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DETERMINATION OF THE COLOR STABILITY OF AN ENVIRONMETALLY-FRIENLY WOOD STAIN FROM SAFFRON (*CROCUS SATIVUS* L.) EXTRAKTS UNDER UV EXPOSURE

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ABSTRACT

This study was designed to develop an environmentally friendly wood stain by natural pigments from saffron (*Crocus sativus* L.) and determine the color stability of this stain to UV light irradiation. Wood stains derived from saffron were prepared by using pure extracts of saffron and saffron extracts with two kinds of mordants, iron and alum. Scots pine (*Pinus sylvestris* L.) and Turkish oriental beech (*Fagus orientalis* Lipsky) wood specimens were used for the study. After treatment with the stain, wood specimens were exposed to UV light irradiation for periods of 500, 1000 and 1500 hours. Results showed that saffron extract with or without mordants as a stain for wood provided some stability to color change after UV irradiation. Furthermore, it was found that treatments with both mordants resulted in much more the color stability compared to saffron treatments without any mordant.

KEY WORDS: natural wood stain, photodegradation, color changes, mordants, saffron (*Crocus sativus* L.)

INTRODUCTION

People are exposed to numerous types of pollutants in modern environments. Wood based products and decoration elements are potential sources for a number of volatile organic compounds (VOCs) indoors. Many chemical components are used in the wood finishes and coatings industry. Salthammer et al. (1998) identified about 150 different VOCs. These pollutants are emitted from different sources that some of them are floor coverings, wood-based panel, furniture, solid woods, wood stains and paints are to be important in the these sources (Cheng and Brown 2003).

A large number of preservative and stain compounds have been introduced to the market; however, many of them have not gained commercial acceptance, because of chemical toxicity, low efficacy, high cost, or corrosiveness (Murphy 1990). Most compounds belong to the group of typical solvents and are chemically inert under normal conditions. However, a number of substances are known as secondary emission products or reactants (Salthammer 2002). These wood stains and preservatives are potentially included in waste wood and are one of the persistent pollutants that have raised concerns about health effects on humans and wildlife (Asari et al. 2004).

Nowadays, there is a growing interest in the revival of natural stains in textile staining; arguments based around keywords such as sustainability, green chemistry, improved eco-balances and thereby leading to niche products for special markets (Bechtold et al. 2007). Because natural stains are generally environmentally friendly and have many advantages over synthetic stains with respect to production and application (Luciana 1997).

The introduction of natural stains into wood products for staining and finishing processes is the alternative solution for eliminating environmental pollutants. A number of stain crops continue to be grown in the Mediterranean region. One example is saffron. Natural pigments from Crocus sativus stigmas were used for the dyeing of cotton, wool (Liakopoulou 1998), and wood (Goktas 2007) and historical map.

Saffron **(***Crocus sativus* L.**)** is a bulbous perennial of the iris family (Iridaceae) treasured for its golden-colored, pungent stigmas. Saffron is an autumn-flowering geophyte and its long scarlet stigmas were highly valued for flavouring foods and for colouring them golden-yellow. They were used as a dye, in perfumes, and as a drug as well as for culinary purposes (Molina et al. 2005, Abdullaev 2004, Winterhalter and Straubinger 2000, Rios et al. 1996, Liakopoulou 1998). One of its principal coloring pigments is crocin, which is easily soluble in water. In addition to crocin, saffron contains crocetin ($C_{20}H_{24}O_4$) as a free agent and small amounts of the pigment anthocianin, α-carotene, β-carotene, and zegxantin (Abdullaev and Espinosa-Aguirre 2004, Tarantilis and Polissiou 1996).

The objectives of this study were to develop an environmentally-friendly natural wood stain derived from saffron and to determine its color stability under UV light irradiation.

