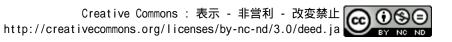
### Studies on Quilt Conservation of Basic Fading Characteristics Derived from Environmental Factors

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| journal or        | 共立女子大学・共立女子短期大学総合文化研究所紀   |
| publication title | 要   |
| volume            | 20  |
| page range        | 1-14  |
| year              | 2014-02   |
| URL               | http://id.nii.ac.jp/1087/00002966/  |



### Studies on Quilt Conservation of Basic Fading Characteristics Derived from Environmental Factors

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#### Abstract

The conservation of works of quilt was investigated from standpoint of evaluation of their fading caused by environmental pollution and light radiation. The characteristics of Japan Industrial Standard blue ribbon in comparison with present and proposed AATCC blue ribbons on exposure of oxides of nitrogen and wavelength sensitivity of AATCC blue wool lightfastness standards under light radiation. Blue ribbons dyed with Disperse Blue 3, Disperse Blue 56 and Disperse Violet 1 were examined by exposure to different times by concentrations of oxides of nitrogen. The results indicate that Disperse Blue 56 may be more appropriate than Disperse Violet 1, because Disperse Blue 56 fading was moderate whereas Disperse Violet 1 faded too rapidly. Moreover, the lightfastness of the AATCC Blue Wool L2 and L4 standards was examined with respect to wavelength sensitivity. Both Blue Wool Standards displayed peak maxima at 245 and 294 nm. The results indicated that UVA and UVB had a significant fading effect, whereas visible light caused fading to a small extent. It is an experimental evidence that the standards would unlikely response to sun light intensity at every wavelength. Specific wavelengths caused Blue wool to significantly fade, suggesting that the total irradiated UV energy may not be an appropriate index.

#### **1. Introduction**

Environmental factors such as air pollution and sun light radiation can cause fading of dyed fabrics of quilt. Specifically, the fading effects of oxides of nitrogen have received attention [1-6], because they are emitted from many sources such as motor vehicles, factories in urban areas, cooking, and heating facilities in the domestic environment. Oxides of nitrogen in cigarette smoke also have the potential to induce fading in some closed environments. Blue ribbon dyed with Disperse Blue 3 (ISO 105-G01 and G04) [7] has been supplied by the American Association of Textile Chemists and Colorists (AATCC) as a standard for evaluating fading caused by exposure to oxides of nitrogen. On the other hand, in Japan, blue ribbon is dyed with Disperse Blue 56 (JIS L 0855) instead of Disperse Blue 3, because the chemical nature of Disperse Blue 3 is associated with some human health risks. Recently, the AATCC reported their examination of Disperse Violet 1 as a candidate dye for a new revised ribbon. In this report, the characteristics of blue ribbon fading were investigated on exposure to oxides of nitrogen to elucidate the fading nature of these dyestuffs, including the time dependency of fading.

Moreover, light irradiation is one of the most influential factors in the fading of dyestuffs [8, 9]. Many approaches have been reported to investigate lighfastness. Most lightfastness experiments were carried out under accelerated conditions using artificial light sources like carbon and xenon arc lamps instead of direct solar radiation. In these experiments, lightfastness standards such as the AATCC Blue Wool lightfastness standards [10], the Japan Industrial Standard Blue Scales [11] and the British dyed-wool light-fastness standards [12] were used to measure the accumulated light intensity. The performance of these blue standards have been examined since the 1950s [13, 14]. A question arose concerning whether a UV narrow band in the sunlight spectral regions may cause greater fading than the visible light region despite its negligible intensity compared to the total solar energy recorded. It was pointed out that measurement of the active wavelengths was necessary to better understand lightfastness testing results [15-18]. However, information given about the wavelength dependence of fading has been insufficient for blue standards. The use of blue wool standards is not limited to dyed fabrics. The standards have also been applied as fading references to evaluate various material deteriorations such as wool

