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Natalie Boruvka

Queen's University, Art Conservation Program, 15 Bader Lane, Kingston, ON K7L 3N6, Canada; nboruvka@hotmail.com

The term foxing is used to describe red-brown spots that develop on some paper objects over time. Recent research provides some evidence that foxing results from localized accelerated oxidation of cellulose. In this project, foxed book paper was exposed to accelerated ageing conditions to study potential changes to the foxing stains with ageing. The appearance of the selected stains was described in normal and UV light before, during and after ageing. The UV fluorescence of the stains was also monitored using a fluorescence spectrometer. Accelerated ageing caused the foxing stains to increase in discoloration in normal light and also changed their appearance in UV light. The UV fluorescence of the foxing stains decreased with ageing. Decreased fluorescence was accompanied with a shift of the peak maximum to a longer wavelength, indicating that chemical changes to the stained paper are occurring with accelerated ageing. Observation of stain development, correlated with changes in UV fluorescence, support the foxing formation theory that areas with strong UV fluorescence are precursors to discoloured foxing stains, which exhibit weaker fluorescence. The results of this experiment are considered preliminary since paper from only one book was studied.

Les rousseurs sont des taches rouge-brun qui se développent sur certains papiers au fil du temps. De récentes recherches démontrent que les rousseurs seraient causées par une oxydation localisée accélérée de la cellulose. Pour cette étude, quelques pages d'un livre touchées par les rousseurs ont été exposées à des conditions de vieillissement accéléré pour étudier les changements potentiels attribuables au vieillissement. L'aspect de taches sélectionnées a été décrit dans des conditions de lumière visible et sous rayonnement ultraviolet, et ce, avant, pendant et après le vieillissement. La fluorescence ultraviolette des taches a aussi été vérifiée à l'aide d'un spectromètre à fluorescence. Le vieillissement accéléré a causé une augmentation de la coloration des rousseurs sous un éclairage en lumière visible et a également modifié leur apparence sous rayonnement UV. La fluorescence ultraviolette des rousseurs a diminué avec le vieillissement. Cette diminution a été accompagnée d'une translation de la crête du spectre de fluorescence vers une plus grande longueur d'onde, ce qui indique que le vieillissement accéléré provoque des modifications chimiques dans les rousseurs. Cette étude a démontrée une corrélation entre l'accentuation visuelle des rousseurs et des changements dans leur fluorescence ultraviolette, ce qui appuie la thèse que des zones à forte fluorescence ultraviolette sont précurseures de l'apparition des rousseurs, lesquelles présentent à leur apparition une plus faible fluorescence. Les résultats de cette expérience sont considérés comme préliminaires, car les pages d'un seul livre ont été étudiées.

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Introduction

Foxing stains are a common problem in paper conservation and, despite decades of research, their cause is still not understood.[1] Recently, researchers have been focusing on the connection between foxing stains and other paper discoloration phenomena such as yellowing with degradation, and tideline staining that forms at wet-dry interfaces.[2-7] Based on these newer studies, all three types of staining appear to be related to cellulose oxidation.[2-12]

While cellulose oxidation is known as one of the main chemical reactions in natural paper ageing, it is only recently that foxing stains have been shown to exhibit pronounced cellulose oxidation.[8-12] Studies using infrared spectroscopy have found that foxing stains contain chemical groups indicative of cellulose oxidation such as double and triple carbon bonds and carbonyl groups.[8,9] Researchers propose that localized stains arise in areas of the paper that have more amorphous cellulose chains, the latter being more susceptible to oxidation.[9]

Foxing and Discoloured Paper

General paper discoloration and foxing stains were linked in a study of the optical response of various papers.[12] This study evaluated the optical reflectance spectra (250-1150 nm) of several old, discoloured paper samples and individual foxing stains of one paper sample. They found a striking similarity among the shape of the spectra of all the samples including those of the foxing stains. They also found a continuous evolution in the spectra that corresponded with increasing paper discoloration whether the discoloration was widespread or localized foxing stains. They used Principal Component Analysis (PCA) to evaluate the number of parameters involved in the evolution of the spectra. PCA simplifies a dataset by describing the variance in terms of a small number of significant, uncorrelated variables (principal components), although it does not identify what exactly these variables are.[12] The PCA results indicated the presence of two principal components. The first component represented about 92% of the total variance and showed a strong correlation with the degree of paper discoloration. The authors believe these results indicate a common mechanism that causes

both widespread discoloration of paper and foxing, which could be cellulose oxidation, as others have proposed.

