Science & Justice 59 (2019) 498–502

Contents lists available at ScienceDirect

Science & Justice

journal homepage: www.elsevier.com/locate/scijus

Investigating the effect photodegradation has on natural fibres at a microscopic level☆

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ARTICLE INFO

Keywords:
Forensic science
Fibre examination
Photodegradation

ABSTRACT

It is a known fact that when fabric is left exposed to sunlight photodegradation occurs. However, no study has ever looked at the photodegradation that occurs to individual fibre filaments as commonly recovered from a scene of crime. To look at photodegradation of individual fibres, wool and cotton fabric were dyed using CI Acid Red 27 and CI Direct Red 80 respectively at two depths of shade, 0.25% and 2.0% owf. Pieces of fabric and individual fibre samples were then placed in a Light Fastness Q-Sun 1000 Xenon test chamber which simulated exposure to sunlight over two time periods, 64 h (equivalent to one weeks sun exposure) and 128 hrs (equivalent to two weeks sun exposure). The resulting pieces of fabric and fibres where then examined using high power comparison microscopy, as well as graded for colour fading using SDC Grey Scale for Assessing Change in Colour (including half steps). Results show that in both fibre types, photodegradation occurs in all samples, however, the degree of fading is shown to vary within a given fibre population showing it is unpredictable in nature.

1. Introduction

In forensic casework, when a fibre is recovered from a crime scene, a suspect or a victim, the primary interest is to identify its origin. This is vital as fibre evidence has the potential to support the proposition of contact between individuals and objects. When a fibre is recovered from an open-air environment, physical and chemical changes may have occurred to it. The changes can be brought about by a number of environmental mechanisms and may lead to the fibre in question being wrongly eliminated from corresponding to the originating source. This research explores the effect one of these mechanisms, photodegradation, can potentially have on single fibres.

It is common knowledge that when textiles are exposed to sunlight, chemical and physical changes can occur including a degree of colour fading. One of the ways in which colour fading is brought about is by a phenomenon known as photodegradation [1–3]. Photodegradation is attributed to be as a result of ultraviolet (UV) radiation and visible light originating from the sun with UV radiation being the predominant factor [1,3–5]. There are four classified types of UV radiation, namely UV-A, UV-B, UV-C and vacuum UV. UV-C and vacuum UV are blocked by the stratosphere whereas UV-A and UV-B reach the earth's surface and cause photodegradation [4]. Degradation arises from the destruction and formation of covalent bonds present in the fibre polymer. This can take place in both the crystalline and non-crystalline structures of the fibre [6].

As well as the fibres themselves, dyes are also affected by UV radiation. The extent to which a dye resists fading when exposed to light, known as a dye's lightfastness, is affected by a number of factors. These are numerous and include the wavelength of the radiation present, the dye's molecular structure, its physical state, its concentration, the type of fibres the dye is present on and the mordant used. Climatic factors such as temperature and humidity also play an important role in the determination of the lightfastness of the dye. Similar to the effect on fibres, UV radiation may chemically change the molecular structure of the dye thus giving rise to spectral and chromatographic changes [7–9].

The two most frequently encountered natural fibres in forensic casework are cotton and wool [10,11]. These two natural fibre types are easily shed upon contact and, as such, are readily transferred from one surface to another. UV radiation has been documented as having a significant impact on wool by causing photo-yellowing of the fibre [4–6,12–16]. Photo-yellowing is mainly attributed to wool being made from the protein keratin [17] with several publications, including Duffield and Lewis [15], Dyer et al. [16] and Simat and Steinhart [18], stating that the cause is due to the amino acids tryptophan and tyrosine. Millington [6] states that photo-yellowing is influenced by the wavelength of the radiation incident on the material, the presence of oxygen

☆ This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.
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https://doi.org/10.1016/j.scijus.2019.04.002
Received 7 August 2018; Received in revised form 11 April 2019; Accepted 14 April 2019
1355-0306/

and water and the treatment the material would have undergone during the manufacturing phase. Photo-yellowing is not a consideration when considering cotton fibres.

