IN SEARCH OF A SUITABLE COATING FOR PYROGRAPHY

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Abstract:

This paper presents the results of an experiment made to examine the discolouration of pyrography, exposed to natural light aging, after coating it with one of two traditional surface finishes. Strips of wood material made of English sycamore (Acer pseudoplatanus) were 'scorched' in a controlled manner at various temperatures to produce different shades from light to dark. This method produced consistent and comparable colour scales for the purpose of testing. Samples were then coated with an oil solution, shellac, or left uncoated and exposed to natural light aging for 110 days/nights. Overall, the sample coated with the oil solution returned the lowest colorimetric colour differences for segments 'scorched' at 350°C and above. Yet, from a visual perspective, via microscopy, it was found that the use of either coating was beneficial for the longevity of the surface 'scorching', in comparison to the sample left uncoated. Neither coating seemed to retard fading for pyrography 'scorched' at lower temperatures. However, it must be considered that the use of either of these treatments will eventually reduce contrast in the image as the coatings darken and yellow further in natural light.

Key words: pyrography; surface coatings; colour change; oil; shellac.

INTRODUCTION

Pyrography and poker work are largely considered to be the generic names for a collection of techniques, used to make pictures and designs by 'scorching' a receptive surface to various shades of brown with a hot tool. Although objects can be found made of other organic materials in museum collections, such as leather, paper and velvet (Millis 2004), this paper deals with pyrography when applied to a wood substrate. Wood was clearly the most popular support for this work throughout history, and it is still much favoured today. Fig. 1(a) pictures a pyrography panel by Joseph Smith, c. 1820. Thought to be made of sycamore, it is after an original painting by Willem Drost (1633-1659) dated 1654. However, this panel might well have been worked from the mezzotint engraving published by William Pether (c. 1738-1821) on 1 August 1768, which is also shown in Fig. 1(b). Pether made engravings of a number of paintings, attributed at the time to Rembrandt van Rijn (1606-1669). Until the end of the eighteenth century, the Drost painting was attributed to Giorgione (d. 1510) (Bikker 2005).

a	*b*

Fig. 1
(a) 'Portrait of a Man with a Plumed Beret', by Smith c. 1820. Photograph by Susan M Millis (b)
The mezzotint print, by William Pether, 1768, AN841924001 ©The British Museum.

Contrary, perhaps, to popular belief, in a previous article (Millis 2013) it was shown that uncoated decoration made by pyrographic methods is subject to significant fading when exposed to direct solar

radiation, which has the potential to dramatically reduce the aesthetic appeal in a few short months if left unchecked. This is also dependent on the species, density, cut, and moisture content, of wood selected as a support, and the temperature at which it was made. There are certain factors governing how the pyrographic image might be seen to deteriorate. Perhaps, one of the main drawbacks is caused by the way a light-coloured wood surface oxidises on exposure to light, producing yellow-coloured deterioration products in the lignin fraction, particularly. Many of these are thought to be ortho and para quinonoid structures (Feller 1971, Hon 1991). For further explanation of this issue, it is important to note that at a microscopic level, and especially when made at low temperatures, pyrography does not affect all of the surface molecules to the same degree, as can be seen in Fig. 2. This is because of the difference in thermal reactivity between molecules. Therefore, as illustrated by the arrows in the image, there are still areas that can be oxidised by light in the expected way. The question here is can light-coloured pyrography be thought to be fading where, in truth, the development of these structures in the molecules unaffected by heat is effectively obscuring it?
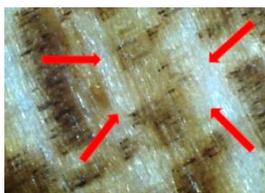
Fig. 2.
A lightly 'scorched' surface at x400 magnification.

