INVESTIGATION INTO THE EFFECT OF FUMIGATION BY ETHYLENE OXIDE ON THE COLOR OF COTTON

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Abstract

In order to determine the effect of ethylene oxide treatments on the physical properties of cotton fiber, mainly color, cottons of varying color characteristics where sourced and fumigated. Commercial quarantine treatments were carried out for 5 hours at 50°C and for 24 hours at 21°C, and the cottons were then tested by various methods to detect any differences. It was found that ethylene oxide treatments had no effect on physical properties such as length, strength and Micronaire of the fiber. The treatments did however result in a permanent change in the color value and subsequently the color grade of USDA Upland cottons. In most cases the reflectance value (Rd) decreased while the yellowness (+b) remained unaffected, which in essence means that the fiber has become darker. These changes in the reflectance values will result in the HVI instrument wrongly classifying the cotton one grade higher (i.e. worse). Color change detected in the Pima cotton did not appear to be permanent, and damage by ethylene oxide on Australian Upland cotton appeared not to be as apparent as noted with USDA calibration cottons. Further work is required to better understand the observed effects of the ethylene oxide fumigation treatments.

Introduction

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 as an island nation is rapidly changing as the barriers of time and distance become less relevant and international travel and trade increase. With this comes increased risk of exotic pests and diseases entering Australia, which can seriously affect its unique environment, native flora and fauna, tourism and lifestyle.

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. These protective measures are undertaken by the Australian Quarantine Inspection Service (AQIS).

Whilst a permit is not necessarily required to import cotton lint (AQIS, 2012), all imported cotton needs to be treated (sanitized) to ensure that the consignment is free of live insects, soil and other debris or verified that any quarantine risk material present will be dealt with during processing. The quarantine treatments used can be either by gamma irradiation or chemical fumigation. Previous studies have shown that gamma irradiation affects the physical properties of cotton and its subsequent processing performance, which has led to the suspension of treating cotton samples with gamma irradiation in Australia (van der Sluijs and Church, 2013; van der Sluijs et al., 2011).

There are currently three chemical treatments prescribed by AQIS;

- Fumigation with ethylene oxide under an initial minimum vacuum of 50 kilopascals at 1200 g/m³ for 5 hours at 50°C.
- Fumigation with ethylene oxide under an initial minimum vacuum of 50 kilopascals at 1200 g/m³ for 24 hours at 21°C.
- Fumigation with methyl bromide at a rate of 32 g/m³ for 24 hours at 21ºC, above normal atmospheric pressure. As methyl bromide is considered an ozone depleter it is in the process of being withdrawn.

Although Australia is a net exporter of cotton, a large number of cotton samples are still imported into Australia on a yearly basis mainly to calibrate and evaluate instruments that objectively measure fiber properties. The Australian cotton industry, through its five local classing facilities, has been participating in a number of international Round Trials for a number of years. The performances of the classing facilities, particularly in terms of results from High Volume Instruments (HVI) that participate in these Round Trials, are assessed as an industry. Although the instruments have performed particularly well in the Round Trials with a number of the instruments in the top 20 and

with most instruments consistently below (i.e. better than) the worldwide average, it has become apparent that the color results (reflectance Rd and yellowness +b) of the Australian HVI instruments participating, are consistently different from the worldwide average.

Previous industry trials have indicated that fumigation treatments by ethylene oxide may affect the color of cottons. A desktop review of the literature concluded that there have been no significant studies conducted in the past to determine the effect of fumigation on the physical properties of cotton lint. A study by the British Museum, that uses ethylene oxide as a fumigant for ethnographic objects found that ethylene oxide does reduce the strength of paper, cotton and silk yarns but has no affect on wool (Green and Daniels, 1987).

In this paper we present the results of preliminary trials with various cottons to determine what effect fumigation treatments by ethylene oxide have on the physical properties of cotton fiber, particularly in regards to the color of cotton fiber and whether this change in color is permanent.

Materials and Methods

In order for an extensive trial to be conducted we sourced a range of calibration cotton from the United States Department of Agriculture (USDA), ranging from Upland White (11-71) to Spotted (23-63) and Tinged (34-54) as well as Pima cotton (1-6, with 1 being the best and 6 the worst grade). We received a total of 25 calibration cottons covering a wide spectrum of color grades. Two 250-gram samples for each color grade were used in this trial to allow for multiple HVI testing.

Prior to forwarding the samples to Australia for treatment and further analysis, the USDA tested the various samples on their master colorimeter. Eight measurements were taken per sample with each measurement made on a different piece/face. Upon arrival the untreated samples were also tested on a HVI 1000 by an industry certified classing facility. As the color of Australian Upland cotton is somewhat different to the USDA cotton (similar Rd but lower +b) we included three samples, which represent typical Australian Upland cotton in the trial. As one would expect there are no real differences in the results between the two facilities. The averages of the eight measurements, as tested by the two classing facilities are shown in Table 1.

The samples were fumigated using ethylene oxide by an accredited company according to AQIS stipulations.

After the fumigation treatment the samples were tested on the HVI instrument four times. The first test was conducted 5 days after treatment, the second test 40 days after treatment, the third test 60 days after treatment and the last test 90 days after treatment. In between these tests the samples were placed in trays and stored in a conditioned room.

Fiber Testing

Bale 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 (Knoxville, USA) 1000 High Volume Instrument (HVI), as per ASTM D5867, for Micronaire, staple length, length uniformity, staple strength, elongation and color. Cotton color is represented by the two measurements Rd (Reflectance) and +b (Yellowness). Prior to the commencement of the ginning season this instrument was qualified using the USDA HVI qualification standards and prior to testing each lot; five tests were conducted with the central tile to ensure that color readings are within tolerance.

