the corresponding untreated controls were extracted for six hours in toluene/ethanol (2/1) using a Soxhlet extractor. Husks and impurities were removed and 200 mg of the remaining material was transferred to a beaker and mixed with 10 ml of a 10% peracetic acid solution whose pH had been preliminarily adjusted to 4.8 with NaOH. The reaction was performed for 30 minutes at 75°C and the solution cooled on ice and filtered. The cotton samples were then washed three times with 100 ml deionised water and once with 100 ml acetone/ethanol (1/1). The samples were then air dried at ambient temperature.
Size-exclusion chromatography (SEC), a proven and effective technique for measuring molecular weights (MW), was then performed on 15 mg of each dried cellulose sample treated with peracetic acid. Cellulose was swollen in water and solvent exchanged three times with dry N, N-dimethylacetamide (DMAc) before the addition of 2.1 ml of an 8% LiCl/DMAc solution. Ethylisocyanate (0.22 ml) was then added to the mixture and fully dissolve the cellulose during 5 days incubation at room temperature. The cellulose solutions were then analyzed by SEC using a 2690 Separation Module (Waters Corp.) equipped with 4 x Mini-Mix-A (20 μm; 4.6x250 mm) columns (Polymer Laboratories) as described by Berthold et al., (2004).

Results

Physical Results

By any measure, the fibre properties of all three cottons used in this study can be considered as good quality and above the Australian base grade\(^1\). Whilst there were only small differences in fibre length properties between the saw ginned Sicala 350B and the roller ginned Pima A8, (Table 1), the Pima cotton had much higher bundle tenacity and was inherently finer (Table 2), which would have positively affected the bundle tenacity result. The Sicala 350B had relatively high bundle tenacity for an Upland cotton.

The fumigation treatments by either ethylene oxide or methyl bromide had little or no significant effect on the physical properties of the cotton fibre. However gamma irradiation, even at the lower dosages, did have an effect on the physical properties of the fibre, with these effects becoming more apparent and significant as the dosage strength increased (Table 5 and Figures 1 to 3).

In the case of the Upland cotton, Sicala V2R, the strength of the fibre reduced by almost 3 cN/tex (10%) from 29.8 cN/tex to around 27.0 cN/tex after gamma irradiation of 19.2 and 20.8 kGy. With an irradiation dosage of 28.6 kGy the fibre strength reduced by nearly 5 cN/tex (16%) to 25 cN/tex with a further reduction in fibre strength of around 7 cN/tex (24%) to 22.7 cN/tex with a dosage of 56.9 kGy. A dosage of 74.2 kGy resulted in a reduction in fibre strength of almost 9 cN/tex (29%) to 21.1 cN/tex. This decrease in fibre

\(^1\) Upland base grade quality is staple length > 1.130 inch, strength > 29 cN/ten and Micronaire in the range of 3.5-4.9.

ELS base grade quality is staple length > 1.350 inch, strength > 44 cN/ten and Micronaire in the range of 3.5-4.1.
strength corresponded with a gradual decrease in fibre elongation; with a 1.0% decrease in elongation from 6.1% to 5.1% with a dosage of 28.6 kGy and almost a 2% decrease in elongation to 4.2% with a dosage of 56.9 and 74.2 kGy. The Micronaire, maturity, fibre fineness and nep content were not affected by the gamma irradiation. Fibre length was also not significantly affected however the short fibre index (SFI)\(^2\) increased significantly at the 28.6 kGy dosage, gradually increasing by subsequent higher dosages. This in turn also had an effect on length uniformity which also tended to decrease at the 28.6 kGy dosage, decreasing with subsequent higher dosages. There was a slight impact on the colour of the cotton although the affect was minimal as the colour deteriorated from Good Middling White to Good Middling Light Spotted cotton as the gamma irradiation dosages increased.

