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SURFACE COATING PYROGRAPHY: A PRELIMINARY INVESTIGATION WITH UV ADDITIVES

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Abstract:

This paper presents the results of an experiment made to examine the photo-discolouration of pyrography, after applying coatings containing UV inhibitors. 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 generated consistent and comparable colour scales for testing purposes. In this test, a sample scale was coated with a 2% solution of Lignostab® 1198, a hindered amine light stabiliser (HALS) pre-treatment, followed by 10% Regalrez® 1126, in white spirit, with a 40% solution of the same type as a topcoat. Both Regalrez® coatings contained Tinuvin® 1130, a UV absorber. The sample was then exposed to natural light aging for 110 days/nights, and compared with uncoated, shellac coated, and oil coated samples. It was found that significant colour changes took place. However, the coatings prevented the development of yellow chromophores, in the wood molecules not affected by heat, leaving the surface brighter and more vibrant than the other samples. Though the coating failed at 33 days, producing defects in the top layer, it continued to protect the wood colour for the full 110 days. However, it did not protect the pyrography.

Key words: *pyrography; surface coatings; colour change; Tinuvin®; Lignostab®.*

INTRODUCTION

Pyrography is undoubtedly one of the world's oldest decorative techniques, yet so little has been written about the chemistry of the reaction products forming the image, and the way these molecules respond to surface coatings and light exposure. The longevity of every image relates directly to the exact conditions and methods of formation, most importantly in this case the species and cut of the wood, and the temperature at which it was made. This observation is supported by Sandberg and Kutnar (2016) when discussing the recent developments in the manufacture of thermally modified timber (TMT)… 'The exact method of treatment can have a significant effect on the properties of the modified wood'… Furthermore, while investigating wood charcoal, Labbé *et al.* (2006) discovered that…'The characteristics of the wood charcoal depend, not only on the wood species, but also on the carbonisation temperature'… It is the temperature that determines whether aliphatic or aromatic molecules are formed on the surface, and aromatic molecules are known to be more stable (Daintith and Martin 2005). Today, it could be speculated that many of the electrically powered tools developed and manufactured for the pyrographic artist, are far too delicate to make a truly lasting impression on a wood surface, particularly if they are temperature regulated.

This was not so in the past. Some two hundred years ago, when pyrography probably gained its highest stature as an art form, artists used simple metal tools, of various shapes and sizes, heated in a charcoal burner, often with asbestos yarn bound handles (Pinto 1960). Thus, there was no heat control as such; these artists had to depend on the length of time the tool was away from the heat source, and work with speed. Consequently, experience was the key element to success. However, there was also another method of working, which seems to have appeared sometime during the 1830s. This technique involved the artist charring the entire wood surface, perhaps to various depths as suggested by Pinto (1960), with a blowlamp or oil of vitriol (sulphuric acid), and then lifting out the lighter parts of the image in relief, using chisels, gouges, knives, abrasive papers, and even fragments of glass. The method was referred to as 'xulopyrography' in the Illustrated Cyclopaedia (sic) of The Great Exhibition of 1851, where the work of Lieutenant Ralph Marshall was described (Anon 1852). Some of Marshall's work can be found in the Pinto Collection at the Birmingham Museum and Art Gallery (https://www.birminghammuseums.org.uk/bmag). Thus, it is likely to be because of these extreme methods of working that some of the pictures have survived to the present day.

Figure 1(a) shows a panel made with this technique, by an as yet unknown artist. It is after an original painting by James Sant CVO, RA (1820-1916), which was then engraved in the mezzotint technique by Samuel Cousins RA (1801-1887). It is most likely that the artist worked directly from the print, rather than the painting, and a copy is also shown here (Fig. 1(b)).

a *b*

Fig. 1.
(a), Pyrography panel by unknown artist, c.1855. Owned and photographed by Fraser Cleminson. (b) 'Speak Lord for thy servant hears', mezzotint, by Samuel Cousins RA, c.1854, © Collection of the Art Gallery of Greater Victoria (AGGV 2019).