Infrared spectroscopy analysis

Infrared spectra were collected at a resolution of 4 cm^{-1} using a Perkin Elmer (UK) System 2000 Fourier-transform infrared (FTIR) spectrometer fitted with narrow band Mercury Cadmium Telluride detector. Attenuated Total Reflectance (ATR) spectra were obtained from the cotton fibers using a Specac (UK) 11900 variable angle accessory and a ZnSe internal reflectance element. Spectra were obtained from the extracts as cast films on KBr salt plates. The solvent was allowed to evaporate at room temperature. All samples were analyzed in duplicate.

Table 1. Average color values for the various cotton grades prior to treatment

USDA Grade	USDA Rd	USDA +b	AUS Rd	AUS +b
11	80.6	9.2	80.7	9.3
21	78.6	9.4	78.7	9.6
31	75.0	8.8	75.1	9.1
41	72.8	7.0	72.4	7.3
51	67.5	6.9	67.9	6.9
61	62.5	6.8	62.9	6.9
71	56.3	7.4	56.1	7.5
23	72.4	11.1	72.2	11.4
33	72.0	10.4	72.2	10.5
43	66.8	10.4	67.1	10.5
53	59.4	10.2	60.8	10.3
63	59.0	9.4	59.9	9.7
34	64.5	13.0	64.9	13.1
44	62.3	12.8	62.9	13.0
54	57.8	12.9	58.0	12.9
Pima 1A	70.8	12.3	71.0	12.4
Pima 1B	68.7	14.0	68.3	14.1
Pima 2A	68.7	12.2	68.3	12.3
Pima 2B	67.4	13.2	68.1	13.2
Pima 3A	65.4	11.3	65.8	11.4
Pima 3B	64.5	13.2	64.5	13.3
Pima 4	62.7	12.3	63.1	12.5
Pima 5A	62.8	11.4	62.9	11.3
Pima 5B	60.7	11.8	60.8	11.6
Pima 6	59.2	10.0	58.8	10.0
Aus A	*	*	80.2	7.6
Aus B	*	*	73.9	7.1
Aus C	*	*	74.7	5.8

Cotton wax extraction and analysis

The cotton wax of selected cotton samples was extracted in duplicate using the Conrad method (Conrad, 1944) Briefly, cleaned (no vegetable or leaf matter) and conditioned (22^{o}C, 65% relative humidity) cotton samples were Soxhlet extracted with hot ethanol solution (95%) for six hours. Waxes were isolated by extracting the ethanol solution with chloroform and the chloroform then back-extracted with water. The chloroform soluble extracts were analyzed by infrared spectroscopy.

The color of the cotton was assessed both before and after extraction using a Gretag Macbeth Color-Eye 7000A spectrophotometer (Munich, Germany). Any residual vegetable and leaf matter trash was manually removed from the samples prior to analysis. The cotton samples were conditioned (22^{o}C, 65% relative humidity) prior to analysis. To ensure consistent measurement of the loose fibers, a mass of 0.512 g (0.005 g) cotton was evenly compressed to a volume of 3.2 cm^3 in a polymethyl methacrylate disposable cuvette (BrandTech, CT, USA) and capped with a 10 mm Perspex cube with a 1 mm hole drilled through the centre. All samples were analyzed in duplicate.

Gas Chromatography / Mass Spectroscopy (GC/MS)

A headspace analysis method was developed for the detection and quantitation of ethylene oxide on cotton. This method is based on B.5.4 of AS ISO 10993.7-2003 (SA, 2003). Approximately 60 mg of cotton was accurately weighed into 6 mL headspace vials and sealed with Teflon faced caps. Before sampling the vials were placed in an oven at 100°C for 1 hour and then in a block heater for 5 minutes at 80°C. The analysis was carried out on a Varian 3600 gas chromatograph and Saturn 2000 mass spectrometer fitted with a 30 m length x 0.32 mm ID x 0.25 µm film, SGE SOLGEL-WAX column. The headspace was sampled manually with a 100 µL sample taken and injected into the gas chromatograph. During analysis all temperatures were isothermal, injector at 200°C and oven at 35°C. The detection and analysis of ethylene oxide was by the combined response of ions 42 – 44 m/z. All analyses were carried out in duplicate.

Ethylene oxide reference material was purchased as a 50,000 ppm solution in dichloromethane from Supelco. The reference material was diluted in dichloromethane to prepare a standard series. The standards were analyzed by injecting 1 µL of the ethylene oxide standards into headspace vials and analysis was performed in the same manner as the samples. The range of the method was 0.50 – 833 mg/kg of ethylene oxide on cotton with excellent linearity (R^2 = 0.9996) over this range. The limit of detection was calculated as 3x the signal height of the background. Cotton samples spiked with ethylene oxide solution had an average recovery (subtracting the spiked cotton results from the result of the untreated cotton) of 89%.

Results and Discussion

Fiber Results

The HVI results for Micronaire, staple length, length uniformity, short fibre index, staple strength and elongation prior to fumigation and 5 days after fumigation with the two treatments of ethylene oxide showed that the fumigation treatments did not have any effect on the physical properties (not shown), which was the case with previous findings (van der Sluijs and Church, 2013; van der Sluijs et al., 2011). Hence all further HVI testing only measured color. The changes in the color values after fumigation with ethylene oxide for 24 hours at 21^{o}C and 5 hours at 50^{o}C are shown in Tables 2 and 3.