During the textile manufacturing process, lightfastness tests are carried out to determine the degree of fading that occurs on a dyed garment. The degree of colour fading is routinely assessed using the Society of Dyers and Colourists (SDC) Grey Scale for Assessing Change in Colour (including half steps). This type of research has little application to the forensic field, since in the majority of crime scenes fibres are encountered as individual fibre filaments as opposed to finding the whole garment. Subsequently, this research is tailored to assess the degree of fading which occurs to individual fibres when exposed to UV radiation and provide valuable information to the forensic fibre examiner as to what may be expected when fibres are exposed to sunlight for a sustained period of time.

2. Materials and methods

2.1. Fibre types

Wool and cotton were the two natural fibre types used for this research. As previously stated, wool is a protein fibre that is derived from sheep. These fibres can be dyed with various dyes such as acid dyes, reactive dyes and chrome dyes [19]. Cotton is a type of cellulosic fibre found attached to the seeds of plants pertaining to the genus *Gossypium*. These fibres can be dyed with a number of different dye types such as direct dyes, reactive dyes, VAT, sulphur and azoic dyes [17]. It has been noted that during the dyeing process of both these fibre types, uneven dyeing can occur. Non-uniform dyeing of wool is caused when the cuticle of the fibre is damaged by chemical reagents during the dyeing process or abrasion [19], whereas in the case of cotton uneven dyeing is a result of either uneven packing of the cellulose chain throughout the fibre, or due to the presence of immature or dead fibres in a batch [20].

2.2. Dyeing profile and ageing of the fibres

CI Acid Red 27 was used for dyeing the wool and CI Direct Red 80 for dyeing the cotton. Dyes were chosen for their lower recorded light fastness within the textile industry allowing for greater potential for photodegradation to be explored within this research. Albegal B acted as the auxiliary for CI Acid Red 27 whereas sodium chloride for CI Direct Red 80. Each fibre type was dyed at two different depths of shade namely, 0.25% owf (on weight of fibre) and 2.0% owf. The two depths of shade were chosen to represent pale (0.25% owf) and more deeply dyed (2.0% owf) textile fibres. The fibres were dyed at a 10:1 liquor-to-fibre ratio following the dyeing profile shown in Fig. 1. The dyeing was carried out in a Roaches Pyrotec – S Dyeing Machine.

Once the dyeing process was finished, the cotton and wool fabric was dried in an oven chamber at 60 °C. The dyeing profile represents that used within the textile industry and produced samples that appear evenly dyed on visual inspection at garment level. Microscopic examination of the dyed fibres showed slight variation between the fibres composing the samples but these were only slight (no more than 1 step on the SDC Grey Scale for Assessing Change in Colour scale).

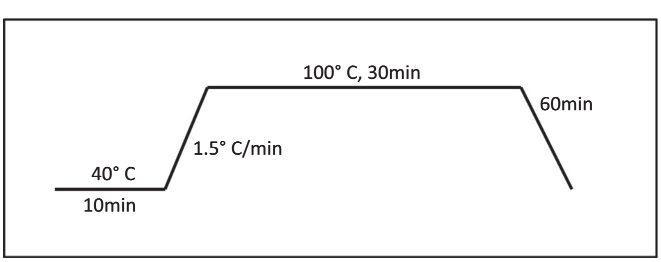

Fig. 1. Dyeing profile for the application of CI Acid Red 27 to wool and CI Direct Red 80 for cotton. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In order to be able to establish if fading at a garment level is different to fading at a fibre level, two pieces of material (1 cm by 2 cm approximately) were taken from each fabric. In order to investigate individual fibre fading, two sets of fibre tapings were also taken from each fabric using J-Lar tape. A Light Fastness Q-Sun 1000 Xenon test chamber was used to simulate exposure to sunlight with the Society of Dyers and Colourists' standardised blue wool samples used as measurable standards. The first set of samples were left in the instrument for 64 h, simulating a week of exposure to sunlight, whereas, the second set of samples were left for 128 h, simulating two weeks of exposure to sunlight. Where individual fibre filaments were exposed to sunlight simulation, the J-Lar tape was placed in the machine with the adhesive side exposed upwards to allow direct exposure of the fibre filaments. An unexposed fibre sample was also utilised as a control and point of reference.