Foxing and Tideline Stains

Stains that result on paper at a wet-dry interface are commonly referred to as tidelines. In a literature review of water-stained cellulosics, Hutchins speculated that foxing occurs by the same browning mechanism as tidelines.[2] This idea was revived by Ligterink *et al*. in their investigation of the spotting and discoloration found in 100 different books.[3] They proposed that staining, including foxing, and general discoloration of paper occur by the same mechanism. In the case of foxing, they suggested that local condensation or "condensation points" in the book can lead to discoloration by a wet-dry interface mechanism. The formation of condensation points would be influenced by humidity, temperature, paper porosity and other irregularities in the paper. More recently, researchers have studied tideline stains on paper produced in the laboratory.[5-6] Experiments have shown that, like foxing, localized cellulose oxidation occurs in tideline stains.[5-6] Although they admit that more research is still required to fully understand the formation mechanism of tidelines, they suspect that the formation mechanism of tidelines is related to that of foxing stains.

UV Fluorescence and Paper Discoloration

UV fluorescence is also another common characteristic shared by foxing stains, tideline stains and naturally yellowed paper. Choisy *et al*. studied the UV fluorescence of 154 foxed paper samples (18^{th} to 20^{th} century).[8] Among the 154 samples, the fluorescence spectra for the foxing stains typically had a single peak emission between 420 nm and 440 nm with an excitation of 365 nm. The authors believe that this indicates a common fluorescent chemical structure among all the foxing stains in all the samples.

A study was conducted by Pedersoli *et al*. to characterize the UV fluorescence of paper at a wet-dry interface.[13] They found increased UV fluorescence in the tideline compared to areas above and below the tideline. The tideline spectra contained a single emission peak at 440 nm with excitation at 254 nm and 340 nm. The spectra were similar to those previously obtained for foxing stains[8] and artificially aged papers.[4] Pedersoli *et al*. suggest there is a common degradation mechanism among naturally and artificially aged paper, foxing stains and tidelines at wet-dry interfaces.[13]

UV Fluorescence and Stain Development

In UV light, the fluorescence of foxing stains can vary in colour from white to yellow and orange. In general, fluorescence appears to be most intense in spots that are not visible or barely visible in normal light, while foxing that has the deepest colour in normal light exhibits little or no fluorescence under UV light. Many researchers have proposed that UV fluorescence is related to the development of foxing.[4,7,8] In the earliest stages, spots or "foxing precursors" will show the most intense fluorescence, but as they develop over time, the fluorescence will decrease as discoloration, visible in normal light, increases. The relationship between foxing formation and UV fluorescence has never been verified experimentally.

The same relationship between discoloration development and UV fluorescence has been observed in paper yellowing and tideline formation. Pedersoli *et al*. conducted a study to relate the browning of paper from artificial ageing to changes in the UV fluorescence.[4] New samples of a cotton linter paper and a bleached chemical wood pulp were put under specific ageing conditions. With ageing, the UV fluorescence initially increased and then levelled off or decreased over time. Colour analysis of the paper samples showed a shift in colour to yellow after ageing for both samples. They suggest that the pronounced discoloration and UV fluorescence seen in foxing may be due to locally more degraded cellulose in paper.