In a previous paper (Millis 2013), the surface chemistry of pyrography was discussed, and it was also shown that an unprotected surface supporting the decoration suffers extreme fading when exposed to natural light aging for 110 days. Furthermore, a later paper (Millis 2017), indicated that two traditional surface coatings, in this case shellac and linseed oil, could moderately retard this deterioration, over a 110 day period, particularly when 'scorched' at temperatures of 375^{o}C and above. This trend has continued, and based on the results of many minor tests (unpublished data), the study has moved forward to investigate an idea for a stabilised coating solution to be developed for pyrography. This paper presents the results of a pilot test in natural light, which could be used as a basis for further research in this area.

It is beyond the scope of this article to disclose and discuss fully the science and background of UV inhibitors. For a comprehensive review of these, the author points the reader to the excellent work by Evans *et al.* (2015).

The Products

The photo-oxidation of lignin has long been a hazard for people working in the wood and paper industries. Therefore, it has received much study, but the observations in the area of timber technology have usually related to exterior furnishings because of the phenomenon referred to as 'weathering'. Thus, according to Dendy (2007), and at the time of her writing, much less work had been achieved in the area for indoor woodwork.

Lignostab® 1198

This product, originally from the stable of Ciba® Speciality Chemicals' ultraviolet technology (now under the auspices of BASF), is purported to bind with lignin to prevent photo-oxidation, in light coloured wood. The substance sold as orange flakes, which readily dissolve in water, should be applied to bare wood in a 1-3% aqueous or aqueous/alcohol solution, as a pre-treatment before coating. The company literature also states that Lignostab® can be successfully used to stabilise dye-tinted or micronised pigment-stained wood (Ciba 2009). Figure 2, illustrates the chemical structure for some commercial hindered amine light stabilisers (HALS) (Schaller and Rogez 2006).

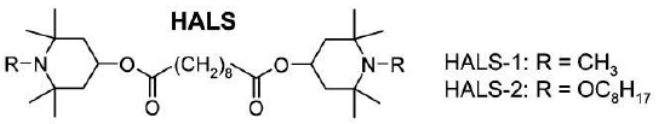

Fig. 2.
The structure of some typical HALS products (Schaller and Rogez 2006).

Tinuvin®

Alongside this product, Ciba® developed a range of additives under the name of Tinuvin®. The author became aware of Tinuvin® during the late 1980s and since then the product technology has evolved extensively. It incorporates a network of ultraviolet inhibitors; some of which prevent the surface coating from yellowing, cracking and generally deteriorating via ultraviolet radiation (HALS); other types help to protect the surface colouration of the timber by absorbing the energy and releasing it as heat (UVA). It has also been noted that there is a synergising effect achievable when combining certain HALS with UVAs in one solution, offering further improved performance (Schaller and Rogez 2006, Shenoy and Marathe 2007).

Deller (1998) tested the possibility of adding Tinuvin® 292, a HALS additive, and Tinuvin® 328, an ultraviolet absorbing compound, to French polish. He concluded that Tinuvin® 328 inhibited the orange fluorescence seen in shellac, which he felt was a desirable quality in the resin. Thereafter, he continued to use Tinuvin® 292 alone. Dendy (2007) tested the effectiveness of Lignostab® 1198 applied to three species of timber. She found that the pre-treatment, in combination with a Tinuvin® stabilised blonde shellac in ethanol, measurably decreased the amount of discolouration, particularly in light coloured timber. In her research, the Tinuvin® products tested were 1130 and 327. Could this be the way forward for pyrography?

Tinuvin® 1130

This is a liquid hydroxy phenol benzotriazole UV absorber, which has outstanding thermal-permanence, good photo-permanence, and is also suitable for waterborne coatings. Figure 3, illustrates the structure (BASF 2019).

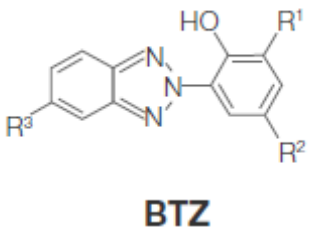

Fig. 3.
The structure of Tinuvin® 1130 (BASF 2019).

Regalrez® 1126 and Kraton® G-1650

Piena (2001) explored the possibility of using a low-molecular weight hydrocarbon resin, Regalrez 1094, as a wood finish, which is used in the conservation of easel paintings. To make it more flexible he combined Kraton® G-1650, a clear copolymer based on styrene and ethylene/butylene with a polystyrene content of 30% (Kraton Polymers 2007), and he stabilised it against ultraviolet radiation with Tinuvin® 292. However, the resin made the coated object too tacky to handle, which might have been caused by the low glass transition temperature (Tg.) of 33^{o}C. Consequently, he tried Regalrez 1126, which has a higher Tg. of 65^{o}C. This proved to be satisfactory. Piena (2001) also found that Regalrez® can be covered with a more traditional material, such as shellac, or a polymer like Paraloid B-72, as a topcoat. Consequently, manufacture of a coating, for the pilot experiment presented here, was adapted from his work.