Further to this, carbonyl groups are often a main feature in chains made of conjugated double bonds and are generally considered to be the main chromophoric group found in the discolouration of some traditional surface coatings as well. As they form more and more conjugated double bonds, the colour of these chromophores becomes stronger, thus absorbing energy at increasingly longer wavelengths in the visible spectrum rather than the ultraviolet. For further clarity of this point, Feller (1971) draws the reader's attention to acetone, which is colourless CH_3COCH_3, diacetyl, which is yellow $CH_3COCOCH_3$, and triketopentane, which is yellow-orange $CH_3COCOCOCH_3$. This example shows how the addition of just one carbonyl group in a conjugated chain can cause the molecule to respond to a longer wavelength. Thus, pyrography 'scorched' at low temperature settings and protected with a surface treatment, might also be disguised by this discolouration occurring in the coating. This will leave the pyrographic artist contending with not only that their work fades but also that parts of the wood yellow simultaneously and if the work is coated, changes occurring in the coating could potentially render their work almost indistinguishable, in a short space of time.

Surface Coating
The application of a surface coating to any artwork is a very personal decision. Much is dependent on how the artist visualizes the final object. For example, for a dark pyrographic, framed work, where most of the surface is 'scorched', there would be little need to retard the photo oxidation of the bare wood. Therefore, there would be several finishing options for the artist to consider. Yet, in the current author's case, the objects are free standing so any coating application needs to withstand regular handling. Recommendations, from practitioners, can be found in the literature for incorporating resins derived from polyurethane, alkyl and acrylic resins (Poole 1995), as well as wax paste and varnishes containing UV inhibitors (Irish 2010). First, however, the overall question must be answered, to finish or not to finish?

OBJECTIVES
To help make that choice, this paper investigates the application of two simple surface coatings, to see if they offer any benefit for the longevity of pyrography artwork, during exposure to direct solar radiation filtered through window glass. Research examining the light resistance of coated samples has not been published previously in academic circles. Therefore, this study offers a contribution to the available knowledge of pyrographic surfaces.

METHOD, MATERIALS AND EQUIPMENT
Wood samples
The term 'samples' in this case, refers to strips of wood material supporting surface colour change as a direct result of heating with a hot tool. Samples made from English sycamore (*Acer pseudoplatanus*) were examined in this project.
The sycamore wood was sawn into sheets averaging in size 405mmx205mmx1.2mm (longitudinal by radial by tangential). They were abraded with P320 carbide paper, followed by 00 'flour' glass paper, to a

smooth surface. Assessment was made by touch. Moisture content of 8.4% was determined using the oven dry method as defined by BS EN 13183-1:2002, and density calculated at 631kg/m^3, based on the oven dried material.

Three wood strips per sheet were 'scorched' at a range of temperatures from 200°C to 450°C with incremental changes of 25°C. The 'scorching' method was the process used in previous work that utilised a temperature controlled stylus, which was driven from side to side in a smooth and linear fashion at a uniform speed, leaving an impression on the surface. Each temperature segment was 40mm wide and, a minimum of 20mm deep. This method produced consistent and comparable gradient scales for the various temperatures and one untreated section to act as a control. All samples were stored in the testing environment to equilibrate with the conditions for 14 days. The scales were then individually cut from the sheets and prepared for use (Millis 2013).

Guides to coating
The coating solutions considered in this research were traditional; linseed oil and shellac. These were chosen to represent the type of wood finish likely to have been used on pyrographic artefacts in the past, for protection.

Shellac
The links with shellac are grounded in furniture history and conservation. Lewis (1979) and Hahn (1994) both advised using it to protect objects of historical American pyrography. The panel shown in Fig. 1(a) was originally coated with a plant resin. However, UVA fluorescence also detected a quantity of shellac covering the central area, possibly put into place during a past conservation treatment. When the coatings were removed it became clear that it had given the piece fair protection, as the very gentle shading forming the facial details was still detectable with the naked eye. Previously, this shading had been concealed by the coatings.

Advantages
Shellac is relatively easy to apply. It is available in different grades and colours. It should remain reversible, though time promotes a gradual reduction in this property (Rivers and Umney 2003).

Disadvantages
Shellac discolours with light exposure, which will enhance the effect of yellowing observed in the plain surface of light-coloured wood. Upon removal, the polar solvents used will affect the pyrographic image, causing some inevitable colour loss (Millis 2012).

