

UNDERSTANDING PYROGRAPHY, THE PHOTOCHEMISTRY OF 'SCORCHED' DECORATION

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Abstract:

This paper examines the discolouration of pyrography artwork applied to three different wood species when exposed to natural light. Samples were 'scorched' in a controlled manner at a range of temperatures to produce different shades from light to dark. This allowed comparisons to be made between different wood species and different temperatures. It was elucidated that pyrography is the result of several processes developed between migrating extractive substances and coloured reaction products formed through the thermal degradation of wood components, which combine in caramelisation and Maillard reactions. Each species was shown to react differently. The results confirm that these colours, caused through the 'scorching' process, are extremely sensitive during light exposure. Light induced colour change was more profound for segments 'scorched' at 350°C, particularly for the hardwood species. Overall, samples made of Douglas fir were found to discolour the least during exposure to natural light.

Key words: Pyrography, colour change, kiln brown stain, protein, colorimetry.

INTRODUCTION

The interaction of wood and heat has been cultivated from pre-historical times to the present day. Therefore, it is not surprising to find that the mechanisms at play between them have found application in the world of art. With wood as the substrate and heat as the 'paint', pyrography, also known as pokerwork, has without doubt existed in most civilisations throughout time. This type of work has often been thought of as a folk art, a decorative technique applied particularly to signs, trinkets and utilitarian ware (Pinto and Pinto 1970). Yet, it has also been used to produce artistically competent pictorial panels, predominantly during the eighteenth and nineteenth centuries and it is these pictures particularly that may well present challenging conservation issues in the future (Millis 2012), Fig. 1(a). illustrates a pyrography panel made by Smith c.1829, which is after an original painting by Annibale Carracci (1560-1609), also shown here in Fig. 1(b).



a



b

Fig. 1

a - 'The Dead Christ Mourned', by Smith c. 1829. Photograph by Susan M Millis; b - The original painting, NG2923 The Dead Christ Mourned ('The Three Maries') by Annibale Carracci c. 1604. Presented by Rosalind Countess of Carlisle, 1913. Photograph ©The National Gallery, London.

Although the science of pyrography may be a little known field, thermally modified wood (TMW) has been and is today the subject of much research particularly for improving the stability and durability of wood. One point that these researchers do agree on is that the colour is not permanent when exposed to light (Jämsä and Viitaniemi 2001, Sunqvist 2004, Hill 2006). Contrary to popular belief, the pyrographic image is also fugitive (not light fast), especially where it has been created at low temperatures. It suffers extreme fading in both UV and visible light, with some shades disappearing completely. In order to understand this shortfall it is first necessary to learn more about the process of surface 'scorching' and how heat applied in this way affects the substrate. Even though the chemical reactions caused by pyrography are perhaps very similar, because of the difference in production methods they cannot be described as the same as those occurring in TMW. For example, industrial thermal modification is usually carried out in a low oxygen environment, often incorporating moisture in the form of steam and it has also been modified by using hot oil. Each of these techniques will produce different reaction products and in all cases the wood will be modified throughout the length and breadth of the timber. Pyrography is a surface modification usually produced with a hot tool. In this method a thin char layer is produced on the surface. These differences between the TMW and pyrography are described further in Fig. 2. The images were taken with a digital microscope set at a magnification of x400. Fig. 3 illustrates the tangential face of sycamore, indicating the nature of the surface after lightly 'scorching' with an electrically heated hand tool.

Kiln brown stain

It is known from the work of McDonald, *et al.* (2000) that a condition referred to as kiln brown stain (KBS), a staining which occurs at the fibre evaporation front during the high temperature kiln drying of radiata pine (*Pinus radiata*), is largely the result of migrating sap and extractives that then combine in caramelisation and Maillard reactions. Whereas caramelisation is formed through combining sugars, the Maillard reaction entails the coupling of sugars with amino acids, which through subsequent reactions produces high molecular-weight nitrogenous melanoidins. As the concentration of nitrogen on the surface would already be increased, through free water movement, all that would be required is heat to initiate both of these reactions. However, KBS is often thought to occur just below the wood surface. To clarify this point, McCurdy, *et al.* (2005) first planed the wood surface to remove any tracheids damaged in preliminary cutting. This caused the discolouration to form at the wood surface and allowed the researchers to measure colour change with a surface reflectance spectrophotometer at several stages during the drying process.