MATERIAL AND METHODS

The specimens of beech (*Fagus orientalis* Lipsky) and Scots pine (*Pinus sylvestris* L.) sapwood were used in this study. Vertical grain specimens (10 (radial) x 100 (tangential) x 150 (longitudinal) mm) were cut and conditioned at 20 ± 2°C and 65 ± 5% relative humidity to reach equilibrium moisture content.

Dried saffron stigmas were obtained from a commercial company in Milas/Muğla-Turkey.

Air-dried stigmas of saffron (100 g) mixed with 3000 ml of water were heated under reflux at about 100°C for 3 h. The suspension was filtered by using filter paper with the millipore filter paper, 0.65 micro metre pore size and a sample of 500 ml of the filtrate was taken for treatment. Volume loss due to evaporation was compensated by the addition of water at the end of the extraction to retain the initial volume.

Mordants used in this study are ferrous sulfate ($FeSO_4.7H_2O$ (technical grade 96% purity, Merck)) and alum ($KAl(SO_4)_2.12H_2O$ (puriss. p.a. Fluka)). They were mixed with aqueous solution of saffron extracts to give final concentrations of 30 g L^{-1} for iron and 50 g L^{-1} for alum mordants (Guzel and Akgerman 2000).

The prepared stains were separated into three parts stains, namely, saffron extract with iron mordant, saffron extract with alum mordant and control without mordant, then heated to 60°C. The wood panels were immersed into the stain solutions just mentioned above for 30 min. Any extra solution left on the specimens was removed with a clean cloth. Specimens were then left to dry at 20±3°C in a vertical position.

The CIELab system (CIE 1976 $L^*a^*b^*$) was used to monitor the color change of the specimens after periods of 500 h, 1000 h, and 1500 h of UV light exposure.

Color measurements were determined according to ISO 7724. The CIELab system is described by three parameters: L^* axis represents the lightness, a^* and b^* are the chromaticity coordinates; $+a^*$ is for the red, $-a^*$ for green, $+b^*$ for yellow, $-b^*$ for blue and L^*varies from 100 (white) to zero (black).

L^*, a^*, and b^* color coordinates of each sample were determined before and after exposure to UV light irradiation. The color was measured on a color reader (Konica Minolta-Color Reader CR-10) using a D65 light source and 10 mm for sample diameter. These values were used to calculate the color differences (ΔE^*) as a function of the UV irradiation period according to the following equation:

$$\Delta L^* = L^*_f - L^*_i \tag{1}$$

$$\Delta a^* = a^*_f - a^*_i \tag{2}$$

$$\Delta b^* = b^*_f - b^*_i \tag{3}$$

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{4}$$

Where, ΔL^*, Δa^* and Δb^* are the changes between the initial (i) and the final (f) values. L^*, a^* and b^* contribute to the color change ΔE^*. The higher the value of ΔE^* is, the greater the discoloration

RESULTS AND DISCUSSION

Color changes of beech and Scots pine wood samples were shown in Tab. 1 and depicted in Figs. 1, and 2. Positive values of Δb^* indicate an increment of yellow color and negative values show an increase in blue color. Positive values of Δa^* indicate a tendency of wood surface to reddish while negative values mean a tendency toward green.

Tab. 1: Color changes of treated and untreated wood species exposed to 1500 h UV irradiation