The tolerance limits permitted by the CCAA for Rd is +/- 1.0 unit and for +b is +/- 0.6 units. The changes in color that are above this limit have been highlighted in yellow, while changes on the limit are highlighted in light blue. From the results it can be seen that it is mainly the reflectance of the cotton that has been affected irrespective of the fumigation method. In most cases the reflectance value has decreased which means that the cotton has become darker. It is also apparent that the cotton that seems to be affected is the Upland USDA cotton Grades 11, 21 and 31 as well as the USDA cotton grades Pima 1A-3B. It is interesting to note that the Australian cotton, which is generally whiter than the USDA cotton, seemed unaffected by the fumigation treatments, with only a slight change to the +b value, with the cotton becoming slightly yellower.

By comparing these changes to the USDA Upland and Pima color charts (not shown) that are uploaded in all HVI instruments, one finds that these small changes can affect the color grade results. These changes in the reflectance values will result in the HVI instrument wrongly classifying the cotton one grade higher (i.e. worse). For example, the Grade 11 cotton will be graded 21 and the 21 will be graded 31. This will lead to the instrument failing to calibrate and also unable to qualify the instrument. As the change in reflectance for the USDA Upland cottons has remained for more than three months (90 days), it appears that this change is permanent. In contrast, after 60 days the color of the USDA Pima cottons has reverted back to its pre-fumigation state.

Table 2: Color changes after treatment with ethylene oxide after 24 hours at 21°C

	Prior	Prior	5 days	5 days	40 days	40 days	60 days	60 days	90days	90 days
USDA	AUS	AUS	Change	Change	Change	Change	Change	Change	Change	Change
Grade	Rd	+b	Rd	b+	Rd	b+	Rd	b+	Rd	b+
11	80.7	9.3	-1.4	0.5	-1.6	0.4	-1.4	0.4	-1.3	0.3
21	78.7	9.6	-1.2	0.5	-1.5	0.2	-1.2	0.2	-1.3	0.2
31	75.1	9.1	-0.9	0.5	-1.1	0.4	-1.0	0.2	-0.5	0.4
41	72.4	7.3	-0.2	0.3	-0.2	0.4	0.4	0.3	0.0	0.1
51	67.9	6.9	-0.3	0.3	-0.8	0.4	-0.6	0.2	-0.5	0.4
61	62.9	6.9	0.5	0.1	0.5	0.3	0.6	0.3	0.5	0.4
71	56.1	7.5	0.1	0.2	0.0	0.1	0.2	0.1	0.4	0.1
23	72.2	11.4	-0.6	0.5	-0.8	0.5	-0.5	0.6	0.0	0.4
33	72.2	10.5	-0.4	0.4	-0.6	0.3	-0.2	0.4	-1.0	0.4
43	67.1	10.5	0.1	0.2	-0.3	0.1	0.0	0.1	0.1	0.2
53	60.8	10.3	-0.7	0.1	-0.5	0.0	0.0	0.1	-0.5	0.2
63	59.9	9.7	-0.2	0.2	-0.2	0.1	-0.2	0.0	-0.6	0.3
34	64.9	13.1	-0.5	0.2	-0.7	0.0	0.2	0.0	-0.3	0.0
44	62.9	13.0	-0.7	0.0	-0.6	-0.2	-0.4	-0.2	-0.5	-0.2
54	58.0	12.9	-0.6	0.0	-0.3	-0.1	0.0	-0.1	-0.1	0.0
Pima 1A	71.0	12.4	-1.3	0.3	-1.4	0.1	-0.8	0.3	-0.5	-0.1
Pima 1B	68.3	14.1	-0.8	0.1	-1.1	0.0	-0.8	0.1	0.8	-0.4
Pima 2A	68.3	12.3	-1.0	0.1	-1.6	0.1	-1.0	0.4	-0.3	0.3
Pima 2B	68.1	13.2	-1.0	0.2	-1.0	-0.1	-0.9	0.2	-0.3	-0.4
Pima 3A	65.8	11.4	-0.8	0.1	-1.0	0.0	-0.5	0.1	0.2	-0.4
Pima 3B	64.5	13.3	-1.2	0.6	-1.5	0.5	-0.8	0.8	-0.9	-0.1
Pima 4	63.1	12.5	-0.5	0.3	-1.0	0.2	-0.8	0.0	-0.7	0.1
Pima 5A	62.9	11.3	-0.9	0.4	-0.9	0.5	-1.1	0.5	-1.5	0.5
Pima 5B	60.8	11.6	-0.3	0.6	-0.9	0.4	-0.4	0.4	0.7	0.4
Pima 6	58.8	10.0	-0.3	0.5	-1.5	0.2	-0.6	0.2	0.9	0.1
Aus A	80.2	7.6	0.0	0.3	-0.8	0.3	-0.4	0.4	-0.3	0.3
Aus B	73.9	7.1	-0.1	0.5	-0.5	0.4	0.1	0.5	-0.1	0.6
Aus C	74.7	5.8	-0.1	0.3	-0.4	0.6	0.1	0.8	0.2	0.5

The changes in color that are above this limit have been highlighted in yellow, while changes on the limit are highlighted in light blue.