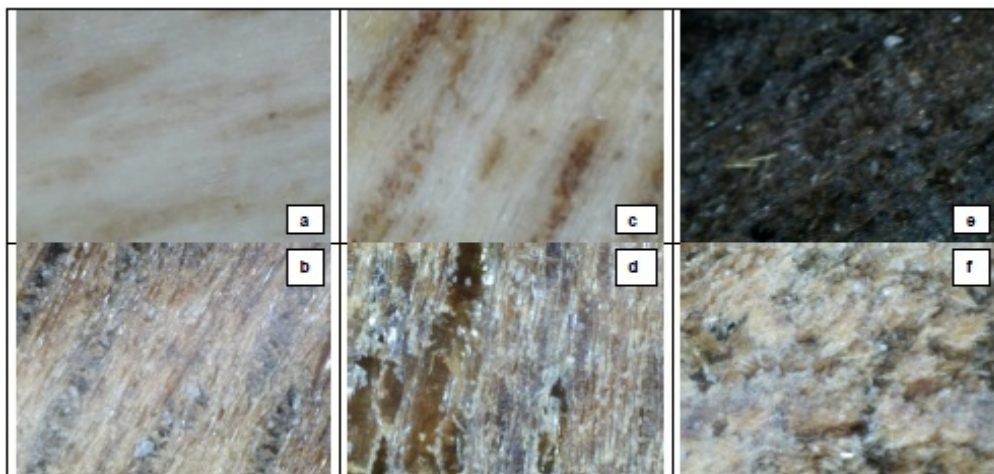


Fig. 2

Images of sycamore and TMW (American birch) wood blocks.

a - tangential face of sycamore 5mm away from transverse face after immersing it end-grain downwards in hot sand (270°C) for three minutes; b - tangential face of TMW; c - tangential face of sycamore 3mm away showing darkening uniseriate and multiseriate rays; d - TMW, the ray cell contents appear to have evaporated; e - the transverse face of 'scorched' sycamore; f - the transverse face of TMW (rough-cut).

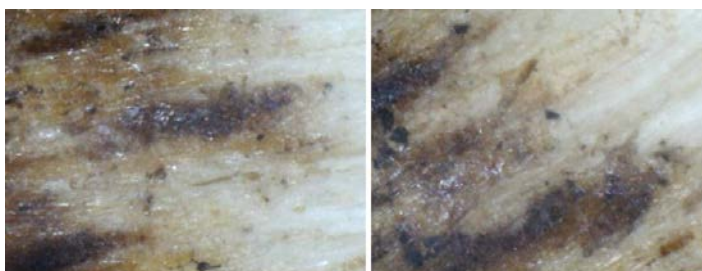


Fig. 3

Lightly 'scorched' tangential face of sycamore, showing the distribution of thermally deteriorated parenchyma cells amid slightly browned fibres.

Protein

Though, it is largely acknowledged that glycoproteins with a high content of hydroxyproline are significant cell wall elements in higher plants, the presence of amino acids and nitrogen in lignocellulosic materials is often underestimated. The middle lamella and primary cell wall ostensibly contain the most glycoprotein and these are the areas that encompass the most lignin at a later stage. The nitrogen content of wood is largely derived from this protein (Dill, *et al.* 1984). Bao, *et al.* (1992) studied a pine extensin-like protein (PELP) located in the active cells of loblolly pine (*Pinus taeda*) in which several amino acids were found. The two with the largest mol-% values were proline and hydroxyproline with 24.04 and 11.47 respectively. They concluded that PELP remained imbedded in the mature wood of loblolly pine years after the tree has been felled and the wood processed. Even though the nitrogen content is low in wood, it would seem that this protein remains inaccessible, being protected by the carbohydrates and lignin. The researchers concluded that retrieval of nitrogen from these proteins may not be viable unless degradation of the cell walls occurs.