OBJECTIVES

Therefore, the purpose of this study was to examine the effects that a coating solution containing UV inhibitors has on the stability of pyrographic decoration, when exposed to a maximum of 110 days of natural light aging. As such, it offers a contribution to the available knowledge of pyrographic surfaces, and an initial basis for further research.

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 405mm x 205m x 1.2m (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, Millis 2017).

Manufacture and application of coatings, Sample P. 1

Samples of two products, which were manufactured and distributed by Ciba® Speciality Chemicals at the time, were provided for this experiment; Lignostab® 1198, and Tinuvin® 1130. A sample of Kraton® G-1650 was supplied by Kraton Polymers UK Limited. A quantity of Regalrez® 1126 was purchased commercially.

Pre-treatment: 2g of Lignostab® 1198 dissolved in 98 ml of distilled water. Undercoat: 10g of Regalrez® 1126, combined with 0.2g of Kraton® G-1650 (2%) and 0.2g of Tinuvin® 1130 (2%), dissolved in 90g of white spirit (GPR). Top coat: 40 g of Regalrez® 1126, combined with 4g of Kraton® G-1650 (10%) and 1.2g of Tinuvin ®1130 (3%), dissolved in 55g of white spirit. Using 10% of Kraton® G-1650 was recommended to make the topcoat more scratch resistant (Piena 2001).

Six coats of the Lignostab® 1198 solution were brushed on sample P. 1, allowing each coat to air-dry in between. Where 'scorched' at higher temperatures, the surface became increasingly hydrophobic. Twelve coats of 10% Regalrez® solution, were brushed on the sample, allowing drying after each application. No build-up was visible, with the naked eye, on the surface. Three coats of 40% Regalrez® solution, were applied in the same way, as a top coat.

Earlier minor tests had indicated that the 40% solution was liable to soften on exposure to heat. Therefore, the coated sample was placed in the freezer for two weeks, prior to exposure, as an attempt to aid hardening (Scarlett 2009).

Figure 4, shows sample P.1, after coating and before exposure. 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 application of the Lignostab® pre-treatment noticeably darkened the wood surface, affecting the control segment particularly.

Fig. 4.
Sample P. 1, after coating application, showing the effect of heating on wood colour.

Natural light aging

As the purpose of this test was to replicate the effects of light exposure on pyrographic decoration in a usual interior situation, the term 'natural light aging' refers to exposing the samples 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 April and October (Millis 2017).

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, these results were not comparable to those produced in natural light (Millis 2017).

Exposure

In this case, the wood sample colour scale was divided into two even-width vertical strips, and mounted on foam core board by covering the left side section with a foil sleeve 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 the sample with two brass tacks (Fig. 5). Then the right halves of the sample were exposed to natural light aging for 110 days/nights. The left side of the sample acted as a control only.

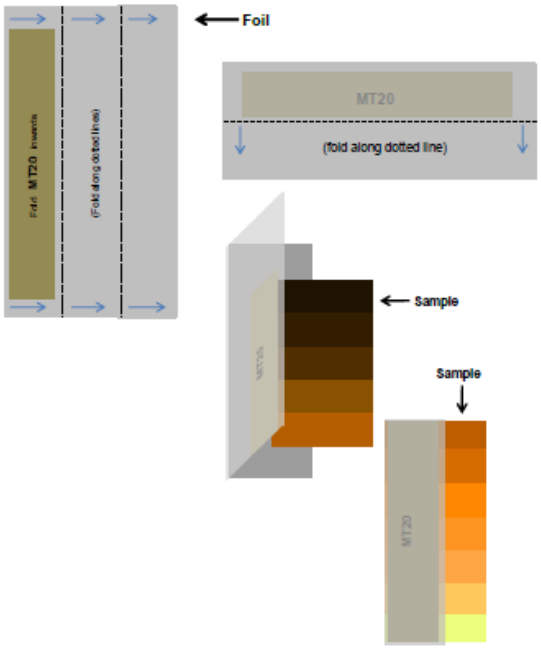

Fig. 5.
Natural light aging, sample preparation plan (Millis 2012).