Table 3: Color results for samples after treatment with ethylene oxide at 5 hours at 50°C

	Prior	Prior	5 days	5 days	40 days	40 days	60 days	60 days	90days	90 days
USDA	AUS	AUS	Change	Change	Change	Change	Change	Change	Change	Change
Grade	Rd	+b	Rd	b+	Rd	b+	Rd	b+	Rd	b+
11	80.7	9.3	-1.1	0.2	-1.4	0.1	-1.1	0.5	-1.5	0.2
21	78.7	9.6	-1.1	0.3	-1.6	0.1	-1.2	0.2	-1.3	0.1
31	75.1	9.1	-0.7	0.3	-1.2	0.1	-0.8	0.3	-1.3	0.3
41	72.4	7.3	1.4	0.0	1.0	0.1	1.2	0.2	0.3	0.2
51	67.9	6.9	-0.4	0.3	-1.1	0.1	-0.7	0.3	-0.6	0.3
61	62.9	6.9	0.6	0.2	0.0	0.1	0.2	0.3	0.6	0.2
71	56.1	7.5	0.2	0.0	0.3	-0.1	0.6	0.0	0.4	0.1
23	72.2	11.4	-0.3	0.4	-0.2	0.1	-0.1	0.3	-0.5	0.5
33	72.2	10.5	-1.0	0.3	-1.3	0.2	-0.6	0.3	-0.2	0.3
43	67.1	10.5	-0.1	0.0	-0.3	-0.2	0.1	0.2	0.0	0.1
53	60.8	10.3	-0.4	0.0	-0.9	-0.1	-0.5	0.1	-0.5	-0.1
63	59.9	9.7	-0.1	0.1	-0.6	0.0	-0.1	0.2	-0.4	0.1
34	64.9	13.1	-1.0	0.1	-1.3	-0.1	-0.5	-0.1	0.2	0.0
44	62.9	13.0	-0.8	-0.1	-0.6	-0.2	-0.3	-0.2	-0.4	-0.1
54	58.0	12.9	-0.6	0.0	-0.6	-0.2	-0.1	-0.1	-0.3	-0.2
Pima 1A	71.0	12.4	-0.6	-0.1	-0.9	0.1	-0.5	0.2	-1.1	0.2
Pima 1B	68.3	14.1	0.5	-0.3	-0.1	-0.3	0.3	-0.5	-0.9	0.0
Pima 2A	68.3	12.3	-0.3	0.3	-0.6	0.0	-0.3	-0.1	-0.9	0.1
Pima 2B	68.1	13.2	-0.9	0.0	-1.0	-0.2	-0.5	0.0	-1.3	0.1
Pima 3A	65.8	11.4	-0.2	-0.2	-0.7	0.0	-0.1	-0.2	0.0	0.1
Pima 3B	64.5	13.3	-1.1	0.2	-1.6	0.2	-0.5	0.2	-1.2	0.5
Pima 4	63.1	12.5	-0.6	0.0	-1.0	-0.1	-0.5	0.0	-0.7	0.2
Pima 5A	62.9	11.3	-1.0	0.2	-1.7	0.5	-1.4	0.4	-0.8	0.7
Pima 5B	60.8	11.6	0.6	0.2	0.1	0.1	0.3	0.4	-0.7	0.2
Pima 6	58.8	10.0	1.0	0.0	0.7	0.0	1.2	0.1	0.5	0.4
Aus A	80.2	7.6	0.1	0.1	-0.7	0.2	-0.3	0.3	-0.5	0.5
Aus B	73.9	7.1	-0.1	0.2	-0.5	0.3	-0.1	0.4	-0.3	0.6
Aus C	74.7	5.8	0.1	0.4	-0.4	0.3	0.2	0.4	0.2	0.7

The changes in color that are above this limit have been highlighted in yellow, while changes on the limit are highlighted in light blue.

Infrared analysis of cottons

There are three ways in which ethylene oxide can interact with cotton after a fumigation treatment.

1. Ethylene oxide can be retained unchanged within the cotton. This residue may persist for some time before final disappearance as a result of volatilization.
2. The formation of small molecules including ethylene chlorohydrins, bromohydrin and ethylene glycol. These species form by the reaction of ethylene oxide with inorganic halides or water present within the cotton.
3. Ethylene oxide can react with the hydroxyl groups of the cotton itself forming alkylated or hydroxyethylated derivatives. The reaction of ethylene oxide with foodstuffs has been known to affect color, taste and texture (Scudamore and Heuser, 1971).

Among the possible reactions presented above, a few can take place under the mild conditions of fumigation. Hydrolysis of ethylene oxide by water present in the cotton and surrounding air can be catalyzed by acid, which is likely present in raw cotton from the microbial degradation of plant matter. The presence of acid would also likely catalyze the reaction of ethylene oxide with the hydroxyl groups of the cellulose molecules comprising the cotton. Ethylene oxide can undergo a polymerization reaction forming low molecular weight glycols. This reaction is accelerated by the presence of water (Green and Daniels, 1987).

Infrared spectroscopy was used to determine if any chemical or structural differences could be detected between the ethylene oxide and untreated cottons that exhibited color differences. Infrared spectroscopy can be used to detect ethylene oxide in the gas phase at pressures lower than 5 mm Hg (Thompson and Cave, 1951). The technique is sensitive to chemical changes to the cotton such as the derivatization described above as well as fiber oxidation and the degree of perfection in the lattice structure of the crystalline regions (van der Sluijs and Church, 2013).

Infrared spectra were obtained from the cotton samples using the Attenuated Total Reflectance (ATR) technique, which provides information from the top few microns of the fiber surface. Typical ATR spectra are shown below.