		Before exposure			500 h				1000 h				1500 h			
Wood	Stain materials	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE*	ΔL*	Δa*	Δb*	ΔE*	ΔL*	Δa*	Δb*	ΔE*
Beech	Control (without stain)	70,30	10,10	24,20	-1,20	-0,10	-1,10	1,63	-1,10	0,10	-1,10	1,56	-2,00	-0,10	-1,70	2,63
	Saffron (without mordant)	65,00	10,90	41,20	-1,40	1,00	-7,60	7,79	-1,00	1,10	-6,70	6,86	-1,20	1,00	-7,50	7,66
	Saffron + Alum	61,95	13,85	44,40	-2,50	0,50	-4,05	4,79	-2,85	0,75	-6,30	6,96	-3,10	0,90	-6,90	7,62
	Saffron + Iron	43,25	3,85	18,0	-1,65	0,05	-2,45	2,95	-1,80	1,15	-2,90	3,42	-2,70	-0,05	-4,15	4,95
Scots Pine	Control (without stain)	79,75	8,10	25,85	-6,15	3,65	0,15	7,15	-7,20	4,00	0,00	8,24	-8,35	4,45	04,00	9,47
	Saffron (without mordant)	74,10	8,90	51,10	-5,50	3,55	-14,45	15,86	-5,00	3,75	-12,55	14,02	-6,30	4,00	-15,35	17,07
	Saffron + Alum	70,80	12,85	51,00	-4,90	2,55	-7,15	9,04	-5,60	3,00	-8,15	10,33	-6,80	3,15	-10,15	12,62
	Saffron + Iron	48,10	8,40	25,90	-2,85	0,15	-3,60	4,59	-3,60	0,15	-5,05	6,20	-4,35	0,00	-5,85	7,29

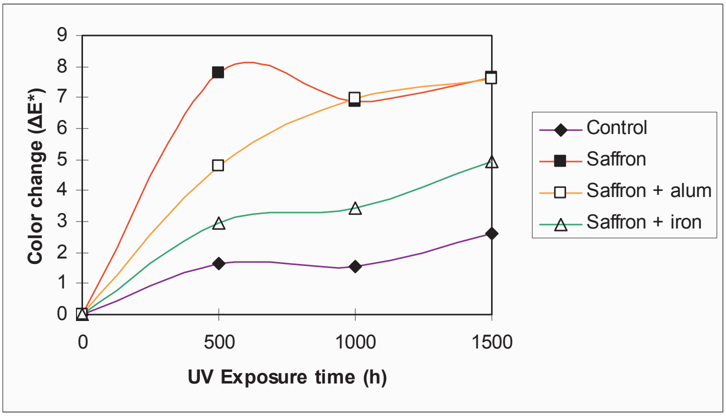

Fig. 1: Color changes of treated and untreated beech after UV exposure

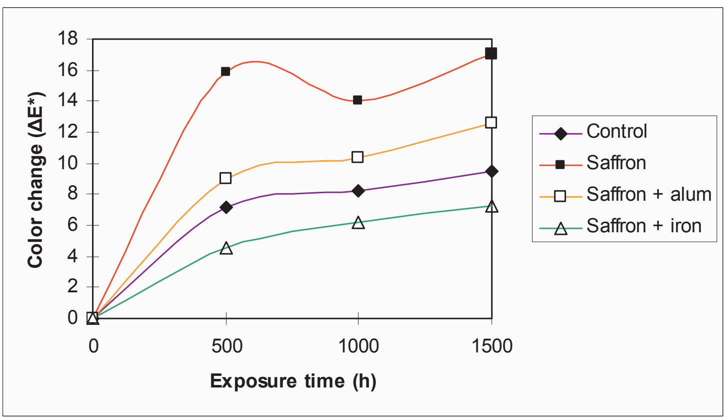

Fig. 2: Color changes of treated and untreated Scots pine after UV exposure

The lowest values of ΔL^* were obtained for the untreated (without stains) Scots pine specimens after 1500 h exposure. All the other treatments of Scots pine caused less changes in the lightness (ΔL^*) than the control specimens. The negative lightness stability (ΔL^*) values occur during the UV exposure because the surface becomes darker. The reason is that photodegradation by UV light induces changes in chemical composition, particularly in the lignin, and subsequent color changes (Feist and Hon 1984). This event occurred by free radicals that generated in wood by light rapidly interact with oxygen to produce hydroperoxides which in turn are easily decomposed to produce chromophoric groups such as carbonyls, carboxyls, quinones, peroxides, hydroperoxides, and conjugated double bonds (Feist and Hon 1984). So, the lowest values of ΔL^* that is the most sensitive parameter of the wood surface quality on the irradiation (Temiz et al. 2005).