yellowing, fading of water colors, photodamage of human hair and to perform instrumental solar radiation measurements. As mentioned above, sets of blue wool standards have been widely used in light dosimetry to qualitatively evaluate light induced damage. However, they have occasionally failed to give a proper prediction of fading characteristics. Crews [19-21] also found the inadequacy of blue wool standards on their sensitivity in the visible light. Some failures are considered to be due to the lack of knowledge regarding the wavelength sensitivity of blue wool standards. Ideally, the correlation between fading characteristics generated using artificial and natural sunlight would be expected to be consistent. In certain cases, however, total energies emitted by the lamp and by the sun are not well correlated. This may lead to contradicting data because materials adsorb at their defined wavelengths. Measuring the fading or deterioration resulting from different radiant wavelengths is necessary to better understand photodamage. As noted above, most fading experiments were performed under accelerated conditions using polychromatic light sources. However, it is important to understand the photosensitivity of a material to a specific wavelength, because photoreactions generally depend on specific wavelengths that relate to the bonding energy of molecules. Identifying these specific wavelengths is useful when investigating processes that promote material degradation. Therefore, knowing spectral sensitivities is crucial in photodegradation control. Investigations on the wavelength dependence of a given reaction or a process have been applied to biological systems, erythema in human skin, and polymer materials. However, studies related to the fading of dyestuffs and fabrics have been scarce. This may be partly due to limitations of instrumental availability and recognition of serious necessity on their fading evaluation. In this study, the fading characteristics of AATCC Blue Wool lightfastness standards were investigated in terms of radiant energy on exposure to monochromatic light. The sensitivity of the standards to radiant wavelengths with respect to fading was determined. We would like to provide some clues to detailed discussion on some contradicting questions for assessing materials that exhibit sensitivity to both visible and ultraviolet radiations such as wool yellowing and bleaching, some colorants, and natural dyes.

#### 2. Experimental

# 2. 1. Characteristics of fading of blue ribbons on exposure of oxides of nitrogen

#### 2.1.1.Blue ribbons

Blue ribbons of Japan Industrial Standard (JIS), Disperse Blue 56 and AATCC, Disperse Blue 3 were used in the experiments. In addition, blue ribbon dyed with Disperse Violet 1 was obtained by two methods. In the first, it was prepared as a trial specimen dyed in our laboratory. And in the other it was distributed as a round robin specimen by AATCC. Commonly, the substrate used in this experiment is cellulose acetate.

#### 2. 1. 2. Exposure to oxides of nitrogen

Specimens were exposed simultaneously to oxides of nitrogen produced by the chemical reaction of sodium nitrite and sulfuric acid solutions according to the procedure described in ISO 105-G01 and G04 (Figure 1). Two sets of specimens were selected for the experiments. The first set consisted of JIS, Disperse Blue 56; AATCC, Disperse Blue 3; and a trial specimen dyed with Disperse Violet 1 in our

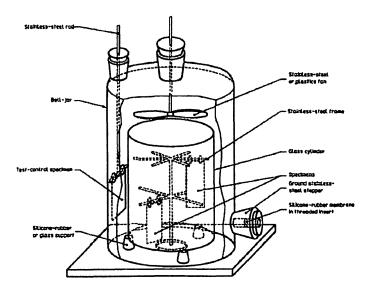


Figure 1. Test apparatus for the exposure of oxides of nitrogen to dyed specimen.

laboratory. The second set consisted of JIS, Disperse Blue 56; AATCC, Disperse Blue 3; and an AATCC round robin Disperse Violet 1 specimen.

#### 2. 1. 3. Grading of color change

The gray scale (JIS L 0804, ISO 105-A02) was used to assess changes in specimen color. Grading at every 1/2 of an integer scale on the gray scale is given in ordinary judgments, and this method used for the second set of specimens. But for the first set of specimens, grading at every 1/4 of an integer scale on the gray scale was applied.

### 2. 2. Wavelength sensitivity of AATCC blue wool

#### 2. 2. 1. Blue Wool Materials

AATCC Blue Wool L2 and L4 lightfastness standards were used in this experiment. As described in the AATCC technical manual, these standards were prepared by blending different proportions of wool dyed with the very fugitive Erio Chrome Azurole BA dyestuff (C.I. 43830) and wool dyed with the fast Indigosol Blue AGG dyestuff (C.I. 73801).