Linseed oil
The use of an oil to coat contemporary pyrography, was recommended to the current author by a colleague (Muradian 2004), as a successful method of protection, which prompted the original study. Furthermore, Walsh (1992) clearly encouraged her readers to use furniture oil to clean and protect historic objects of Australian pokerwork. So, there is evidence to show that others have believed oil to be a suitable coating for pyrography. In the experiment described here, linseed oil was selected because of the strong association that it has in both furniture and easel painting history. However, from a conservation perspective, oil would not usually be considered appropriate for coating works of art.

Advantages
Oil is easy to apply, and miscible with aliphatic and aromatic solvents such as toluene and white spirit. It will saturate the overall colours of the work. It does not appear to cause harm to the pyrographic surface (Millis 2012).

Disadvantages
Linseed oil becomes increasingly darker with light exposure and cross-links severely. It will strongly colour the untouched parts of the image, thus reducing contrast. It is most likely to become intractable from the surface (Williams 2003), or need polar solvents (Rivers and Umney 2003), perhaps dichloromethane (Sawyer 2017), to remove it. These will damage the surface. Winter (1983) noted that carbon pigments retard the free radical drying mechanism observed in the oil vehicle. This was considered to be a quenching reaction caused by free radicals in the carbon pairing with those in the oil. Therefore, as carbonaceous radicals are likely to be involved in the pyrographic surface, the image may become tacky and pick up particulate matter.

Manufacture and application of coatings
The two traditional surface coatings were made from raw materials.

Shellac
100g de-waxed blonde shellac (ground), in 300ml Industrial Methylated Spirits (IMS), VWR, GPR, 98/99% w/w total alcohols. A coating of shellac varnish was applied to two of the 'scorched' samples by brush, followed by a second coating an hour later.

Linseed oil
100ml of boiled linseed oil, in 100ml of Stoddard Solvent, a white spirit/hydrocarbon solvent, VWR, GPR. An initial coating of the oil solution was applied to two of the 'scorched' samples by brush, followed by a second coating an hour later.
Two samples were left uncoated.
Fig. 3, shows part of a sample scale made of sycamore, which was coated with shellac. It was soon to be realised that segments 'scorched' at less than 325°C were completely reversed in the test, and there were only small differences in colour between those 'scorched' at the highest temperatures. Therefore, as an aid to clarity in the results presented here, they are not mentioned further. In this image, each segment of interest is marked with the temperature of execution, showing clearly the influence that heat has on the colour of wood. The segment marked with brackets is shown here for colour information only.

Fig. 3.
A colour scale produced of English sycamore, coated with shellac, showing the effect of heating on wood colour.

Three colour scales, one uncoated, one shellac coated and one oil coated, were stored in complete darkness until the end of the testing process, to act as overall control samples.

Natural light aging
The purpose of this test was to replicate the effects of light exposure on pyrographic decoration in a usual interior situation. To that end, the term natural light aging refers to exposing the samples together day and night, through window glass, on a south-westerly facing window sill for 110 days/nights. At location 51.680, -0.802, and an altitude of 204.0m above mean sea level. Exposure took place between June and October.

Why use natural light?
Whereas it might be thought that using an accelerated aging process would produce faster and more reproducible data, it is largely dependent upon the light source available. Searle (1994) states quite clearly that…'the type of light source used in durability testing significantly influences the stability ranking of materials as well as the mechanisms and type of degradation'. Many tests were conducted, during the overall research project, under a metal-halide UVA lamp (https://www.hoenlegroup.com). However, the results were not comparable to those produced in natural light.
The display was based on British Standards Institute BS EN ISO 105-B01:1999 and set up as follows: The standards were met as closely as possible. The wood sample colour scales were divided into three even-width vertical strips with a pencil and mounted together on foam core board by covering the centre section with a strip of card, lined with MT20 ultraviolet protective film (http://www.sun-x.co.uk/products/mt20-dark-neutral-uv-window-film), which was secured in place over each sample with two brass tacks (Fig. 4, Cover A). The left and right thirds of each sample were exposed to natural light for 50 days/nights. Then the right third was covered with lined card in the same way (Cover B) and the left third was exposed for an extra 60 days/nights. Therefore, for each sample, the right third was exposed for 50 days/nights, the left third was exposed for 110 days/nights and the centre third was not exposed to light (Millis 2013).
Light exposure for the 110 day period was quantified in lux as 10,326,000, by monitoring an in situ LightCheck® dosimeter (http://keepsafe.ca/LightCheckHome.htm), and was based on the results of four trials. No attempt was made to measure UV radiation, and the control of temperature and relative humidity were beyond the scope of the study (Millis 2013).