Light exposure for the 110 day period was quantified in lux as 10,326,000, by monitoring an in situ LightCheck® dosimeter, 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, Millis 2017).

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, Millis 2017).

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 8 mm measuring area, was index set to use D65 illumination and calibrated to a 2^{o} 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 equation (1) (for full method see BS EN ISO 105-J03:1997).

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 with a UV stabilised finish. As the slight colour changes developed at temperature settings from 325^{o}C and below were reversed by the test, these segments will not be mentioned further.

(1)

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

$$Where \quad \Delta L^* = L^*_T - L^*_R$$

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

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

R = Reference sample (before exposure)

T = Test sample (after exposure)

RESULTS AND DISCUSSION

The colour changes that took place in the samples were the direct result of exposure to natural light aging, 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 *ClE*ΔE^*_{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, Millis 2017).

Table 1

Colour parameters of selected segments, for sample P. 1, before exposure to natural light aging, with colour difference values recorded after exposure (grey)

Sycamore	Temperature	(a) Colour measurements before exposure			(b) Colour differences after exposure			
					50 days		110 days	
		*L**	*a**	*b**	ΔE^*_{ab}	*ΔL**	ΔE^*_{ab}	*ΔL**
P.1	**Control**	**66.46**	**9.77**	**24.94**	**7.07**	**6.18**	**10.78**	**9.44**
	350°C	**53.87**	**11.68**	**24.26**	**12.52**	**12.21**	**17.50**	**16.84**
	375°C	**42.76**	**14.10**	**22.77**	**13.44**	**12.25**	**20.41**	**19.25**
	400°C	**32.14**	**12.85**	**13.92**	**14.37**	**10.44**	**22.46**	**17.99**
	425°C	**25.06**	**7.29**	**4.37**	**10.91**	**6.62**	**18.26**	**12.48**
	450°C	**23.21**	**1.96**	**0.48**	**5.93**	**3.38**	**11.29**	**7.25**

Examination of the data shows that significant colour change took place during exposure. However, it is not until these data sets are compared with other samples that it becomes possible to fully comprehend the results. The first chart, pictured in Fig. 6, represents the absolute colour differences caused by exposure, at the end of the testing phase (ΔE^*_{ab}). In this chart, sample P. 1 is presented alongside samples shown in previous work (Millis 2017); uncoated, shellac coated and linseed oil coated sycamore. Colour coordinates for the latter samples are shown in Table 2(a), with the differences thereof in Table 2(b). Starting with the control segment (not treated with heat), it can be seen that major lightening of the wood surface took place in sample P. 1, which amounted to a lightness difference of 9.44, and ultimately to an absolute colour change value of 10.78. Even though there were large overall colour differences recorded for the uncoated, shellac coated and oil coated control segments, these were caused by significant increases in yellowing (+b axis), and changes in lightness were minimal. Colour differences continued to rise for segments 'scorched' at 350°C (ΔE^*_{ab} 17.50) and 375°C (ΔE^*_{ab} 20.41), equalling the value for the uncoated sample at 375°C (ΔE^*_{ab} 20.64), while the oil coated sample returned the lowest values. However, at 400°C, it is clear that the stabilised segment returned the highest amount of colour change (ΔE^*_{ab} 22.46) for all four samples. Colour change began to drop slightly for the stabilised segments 'scorched' at 425°C and 450°C, but continued to remain significant.

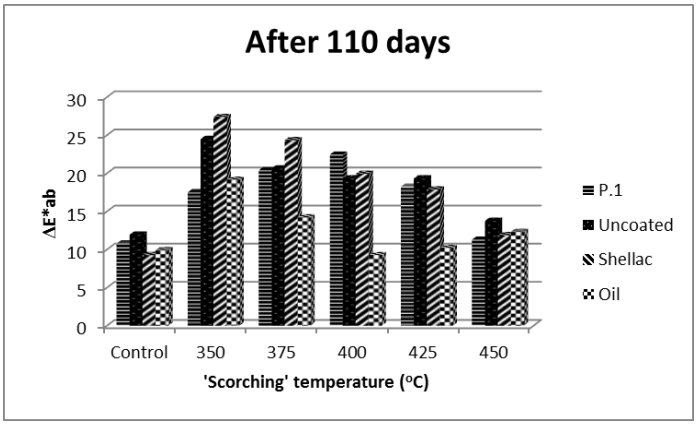

Fig. 6.
Overall colour differences for the samples, at the end of the testing phase.