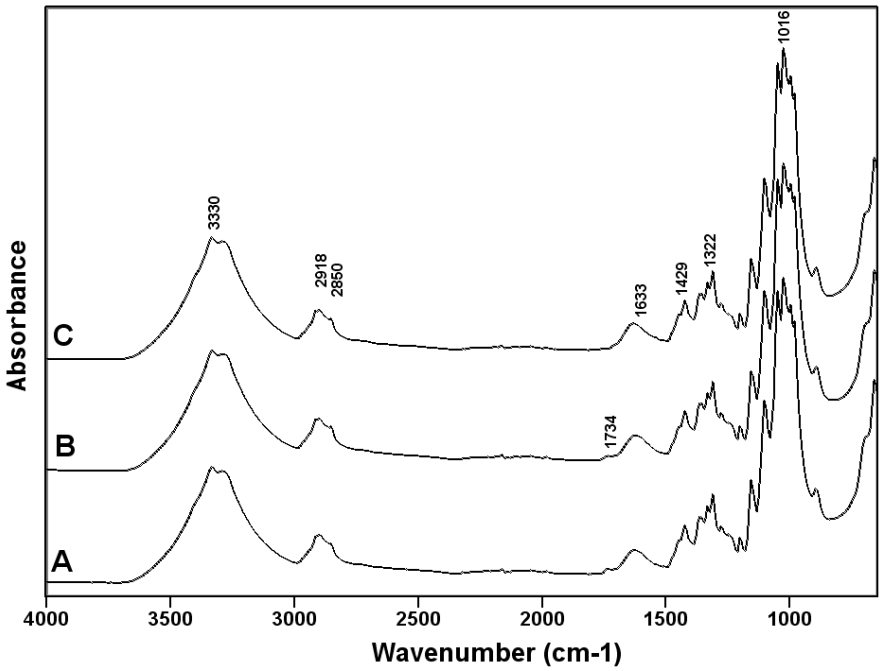


Figure 1. Infrared ATR spectra obtained from cotton fiber samples: A) Aus B untreated, B) Aus B treated at 21°C after 5 days and C) Aus B treated at 50°C after 5 days.

The spectral features can be assigned as follows: 3330 cm^{-1} intermolecular hydrogen bonded O-H stretching, 2918, 2860, 1439 and 1322 cm^{-1} vibrations of the CH_2 groups, the strong multi-component feature centered near 1016 cm^{-1} C-O-C β-glycosidic linkages, alcoholic C-O stretch and C-C and C-O-C ring modes (Abidi et al., 2008).

The only differences found between the spectra shown in Figure 1 can be attributed to minor differences in adsorbed water (1633 cm^{-1}) and in ester content (1734 cm^{-1}), the latter likely being a fatty acid ester contaminant. These features were found to vary randomly, even between sub-samples of the same cotton and thus cannot be related to the effects of the treatments. No evidence of residual ethylene oxide or any of its reaction products could be detected.

Extraction and analysis of cotton wax

Cotton wax extractions were undertaken in an attempt to determine if the color changes detected in the cotton by the HVI measurements could be associated with the degradation of the layer of cotton wax on the fiber surface or the reaction of the cotton wax with the ethylene oxide. If the observed color changes are associated with changes in the cotton wax, the removal of the wax should return the fumigated cotton to the same color state as that of the untreated wax after extraction.

Color measurements were made for cotton fibers both before and after extraction. Yellowness Index (YI-E313), Δb* and ΔE (CMC 2:1) were determined. Reflectance (Rd) was not determined for these samples, however L* values have been shown to strongly correlate with Rd values (Rogers et al., 2008). The results are shown in Table 4.

Table 4. Typical mean color differences obtained after wax extraction by the Conrad method

Sample	Delta (Δ)			
	YI-E313	b*	E (CMC 2:1)	L*
Aus B Untreated 5 days	-1.02	-0.33	0.68	1.62
Aus B Untreated 60 days	0.45	0.21	0.20	-0.03
21°C Aus B 5 days	0.28	0.26	0.53	1.33
21°C Aus B 60 days	0.28	0.20	0.27	0.54
50°C Aus B 5 days	-0.52	-0.15	0.4	0.94
50°C Aus B 60 days	-0.88	-0.34	0.36	0.32

There are no significant differences between the yellowness of the extracted and un-extracted cottons at the 95% confidence limit. The ΔL* results suggest that the extraction of the cotton wax has increased the brightness of the cotton irrespective of whether the cotton was fumigated or not. The effect appears to be reduced for the aged cotton but none of the ΔL* values obtained for the treated and untreated pairs are statistically significant at the 95% confidence limit.

The extracted wax was analyzed by infrared spectroscopy, as due to its low concentration on the cotton fibers surface very little information about its chemical state would be gleaned from the infrared spectra obtained from the cotton itself. Typical spectra of the extracted waxes are shown in Figure 2.