In the case of the Long Staple Upland cotton, Sicala 350 B, the strength of the fibre also reduced by almost 3 cN/tex (9%) from 31.5 cN/tex to 28.8 cN/tex after gamma irradiation of 19.2 kGy. With an irradiation dosage of 28.6 kGy the fibre strength reduced by nearly 5 cN/tex (16%) to 26.6 cN/tex with a further reduction in fibre strength of almost 8 cN/tex (25%) to 23.6 cN/tex with a dosage of 56.9 kGy. This decrease in fibre strength corresponded with a gradual decrease in fibre elongation; with nearly a 1.0% decrease in elongation from 5.2% to 4.3% with a dosage of 28.6 kGy and almost a 1.5% decrease in elongation to 3.8% with a dosage of 56.9 kGy. The Micronaire, maturity, fibre fineness and nep content were not affected by the gamma irradiation. Fibre length was also not significantly affected however the SFI tended to increase significantly at the 28.6 kGy dosage, gradually increasing by subsequent higher dosages. This in turn also had an effect on length uniformity which also tended to decrease at the 28.6 kGy dosage, decreasing with subsequent higher dosages. There was a slight impact on the colour of the cotton although the affect was minimal as the colour deteriorated from Strict Middling White to Good Middling Light Spotted cotton as the gamma irradiation dosages increased.

In the case of the Extra Long Staple cotton, Pima A8, the physical properties of the fibre were dramatically affected by gamma irradiation. The strength reduced by almost 5 cN/tex (11%) from 44.5 cN/tex to 39.4 cN/tex after gamma irradiation of 19.2 and 20.8 kGy. With an irradiation dosage of 28.6 kGy the fibre strength reduced by almost 9cN/tex (20%) to 35.5cN/tex. With a

\(^2\) The proportion by mass of fibres shorter than one half inch.
dosage of 56.9 kGy the fibre strength reduced by nearly 14cN/tex (31%) to 30.9cN/tex. A dosage of 74.2 kGy resulted in a reduction in fibre strength of almost 18cN/tex (40%) to 26.7 cN/tex. This decrease in fibre strength corresponded with a gradual decrease in fibre elongation; with a 1.0% decrease in elongation from 6.4% to 5.4% with a dosage of 28.6 kGy and almost a 2% decrease in elongation to 4.9% with a dosage of 74.2 kGy. The Micronaire, maturity, fibre fineness and nep content were not affected by the gamma irradiation. Fibre length was also not significantly affected however the SFI tended to increase significantly at the 28.6 kGy dosage, gradually increasing by subsequent higher dosages. This in turn also had an effect on length uniformity which also tended to decrease at the 28.6 kGy dosage, decreasing with subsequent higher dosages. There was no impact on the colour of the cotton as Pima cotton is naturally creamier coloured cotton than Upland cotton and gamma irradiation did not seem to make any difference to the colour.

The extent of the decrease in fibre strength and elongation due to various quarantine treatments is graphically illustrated in Figure 1 and 2. Figure 3 provides a graphical illustration of the increase in SFI due to the various treatments.

The results clearly indicate that the physical fibre properties of the cotton such as; strength, elongation, length uniformity, short fibre and to a lesser extent colour is affected by gamma irradiation. The study has shown that gamma irradiation affects normal Upland, Long Staple Upland as well as Extra Long Staple cotton. In actual fact the affects of gamma irradiation was more pronounced on Extra Long Staple cotton. This is of major concern to importers and of grave concern to spinners, as fibre properties required to process high quality yarn efficiently (strength) are affected.
Table 5 – Fibre results for Upland cotton after treatment by the HVI 1000