Table 2

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

Sycamore	Temperature	(a) Colour measurements before exposure			(b) Colour differences after exposure			
					50 days		110 days	
		*L**	*a**	*b**	ΔE^*_{ab}	ΔL^*	ΔE^*_{ab}	ΔL^*
Uncoated	**Control**	78.43	6.70	16.78	8.52	-1.43	11.94	-1.91
	350°C	39.71	10.80	13.63	20.03	14.81	24.49	17.68
	375°C	35.73	7.72	8.56	16.23	9.94	20.64	13.07
	400°C	35.72	5.97	6.11	14.80	8.97	19.34	11.94
	425°C	36.26	5.81	6.25	14.35	8.98	19.33	12.22
	450°C	34.32	3.69	3.84	9.77	5.74	13.76	8.35
Shellac	**Control**	73.78	7.59	22.48	6.0	0.57	9.28	1.25
	350°C	36.81	12.22	16.28	22.86	17.01	27.39	20.42
	375°C	30.83	9.27	9.23	19.60	11.73	24.35	15.02
	400°C	28.81	6.68	5.62	15.19	8.51	19.94	11.78
	425°C	28.38	5.53	5.22	14.02	8.07	17.88	10.44
	450°C	26.73	1.89	1.42	8.52	3.74	11.87	6.30
Oil	**Control**	75.81	8.90	26.57	6.35	-3.10	9.90	-3.18
	350°C	31.78	9.22	8.40	14.88	8.84	19.14	11.39
	375°C	28.24	4.42	2.93	11.01	5.50	14.21	7.31
	400°C	27.94	1.88	0.73	5.57	1.82	9.25	3.76
	425°C	27.85	2.53	1.08	6.31	2.34	10.20	3.94
	450°C	29.22	3.34	1.56	8.09	2.97	12.32	5.11

To aid in the clarity of this investigation, the segments at two temperature settings were examined further, 375°C and 400°C. These were chosen because they reflect the colour shades often preferred by a pyrographic artist working today, to give contrast to their work. Figure 7, highlights the results for the segment 'scorched' at 375°C, featuring the four samples. In this chart, the absolute colour difference values are shown at the lower benchmark of 50 days, alongside those realised at 110 days. Initial examination reveals that the largest portion of colour change occurred during the first 50 days of exposure, for all samples, after which the rate of change slowed. If the two data points representing the uncoated sample, are taken as the 'standard' for colour change, meaning that without a surface coating at all, the amount of difference expressed by these values would be equal to the amount expected to be found in a pyrographic image subjected to 110 days of exposure to unrestricted daylight, then a suitable coating solution must return lower amounts of colour change than those shown here. The stabilised coating returned a lower amount of colour change during the first 50 days, nevertheless during the second part of the test, colour change increased to match the result for the uncoated sample. The data points representing the shellac coated sample returned the highest amount of colour change for that segment. However, this was thought to have been caused by changes in the coating, as well as those occurring at the wood surface. Moving onward, observations for the segment 'scorched' at 400°C, shown in Fig. 8, indicate an unequalled rise in colour change for the stabilised segment, sample P. 1, when compared to the other three samples. The lowest amounts of colour change, for both segments, were recorded by the oil coated sample.

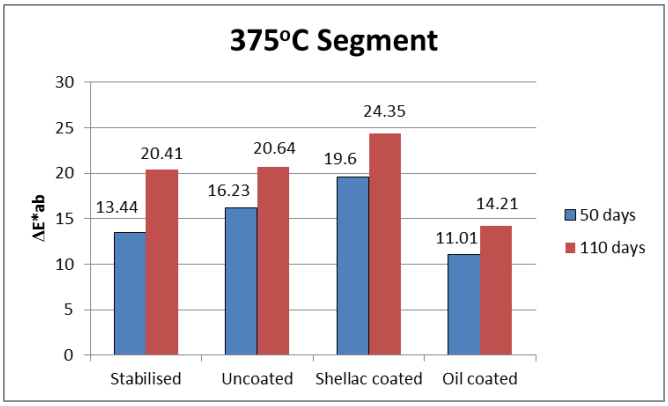

Fig. 7.
Absolute colour differences for the segments, 'scorched' at 375°C, after 50 days, and at the end of the testing phase.