Tidelines in their earliest stages of formation fluoresce in UV light, but do not show any visible discoloration in normal light, which is similar to the theorized foxing precursor.[5,6] Studies have shown that if a sample of paper exhibiting such a tideline is put under accelerated ageing, brown discoloration visible in normal light will develop after ageing accompanied by a visual decrease in UV fluorescence.[5,6]

Outline of this Study

The effect of accelerated ageing on pre-existing foxing stains on paper was considered for the present study. Foxed book paper was subjected to accelerated ageing (80°C, 65% RH) for 23 days and selected stains were observed in normal and UV light and measured with a UV fluorescence spectrometer. Since accelerated ageing had been previously shown to induce tideline stain development and paper yellowing, its effect on existing foxing stains and potential precursors was of great interest. This experiment was the first to study changes to foxing stains on paper under accelerated ageing.

Materials and Methods

Foxed Book Paper

Foxed paper from one book was selected for this experiment. This allowed for the selection of a sufficient number of foxing stains for the investigation, all originating on the same type of paper. The experiment was limited by the fact that only one type of foxed paper sample was examined, but still provides useful preliminary results.

The book was printed in letterpress type on both sides of a handmade laid paper. There was no indication of date on any of the pages. The book was printed in Italian, and therefore, presumed to be Italian in origin. The title page read "OMELIE di S. Gio. Grisostomo." The paper was analyzed using polarized light microscopy, various spot tests and Fourier transform infrared spectroscopy (FTIR). The microscopy results showed that the paper was made from bast fibres, such as flax, indicating

that it is rag paper. The pH of the paper was near neutral. The size used on the paper was not identified. Spot tests for rosin, alum and starch were all negative. The FTIR spectrum of the paper (collected with a Nicolet FTIR Spectrometer AVATAR 320 FT-IR equipped with a Golden Gate Attenuated Total Reflection (ATR) single pass diamond) did not include any protein peaks that might indicate the presence of a gelatin size. The paper might date from the 18th century to the early 19th century based on its manufacture, fibre type and neutral pH.[14]

Selection and Classification of Stains for Monitoring

The spots that were monitored over accelerated ageing were divided into the following four groups based on the degree of staining:

- None (unaffected areas), 24 spots selected.
  Unaffected areas that showed no staining in normal light and no visible fluorescence in UV light.
- Weak Foxing, 25 spots selected.
  Spots that were not visible to barely visible in normal light and fluorescent in UV light.
- Moderate Foxing, 27 spots selected.
  Spots that were visible in normal light and fluorescent in UV light.
- Intense Foxing, 26 spots selected.
  Spots that were visible in normal light, darker in colour than moderate foxing, and with weak fluorescence in UV light.

The spots selected for each group were all from the same 12 pages of the book. The unaffected areas served as a control group to ensure that any changes observed were unique to the groups that exhibited foxing.

Accelerated Ageing

The 12 pages of foxed book paper with the selected foxing stains were aged in a temperature and relative humidity chamber (DESPATCH LEA 1-69) set to 80°C and 65% relative humidity following the ISO standard ISO 5630-3 1996, for a total of 23 days. It has been previously shown that the rate of accelerated ageing of paper is increased when the paper is aged in stacks instead of individual hanging sheets.[15,16] The stacked paper configuration was chosen for this experiment in order to obtain the greatest amount of ageing in the relatively short ageing time of 23 days that was allotted for the experiment. The pages were stacked in the original order they appeared in the book and placed between six pages of the book paper at the top and bottom. The entire pile of paper was sandwiched between pieces of polyester webbing and two pieces of Plexiglas. The paper was aged in the Plexiglas sandwich, which was placed on a rack in the ageing chamber.

At 5, 10, 15 and 23 days, the paper was removed from the chamber and left at ambient conditions overnight. All the testing was conducted the following day and the paper was returned to the chamber in the same configuration.

Observations in Normal and UV Light

The selected spots for all groups were examined before, during and after ageing using the following methods. In normal light (fluorescent room lights and the light from a desk lamp with an incandescent bulb), the colours of the spots were scored using a custom foxing colour scale (**Figure 1**). The scale was created from foxing stains found on the book paper, with 0 being an unaffected area of paper and 5 being the darkest foxing stain observed in the book. A brief description of the appearance of the spots was recorded and the paper was photographed with a digital camera with tungsten lighting. Since the foxing stains were much smaller than the port of the colorimeter available, colour was only assessed visually by one observer, against the custom foxing colour scale.