Colour measurement

As the colour of pyrography is heterogeneous, for accurate colour comparison to be made, it was essential to make sure that the colorimeter was sited at the same place each time a reading was taken. This was because of the influence wood grain has on the surface colour. To aid in this, a template was made from Perspex. It consisted of a shallow tray with built-up sides and was 45mm wide in the centre, just large enough to insert the sample. Another piece of Perspex fitted closely inside, into which three 22mm holes were bored; one to the left, another to the right and a third in a central position. These allowed enough room for the tip of the colorimeter to be sited flush with the sample. Paper rulers were adhered to each rim of the template, which permitted pin-point accuracy to be observed. Only readings made in the same position of the same sample were compared (Millis 2013).
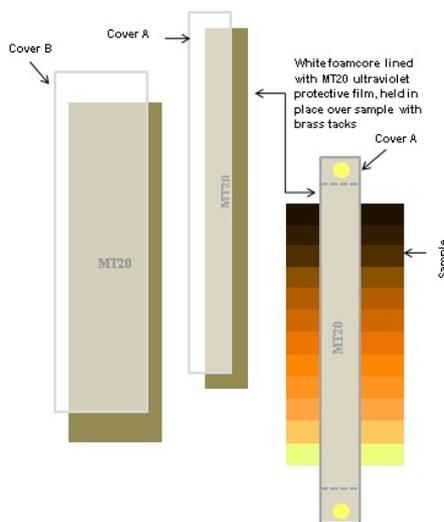
Fig. 4.
Natural light aging, sample preparation plan (Millis 2012, Millis 2013).

A Konica Minolta Chroma Meter CR-300 was used to monitor changes in the surface colour of the 'scorched' samples. The measuring head of the instrument incorporated an 8mm measuring area, was index set to use D65 illumination and calibrated to a 2° observer angle. Calibration was performed at the start of each measuring session. Measurements were taken from the left side, right side and the centre section, making a total of 36 readings for each sample scale, covering the full twelve segments of colour change. The colorimeter, fitted with a 22mm light protection tube (CR-A33a), was index set to take three tristimulus measurements and then calculate a mathematical average for the segment. The *CIE L*a* b** (1976) colour space was selected for interpretation. For this system *L** represents lightness and is on a scale of 100, where *L** = 100 is white and *L** = 0 is black. The *a** measurement characterises the green (- *a**) red (+ *a**) axis and *b** the blue (- *b**) yellow (+ *b**) axis. All measurements taken were absolute. Total colour change was calculated from these measurements by using the following equation (1) (for full method see BS EN ISO 105-J03:1997):

$$\Delta E *_{ab} = \sqrt{(\Delta L*)^{2} + (\Delta a*)^{2} + (\Delta b*)^{2}}$$ (1)

$$Where \quad \Delta L* = L *_{T} - L *_{R}$$

$$\Delta a* = a *_{T} - a *_{R}$$

$$\Delta b* = b *_{T} - b *_{R}$$

R = Reference sample (before exposure)
T = Test sample (after exposure)

Before exposure began the colour parameters were determined for each segment, with relevant examples presented in Table 1(a). Subsequent measurements were mathematically compared to these data sets in order to gain an accurate insight to the photochemical stability of the pyrographic image after surface coating.

RESULTS AND DISCUSSION

The colour changes that took place in the samples were the direct result of exposure to natural light, through window glass, for 110 days and nights. They are presented here in chart form with the accompanying computational colour differences shown in Table 1(b). In these charts, 0 represents no change in colour at all. A difference of just $CIE\Delta E^*_{ab}$ 3 has been determined to be the minimum value of colour change that can be recognised by the human eye (Hon and Minemura 1991, Sundqvist 2004, Millis 2013). The first chart, pictured in Fig. 5, represents the absolute colour differences caused by exposure, at the end of the testing phase (ΔE^*_{ab}).