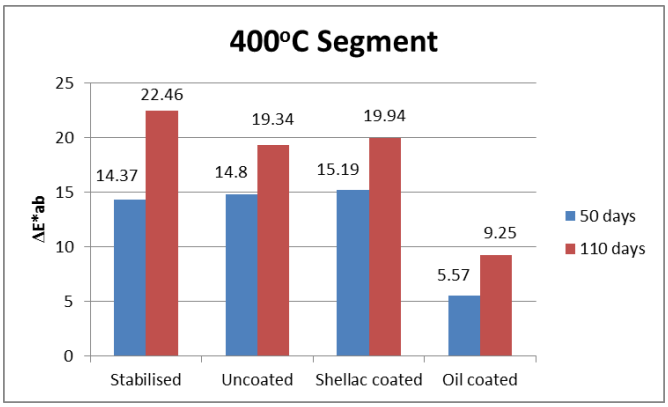

Fig. 8.
Absolute colour differences for the segments, 'scorched' at 400°C, after 50 days, and at the end of the testing phase.

Percentage change

The percentages of colour change after 50 days of exposure, for the four samples, are listed in Table 3. For the segment 'scorched' at 375°C, the lowest percentage change was achieved by the stabilised sample P. 1, at 66%, with the uncoated sample at 79%, the shellac coated sample 80%, and the oil coated sample 77%. For the 400°C segment, they were 64%, 76% 76% and 60%, respectively. These results suggest that the stabilised coating slightly retarded the rate of colour change for both segments. However, the lowest percentage change for the segment 'scorched' at 400°C was achieved by the sample coated with linseed oil, at 60%.

Visual interpretation

Figure 9, illustrates sample P.1, after exposure to 110 days and nights of natural light. It is clear from this image that significant lightening of the wood surface, as well as fading, took place during the experiment. It is also apparent that the coating inhibited the production of yellow chromophores in the control segment, and the wood molecules unaffected by heat. Defects in the coating, which had started to appear after 33 days, were particularly visible on the control segment and indicated that perhaps the development of the coating was inadequate or, conceivably, 40% Regalrez® 1126 in white spirit was not suitable as a top coat for the conditions presented in the testing environment. This had not occurred with a 10% solution in white spirit, when exposed to 'simulated sunlight' in the Dr Hönle UVA aging unit. To the contrary, the surface survived the excessive heat levels exceptionally well.

Table 3

The percentage colour change at 50 days, for the segments 'scorched' at 375°C and 400°C

Sample	Temperature	Percentage change at 50 days
Stabilised	**375°C**	**66%**
Uncoated	**375°C**	**79%**
Shellac coated	**375°C**	**80%**
Linseed oil coated	**375°C**	**77%**
Stabilised	**400°C**	**64%**
Uncoated	**400°C**	**76%**
Shellac coated	**400°C**	**76%**
Linseed oil coated	**400°C**	**60%**

However, for sample P. 1, the coating remained soluble, and the overall appearance of the surface was much richer, more vibrant in colour than that of the uncoated, shellac coated, and oil coated samples. Figure 10, pictures sample P. 1, after coating removal, together with the uncoated sample. Though yellowed, examination suggests that the pyrography on the uncoated sample has faded slightly less in this case.

Fig. 9.
Sample P. 1, at the end of the testing phase.

Fig.10.
Sample P. 1 (below) after coating removal, together with the uncoated sample.

A pyrographic surface presents a very difficult proposition to protect. This is because the surface contains a large assortment of molecules at various stages of charring and carbonisation (Shafizadeh 1984). These molecules are very unstable and require only low levels of energy for bonds to be broken, resulting in loss of colour. Because it is so complex, it is unlikely that a single coating of any type and thickness will be able to arrest all levels of colour change due to this art form. This means that a compromise has to be reached, which will afford some degree of protection for the majority of the surface colour. As mentioned previously (Millis 2017), applying a surface coating to any art work is a very personal decision, and it is often dependent on the particular object needing the treatment. The Regalrez® 1126, provided a good surface when used in a 10% solution with white spirit, and previous work has determined that white spirit causes less damage to pyrography, than more polar solvents (Millis 2012). When considering the issue from another standpoint, as extractives are undoubtedly part of the pyrographic image, and it is well known that historic pigments containing them and the products of incomplete combustion, such as bistre, are fugitive in light (Winter 1983), could an extractive stabiliser be more successful, as demonstrated by Passauer *et al*. (2015)? Or, perhaps, a red-shifted ultraviolet absorber? Whatever the choice, it is clear that much further testing is needed to establish the way forward if using UV technology is the preferred path.