2.3. Examination of fading

A high power comparison microscopy was used to assess the degree of colour fading of the individual fibre samples allowing a visual comparison of the control sample to an aged fibre. The high power comparison microscope utilised was a Leica DMR. In order to estimate the fading that had occurred, the SDC Grey Scale for Assessing Change in Colour (including half steps) were used. This scale is from 1 to 5 and includes half steps where 1 indicates that major fading difference is noted between the control and sample and 5 indicates that no fading has occurred.

3. Results

3.1. Visual comparison

Visual comparisons were carried out between the fabric samples subjected to photodegradation and their respective controls using the SDC Grey Scale for Assessing Change in Colour (including half steps). Both wool and cotton fabric, at the two depths of shade, visually showed that a small degree of fading had occurred; this was more pronounced at 128 h of exposure compared to 64 h of exposure as seen in Table 1.

It is worth noting that at a fabric level any suggestion of uneven dyeing was not observed as would be expected when following industry guidelines for dyeing.

3.2. High power comparison microscopy

Single fibre samples were recovered from the fabric samples and these, as well as the single aged fibre samples, were examined against the control samples using high power comparison microscopy. The single fibres from the unaged samples showed very slight variation of dyeing across the sample when examined microscopically. This was not beyond what a forensic fibre examiner would expect to observe within casework and the fibres were considered to be dyed to an acceptable industry level.

Table 1
Recorded degree of fading for fabric samples measured using the SDC Grey Scales for Assessing Change in Colour.

Fibre type	Depth of shade (%)	64 h of exposure	128 h of exposure
Wool	0.25	4	3/4
	2.0	4/5	4
Cotton	0.25	4/5	4
	2.0	4/5	4

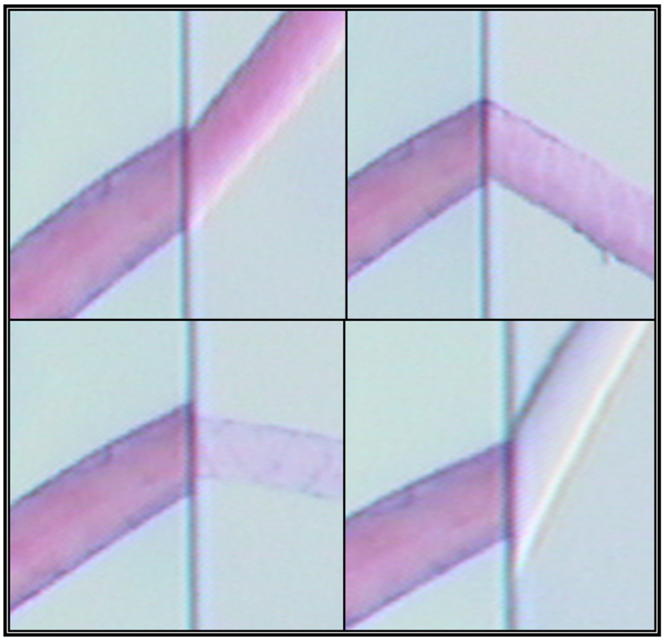

Fig. 2. The degree of fade of wool samples dyed to 0.25% owf (both single fibre and fibres from fabric samples at both 68 and 128 h) - 4/5 (top-left), 3/4 (top-right), 2 (bottom-left) and 1 (bottom-right).