Table 1

Colour parameters of selected samples before exposure to natural light, with colour difference values recorded after exposure (grey)

Sycamore	Temperature	(a) Colour measurements before exposure			(b) Colour differences after exposure			
		L^*	a^*	b^*	ΔE^*_{ab}	ΔL^*	Δa^*	Δb^*
Uncoated	**Control**	78.43	6.70	16.78	11.94	-1.91	0.09	11.79
	325°C	52.20	11.88	20.79	21.52	18.07	-2.09	11.05
	350°C	39.71	10.80	13.63	24.49	17.68	2.03	16.83
	375°C	35.73	7.72	8.56	20.64	13.07	4.37	15.36
	400°C	35.72	5.97	6.11	19.34	11.94	4.68	14.47
Shellac	**Control**	73.78	7.59	22.48	9.28	1.25	0.26	9.19
	325°C	50.43	12.62	24.48	22.53	19.54	-2.11	11.02
	350°C	36.81	12.22	16.28	27.39	20.42	1.69	18.17
	375°C	30.83	9.27	9.23	24.35	15.02	5.53	18.35
	400°C	28.81	6.68	5.62	19.94	11.78	6.15	14.87
Oil	**Control**	75.81	8.90	26.57	9.90	-3.18	1.7	9.22
	325°C	39.56	13.30	17.53	22.33	16.30	0.74	15.24
	350°C	31.78	9.22	8.40	19.14	11.39	5.09	14.51
	375°C	28.24	4.42	2.93	14.21	7.31	6.20	10.49
	400°C	27.94	1.88	0.73	9.25	3.76	5.43	6.47

On first examination, it is clear that significant colour changes occurred in all samples. Starting with the control segments (not treated with heat), it is evident that the sycamore wood experienced colour change directly, showing an overall colour change value (ΔE^*_{ab}) of 11.94 for the uncoated sample, 9.28 for the shellac coated sample, and 9.90 for the oil coated sample. There is visual evidence to show that most of this occurred by a marked increase in yellowing, for all three samples, which is supported by the data presented in Table 1(b) (Δb^*). Yet, it is also important to point out that the addition of the coatings had changed the optical properties of the samples before exposure began, increasing the yellowness ($+b^*$) by 34% (shellac) and 58% (oil), while there were also differences in the L^* and a^* axes. This can be seen in the 'opening' data, Table 1(a).
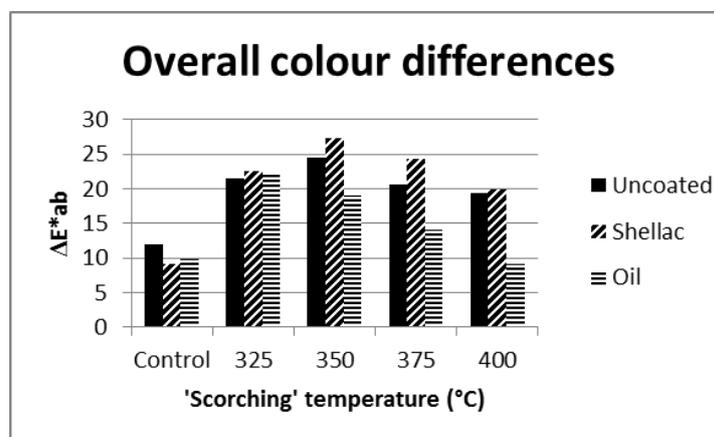
Fig. 5.
Overall colour differences for the samples, at the end of the testing phase.