The rate of color change in surface of both wood species (treated and untreated) after UV light irradiation occurred rapidly for during the first 500 h period then slowed to only small changes at 1000 to 1500 h. When wood is exposed to the outdoors or in artificial UV light for a relatively short period, changes in brightness and color are readily observed (Feist and Hon 1984, Kamdem and Grelier 2002).

The lowest color changes (ΔE^* = 2,63) were determined for the untreated beech specimens Meanwhile the highest color changes (ΔE^* = 17,07) were determined for the Scots pine treated with saffron (without mordant) extracts. The magnitudes of the color change in the both treated wood specimens were higher when compared to those of untreated ones. In other words, saffron extracts without mordants as a stain for wood didn't contribute to the color stability. The reason of this high color changing is, due, most probably, to crocetin, which are major ingredient in the flowers of Crocus sativus (Abdullaev and Espinosa-Aguirre 2004, Tarantilis and Polissiou 1996). Crocetin is a natural carotenoid dicarboxylic acid that has a deep red color and forms crystals with a melting point of 186°C. Crocin is the chemical ingredient primarily responsible for the color of saffron. Moreover, carotenoids can be damaged by temperature and light in the short time (Stahl et al. 2000). Therefore, the carotenoids damaged under UV light exposure gave low fastness degrees in the study. However, the saffron extract with both mordants used here contribute the higher color stability than the extract without mordants mixture. The reason for this color stability may be the presence of mordants. The presence of metal ions promotes free radical formation (Feist and Hon 1984) of wood components even when they are exposed to light. The stabilization of lignin by iron was reported to occur through the formation of iron-lignin complex (Kamdem and Grelier 2002). Olmez (2004) reported that iron and alum mordants contributed color stability of wool yarn stained by saffron extract.

Generally, the color changes values of Scots pine (treated/untreated) were higher than those of the beech wood (treated/untreated). In UV experiments, softwoods showed greater color change than hardwoods (Sahin 2002). The reason for the differences between two wood groups may be due to the differences of chemical compositions of the two different woods (hardwood and softwood) (Sogutlu and Sonmez 2006, Temiz et al. 2005). That is to say, in general softwoods have 2-10 % more lignin than hardwoods. From the major wood constituents, lignin contributes with 80-95 % to the UV absorption coefficient of wood (Tereza et al. 2004). Lignin has aromatic, phenolic and carboxylic groups that absorb rays of different energy levels. In contracts, cellulose is not sensitive to UV light of wavelengths longer than 340 nm (Feist and Hon 1984). So, it is possible to say that the color change of Scots pine (softwood) would have to be higher than the beech wood (hardwood) because of the lignin degradation. Consequently, most of the components in wood are obviously capable of absorbing enough visible and UV light to undergo photochemical reactions leading ultimately to discoloration and degradation (Feist and Hon 1984). However, the roughness of color stabilized wood is a complex phenomenon because wood is an anisotropic and heterogeneous material. Several factors, such as anatomical differences, growing characteristics, machining properties, pre-treatments (e.g. steaming, drying, etc.), can affect the color stability (Temiz et al. 2005).

CONCLUSIONS

This study dealt with UV color stability characteristic of wood treated with plant-based stains derived from saffron extracts. The stain was applied in three different forms, which were natural (without mordant), saffron + iron and saffron + alum mixtures. Generally, stain methods showed higher color changes compared to the untreated specimens of beech and Scots pine after 1500 h exposure in UV irradiation test cycle. Saffron extracts as a wood stain contributed to color changing. After 1500 h of exposure, untreated beech specimens provided the lowest color changes. The results demonstrated that treatments with two mordants retarded much more the total color change compared to saffron treatments without any mordant. Color changes of treated and untreated Scots pine specimens were higher than those of both treated and untreated beech wood.

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