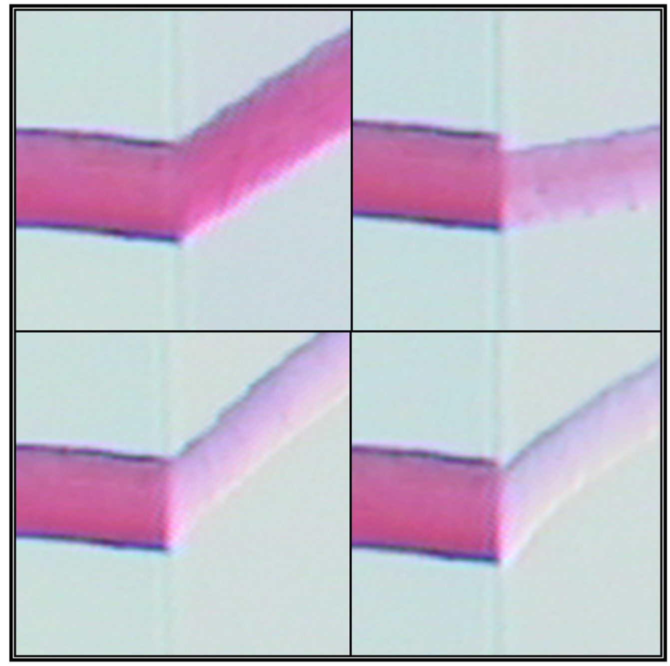

Fig. 3. The degree of fade of wool samples dyed to 2% owf (both single fibre and fibres from fabric samples at both 6 and 128 h) - 5 (top-left), 4 (top-right), 3 (bottom-left) and 2 (bottom-right).

3.2.1. Wool samples dyed to a depth of 0.25% owf

Microscopic examinations of both the single fibre and fibres from the wool sample at the two times of ageing (64 and 128 h) showed variance in their degree of fading when compared to the control sample. A degree of fading ranging from 4/5 to 1 was noted for all samples as shown in Fig. 2. It was also noted that the fibres which were recovered from the aged fabric at both time variations showed inconsistent colour distribution not only throughout the sample population but in some fibres across their length.

3.2.2. Wool samples dyed to a depth of 2.0% owf

Microscopic examination of both the fibres from the wool sample and the single fibre samples showed that, in general, little fading occurred at both 64 and 128 h. The majority of fibres were recorded with a degree of fade of 5 showing that no apparent fading had occurred although some were noted in all samples with a rating of between 4/5 and 2 as shown in Fig. 3. The fibres examined from the fabric sample aged for 64 h showed the least fading with only two fibres examined showing fading of a grading of 3/4 with the remaining fibres showing no fading. The greatest variation and degree of fading was evidenced in the single fibres which were aged for 64 and 128 h suggesting that single fibres are more susceptible to ageing than those within a fabric sample; fading ranged from 5 to 2 for these samples.

3.3. Cotton samples dyed to a depth of 0.25% owf

Microscopic examinations of both the single fibre and fibres from the cotton sample at the two times of ageing (64 and 128 h) showed evidence of variance in their degree of fading when compared to the control sample. All four sample populations showed evidence of fading across the length of the fibres, this is evidenced in Fig. 4 which shows the control sample on the left and the degree of fading observed across one fibre length on the right. This suggests that the orientation of the fibre towards the light source may be a significant factor in fading with fibres that are a combination of within the fabric weave and on the uppermost layer of the weave displaying mixed degrees of fading across the fibre length.

A degree of fading ranging from 4/5 to 1 was noted for all samples as shown in Fig. 5. The result shows that it is not possible to predict the degree of fading that fibres will undergo whether they are within a cotton sample or if they are single fibre filaments.

3.3.1. Cotton samples dyed to a depth of 2.0% owf

Microscopic examinations of both the single fibre and fibres from the cotton sample at the two times of ageing (64 and 128 h) showed little fading in general with most samples achieving a rating of 5 thus demonstrating no fading. There are a number of fibres within all four population groups which have faded considerably and unevenly across the fibre length with fading ratings from 4/5 to 1 as show in Fig. 6. The fading does not appear to be more apparent or prevalent in any one sample.