Pyrography is such a destructive technique, albeit minor, and on timber it seems to be a similar process, combined with the caramelisation and Maillard reactions occurring in the breakdown products of wood fibres and, particularly, in lignin. By developing in this way, a thin layer is formed on the wood surface, which is largely hydrophobic owing to increased lignification (Millis 2012). In light of the work of Bao *et al.* (1992) and Dill *et al.* (1984) it is feasible to accept that these Maillard reactions do occur in wood. Evans, *et al.* (2004) studied the effects that nitrogen has on the formation of char from biomass, via the Maillard reaction between carbohydrates and particularly proline. They discovered that proline reacts vigorously and accelerates char formation more than other amino acids and at lower temperatures. In conclusion, these researchers confirmed that the Maillard reaction tends to leave increased amounts of nitrogen in the char. It is also important to note that the process of 'scorching' increases the amount of products that can be extracted by solvent application (Pervan *et al.* 2006, Millis 2012). In addition to this, Pervan *et al.* (2006)

record, that in high temperature steam drying, an increased amount of extractives occurs as a result of the hemicellulose fraction breaking down. Having been produced by thermal deterioration, these coloured reaction products contain a large number of free radicals, which may then take part in later reactions involving colour change, by combining with those newly created during light exposure (Deka and Petrič 2008).

Focusing on three wood species, this investigation determines the photochemical issues in practical terms by examining pyrography samples during exposure to natural light.

EXPERIMENTAL

Wood samples

Three species of timber were examined: English sycamore (*Acer pseudoplatanus*), Common apple (*Malus pumila*) and Douglas fir (*Pseudotsuga menziesii*). Prior to manufacture, the wood was cut into sheets, approximately 1mm thick and abraded with P320 carbide paper, followed by 00 'flour' glass paper to a smooth surface. The moisture contents of 8.4%, 7.7% and 7.5% respectively, were determined by the oven dry method as defined by BS EN 13183-1:2002 and thus the oven dry density was calculated at 631kg/m³ (sycamore), 544kg/m³ (apple) and 440kg/m³ (Douglas fir), with the following equation (1).

$$d = \text{mass} / \text{volume} \text{ [kg / m}^3\text{]} \quad (1)$$

The apparatus developed for the heat treatment, shown in Fig. 4, comprised:

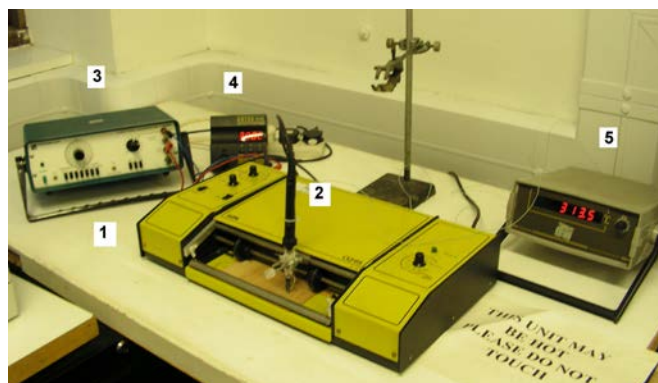


Fig. 4
Sample making apparatus.

1. Chart Recorder. A modified chart recorder where a wood panel was slowly drawn through. The chart recorder pen was replaced by a temperature controlled heating element with a sensing thermocouple placed behind the very tip. The heating element was driven from side to side in a smooth and linear fashion by an external ramp generator.

2. Modified soldering iron with Type K miniature open junction thermocouple inserted in tip. Weight 103g, tip radius (in contact with the wood) 0.20mm.

3. Feedback Function Generator, used to control the action and speed of the modified pen (0.04m/sec).

4. ANTEX 690SD Setting thermometer. The thermometer regulated the temperature of the soldering iron and could be adjusted to any temperature between 0°C and 450°C.