The spots were also examined in darkness using a UV light stand (CIE Design Limited UV Vertical Luminaire) with two UV longwave blacklight tubes that emit in the range of 355 to 360 nm. A brief qualitative description of the perceived colour, intensity and appearance was recorded.

UV Fluorescence Spectroscopy

The UV fluorescence of the foxing stains and unaffected areas were measured with an in-house assembled, fiber-optic based fluorescence spectrometer.[17] It used a UV-LED light source (Nichia Inc., Southfield, MI) for excitation at 373-393 nm and an Ocean Optics SF2000 spectrometer (Ocean Optics, Dunedin, FL). The spectrometer has a charge-coupled detector (CCD) operating with a 100 ms signal integration time.

The head of the fibre optic probe was positioned perpendicular to the paper at a distance of approximately 0.5 cm. The light source created a circle of illumination with a diameter of 0.3 cm. The paper was positioned so the spots were centered in the circle of illumination created by the light source to collect the fluorescence spectrum. The fluorescence spectrum data was collected from 300 nm to 1000 nm using OOI Base 32 software.

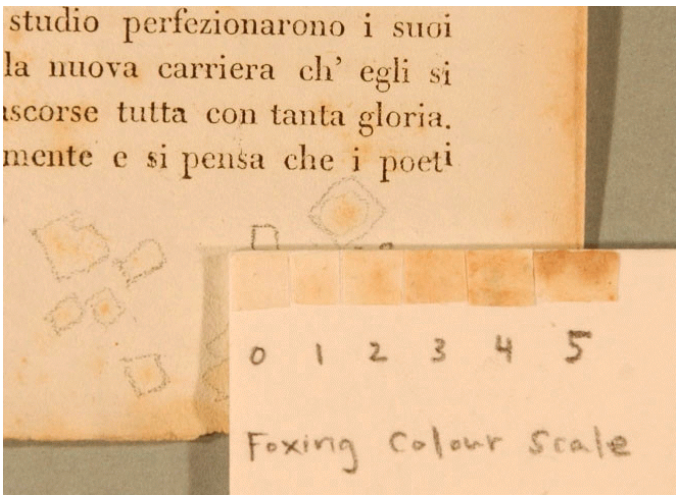

Figure 1. Custom foxing colour scale from 0 (unaffected) to 5 (dark foxing stain).

Statistical Analysis of UV Fluorescence Data

Statistical analysis was carried out using the R software environment.[18] To visually assess the maximum fluorescence and corresponding wavelength across both time and foxing groups, line graphs depicting sample averages against time were created. 95% confidence intervals for the averages among the samples that underwent accelerated ageing were also plotted using error bars.

The distance or amount of overlap between two confidence intervals may indicate significant differences; however, this approach has been shown to be a poor substitute for formal hypothesis testing.[19] Consequently, hypothesis tests were performed to determine whether the differences in the sample averages of maximum fluorescence and corresponding wavelength across foxing groups were statistically significant, or simply due to random variation.

With three foxing groups and five time points, the design called for numerous hypothesis tests. As a result, two standard methods were adopted to address the issue of multiple comparisons. The first, known as Fisher's least significant difference, was to perform a preliminary overall test for differences in averages across foxing groups.[20] Due to the repeated observations over time, the overall test used was the F-test from repeated measures ANOVA (Analysis of Varience). Provided that the F-test indicated a significant difference, Welch's t-tests were performed to compare individual pairs of foxing groups. The Welch's t-test used a non-pooled estimate for variance with the null hypothesis: "foxing level group averages are equal" and alternative hypothesis: "foxing level group averages are unequal." The second multiple comparison technique employed was Bonferroni's adjustment, where the t-test p-values were multiplied by the number of tests.[20] A p-value less than 0.05 was considered indicative of a statistically significant difference.