#### 2. 2. 2. Exposure to light sources

Samples were irradiated with monochromatic light using a JASCO CRM-FD spectroirradiator (Figure 2). The spectroirradiator was equipped with a 300 W xenon arc lamp with an ellipse half sphere mirror to collect light emission. Radiation from this source was converted into monochromatic light using a diffraction lattice grating with 1200 lines/mm. The wavelength dispersion was about 2 nm mm<sup>-1</sup> and the slit was set to 2 mm, resulting in an accuracy of about 4 nm for each irradiation wavelength. The specimens were placed in an appropriate position in a sample holder and exposed to monochromatic radiations interspaced by about 16 nm within the 220-700 nm wavelength

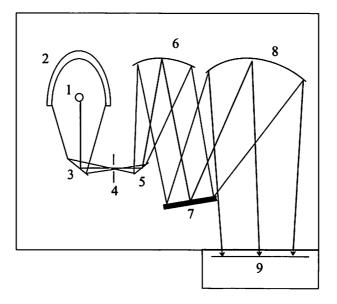


Figure 2. Schematic diagram of the spectroirradiator: (1) Xenonarc lamp; (2) elliptical sphere mirror; (4) slit; (7) diffraction grating; (9) sample holder. (3), (5), (6), and (8) are mirrors.

range. The light intensity in W m<sup>-2</sup> nm<sup>-1</sup> was periodically measured for each wavelength using a photometer.

The photometer was an advanced device which consisted of a thermopile detector attached to the spectroirradiator. Light exposures were carried out at temperatures and relative humidity ranging from 20 to 25°C and from 50% to 70%, respectively.

#### 2. 2. 3. Evaluation of fading

The specimen color change was measured using a Minolta Model CM-3700d color analyzer with a 4×7 mm<sup>2</sup> viewing aperture. The amount of fading was evaluated in terms of color difference and calculated using the following formula proposed by the CIE Committee in 1976:  $\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ , where  $\Delta L^*$  is the lightness-darkness difference,  $\Delta a^*$  is the redness-greenness difference, and  $\Delta b^*$  is the yellowness-blueness difference.

# 2. 2. 4. Compilation of radiant wavelength sensitivity

The accumulated energy (J m<sup>-2</sup> nm<sup>-1</sup>) was calculated in light intensity (W m<sup>-2</sup> nm<sup>-1</sup>) by exposure time for each exposure wavelength, because the light source did not radiate at the same intensity at each wavelength. For a specimen, the relationship between accumulated radiant energy and color difference was examined in a time sequential experiment at each exposure wavelength. Then, a smooth curve was drawn to give a representative fading characteristic. Color difference data under a specified radiant energy was read out from the curve to obtain wavelength sensitivity characteristics at each exposure wavelength.

#### 3. Results and discussion

# 3. 1. Characteristics of fading of blue ribbons on exposure of oxides of nitrogen

Figure 3 shows the gray scale evaluation results with increasing exposure time to oxides of nitrogen for the first set of specimens (ribbons dyed with JIS, Disperse Blue 56; AATCC, Disperse Blue 3; and a trial specimen of Disperse Violet 1). The AATCC Disperse Blue 3 specimen showed moderate fading. On the other hand, the JIS, Disperse Blue 56 specimen showed better fastness to fading, but the Disperse Violet 1 trial specimen showed the less fastness on exposure to oxides of nitrogen. For all the specimens, the fading characteristics against time seem to exhibit a curved, and not a linear relationship. Figure 4 shows the fading characteristics of a same specimen set under a more concentrated condition of oxides of nitrogen. Figures 3 and 4 seem to be consistent.

Figure 5 shows the fading results for the AATCC round robin Disperse Violet 1 specimen compared with the JIS, Disperse Blue 56 specimen on the basis of standard fading of the currently used AATCC, Disperse Blue 3 specimen. The exposure was stopped when fading of the AATCC, Disperse Blue 3 specimen reached the AATCC designated standard for fading.