Table 4, presents the overall colour differences, together with the differences that occurred in the b* axis, observed for the left, covered, side of sample P. 1, which acted as an overall control for the duration of the test. Also shown are the results for the uncoated, shellac coated and oil coated control samples, which were stored in complete darkness for the entire experimental phase. Whereas the shellac and oil coated samples had increased in yellowness, no such change had occurred for sample P. 1. However, a slight but

consistent rise in lightness had contributed to the final results. This suggests that very slight bleaching occurred in the dark for all segments of this sample.

Table 4

Overall colour differences seen in the control samples at the end of the testing phase, compared with the covered side of sample P. 1

Segment Temperature	P. 1 Covered side			Uncoated		Shellac coated		Oil coated	
	ΔE^*_{ab}	ΔL*	Δb*	ΔE^*_{ab}	Δb*	ΔE^*_{ab}	Δb*	ΔE^*_{ab}	Δb*
Control	2.51	2.37	0.59	1.14	0.78	2.53	2.26	5.74	5.49
350°C	3.19	3.17	0.07	1.58	1.20	1.76	1.32	1.91	1.37
375°C	3.27	3.25	0.33	1.56	1.06	1.50	1.17	1.50	1.06
400°C	2.54	2.31	0.69	0.53	0.05	1.46	0.80	0.33	0.15
425°C	2.48	2.19	-1.00	0.70	0.14	1.82	1.14	0.60	0.32
450°C	2.00	1.65	-1.08	0.33	0.12	1.02	0.56	0.30	0.20

CONCLUSION

The photo-discolouration of pyrography samples applied to English sycamore, and finished with a coating system containing UV inhibitors, has been investigated, and compared to uncoated, shellac coated, and linseed oil coated samples. After irradiation, it was clear that large colour changes had occurred. Nevertheless, the coating prevented the development of yellow chromophores in the molecules not affected by heat, leaving the surface looking brighter and more vibrant than the other samples. Unfortunately, this coating failed at 33 days, producing bubble-like defects in the top layer. Yet, even so, it continued to protect the wood from yellowing for the full 110 days. In spite of this, the coating did not seem to offer any protection to the pyrography, and at 400°C, it might have been the cause of the increased amount of colour change recorded. However, for the segments 'scorched' at 375°C and 400°C, the stabilised coating seemed to slightly retard the percentage of colour change that occurred over the first 50 days. Consequently, much further research is needed, to fully understand if UV inhibitors are useful for pyrographic surfaces, or if they are, indeed, harmful.

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REFERENCES

Anon (1852) The Crystal Palace, and its contents: an illustrated cyclopaedia of the Great Exhibition of the Industry of all Nations. BLIXG. Embellished with upwards of five hundred engravings. With a copious analytical index. W M Clark, 16 & 17, Warwick Lane. Online at: http://www.archive.org

Art Gallery of Greater Victoria (2019) Speak Lord for thy Servant Hears, c.1854. jpg. Online at https://commons.wikimedia.org/wiki/File:Sant-cousins.jpg

BASF SE (2019) Coatings that stay looking good. BASF Brochure. Online at: https://www.btc-europe.com/fileadmin/.../Tinuvin_Chimassorb_Lignostab_EN.pdf

British Standards Institute (1997) BS EN ISO 105-J03:1997. Textiles – Tests for colour fastness. Part J03. Calculation of Colour Differences. BSI

British Standards Institute (2002) BS EN 13183-1: 2002. Moisture content of a piece of sawn timber. Determination by oven dry method. BSI

Ciba Inc (2009) Ciba® Lignostab® 1198 Wood Lignin Stabilizer. Paints and Coatings. Company literature