Results and Discussion

Observed Changes in Foxing Stains in Normal and UV Light with Accelerated Ageing

Changes Observed in Normal Light

The results of this experiment showed that it was possible to induce foxing stain development in foxed book paper exposed to accelerated ageing conditions of 80°C, 65% RH over 23 days. Many of the spots became darker in colour as indicated by an increased colour scale score. **Table I** summarizes the degree of colour change that was observed for each group based on the customized foxing colour scale. As seen in **Table I**, some of the spots with weak foxing that were not visible before ageing became more visible in normal light after ageing. Accelerated ageing also caused the colour of most of the spots with moderate and intense foxing to deepen. The intense foxing spots showed a smaller degree of change compared to the moderate foxing spots. This might be expected since these are the more developed stains. The unaffected areas did not change in appearance in normal light over the 23 days of accelerated ageing.

Changes Observed in UV Light

Spots that became more visible in normal light also changed in appearance in UV light with accelerated ageing. These changes were often from white to yellow and yellow to orange fluorescence. Some spots with moderate and intense foxing developed orange and orange-brown centres in UV light with ageing that corresponded with the areas of the spots that were more visible in normal light. In UV light, some intense foxing stains appeared fainter and duller with ageing and became difficult to see. Meanwhile, the overall appearance of the unaffected areas in UV light did not change with accelerated ageing.

The changes that were observed in the foxing stains in UV light agree with a popular foxing formation theory in the research literature.[4,7,8,13] In general, the perceived colour in UV light changed from white to yellow to orange with accelerated ageing. Weak foxing spots were of particular interest in this experiment since they represented the foxing precursors defined in the foxing formation theory. These areas were selected because they showed strong UV fluorescence with little to no staining in normal light. After accelerated ageing, many weak foxing spots that were initially barely noticeable did become more visible in normal light.

The qualitative observations of accelerated ageing on the foxing stains are similar to the results obtained for studies in which tideline stains on paper were exposed to accelerated ageing.[5,6] In those experiments, if a few drops of water were used to create a wet-dry interface in a paper sample, upon drying, a ring fluorescent in UV light would appear, but little to no discoloration would be visible in normal light. Exposing the samples to accelerated ageing (80°C, 65% RH for 24 days[5] or 80°C, 50% RH for 28 days[6]) caused the fluorescent rings to develop into brown tideline stains visible in normal light. With ageing, the UV fluorescence of the rings changed from blue to yellow and the intensity, after an initial increase, decreased and eventually disappeared.[6]

Researchers have proposed an explanation for the relationship between paper discoloration and UV fluorescence. In general, oxidation introduces double bonds in cellulose that can form a conjugation system capable of absorbing light.[1,6] Initially, a short conjugation system will absorb in the UV range and fluoresce in UV light.[1,6] With further oxidation of the cellulose, the conjugation system extends in length and begins to absorb longer wavelengths.[1,6] Eventually, the system starts to absorb visible light causing discoloration in normal light to appear.[1,6] This theory fits with the foxing formation theory and the foxing stain development observed in this experiment. It also attributes the UV fluorescence and visual discoloration of various paper browning phenomena, including foxing, to cellulose oxidation.

Table I: Visually-assessed Changes in Colour Scale Score for Monitored Foxing Stains Exposed to Accelerated Ageing.*

Initial Foxing Level	Number of Spots Examined	Observed Change in Colour Scale Score** after Accelerated Ageing	Number of Spots with Observed Change
Weak (Spots that were not visible to barely visible in normal light and fluorescent in UV light)	25	No change	8
		Perceptible change (0.5 unit increase)	11
		Noticeable change (unit increase greater than 1.0)	6
Moderate (Spots that were visible in normal light and fluorescent in UV light)	27	No change	3
		Perceptible change (0.5 unit increase)	5
		Noticeable change (unit increase greater than 1.0)	19
Intense (Spots that were visible in normal light, darker in colour than moderate foxing, and with weak fluorescence in UV light)	26	No change	5
		Perceptible change (0.5 unit increase)	9
		Noticeable change (unit increase greater than 1.0)	12
None (No staining in normal light and no visible fluorescence in UV light)	24	No change	24

* Ageing conditions: 80°C, 65% RH over 23 days.
** Colour scale score was assessed visually by comparison to the custom foxing colour scale shown in **Figure 1**. The scale was created from foxing stains found on the book paper, with 0 being an unaffected area of paper and 5 being the darkest foxing stain observed in the book.