From the results in those figures, it seems that Disperse Blue 3 is the most suitable dye for a standard ribbon among those tested in this study as shown in Figure 6. Notably, Disperse Blue 3 was used in a former standard ribbon as the Japan Industrial Standard. The currently used JIS ribbon was shown to have more stable fastness. The AATCC-proposed Disperse Violet 1 dye was shown to have very low fastness. Studies on Quilt Conservation of Basic Fading Characteristics Derived from Environmental Factors

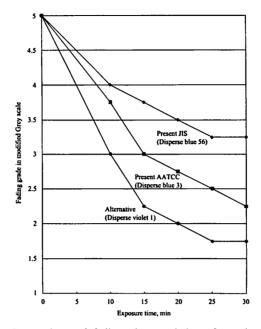


Figure 3. Comparison of fading characteristics of standard ribbons, present JIS (Disperse blue 56), present AATCC (Disperse blue 3) and alternative (Disperse violet 1), under the exposure to oxides of nitrogen produced in a standard diluted method.

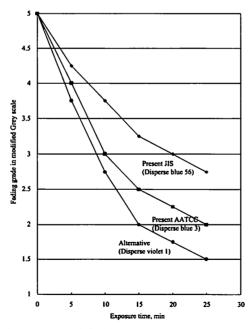


Figure 4. Comparison of fading characteristics of standard ribbons, present JIS (Disperse blue 56), present AATCC (Disperse blue 3) and alternative (Disperse violet 1), under the exposure to oxides of nitrogen produced in a standard concentrated method.

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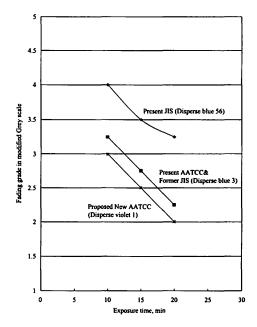


Figure 5. Comparison of fading characteristics of standard ribbons, present JIS (Disperse blue 56), present AATCC (Disperse blue 3) and proposed new AATCC (Disperse violet 1), under the exposure to oxides of nitrogen produced in a standard concentrated method.

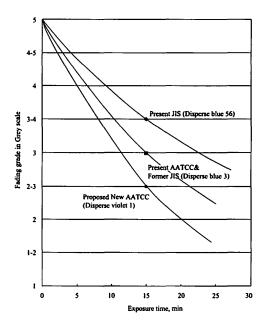


Figure 6. Schematic diagram of fading of standard ribbons, present JIS (Disperse blue 56), present AATCC (Disperse blue 3) and proposed new AATCC (Disperse violet 1), under the exposure to oxides of nitrogen.

Thus judging the standard fading in real time during an experiment would be difficult.

# 3. 2. Wavelength sensitivity of AATCC blue wool

### 3. 2. 1. Color features of Blue wool L2 and L4

Figure 7 shows the reflectance of the Blue wool L2 specimen. With a peak of 27.5% at 450 nm, the reflectance was higher in the 400-500 nm wavelength range compared to other visible light regions, which is a typical feature of blue color. The lowest reflectance was observed to be 3.5% at 615 nm, where the specimen significantly absorbed most radiated light. The difference between the peak and bottom reflectances is large, resulting in a bright blue specimen. Figure 8 shows the reflectance of the Blue wool L4 specimen which displayed a blue color characteristic. However, peak and bottom reflectances in the visible light region were found to be 16.0% at 450 nm and 3.5% at 615 nm, respectively. The difference between these reflectances was small and the peak reflectance intensity was low, resulting in dull blue color on a specimen. 3.2. Fading characteristics of

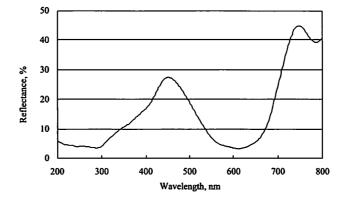


Figure 7. Reflectance spectra of the AATCC Blue Wool L2 lightfastness standard.

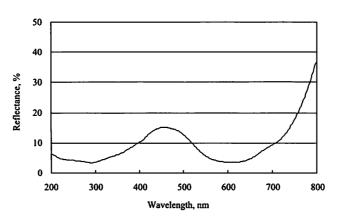


Figure 8. Reflectance spectra of the AATCC Blue Wool L4 lightfastness standard.