4. Discussion

Results acquired from the high power comparison microscopy examinations show that fading of fibres on a fabric level and individual fibre level has occurred. However, in every sample, irrespective of whether the latter fibres originated from the aged fabric or from aged individual fibres, all populations displayed a mixed degree of colour fading. This research shows that significant photodegradation can occur as quickly as the equivalent to a weeks exposure to sunlight (64 h) rendering a matching fibre to appear as a non-colour match to the control source. This may cause a matching fibre to be disregarded as corresponding to a control fibre source highlighting the need for caution when interpreting photodegraded fibres.

In addition to inconsistent photodegradation on exposure to sunlight, inconsistencies were also noted in terms of fading across the lengths of some of the fibres. This can be attributed to two factors, non-uniform dyeing or the fact that the fibre may have had mixed orientation towards the light source with part of the fibre being protected by either being within the fabric weave or on the underside away from the light source. In this research the control fibre source did not exhibit uneven dyeing when examined microscopically so it is assumed that the colour fading in the light exposed samples was due to photodegradation rather than uneven dyeing. The uneven colour distribution seen after

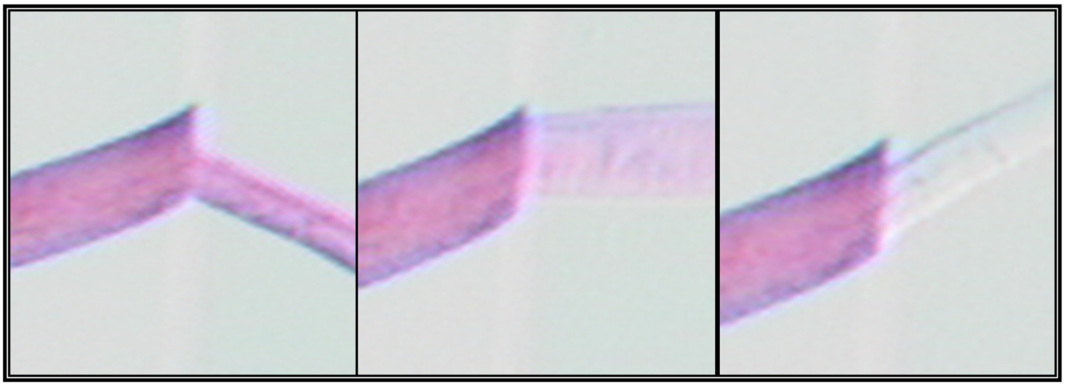

Fig. 4. Variation of fading across one fibre (control fibre on left and single recovered fibre on right).