UV Fluorescence Spectroscopy

The shape and location of the fluorescence peaks are similar among all the foxing stain groups and the unaffected areas of paper. A typical UV fluorescence spectrum obtained for samples in this experiment contains one fluorescence peak which occurs at around 550 nm using an excitation source of 383 nm. **Figure 2** shows fluorescence spectra for an intense foxing stain at 0, 5, 10, 15 and 23 days of artificial ageing. The peak emission occurs at around 550 nm, a longer wavelength compared to the UV fluorescence spectra previously obtained for foxing stains (420-440 nm, $\lambda_{excitation}$= 365 nm; 460nm, $\lambda_{excitation}$= 395 nm),[8] artificially aged paper (445-450 nm, $\lambda_{excitation}$= 365 nm)[4] and tidelines (440 nm, $\lambda_{excitation}$= 340 nm).[13]

Two main trends were found in the UV fluorescence spectra of foxing stains exposed to accelerated ageing. The first was that the fluorescence of the foxing stains decreased with ageing, as visible in **Figure 2**. This decrease is illustrated graphically in **Figure 3**, which shows a plot of the average maximum fluorescence for each group against ageing time. The decrease is more evident in the foxing stains (weak, moderate and intense foxing) compared to the unaffected areas exposed to accelerated ageing. This suggests that the chemical changes within the foxing stains that occur with accelerated ageing do not occur to the same degree in unaffected paper.

UV fluorescence appears to be a significant feature in foxing development. The stains studied in this experiment were initially grouped based on qualitative observations in normal and UV light with the assumption that foxing stain development was inversely related to UV fluorescence. The results of UV fluorescence spectroscopy help to verify this relationship. In

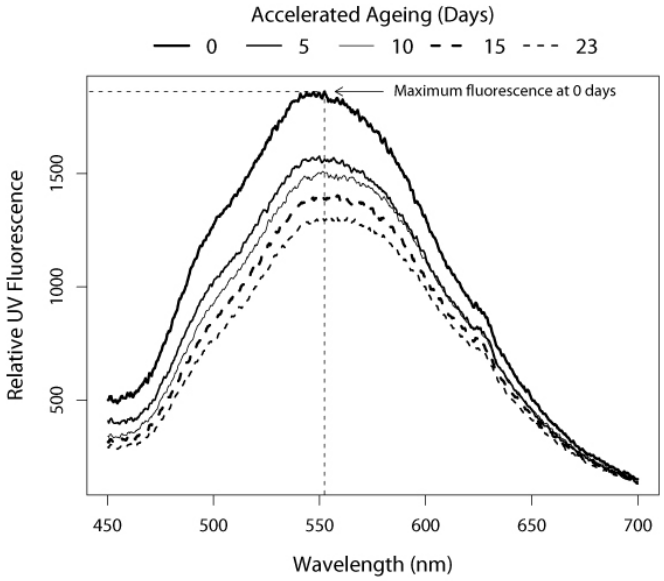

Figure 2. UV fluorescence spectra for an intense level foxing stain over 23 days of accelerated ageing.