<table>
<thead>
<tr>
<th>Variety</th>
<th>Treatment Type</th>
<th>Tenacity cN/tex</th>
<th>Elong %</th>
<th>Length inch</th>
<th>U I %</th>
<th>SFI %</th>
<th>Mic(μg/inch)</th>
<th>Colour Rd</th>
<th>Colour +b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sicala V2R</td>
<td>MB</td>
<td>30.2</td>
<td>6.3</td>
<td>1.162</td>
<td>82</td>
<td>8.8</td>
<td>4.00</td>
<td>80.2</td>
<td>10.0</td>
</tr>
<tr>
<td>Sicala V2R</td>
<td>ETO</td>
<td>29.7</td>
<td>6.1</td>
<td>1.137</td>
<td>82</td>
<td>9.8</td>
<td>4.05</td>
<td>79.2</td>
<td>10.0</td>
</tr>
<tr>
<td>Sicala V2R</td>
<td>19.2 kGy</td>
<td>26.7</td>
<td>5.2</td>
<td>1.203</td>
<td>81</td>
<td>9.9</td>
<td>4.01</td>
<td>81.7</td>
<td>9.2</td>
</tr>
<tr>
<td>Sicala V2R</td>
<td>20.8 kGy</td>
<td>27.3</td>
<td>5.7</td>
<td>1.079</td>
<td>82</td>
<td>10.5</td>
<td>4.08</td>
<td>77.7</td>
<td>11.8</td>
</tr>
<tr>
<td>Sicala V2R</td>
<td>28.6 kGy</td>
<td>25.0</td>
<td>5.1</td>
<td>1.133</td>
<td>81</td>
<td>11.6</td>
<td>4.09</td>
<td>79.7</td>
<td>10.9</td>
</tr>
<tr>
<td>Sicala V2R</td>
<td>56.9 kGy</td>
<td>22.7</td>
<td>4.2</td>
<td>1.166</td>
<td>80</td>
<td>11.9</td>
<td>3.98</td>
<td>80.8</td>
<td>10.6</td>
</tr>
<tr>
<td>Sicala V2R</td>
<td>74.2 kGy</td>
<td>21.2</td>
<td>4.2</td>
<td>1.045</td>
<td>80</td>
<td>14.1</td>
<td>4.10</td>
<td>76.8</td>
<td>13.4</td>
</tr>
<tr>
<td>Sicala 350 B</td>
<td>MB</td>
<td>31.0</td>
<td>5.2</td>
<td>1.285</td>
<td>84</td>
<td>7.7</td>
<td>4.36</td>
<td>79.3</td>
<td>9.0</td>
</tr>
<tr>
<td>Sicala 350 B</td>
<td>ETO</td>
<td>31.0</td>
<td>5.1</td>
<td>1.279</td>
<td>83</td>
<td>7.7</td>
<td>4.26</td>
<td>78.5</td>
<td>9.2</td>
</tr>
<tr>
<td>Sicala 350 B</td>
<td>19.2 kGy</td>
<td>28.8</td>
<td>4.7</td>
<td>1.269</td>
<td>83</td>
<td>8.2</td>
<td>4.36</td>
<td>78.3</td>
<td>9.9</td>
</tr>
<tr>
<td>Sicala 350 B</td>
<td>28.6 kGy</td>
<td>26.6</td>
<td>4.3</td>
<td>1.263</td>
<td>83</td>
<td>8.5</td>
<td>4.35</td>
<td>78.7</td>
<td>10.4</td>
</tr>
<tr>
<td>Sicala 350 B</td>
<td>56.9 kGy</td>
<td>23.6</td>
<td>3.8</td>
<td>1.243</td>
<td>82</td>
<td>9.5</td>
<td>4.35</td>
<td>78.2</td>
<td>11.2</td>
</tr>
<tr>
<td>Pima A8</td>
<td>MB</td>
<td>45.9</td>
<td>6.4</td>
<td>1.370</td>
<td>86</td>
<td>5.9</td>
<td>4.00</td>
<td>74.1</td>
<td>11.5</td>
</tr>
<tr>
<td>Pima A8</td>
<td>ETO</td>
<td>45.5</td>
<td>6.1</td>
<td>1.326</td>
<td>86</td>
<td>5.8</td>
<td>3.93</td>
<td>73.1</td>
<td>12.0</td>
</tr>
<tr>
<td>Pima A8</td>
<td>19.2 kGy</td>
<td>39.6</td>
<td>5.3</td>
<td>1.351</td>
<td>86</td>
<td>6.0</td>
<td>3.95</td>
<td>73.3</td>
<td>12.5</td>
</tr>
<tr>
<td>Pima A8</td>
<td>20.8 kGy</td>
<td>39.2</td>
<td>6.5</td>
<td>1.351</td>
<td>86</td>
<td>5.9</td>
<td>4.00</td>
<td>74.3</td>
<td>11.9</td>
</tr>
<tr>
<td>Pima A8</td>
<td>28.6 kGy</td>
<td>35.5</td>
<td>5.4</td>
<td>1.333</td>
<td>85</td>
<td>6.4</td>
<td>3.98</td>
<td>73.9</td>
<td>12.6</td>
</tr>
<tr>
<td>Pima A8</td>
<td>56.9 kGy</td>
<td>30.9</td>
<td>4.2</td>
<td>1.325</td>
<td>85</td>
<td>6.6</td>
<td>3.90</td>
<td>73.7</td>
<td>13.0</td>
</tr>
<tr>
<td>Pima A8</td>
<td>74.2 kGy</td>
<td>26.7</td>
<td>4.9</td>
<td>1.307</td>
<td>83</td>
<td>7.3</td>
<td>4.05</td>
<td>73.1</td>
<td>13.0</td>
</tr>
</tbody>
</table>
Figure 1 – Affect of Quarantine Treatments on Fibre Strength