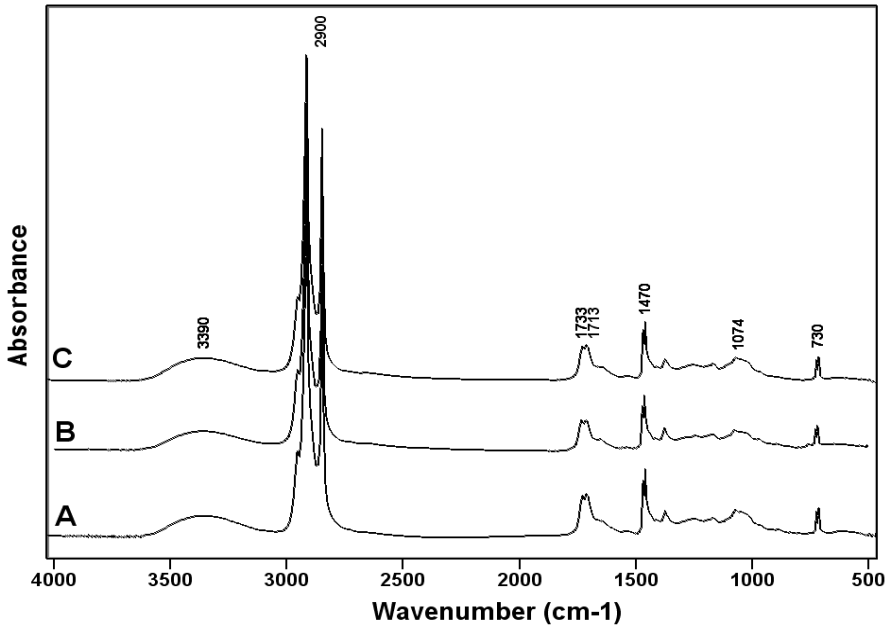


Figure 2. Infrared spectra obtained from cotton wax extracts: A) Aussie 2 untreated, B) Aus B treated at 21°C after 5 days and C) Aus B treated at 50°C after 5 days.

These spectra are typical of cotton wax (Church and Woodhead, 2006) and exhibit dominant CH_2 stretching vibrations near 2900 cm^{-1} with the corresponding deformation and rocking vibrations observed at 1470 and 730 cm^{-1}, respectively. Other significant features include the broad –O-H stretching mode at 3390 cm^{-1}, ester and free acid C=O stretching modes at 1733 and 1713 cm^{-1} and C-O-H stretching modes at 1074 cm^{-1}. These features are indicative of the presence of components including fatty acids and esters, hydrocarbon waxes and fatty alcohols.

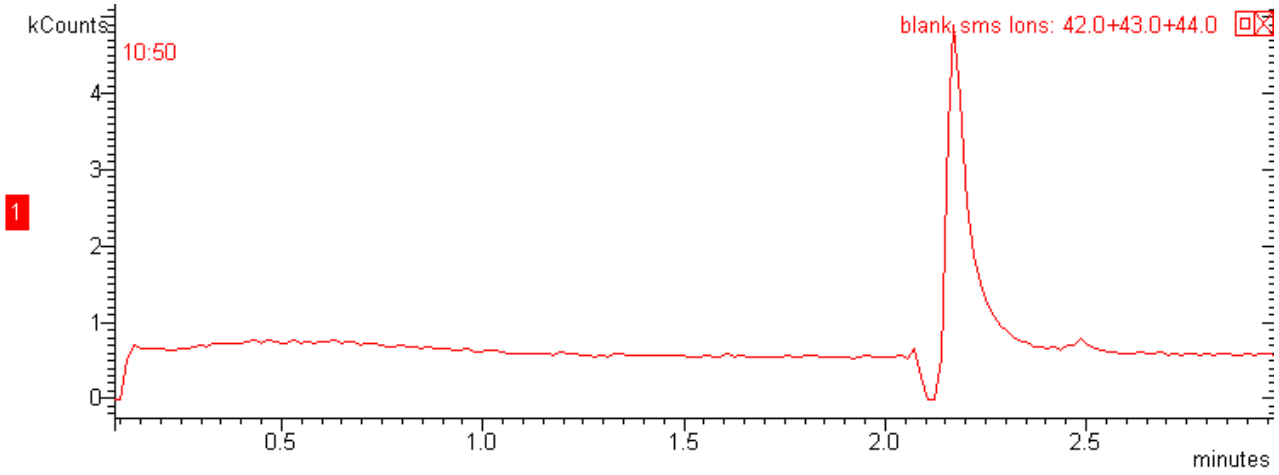
Possible signs of oxidation could include intensity changes in C-O-H, C=O and C-OH stretching vibrations. Ethylene oxide has the potential, in the presence of heat or alkaline catalyst, to react with free fatty acids present in the wax to form mono- and di-esters (Wrigley et al., 1959). This reaction is unlikely under the conditions used during the fumigation process. No change in the relative intensities of free acids to esters can be detected.

In summary, no significant differences can be detected between the cotton fibers or the cotton wax extracts obtained from the treated and untreated samples.