Blue wool L2 and L4 standards under a 294 nm monochromatic light As described in the experimental section, the results shown in Figures 9 and 10 were obtained upon specimen exposure to a narrow radiation band isolated from dispersed polychromatic light emitted from a source. In this case, the irradiance depends on the wavelength because the source does not emit wavelengths of equal intensities. Therefore, varying the exposure time at each wavelength accordingly will make the irradiance to be constant. Figure 9 shows the fading curve for Blue wool L2 under a continuous monochromatic radiation at 294 nm. Fading increased with increasing accumulated radiant energy. Instead of a linear fading rate, the resulting fading rate was found to be curved. Figure 10 shows the fading curve for Blue wool L4 under a continuous monochromatic radiation at 294 nm. Blue wool L4 displays the same characteristic curve as Blue wool L2 with respect to continuous radiation. Figure 11 shows the comparison between Blue wool L2 and L4 fading characteristics. According to the AATCC technical manual, standards with a high number are expected to be twice as colorfast as standards bearing the preceding number.

Blue wool L4 is expected to be more colorfast than Blue wool L2 by a factor of 4. The radiant energy was shown to be reduced by a factor of 4 for Blue wool L4 compared to Blue wool L2 (Figure 11).

Indeed, the two characteristic curves appear almost coincidental. It is confirmed that these characteristics may be identical on the monochromatically radiant energy basis. This kind of argument has not been published so far.

#### 3. 2. 2. Wavelength sensitivity characteristics

The wavelength sensitivity characteristic, also known as an action spectrum, is shown in

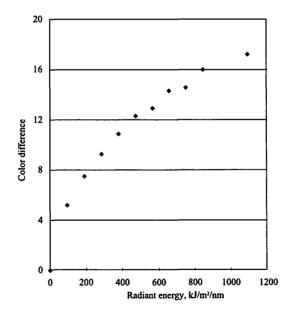


Figure 9. Fading characteristics of the AATCC Blue Wool L2 lightfastness standard under monochromatic irradiation at 294 nm.

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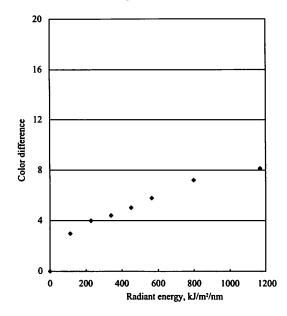


Figure 10. Fading characteristics of the AATCC Blue Wool L4 lightfastness standard under monochromatic light irradiation at 294 nm.

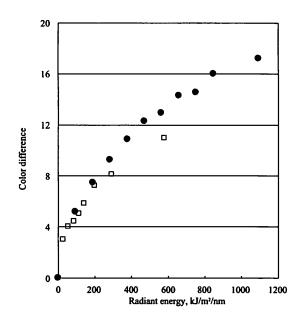


Figure 11. Comparison between the fading characteristics of AATCC Blue Wool L2 ( $\bullet$ ) and L4 ( $\Box$ ) lightfastness standards under monochromatic irradiation at 294 nm as a function of radiation energy. The radiant energy is scaled down by a factor of 1/4 for L4.

Figure 12 for Blue wool L2 lightfastness. In this study, the fading characteristics of the dyed fabrics were compiled when the accumulated radiant energy reached 500 kJ m<sup>-2</sup> nm<sup>-1</sup> for each wavelength in a way as shown in Figure 9. Two intense peaks were observed at 245 and 295 nm in the UVB-UVC range for Blue wool L2 (Figure 12). This suggests that UVA radiation will have significant fading effects, whereas visible light will cause fading to a small extent. This characteristic is consistent with previous results by Crews, who reported that Blue wool L2 was not sensitive to visible light when studying the effectiveness of UV filtering materials. In addition, Yoshizumi et al. suggested that most Blue wool L2 fading under sunlight radiation might be caused by UVA and UVB rays, and that the effect of visible light on fading might be very small [21]. The results obtained in this study provide direct evidence to these previous reports.