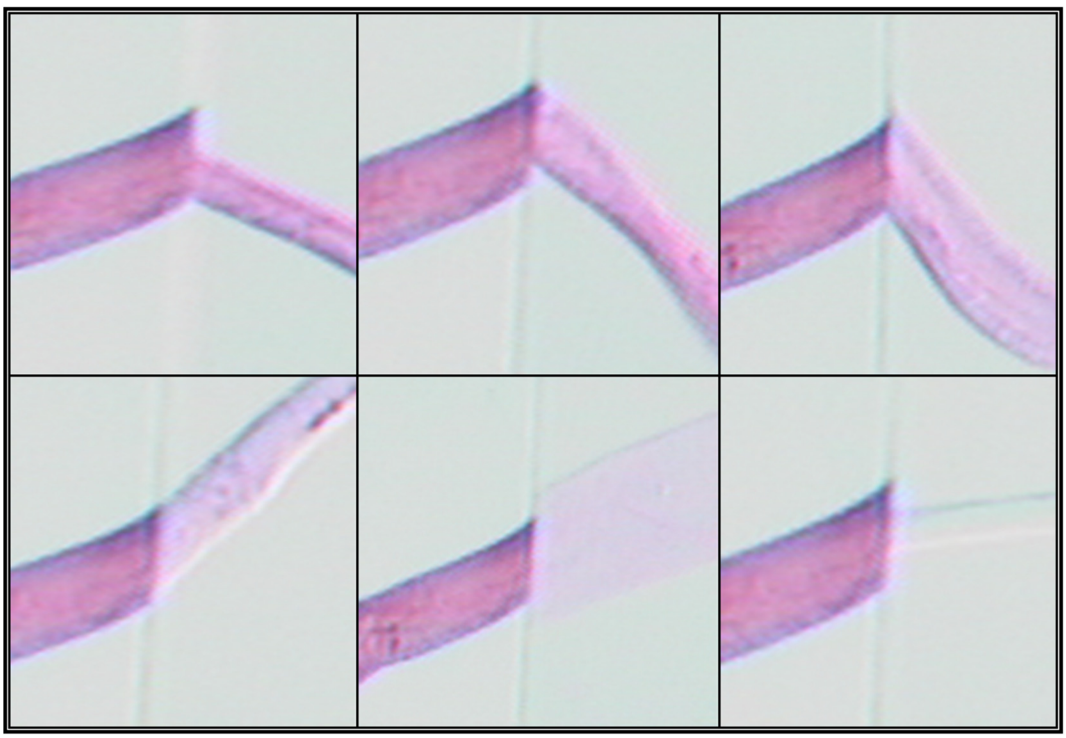

Fig. 5. The degree of fade of cotton samples dyed to 0.25% owf (both single fibre and fibres from fabric samples at both 6 and 128 h) - 4/5 (top-left), 4 (top-centre), 3/4 (top-right), 2 (bottom-left), 1/2 (bottom-centre) and 1 (bottom-right).

exposure to light suggests that the orientation of the fibre surface towards the light plays an important aspect in its colour fading. The inconsistency of colour along a fibre's length may be another factor which could result in missed identification of a corresponding fibre and is another factor the forensic scientist needs to be mindful of.

When investigating both natural fibre types, it could be seen that there were less significantly faded fibres across the population as the depth of shade increased from 0.25% to 2.0% owf. This implies that the lower depths of shade are more susceptible to photodegradation and, therefore, more caution should be employed when interpreting paler fibres.

When a comparison is made between the two fibre types, it appears that the variation in degree of fading is more apparent in cotton than wool samples at the fibre level. In addition, variation across a single fibre was more abundant within the cotton samples suggesting that different fibre/dye combinations will result in differing degrees of colour fading. It is not safe to conclude that cotton may be more susceptible to colour degradation than wool from this research and this is something which would need further exploring.

The results obtained from the visual comparison of the garment samples with its aged fabric counterparts show both the wool and cotton samples exhibit fading after both 64 h (1 weeks sun exposure) and 128 h (2 weeks sun exposure). All the samples showed more fading when exposed for 128 h by ½ degree compared to 64 h. It is important to note that although the degree of fading was consistent across the samples, this is not the case when individual fibres are examined.

This research suggests that any sunlight exposure to an individual fibre will cause photodegradation, a fact the forensic scientist needs to be mindful of when interpreting fibres recovered from a body that has been exposed to an outdoor environment. The scientist may wish to carry out further experimentation on their casework samples if the recovered fibres appear to differ in colour strength to the control sample in order to ascertain a match.