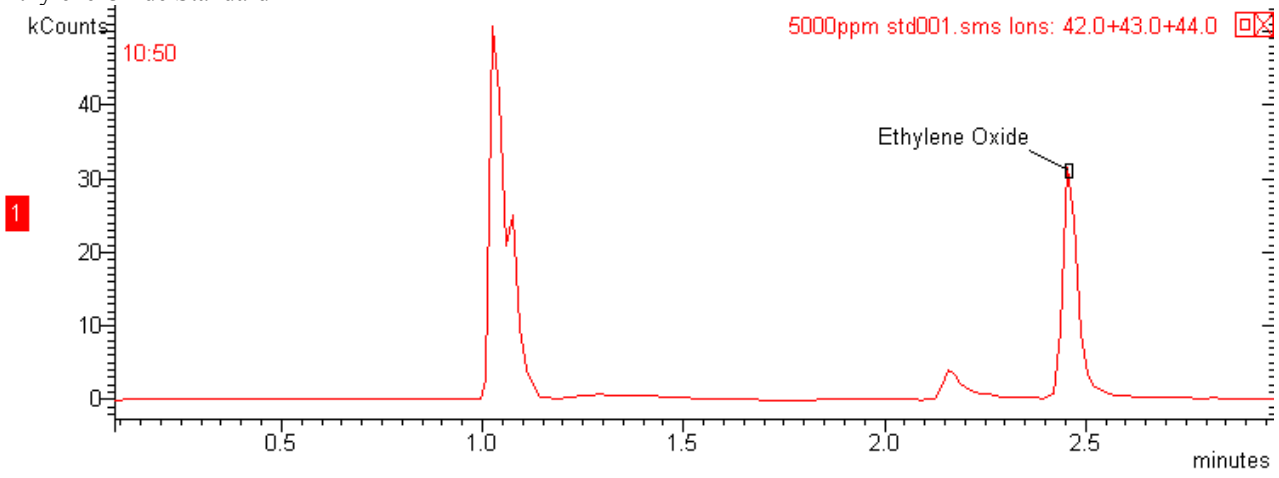
GC/ MS analysis of cotton

GC/MS analysis of the vapors given off by the cotton samples after incubation at 100°C for 1 hour was carried out in order to determine if there was any residual ethylene oxide present from the fumigation. Under the chromatographic conditions used, ethylene oxide had a retention time of 2.46 minutes and the total run time was 3 minutes. Typical chromatograms are shown as Figure 3. The chromatogram shown as the top trace is typical of a blank run where no cotton was present. Only a weak peak is evident at a retention time of about 2.16 minutes. The middle chromatogram trace shows the ethylene oxide standard eluting as expected. The lower chromatogram trace is from the analysis of a cotton sample 3 months after fumigation at 21°C. From this result it is clear that even after open storage under standard conditions there is a residual of ethylene oxide present in the cotton.

Blank – No Cotton in Vial



Ethylene Oxide Standard



Sample – 21°C, Aus B at 3 months

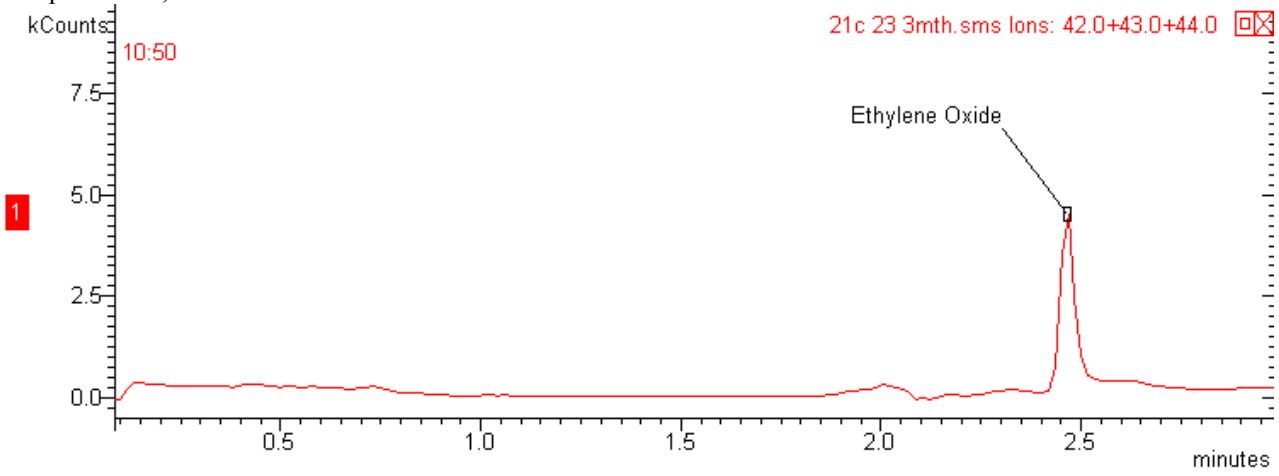


Figure 3. Typical chromatograms: blank chromatogram (top), ethylene oxide standard (middle) and Aus B cotton sample treated at 21°C and sampled after 3 months (bottom).

The average residual ethylene oxide concentration in milligrams per kilogram (mg/kg) detected on the fumigated cotton are given in Table 5. In general the standard deviations were less than 0.5 mg/kg.

Table 5: Average residual ethylene oxide detected after treatment

Sample	Ethylene Oxide concentration (mg/kg)					
USDA Grade	21°C 5 days	21°C 60 days	% change	50°C 5 days	50°C 60 days	% change
11	6.9	7.3	5%	4.1	3.8	-8%
21	4.0	2.8	-29%	4.3	3.9	-10%
31	4.2	11	151%	4.8	3.0	-36%
41	6.0	6.6	10%	3.8	3.5	-8%
51	7.8	7.6	-2%	3.8	2.4	-38%
61	6.3	4.9	-23%	4.3	1.8	-59%
71	6.7	3.7	-45%	2.8	2.1	-25%
23	7.1	4.1	-42%	2.9	1.8	-36%
33	2.6	5.4	110%	3.9	2.7	-32%
43	7.9	2.2	-72%	3.2	4.9	52%
53	11	6.6	-42%	4.3	4.0	-7%
63	8.1	8.4	5%	7.3	3.3	-55%
34	7.0	3.7	-46%	2.7	1.9	-27%
44	6.7	7.2	8%	4.7	4.4	-6%
54	2.4	4.5	87%	1.8	1.5	-19%
Pima 1A	4.1	2.8	-31%	2.4	1.2	-47%
Pima 1B	2.4	1.5	-37%	2.3	4.4	94%
Pima 2A	3.1	2.1	-33%	2.1	1.4	-31%
Pima 2B	6.3	2.4	-62%	3.6	2.0	-45%
Pima 3A	17	3.3	-81%	5.1	2.8	-46%
Pima 3B	8.0	4.1	-49%	2.0	3.5	76%
Pima 4	6.3	2.5	-60%	2.0	3.4	66%
Pima 5A	4.9	3.0	-39%	3.2	2.8	-14%
Pima 5B	2.5	1.2	-50%	3.9	1.8	-53%
Pima 6	2.1	2.4	11%	2.5	2.1	-15%
Aus A	2.3	1.4	-38%	4.0	3.2	-18%
Aus B	4.6	1.6	-65%	6.4	2.7	-58%
Aus C	3.6	2.0	-46%	3.9	2.4	-37%