5. COMARK Microprocessor thermometer 6110. A Type K miniature open junction thermocouple was fitted inside the copper sheath of the modified soldering iron and directly connected to this microprocessor, in order to calibrate the running temperature of the tool.

Each wood strip was 'scorched' at a range of temperatures from 200°C to 450°C with incremental changes of 25°C. Temperature segments were 40mm wide and 20mm deep. This method produced consistent and comparable gradient scales for the various temperatures and one untreated section to act as a control. However, the colour differences between the segments, at both ends of the scale, were often difficult to determine easily with the naked eye. All samples were stored in ambient conditions in the testing environment for 14 days. The scales were then individually cut from the sheets and prepared for use. Fig. 5

shows one sample scale made of Douglas fir. In this image, each segment is marked with the temperature of execution, showing clearly the influence that heat has on the colour of wood (Millis 2012).



Fig. 5

A colour scale produced of Douglas fir showing the effect of heating on wood colour.

One colour scale made of each wood species was stored in the dark, to act as overall 'control' samples, until the end of the testing phase.

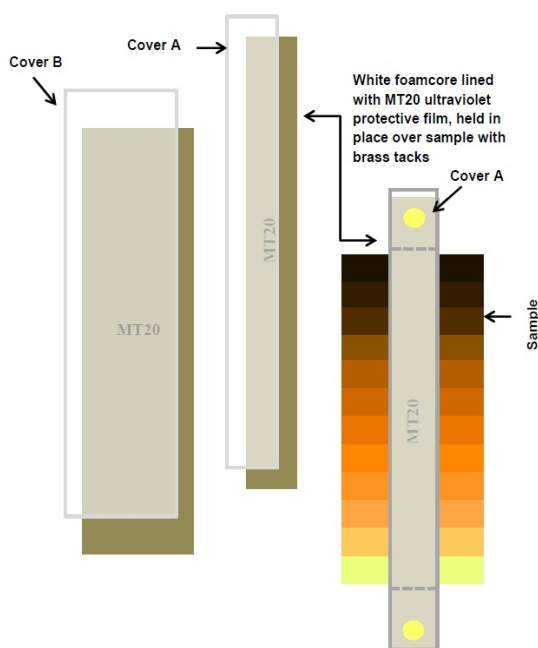


Fig. 6

Natural light aging, sample preparation plan (Millis 2012).

Natural light ageing

The purpose of this test was to replicate/simulate the effects of light exposure on pyrographic decoration in a usual interior situation. To that end, the term natural light ageing refers to exposing the samples together day and night on a south-westerly window sill for 110 days/nights.

The display was based on 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 foamcore board by covering the centre section with a strip of card, lined with MT20 ultraviolet protective film (Sun-X <http://www.sun-x.co.uk>), which was secured in place over each sample with two brass tacks (Fig. 6, 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 to 50 days/nights, the left third was exposed for 110 days/nights and the centre third was not exposed to light.

Light exposure for the 110 day period was quantified in lux as 10,326,000, by monitoring an in situ LightCheck® dosimeter (<http://www.lightcheck.co.uk>), and was based on the results of four trials. Although a certain amount of UV light, over approximately 315nm, would be transmitted through plain window glass, no attempt was made to measure it and the control of temperature and relative humidity were beyond the scope of the study.

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.

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 comprises 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 an overall 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 (proportional blend of three different colour values, which when combined match the shades detected by the human eye) 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 (2) as defined in BS EN ISO 105-J03:1997:

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

Where $\Delta L^* = L^*_T - L^*_R$ (2)

$$\Delta a^* = a^*_T - a^*_R$$

$$\Delta b^* = b^*_T - b^*_R$$

R = Reference sample (before exposure)

T = Test sample (after exposure)

Before exposure began the colour parameters were determined for each segment, with some example measurements presented in Table 1. Subsequent measurements were mathematically compared to these data sets in order to gain an accurate insight into the photochemical stability of the pyrographic image.