Figure 2 – Affect of Quarantine Treatments on Fibre Elongation
Microscopy, X-Ray diffraction and Spectroscopy Results

In order to determine the reason for these large changes in the physical fibre properties samples were analysed by Scanning Electron Microscope (SEM), x-ray diffraction microanalysis, Fourier Transform Infrared Spectrometry (FTIR) and Infrared Analysis.

Scanning Electron Microscope

Four cotton samples (untreated Upland and 74.2 kGy irradiated and untreated Pima and 74.2 kGy irradiated) were analysed. Each sample was placed on an aluminium sample holder and attached using double-sided, conductive carbon tape. These were then coated with approximately 2 nm of chromium to improve electrical conductivity using a Dynavac Xenosput coating system. Images of the samples were acquired using a Hitachi S4300 SE/N field emission scanning electron microscope. The electron beam energy used was 1.2 kV and the working distance was 10 mm. Examination of the images showed no discernable difference between the irradiated and non-irradiated samples.

X-ray diffraction microanalysis

Four cotton samples (untreated Upland and 74.2 kGy irradiated and untreated Pima and 74.2 kGy irradiated) were analysed for qualitative GADDS μ-XRD analysis. Small samples of clean cotton fibre were obtained and twisted together to form a bundle of fibres ~1-2 mm in diameter and ~5 cm long. These bundles were taped securely and tightly to the GADDS transmission stage. XRD Microanalyses from selected spots on the cotton bundles were carried out with a Bruker GADDS (General Area Detector Diffraction System) microdiffractometer. The instrument
uses CuKα radiation (40 mA, 40 kV) with crossed Göbel mirror optics to produce a collimated, parallel, high brilliance beam. The spot size of analysed regions was 300 microns (0.3 mm) in diameter. The recorded diffraction data were converted to conventional XRD diffractograms by integration around the Chi circle of the detector. Phases were identified using the ICDD-JCPDS powder diffraction database.

Normalised, integrated x-ray diffractograms for each of the samples, as extracted from the 2D GADDS data are shown in Figure 4. Cellulose was identified in all the XRD traces. No significant differences in terms of peak intensity, peak width or minor peaks could be identified between any of the samples.