Figure 13 shows the lightfastness characteristic of Blue wool L4. As expected, Blue wool L4 behaved with more lightfastness than Blue wool L2. Like for Blue wool L2, two dominant peaks, which are characteristics of fading, appeared a 245 and 295 nm. This lightfastness characteristic is considered to be acceptable because Blue wool L4 was shown to have a consistent wavelength sensitivity with Blue wool L2. Ultraviolet radiation is known to strongly influence the fading of dyestuffs in general. Quantum chemistry also suggests hat the absorbed photo energy causes dye molecules to undergo photodecomposition. Here, two specified wavelengths were found to distinctly cause Blue wool L2 and L4 to fade. Ultraviolet radiation did not exhibit fading effects on Blue wools as a whole, but fading was highly wavelength dependent. Moreover, the absorption of these specimens around 600 nm would slightly affect fading as suggested by the presence of a small peak around 600 nm in Figures 12 and 13. Discussing the photo molecular aspect of these results in detail is not easy, but experimentally important facts were shown in this study. Blue wool L2 and L4 have been widely used as references to monitor accumulated light exposure. According to these results, the AATCC blue wool lightfastness standards are clearly very sensitive to ultraviolet radiation but insensitive to visible radiation. As noted previously, these standards would not be appropriate for assessing materials that exhibit sensitivity to both visible and ultraviolet radiations such as wool yellowing and bleaching, some colorants, and natural dyes Our results may explain why it is virtually impossible to obtain identical degrees of yellowing from two wool fabric specimens irradiated using two different lamps, regardless of the identical extents of Blue wool fading. On the other hand, as opposed to natural dyes, the lightfastness of commercial synthetic dyes mostly depends on their lightfastness in the ultraviolet region. Therefore, Blue wool standards are considered useful in the evaluation of dyed fabrics. The fading of Blue wool L2 and L4 under monochromatic light irradiation was determined in terms of wavelength sensitivity characteristics to discuss the effects of wavelength on fading. The characteristics were examined as a function of radiant energy.

#### 4. Conclusion

As alternatives to Disperse Blue 3, the for-

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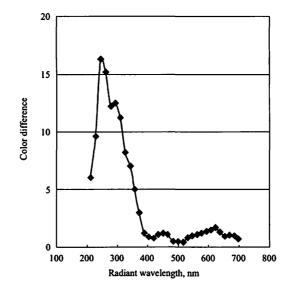


Figure 12. Wavelength sensitivity characteristics for the fading of the AATCC Blue Wool L2 lightfastness standard under a radiant energy of  $500 \text{ kJ m}^{-2} \text{ nm}^{-1}$  at each wavelength.

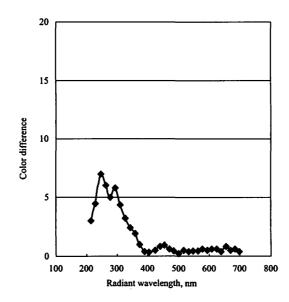


Figure 13. Wavelength sensitivity characteristics for the fading of the AATCC Blue Wool L4 lightfastness standard under a radiant energy of  $500 \text{ kJ m}^{-2} \text{ nm}^{-1}$  at each wavelength.

mer JIS and the current AATCC standard, Disperse Blue 56 and Disperse Violet 1 were examined on exposure to oxides of nitrogen. The results indicate that Disperse Blue 56 may be more appropriate than Disperse Violet 1, because Disperse Blue 56 fading was moderate whereas Disperse Violet 1 faded too rapidly.

The wavelength sensitivity characteristics exhibited peak maxima at 245 and 294 nm for both Blue wool L2 and L4. Therefore, UVA will significantly affect fading, whereas visible light will cause little fading. The photodegradation process was not discussed in detail. These characteristics did not seem to directly relate to their spectral reflectances. We found that irradiation at specific wavelengths caused Blue wool to fade significantly. This result suggests that total irradiated UV energy may not be an effective index. Further research work is necessary to completely understand the nature of Blue wool standards. However, our results present new aspects relative to the fading characteristics of Blue wool, which may provide explanations to controversial fading results.

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