Daintith John, Martin Elizabeth. Eds. (2005) 5th Ed; A Dictionary of Science. Oxford University Press. Oxford, UK

Deller Craig (1998) French polish from a conservator's point of view. Some ideas for a better coating. WAG Reprints Online (Wooden Artifacts Group). Online at: http://www.wag-aic.org

Dendy Jean (2007) The effectiveness of Ciba® Lignostab®1198 Wood Photostabilizing Additive in three wood species. Report MA Conservation. Queens University. Ontario Canada

Evans PD, Haase JG, Shakri A, Seman BM, Kiguchi M (2015) The search for durable exterior clear coatings for wood. Coatings. 2015 (5) 830-864. Online at: http://www.mdpi.com/2079-6412/5/4/830

Hon DN-S, Minemura N (1991) Colour and Discoloration. Wood and Cellulosic Chemistry. Hon DN-S, Shiraishi N. Eds. Marcel Dekker. New York, USA. 395-454

Hon DN-S (1991) Photochemistry of wood. Wood and Cellulosic Chemistry. Hon DN-S, Shiraishi N. Eds. Marcel Dekker. New York, USA. 525-555

Kraton Polymers (2007) Material Safety Data Sheet. Kraton Polymers SEBS G Series Products. Online at: http://www.kraton.com

Labbé Nicole, Harper David, Rials Timothy (2006) Chemical structure of wood charcoal by infrared spectroscopy and multivariate analysis. Journal of Agricultural and Food Chemistry. 54 (10) 3492-3497. Online at: http://www.treesearch.fs.fed.us/pubs/24910

Millis SM (2012) Understanding pyrography: the deterioration and conservation of decorative 'scorched' wood. MPhil thesis. Buckinghamshire New University. Brunel University

Millis SM (2013) Understanding pyrography, the photochemistry of decorative 'scorched' wood. Pro Ligno 9 (4). 684-692. Online at: http://www.proligno.ro/en/articles/2013/4/Millis_final.pdf

Millis, Susan M (2017) In search of a suitable coating for pyrography. Pro Ligno13 (4). 404-413. Online at: http://www.proligno.ro/ro/articles/2017/4/MILLIS.pdf

Passauer L, Prieto J, Müller M, Rössler M, Schubert J, Beyer M (2015) Novel color stabilization concepts for decorative surfaces of native dark wood and thermally modified timber. Progress in Organic Coatings 89 (December 2015). 314-322. Online at: http://www.sciencedirect.com/science/article/pii/S0300944015300291

Piena Hans (2001) Regalrez in furniture conservation. Journal of the American Institute for Conservation. 40 (1) Spring 2001. Online at: http://www.jstor.org/stable/3180013

Pinto Edward H (1960) Pyrography as an Art: Part 1. The Woodworker. March1960. 46-47

Sandberg D, Kutnar A (2016) Thermally Modified Timber: Recent developments in Europe and North America. Wood and Fiber Science. 48. 28-39. 2015 Convention. Special Issue. Society of Wood Science and Technology

Scarlett Justin (2009) Private consultation. 19/5/2009

Schaller Christian, Rogez Daniel (2006) Defended from the sun. European Coatings Journal. 12/2006. 22. Online at: www.european-coatings.com/content/download/60656/693172/version/.../61404.pdf

Searle ND (1994) Effect of light source emission on durability testing. Accelerated and outdoor durability testing of organic materials. ASTM STP 1202. Ketola WD, Grossman D. Eds. American Society for Testing and Materials. Philadelphia, USA. 52-67

Shafizadeh F (1984) The Chemistry of Pyrolysis and Combustion. The Chemistry of Solid Wood. Rowell RM, Ed. Advances in Chemistry Series. American Chemical Society. Seattle, USA. 489-529

Shenoy MA, Marathe YD (2007) Studies on synergistic effect of UV absorbers and hindered amine light stabilisers. Pigment & Resin Technology. 36 (2). 83-89

Sundqvist B (2004) Colour Changes and Acid Formation in Wood During Heating. PhD thesis. Divisions of Wood Material Science, Skellefteå Campus, Luleå University of Technology. Online at: http://ltu.diva-portal.org/smash/get/diva2:999349/FULLTEXT01.pdf

Winter J (1983) The characterization of pigments based on carbon. Studies in Conservation 28 (2). 49-66. Online at: https://www.jstor.org/stable/1506050