![Graph](image_url)

**Figure 4 – Normalised, integrated x-ray diffractograms for each sample extracted from 2D GADDS data.**

**Fourier Transform Infrared Spectrometry (FTIR)**

Four cotton samples (untreated Upland and 74.2 kGy irradiated and untreated Pima and 74.2 kGy irradiated) were cut to fit into a Pike Miracle diamond press in a Bruker Vertex 70 FTIR spectrometer. Absorbance spectra were collected at a resolution of 8 cm⁻¹ with a total of 64 scans per measurement. The results are shown in Figure 5. As can be seen there are no significant differences in terms of peak intensity, peak width or minor peaks could be identified between any of the samples.
Figure 5 – Absorbance spectra for untreated and gamma irradiated cotton

**Infrared Analysis**

Four cotton samples (untreated Upland and 74.2 kGy irradiated and untreated Pima and 74.2 kGy irradiated) were conditioned with the infrared spectra normalized on the 3272 cm⁻¹ H-bonded OH. As shown in Figure 6, 7 and 8 no significant differences were found between the untreated sample and the 74.2 kGy treated samples.
Figure 6 – Infrared spectra for Pima (Red treated, Black untreated)

Figure 7 – Infrared spectra for Upland (Red treated, Black untreated)
Figure 8 – Infrared spectra for LS Upland (Red treated, Black untreated)

**Chemical Results**

**Molecular determination of cellulose**

The estimated Molecular weight (MW) of the non irradiated cellulose samples was of $10^6$ Da for all lines, except the Upland line, which exhibited a significantly lower apparent molecular weight ($7 \times 10^5$ Da) (Figure 9).

Figure 9 - Molecular weight of untreated and gamma irradiated cotton
These MW correspond to a degree of polymerization (DP) of ca 6200 for the Pima and LS Upland lines and 4300 for the Upland line. These differences may reflect genetic variation or different growth conditions although such parameters have never been reported to affect the molecular weight of cellulose from different cotton lines. The actual reason for the observed differences remains unclear. Despite this discrepancy between the Upland line and the two other lines tested here, the trend of the decrease in MW was comparable for all cellulose samples. In particular, the observed apparent molecular weight dropped for all lines from their original value (10^6 or 7 x 10^5 Da) to ca 2.5-3 x 10^5 Da under a dose of 20.8 kGy. Higher irradiation doses were accompanied by a continued decrease in MW, but the observed decrease was more progressive than that observed between the non irradiated samples and those exposed to 20.8 kGy. The apparent MW weight of all cellulose samples decreased from 2.5-3 x 10^5 Da to 10^5 Da when exposed to a total irradiation dose of 74.2 kGy. These results suggest that a 20.8 kGy irradiation dose provokes the breakage of cellulose chains at the most sensitive points probably representing domains of lower crystallinity in the fibrillar structures, while higher doses are required to further decrease the size of cellulose chains from the more crystalline domains of the fibers. The decrease in molecular size is most likely responsible for the observed alteration of the mechanical properties of the cotton fibers upon irradiation. Similar to our data, samples from wood have been shown to exhibit a decreased molecular weight upon increasing irradiation doses compared to the untreated samples while the degree of crystallinity of the cellulose fibers is not significantly modified upon irradiation (Aoki et al., 1977).

**Conclusion**

Experience from within the industry had suggested that sanitary treatments prescribed by AQIS do affect the quality of the cotton, although there had been little direct scientific information available on the magnitude of the damage. In order to determine the effect on the physical properties of the treatments prescribed by AQIS (fumigation with ethylene oxide or by methyl bromide and gamma irradiation), standard Upland, Long Staple Upland and Extra Long Staple cotton were treated.

The fumigation treatments by either ethylene oxide or methyl bromide had little or no significant effect on the physical properties of the cotton fibre. However gamma irradiation, even at the lower dosages, did have an effect on the physical properties of the fibre, with these effects becoming more apparent and significant as the dosage strength increased.

Results show that the physical fibre properties of the cotton such as fibre strength, elongation, fibre length, length uniformity, short fibre and to a lesser extent colour is affected by gamma irradiation. The study has shown that gamma irradiation affects normal Upland, Long Staple Upland as well as Extra Long Staple cotton. In the case of the Upland and Long Staple Upland cotton the strength of the fibre reduced by between 3cN/tex and 9 cN/tex, depending on the dosage. This decrease in fibre
strength corresponded with a gradual decrease in fibre elongation by 1.0 to 2.0%. The Extra Long Staple cotton was dramatically affected by gamma irradiation. The strength reduced by between 5 cN/tex and 18 cN/tex, with a corresponding decrease in fibre elongation of 2%.