5. Conclusion

This study continues to re-affirm that when fabric is exposed to sunlight photodegradation occurs. It can be further stated that

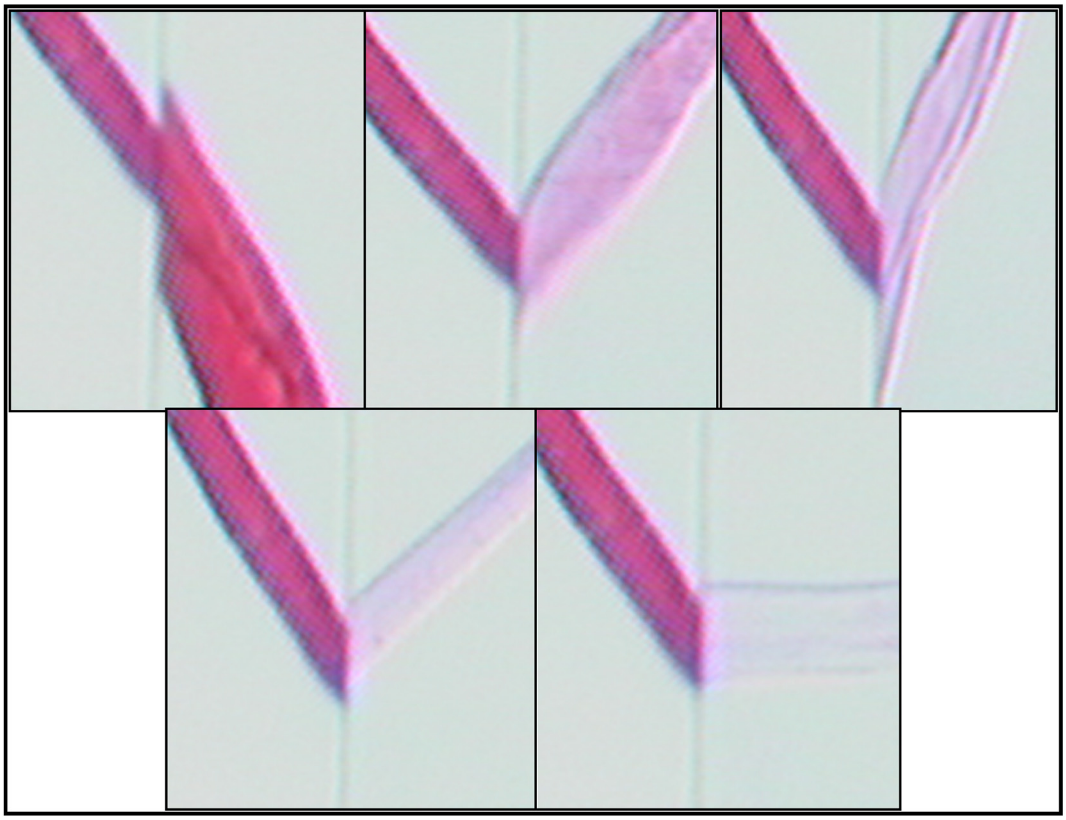

Fig. 6. The degree of fade of cotton samples dyed to 2% owf (both single fibre and fibres from fabric samples at both 6 and 128 h) - 5 (top-left), 3/4 (top-centre), 3 (top-right), 2 (bottom-left), and 1 (bottom-right).

photodegradation also occurs to fibres exposed to sunlight as individual fibre filaments. No major differences were observed for the results obtained for the two fibre types. In general, it was observed that fading was more evident to the fabric or individual fibres dyed at a shade of depth of 0.25% owf.

The photodegradation of fibres has severe implications within the forensic field. When examinations are carried out on fibres which have been exposed to sunlight, there is little research to guide the examiner on how these fibres may have colour faded due to photodegradation. This research demonstrated that fading would occur when a garment is exposed to sunlight or when transferred individual fibres (for example, from a suspects clothing onto the victim) have been left exposed to sunlight. In this respect, when a comparison is carried out between the exposed garment/transferred fibre and a control, the examiner may conclude that the colour of the control fibre does not match the exhibit and wrongly eliminate it from the investigation. This research suggests that if the examiner has a fibre that is the same generic type and appearance but the recovered fibre is paler than the control, there is a possibility that the recovered fibre is a match but has undergone photodegradation due to sunlight exposure.

Acknowledgments

Ken Robinson and Andrew Campbell.

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