Residual ethylene oxide was detected on all cotton samples, although there were no apparent trends, the residual levels of all treated cottons changed with time. For the USDA Upland White cottons treated at 21°C, 57% showed decreased ethylene oxide levels while in the case of the Spotted color cottons 60% showed decreases with time. Thirty three percent of the Tinged color cottons showed decreased ethylene oxide levels. The majority of the Pima cottons, with the exception of Pima 6, showed decreased ethylene oxide levels. All the Australian cottons showed decreases.

For cottons treated at 50°C, a larger proportion was found to have ethylene oxide levels that decreased with time. All of the USDA Upland White and Tinged cottons showed decreased ethylene oxide levels while in the case of the

Spotted color cottons, 80% showed decreases. The majority of the Pima cottons, with the exception of Pima1B, 3B and 4 and all of the Australian cottons also showed decreased ethylene oxide levels with time.

As presented earlier in this report, the USDA cottons whose color was most affected (reduction in Rd) by the fumigation process were the Upland USDA Grades 11, 21 and 31 as well as the Pima USDA cotton grades 1A-3B. The change in the reflectance values of the Upland USDA Grades 11, 21 and 31 appears to be permanent, as the lower Rd values have lasted for longer than 3 months. The ethylene oxide content of a majority of these cottons decreased with time after treatment. The Grade 11 cotton treated at 21^{o}C showed a 5% increase in residual ethylene oxide over the 50 days while over the same time period the cotton treated at 50^{o}C decreased by 8%. For the Grade 21 cotton treated at 21^{o}C, the ethylene oxide residual decreased by 29%, while the same cotton treated at 50^{o}C decreased by only 10%. The Grade 31 cotton treated at 21^{o}C exhibited the largest increase (151%) while the 50^{o}C treated cotton decreased by 36%.

In contrast, the change in the Pima cottons does not appear to be permanent as the Rd values seem to fall within the limits after 60 days of treatment with the treatment of 24 hours at 21^{o}C while the treatment with 50^{o}C seems to have no effect on the Rd values. The majority of these cottons also exhibit decreased ethylene oxide content with time. The ethylene oxide residuals in the Pima cottons treated at 21^{o}C all decreased by a minimum of 31%, while all the Pima cottons treated at 50^{o}C also decreased by a minimum of 31% with the exception of 2B and 3B which increased by a minimum of 76%.

The color of the Australian cotton seemed unaffected by the ethylene oxide treatments with only a slight increase in the +b value, i.e. the cotton became slightly yellower. The ethylene oxide content of all of these cottons decreased with time after treatment.

It is interesting to compare the ethylene oxide residuals detected on the cotton samples to those detected on wheat flour and other comedies including sultanas, cocoa beans, ground nuts and lentils after fumigation treatments. In general it was found that when these materials are freely aired at 25^{o}C, the ethylene oxide levels dropped below a residual of 1 parts per million (ppm) within 14 days (for solids, 1 ppm = 1 mg/kg) (Scudamore and Heuser, 1971). These levels of ethylene oxide are considerably lower than those detected for even the 60 day aged cotton samples. When fumigated wheat was sealed in air–tight conditions a residual of 50-100 ppm was detected after 14 days and trace levels were still found after 90 days. At lower temperatures the ethylene oxide was found to dissipate more slowly.

From the variability of the results reported above and the lower level of ethylene oxide found in wheat and other commodities after fumigation, it is clear that further work needs to be carried out on cotton to further refine our understanding of the effects of the fumigation process. One of the major drawbacks of the current study is that the fumigation and testing was carried out at multiple locations. This required the cotton to be shipped back and forth to different labs several times during the experimentation. Based on the current results it is clear that only color measurements are actually required to further this study and these can be carried out using a spectrophotometer instead of a HVI instrument. It is probable that with more stringent controls of the fumigation process, sample handling and analysis a correlation between ethylene oxide content and cotton color may be found.

Summary

This study has shown that the fumigation of cotton lint with ethylene oxide for 24 hours at 21^{o}C and 5 hours at 50^{o}C, as per AQIS requirement had no effect on the physical properties (such as length, strength and Micronaire) of the fiber. The study however did find that fumigation with ethylene oxide did result in a color change that could subsequently adversely affect the color grade of the cotton. In most cases the reflectance value (Rd) decreased while the yellowness (+b) was unaffected, which in essence means that the fiber has become darker. This was most apparent for the Upland USDA cotton Grades 11, 21 and 31 as well as the Pima USDA cotton grades 1A-3B. These changes in the reflectance values will result in the HVI instrument wrongly classifying the cotton one grade higher (i.e. worse). For example the Grade 11 cotton will be graded 21 and the 21 will be graded 31. This will lead to the instrument failing to calibrate and it will also be impossible to qualify the instrument. While the color changes observed for the USDA Upland cotton appeared permanent, those for the fumigated USDA Pima cottons reverted back to their pre-fumigation state with time. The damage caused by ethylene oxide on Australian Upland cotton was not as apparent as noted for the USDA cottons, with only a slight increase in the +b value, i.e., the cotton became

slightly yellower. Further work is required to better understand the observed effects of the ethylene oxide fumigation treatments on cotton fibers.

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