Analysis by various microscopy methods revealed no noticeable surface damage. However chemical analysis revealed that the molecular weight of Upland, Long Staple Upland and Pima cotton decreases at even the lower dosages (20.8 kGy) and continues to decrease as dosages with gamma irradiation increased. The results suggest that a low irradiation dose provokes the breakage of cellulose chains at the most sensitive points, which probably represents domains of lower crystallinity in the structures. Higher doses then continue to decrease the size of cellulose chains from the more crystalline domains of the fibers. The decrease in molecular size is most likely responsible for the observed alteration of the mechanical properties of the cotton fibers upon irradiation.

Extension Opportunities
It is intended to conduct some spinning and dyeing trials to determine the consequences of quarantine treatments on yarn and fabric quality.

Publications
It is intended to publish an article in the Australian Cotton Grower magazine and also to submit a paper to an international scientific journal for consideration. These results will also be presented to AQIS to encourage them to change their protocols.
Part 4 – Final Report Executive Summary

Quarantine plays a critical role to ensure that Australia remains free from serious pests, weeds and diseases present in other parts of the world. Australia places great importance on quarantine and has among the strongest quarantine measures of any country in the world. Cotton is treated to ensure that consignments are free from live insects, soil and other debris. Depending on the samples the quarantine treatments used can be chemical (fumigation) by either methyl bromide or ethylene oxide or by gamma irradiation at either 50kGray or 25kGray (kGy).

Experience from within the industry suggests that these treatments affect the quality of the cotton, although there is little direct scientific information available on the magnitude of the damage to the cotton. Thus, in order to determine the affect of the various quarantine treatments on the physical properties of cotton lint standard Upland cotton, Long Staple Upland cotton and Extra Long Staple cotton was treated with the various quarantine treatments.

The fumigation treatments by either ethylene oxide or methyl bromide had little or no significant effect on the physical properties of the cotton fibre. However gamma irradiation did have an effect on the physical properties of the fibre.

The results clearly indicate that the physical fibre properties of the cotton such as; strength, elongation, length uniformity, short fibre and to a lesser extent colour is affected by gamma irradiation. The study has shown that gamma irradiation affects normal Upland, Long Staple Upland as well as Extra Long Staple cotton. In the case of the Upland and Long Staple Upland cotton the strength of the fibre reduced by between 3cN/tex and 9 cN/tex, depending on the dosage. This decrease in fibre strength corresponded with a gradual decrease in fibre elongation by 1.0 to 2.0%. The Extra Long Staple cotton was dramatically affected by gamma irradiation. The strength reduced by between 5 cN/tex and 18 cN/tex. This decrease in fibre strength also corresponded with a 2% decrease in fibre elongation.

Analysis by various microscopy methods revealed no noticeable surface damage. However chemical analysis revealed that the molecular weight of the cotton decreases at even the lower dosages and continues to decrease as dosages with gamma irradiation increased. These results suggest that a low irradiation dose provokes the breakage of cellulose chains at the most sensitive points, which probably represents domains of lower crystallinity in the structures. Higher doses then further decrease the size of cellulose chains from the more crystalline domains of the fibers. The decrease in molecular size is most likely responsible for the observed alteration of the mechanical properties of the cotton fibers upon irradiation.

The message from this preliminary investigation is quite clear, if any cotton material needs to be imported into Australia; one must insist on chemical (fumigation) by either ethylene oxide or methyl bromide as gamma irradiation, even at low dosages, severely damages the physical properties of cotton.
References

Acknowledgements

The author gratefully acknowledges the assistance of Vincent Bulone of the Swedish Center for Biomimetic Fiber Engineering and Fredrik Berthold Swedish Paper and Pulp Institute in compiling this report. The support of Steritech and the Auscott Classing facility is also acknowledged. He would also like to thank Mr. Fred Horne for his assistance and Mmes. Susan Miller and Liz Coles for testing the samples are also gratefully acknowledged.