RESULTS

For clarity the results presented here map the colour changes of just three segments from each sample; the control segment (untreated with heat) and the segments 'scorched' at 350°C and 450°C. These were considered to give a good representative insight into the changes occurring in the pyrographic image. The colour changes that took place were a direct result of exposure to natural light for 110 days/nights, and are graphically presented here in a chart with an accompanying table. In this chart, 0 states that there is no change in colour at all. A difference in CIEΔE*ab in the order of 3 units is judged to be the lower threshold for the human eye to distinguish colour change (Hon and Minemura 1991, Sundqvist 2004). The black line of data points in Fig. 7, expresses the overall colour changes which occurred in the experiment (ΔE*ab). Early examination of the data shown in the grey section of Table 1 reveals that in some cases the figures seem significantly high. Plotted together in this way, it is simple to see that the segments 'scorched' at 350°C have changed noticeably more than the others, particularly for the hardwood species, returning 24.49 (sycamore) and 25.64 (apple). Absolute colour change for the same segment made of Douglas fir wood, measured the much lower figure of 12.64. The sycamore segment 'scorched' at 450°C also changed more than the other two species. Overall, the smallest colour changes were observed in the sample made of Douglas fir.

Table 1

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

Wood species	Temperature	Colour measurements before exposure			Colour differences after exposure			
		L*	a*	b*	ΔE^*_{ab}	ΔL^*	Δa^*	Δb^*
Sycamore	Control	78.43	6.70	16.78	11.94	-1.91	0.09	11.79
	350°C	39.71	10.80	13.63	24.49	17.68	2.03	16.83
	450°C	34.32	3.69	3.84	13.76	8.35	3.83	10.33
Apple	Control	65.20	6.16	15.93	10.12	7.14	-0.61	8.03
	350°C	41.10	8.34	12.84	25.64	20.52	2.14	16.11
	450°C	28.77	0.39	-0.28	6.06	2.23	3.98	4.15
Douglas fir	Control	67.61	8.89	22.45	3.34	-0.11	-0.99	3.19
	350°C	36.01	7.20	8.44	12.64	9.09	2.26	8.44
	450°C	31.16	0.94	0.55	2.01	0.32	0.98	1.73

Although the colour difference data reveals the amount of colour shift occurring in the samples, it does not provide information referring to the way the colour has changed. To this end, the parameters ΔL^* , Δa^* and Δb^* are often more useful. As the purpose of the experiment was to assess the colour fading of pyrography, the most important of these measurements was ΔL^* , which shows how much the colour has lightened or whether it has in fact become darker. In this case, examination of the grey data points in Fig. 7, and the accompanying data (Table 1), shows that the sycamore control segment became very slightly darker in colour, while the apple control increased in lightness, returning a figure of 7.14. The data for Douglas fir indicated very little change. However, all the segments 'scorched' at 350°C returned significant increases in lightness, particularly for the two hardwoods; 17.68 (sycamore) and 20.52 (apple). To put this into context, these amounts represent rises of 45% and 50% of the original surface colour respectively. By contrast, the Douglas fir segment presented an increase in lightness of 9.09, which equals a rise of 25%. Measurements for the segments 'scorched' at 450°C were 8.35 (sycamore), 2.23 (apple) and 0.32 (Douglas fir). Changes in the a^* and b^* axes can be viewed numerically when comparing the data in Table 1. Overall, this test established that the 'scorched' colour of the Douglas fir sample was the most resistant to natural light by generally exhibiting low colour differences.

Discussion

It is important to remember that the carbonaceous surface, which forms the pyrographic image, is also heterogeneous in keeping with the wood substrate. Therefore, it will contain multifarious molecules at various stages of charring and carbonisation (Shafizadeh 1984). Though these are all likely to become degraded during light exposure, it is feasible to suspect that the molecules will be affected at different rates thus transforming in structure and function. Therefore, in theory, it could be hypothesised that the change in colour caused by the light exposure could effectively explain the changing chemistry of the surface. However, the point is that these shortfalls result in a microscopically and, often, macroscopically diverse surface colour, which might be difficult to fully characterise with a colorimeter. The template used in this study helped to maintain that the instrument was sited in the same position of each sample every time the colour was measured, but differences in the original wood colour could have affected the results shown here. For example, the Douglas fir sample returned the smallest colour change values for all three of the segments evaluated. However, it is also shown in the results that the original wood colour did not lighten, darken or yellow significantly during light exposure. Whereas, the sycamore wood slightly darkened and yellowed, during exposure, and the apple lightened significantly and yellowed.