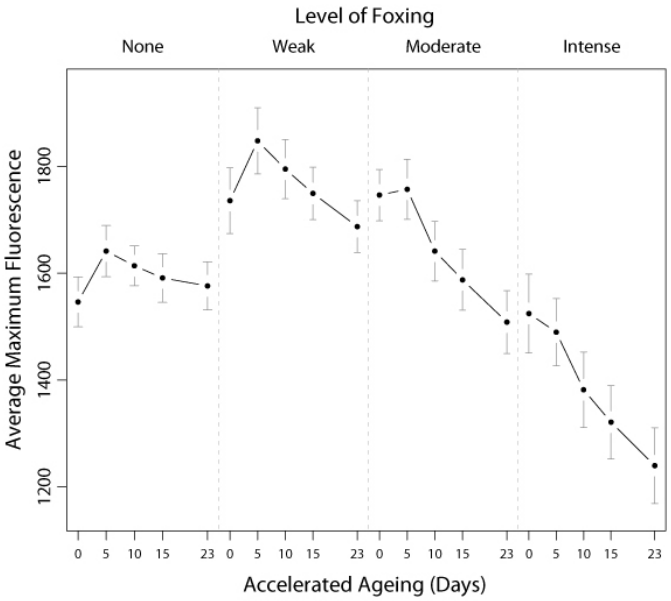

Figure 3. Average maximum fluorescence for foxing levels (none, weak, moderate, intense) against accelerated ageing time in days.

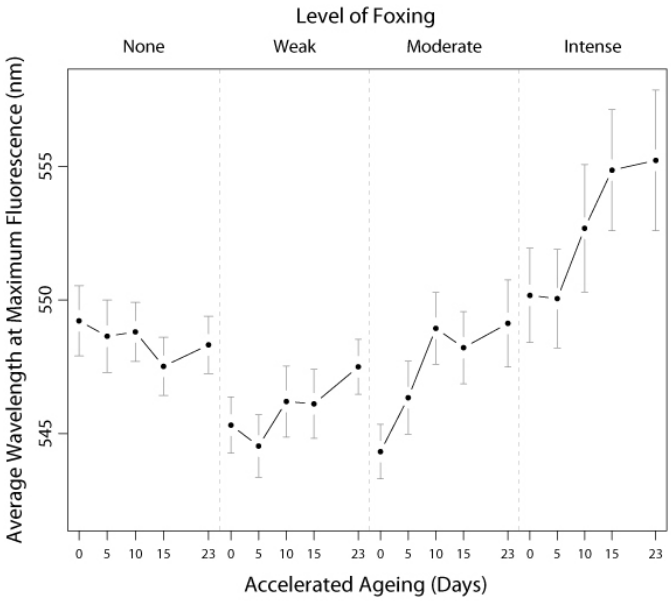

Figure 4. Average wavelength at maximum fluorescence for foxing levels (none, weak, moderate, intense) against accelerated ageing time in days.

Figure 3, the level of fluorescence of the groups are positioned as expected with the weak foxing group showing the highest fluorescence, intense foxing the lowest fluorescence, and moderate foxing an intermediate level. It is interesting that the graphs of weak, moderate and intense foxing levels, placed side by side, show a continual decrease in fluorescence. This could represent the fluorescence of a foxing stain from its earliest stages (weak foxing) to full stain development (intense foxing).

Previous studies involving accelerated ageing of paper have shown that accelerated ageing causes an initial increase in UV fluorescence in paper.[4] This might explain the increase in fluorescence seen in **Figure 3** from 0 to 5 days of accelerated ageing for the unaffected areas and weak foxing groups. There also appears to be a steeper drop in UV fluorescence for the moderate and intense foxing levels with accelerated ageing. This suggests the rate of decrease in UV fluorescence is greater in more developed foxing stains.

The second pattern that was found in the UV fluorescence spectra of the foxing stains was that the maximum of the UV fluorescence peak shifts to a longer wavelength as a function of accelerated ageing. This increase is illustrated by plotting the average of the wavelengths that achieved maximum fluorescence for each foxing level against accelerated ageing time in days (**Figure 4**). The increase is most apparent for the moderate and intense foxing stains.

While decreasing UV fluorescence in the foxing stains was anticipated to occur with accelerated ageing, the increase in UV peak wavelength was an unexpected discovery. This also indicates the occurrence of chemical changes within the foxing stains with accelerated ageing. If increasing UV peak wavelength, like decreasing UV fluorescence, can be considered a feature of more developed foxing stains, it is interesting that the position of the qualitatively classified foxing levels correspond accordingly. At 0 days, the weak and moderate foxing group averages are around 545 nm while intense foxing begins at 550 nm (**Figure 4**). Generally, with ageing, the increase in wavelength appears to be the greatest in the more developed stains with moderate and intense foxing.