For the segments 'scorched' at 325°C, marked fading was observed for all samples, which amounted to a rise of 35% of the original lightness for the uncoated sample, 39% for the shellac coated

sample and 41% for the oil coated sample. Changes in lightness peaked for the segments 'scorched' at 350°C, increasing to 45% (uncoated) and 55% (shellac coated), whereas it dropped to 35% for the oil coated sample. These results are shown in Fig. 6, which maps the changes that occurred in the lightness parameters ($ΔL^*$). This trend continued, with the shellac coated sample providing the largest colour differences throughout. However, colour change dropped notably, for the sample coated with the linseed oil solution, returning an overall $ΔE^*_{ab}$ of 9.25 for the segment 'scorched' at 400°C, compared with 19.34 (uncoated) and 19.94 (shellac coated). This result points to an increase in performance for the oil solution used to protect the surface colour.
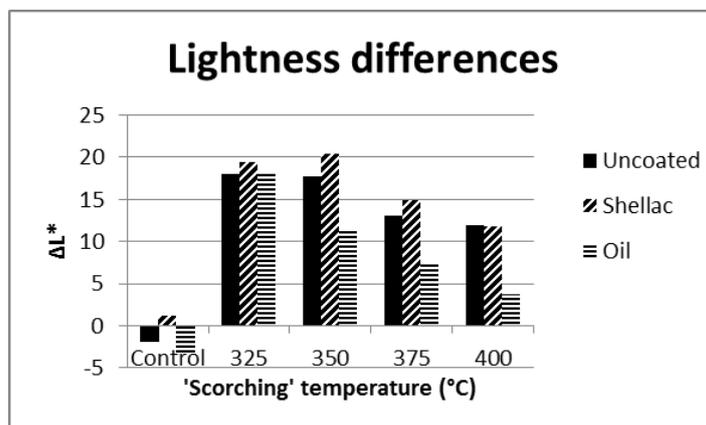
Fig. 6.
Overall lightness differences for the samples, at the end of the testing phase.

Experimental study has demonstrated to the author that, when choosing a surface coating, a completely clear, 'water-white', non-yellowing varnish, or lacquer, is unlikely to be able to provide adequate protection for fugitive (unstable) colouring matter. The UV transmission of glass is affected by the source and the age of the glass. However, it is important to remember that UV rays in excess of 310nm can penetrate it and cause serious, long-term, deterioration to organic and light sensitive materials (Ketola and Robbins 1994). Whereas, UV shielding can be provided by incorporating ultraviolet absorbers, hindered amine light stabilisers, and inorganic nanoparticles, or by glazing with conservation glass or film, from an aesthetic point of view, these will mainly help to prevent a light-coloured wood surface from yellowing. Though, it must be acknowledged that much successful research has been achieved with them, when used to protect a natural wood surface (for a review of the research, see Evans *et al.* 2015). However, according to Passauer *et al.* (2015), these additives are often inadequate to afford reasonable protection to dark-coloured wood surfaces, and in the case of thermally modified timber (TMT), they have been known to accelerate discolouration when compared to unprotected samples. In an earlier paper (Millis 2013), it was elucidated that pyrography is likely to be the result of several processes, developed between migrating extractive substances and the coloured reaction products from the thermal degradation of wood components, which combine in caramelisation and Maillard reactions, thus, forming a crust-like substance on the surface. Consequently, this crust will contain a numerous diversity of labile molecules at various stages of charring and carbonisation (Shafizadeh 1984). These molecules will absorb light strongly. Certainly, it could be speculated that, if products such as furfural or hydroxymethylfurfural are present in the pyrographic image, the use of inorganic nanoparticles particularly, in a coating, might well cause a photocatalytic reaction to occur (Ghasemi *et al.* 2016), ultimately advancing the fading of the image. However, no research with nanoparticles has been achieved by the current author to date. To offer a good level of protection to a substrate from the UVA wavelength range (315-400nm), any ultraviolet absorber would need to have a bathochromic shift and, thus, would impart a yellow cast to the coating. Yet, even this will not protect the surface from the other, most dangerous, wavelength, which according to Searle (1994) is at 405nm, in the violet region of visible light. This is the optimum wavelength for bleaching of yellow chromophores to occur. Moreover, Kataoka *et al.* (2007), determined that the blue region (434-496nm) of visible light is also capable of penetrating wood and causing bleaching effects of the surface molecules, though, in their tests it was not found responsible for the photodegradation of the underlying layers.

Fig. 7.
The three samples at the end of the testing phase (top) uncoated (centre) shellac coated (below) oil coated.