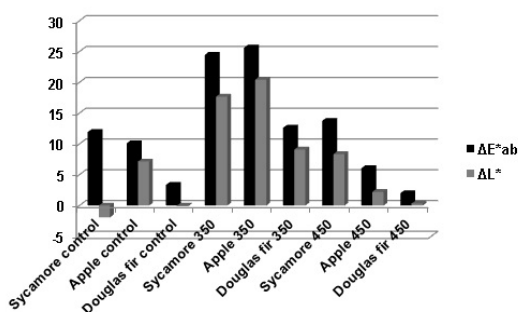


Fig. 7

Black: Absolute colour changes seen in samples after exposure to natural light (ΔE^*_{ab}); Grey: Differences in lightness value after exposure (ΔL^*).

Each wood species also reacts to pyrography differently, ostensibly because of the specific colour and chemistry of the original timber (Millis 2012). Although there are many other contributing factors, such as density, moisture content, fineness of grain and pH value, these differences may well be owing to the presence of a particular extractive, or combination of extractives, in the basic wood structure as explained by Kai (1991). Yet, could this disguise the results? A tristimulus colorimeter works on the basis of measuring overall colour. Therefore, it could be argued that the original wood colour, in this case rather brown, could add to the strength of the measured colour by blending in with the pyrography rather than contrasting against it. Because of these facts, it would seem prudent to employ visual interpretation alongside colorimetry when assessing the fading of pyrography.

The exposed samples are presented together in Fig. 8. Visual examination revealed that all samples were highly affected by the light source, particularly up to the segments 'scorched' at 450°C. All samples also showed strong definition between the earlywood and latewood, which was further enhanced by the 'scorching' process. However, the lower density and, perhaps, the increased lignin content of the Douglas fir indicated that this sample was slightly more affected by the heat overall, which can be seen particularly at low temperatures (Fig. 5). This, in combination with the lower reactivity (usually observed as yellowing) of the Douglas fir timber, as shown mathematically in Table 1 by the control segment, gave rise to less contrast developing between earlywood and latewood. The outcome of this might well be described by a lower mathematical colour change value. The colour of the pyrographic surface of Douglas fir showed to be dull in comparison with the sycamore and apple samples, which had yellowed significantly.



Fig. 8

The three samples after exposure to natural light; sycamore (top), apple (centre), Douglas fir (below) (Millis 2012).

Table 3

Overall colour changes seen in control samples at the end of the testing (ΔE^*_{ab})

Segment	Sycamore	Apple	Douglas fir
Control	1.14	1.03	1.03
350°C	1.58	1.47	0.74
450°C	0.33	0.34	0.43

Table 3, presents the overall colour differences measured for the control samples, which were stored in complete darkness for the duration of the testing phase. Here only very minor changes were observed, which confirms that light exposure is the major influence in the fading of pyrography.

CONCLUSION

The chemistry and photochemistry of pyrography have been investigated, as applied to three wood species. It was determined that pyrography is the result of several processes, developed between migrating extractive substances and the coloured reaction products from the thermal degradation of wood components. By combining in caramelisation and Maillard reactions, a crust-like substance with increased lignification is formed on the wood surface. Each wood species was shown to provide different results both in production of the colour and in the ageing test. It was confirmed that these colours caused through the 'scorching' process were extremely fugitive during light exposure and that these changes were cumulative. Light-induced colour change was more profound when 'scorched' at 350°C, particularly in the hardwood species. Overall, samples made of Douglas fir proved to change the least, demonstrating a greater relative resilience of pyrographic work on that species to light exposure.

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