The observed decrease in fluorescence and increase in peak emission wavelength of the foxing stains with ageing might also be explained by the proposed relationship between paper discoloration and UV fluorescence previously described.[1,6] With ageing, the extension of conjugation systems in the cellulose of the foxing stains causes the absorption of longer wavelengths of light. This change could result in an increase in peak emission wavelength as well as an overall decrease in the level of UV fluorescence, as observed in this experiment.

Statistical Analysis

The repeated measures ANOVA F-tests indicated that the average maximum fluorescence and the average corresponding wavelength observed over time were significantly different among the foxing groups ($p < 0.0001$). As a result, t-tests were performed to assess differences between each pair of groups. Instead of comparing averages at any one-time point, the t-tests compared the average *decrease* in maximum fluorescence and the average *increase* in the wavelength at the maximum fluorescence from day 5 to day 23. A p-value less than 0.05 in the t-tests is indicative of a statistically significant difference.

The t-tests showed that, with the exception of the moderate versus intense foxing, all of the groups were significantly different in terms of the average decrease in maximum fluorescence (**Table II**). In terms of average increase in wavelength, only the differences between none versus weak ($p = 0.0375$) and none versus intense ($p = 0.0016$) levels of foxing were found to be statistically significant (**Table III**).

Table II: Bonferroni-adjusted p-values* of Pairwise Tests for Comparing Decrease in Maximum Fluorescence from Day 5 to Day 23.

Foxing level	None	Weak	Moderate
Weak	0.0005	—	—
Moderate	< 0.0001	0.0046	—
Intense	< 0.0001	0.0324	> 0.9

*A p-value less than 0.05 is indicative of a statistically significant difference.

Table III: Bonferroni-adjusted p-values* of Pairwise Tests for Comparing Increase in Wavelength at Maximum Fluorescence from Day 5 to Day 23.

Foxing level	None	Weak	Moderate
Weak	0.0375	—	—
Moderate	0.0867	> 0.9	—
Intense	0.0016	0.51	0.4667

*A p-value less than 0.05 is indicative of a statistically significant difference.

The statistical analysis showed a significant difference between the unaffected paper and foxed paper in all but one of the pair wise comparisons. Thus, in general, the hypothesis testing verified that foxing groups had significantly greater fluorescence decrease and wavelength increase at maximum fluorescence with accelerated ageing compared to unaffected areas of paper.

Conclusions

This experiment is the first to study the effects of accelerated ageing on foxing stains. The results show that accelerated ageing caused foxing stain development in one type of foxed book paper. Accelerated ageing also appeared to affect the UV fluorescence of the foxing stains studied. The foxing stain fluorescence decreased with ageing and the peak also shifted to longer wavelengths. These changes indicate the occurrence of chemical changes within the foxing stain that take place simultaneously with foxing stain development in normal light (increased visible stain colour). The relationship between the chemical changes and the development of the foxing stains is supported by the fact that areas of unaffected paper, also exposed to accelerated ageing, did not show the same degree of change in appearance in normal light or in their UV fluorescence spectra compared to the foxing stain groups. Since this study only looked at foxing stains from one type of paper they are considered preliminary.

The effect of accelerated ageing on the foxing stains in this experiment can be compared to studies of artificially aged paper and tideline stains on paper.[4-6] Like these studies, the sequence of stain development appeared to begin with an initial increase in fluorescence in UV light followed by discoloration visible in normal light and an eventual decrease in UV fluorescence. The results agree with the theory of a common formation mechanism among foxing, paper yellowing and tideline stains.

A number of previous studies suggest the discoloration in foxing occurs through localized accelerated cellulose oxidation.[8-12] Presumably cellulose oxidation in foxing stains is increased by accelerated ageing, however, further research would be required to verify which chemical reactions cause the development of foxing stains and the associated changes in UV fluorescence.

Researchers have used FTIR in the past to study foxing stains and have found chemical groups indicative of cellulose oxidation.[8-10] It would be interesting to compare FTIR spectra of foxing stains before and after accelerated ageing. This could potentially link the development of foxing with an increase of cellulose oxidation products.

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