The three samples are presented together in Fig. 7, where it is clear to see that all of the identified segments have faded. However, though a subjective determination, the yellowing that occurred in the natural wood was darker and more chromatic for the coated samples, particularly for the one treated with the oil solution, at the bottom of the picture. To investigate further, photomicrographs were taken at x400 magnification, of the exposed segments 'scorched' at 400°C, after the coated samples had been gently solvent cleaned, so as not to abrade and remove the surface. These are presented in Fig. 8. Picture (a) represents the uncoated sample, picture (b) the shellac coated sample, and picture (c) the oil coated sample. Examination of these images shows that the surface of both coated samples appeared darker and more saturated than the uncoated sample, which had greyed throughout. This greying is thought to have been caused by the chemical destruction of the carbonaceous aggregates by electromagnetic radiation.
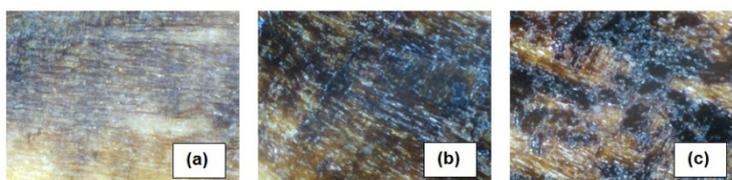
Fig. 8.
The segments 'scorched' at 400°C, at x400 magnification, after exposure (a) uncoated (b) shellac coated (c) oil coated.

Though, the colorimetric data sets for the shellac coated sample did not support it, from a visual perspective, it was determined that both of the surface coatings tested gave some degree of protection to the pyrography, where 'scorched' at temperatures above 350°C. Though, little shielding was apparent for pyrography made at lower temperature settings. While clear, both surface coatings imparted a yellow hue to the samples when applied, and it could be speculated that, as such, the coatings were affording their respective surfaces protection by absorbing the blue region themselves and, thus, reflecting yellow. However, there was no doubt at all that the addition of either coating would eventually reduce contrast in the image by darkening and yellowing further in natural light.

Table 2, presents the overall colour differences seen in the control samples, which were stored in complete darkness for the duration of the testing phase. Examination of the data revealed that dark reactions occurred in both coated samples. However, for the oil coated control segment 5.49 was the difference in the *b** axis, and for the shellac coated control segment, the difference was 2.26. These results determined that the coatings had also yellowed in the dark. Though, it did not seem to affect the pyrography. There is a need for much further work to be achieved in this area.

Table 2

Overall colour differences seen in the control samples at the end of the testing phase

Segment Temperature	Uncoated		Shellac coated		Oil coated	
	$ΔE^{*}_{ab}$	$Δb^{*}$	$ΔE^{*}_{ab}$	$Δb^{*}$	$ΔE^{*}_{ab}$	$Δb^{*}$
Control	1.14	0.78	2.53	2.26	5.74	5.49
325°C	1.33	1.15	3.39	2.86	3.68	3.05
350°C	1.58	1.20	1.76	1.32	1.91	1.37
375°C	1.56	1.06	1.50	1.17	1.50	1.06
400°C	0.53	0.05	1.46	0.80	0.33	0.15

CONCLUSION

The discolouration of pyrography samples applied to English sycamore, and coated with linseed oil and shellac, has been investigated and compared to an uncoated sample, after exposing them to natural light aging for 110 days/nights. Out of the three samples, the linseed oil coated sample returned a consistently lower colour change value, and lower increases in lightness, where 'scorched' at temperatures of 350°C and above. Even though, from a conservation point of view, the use of drying oils would not be recommended, it was determined that linseed oil offered the best protection to pyrography, made at those temperature settings. However, from a visual perspective, the microscopic surface of the shellac coated sample also seemed to be in a superior condition than the uncoated sample, which appeared grey by comparison. This would indicate that shellac also offered some degree of benefit to pyrography, though, in time, both coatings would significantly reduce contrast by contributing further to the darkening and yellowing occurring in the plain wood surface. Neither coating was found to reduce the discolouration occurring in pyrography made at lower temperature settings. It was recognised that there is a need for much further research to be achieved, in the search for the most suitable coating.

ACKNOWLEDGEMENTS

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