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The staining influence of iron (II) sulphate on Norway spruce wood

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Abstract: *The staining influence of iron (II) sulphate on Norway spruce wood* The paper presents the results of research on the colour change of Norway spruce (*Picea abies* L.) wood under the influence of iron (II) sulphate water solution at three different concentrations (1%, 2%, 3%). The tests were perfomed wood showing defects typical of coniferous wood. The aim was to determine the possibility of increasing the usefulness of wood with defects (blue stain, reactive wood). Measurements of color parameters and their changes based on the CIELab color space were carried out. The influence of natural weathering on further staining effect was also determined.
On the basis of the tests carried out, it was shown that iron (II) sulphate causes greying of Norway spruce (*Picea abies* L.) wood and that the concentration of the solution does not have a major effect on color changes. The surface of the aged wood was clearly stained and darkened, with the greatest difference in the samples modified with a 3% solution.

Keywords: Norway spruce, *Picea abies* L., iron sulphate, weathering

INTRODUCTION

During external exposition using uncoated wood has become popular in architecture in order to avoid necessity maintenance such as repainting and to not hummer natural environment (Hundhausen et al. 2020, Lesar and Human 2022). The lack of any protection of the wood surface has its consequences in the form of color changes. Changes in wood color is a natural phenomenon, the causes of which can be divided into two main groups: biotic and abiotic. Biotic factors include the action of insects, fungi, and other microorganisms. The most common wood discoloration caused by fungi in coniferous trees is blue stain, which can be caused by about 100 different species of fungi (Unger et al. 2001). The infected wood changes color to gray, bluish-gray, or even black. There are two types of blue stain: primary, which develops from the time the wood is cut until it is dried, and secondary, which occurs during use (Krajewski and Witomski 2005). Blue stain, despite causing significant discoloration, does not negatively affect the mechanical properties of the wood. However, it is an undesirable characteristic due to its negative aesthetic effect (Humar et al. 2008).

Abiotic factors include weather conditions, such as temperature changes, air humidity, precipitation, wind, oxidation and sunlight radiation. Prolonged exposure to weather conditions leads to graying. Pigments and tannins undergo chemical changes, water-soluble substances are leached out, and wind deposits dust between the loosened surface fibers (Williams 2005). This phenomenon occurs in all tree species and manifests as a superficial color change of the wood to silver-gray, often with a silky sheen. In a study conducted on spruce wood, Müller et al. (2003) demonstrated that the wood surface changes color under the influence of ultraviolet rays. Lignin constitutes 20 to 30% of the wood tissue and absorbs UV rays, leading to its degradation and photodegradation of the -CH2 or -CH(OH) groups. These reactions result in the formation of free radicals, which cause the yellowing of the wood (George et al. 2005).

There are many methods available to limit or prevent wood discoloration, such as oiling or varnishing. In order to maintain the protective properties of the applied substances, periodic reapplication is often necessary, which can be burdensome for large-scale structures. Lacquer coatings also degrade under the influence of external factors (Schaller and Rogez and 2007, Grüll et al. 2011). As wood undergoes dimensional changes, the coatings crack and peel, leaving an unsightly surface exposed to moisture and microbial attacks (George et al. 2005). Pigmented products that form opaque coatings exhibit better durability compared to semi-transparent and transparent ones (Grüll et al. 2014). In recent years, there has been an increasing demand for transparent finishes that preserve the natural grain of the wood. However, as demonstrated by numerous studies, transparent coatings exhibit poor durability in external exposure, averaging up to two years in moderate climates and up to one year in tropical climates (Evans et al. 2015). Many substances used in these methods contain environmentally harmful ingredients. These substances can be released into the environment during product preparation, application, and even during use, for example, through leaching with rainwater. Paints and lacquer products contain environmentally detrimental substances such as volatile organic compounds (VOCs) - 37.28% in solvent-based products, 9.88% in water-based products, and 18.02% in UV-cured coatings (Ke et al. 2020). VOCs, when released into the atmosphere, undergo chemical reactions, producing secondary pollutants and contributing to the formation of photochemical smog (Dybał 2021). Short-term effects of VOC exposure can include respiratory irritation, headaches, or nausea, while long-term exposure (measured in years) can lead to cancer and damage to the nervous system (Alia et al. 2021, Soni et al. 2018).

The color changes of an unprotected wooden facade are uneven and depend, among other factors, on its exposure. Hirche (2014) showed differences in the color changes of wood depending on the geographic orientation of wood surface. Sections of the facade protected by roof overhangs experience slower graying, which can negatively impact the aesthetics of the building due to varying rates of change depending on the location and exposure of wood to external factors. The majority of users desire a uniform appearance of wood across the entire surface of wooden products or structures (Hundhausen et al. 2020). One possible method to reach a homogeneous grey color on wood surface exposed outdoor is to produce stains with a grey color that corresponds to the natural grey of weathered wood. Lesar and Humar (2022) demonstrated that the use of a solution based on iron (II) sulfate and biocides is an effective method for staining and prolonging the lifespan of spruce wood, and such modified wood can be used outdoors in the third usage class. So far, only few studies have been conducted on the color changes of wood caused by the action of iron (II) sulfate (Hundhausen et al. 2020, Jankowska and Kwiatkowski 2022, Lesar and Humar 2022). This paper presents the results of research on the influence of iron (II) sulfate solution concentration on wood color. The tests were performed on wood with defects typical of coniferous wood. The aim was to determine the possibility of increasing the usefulness of wood with defects (blue stain, reactive wood). The obtained results may be used by the industry in the future for more efficient implementation of environmentally friendly architectural solutions. However, to extend the lifespan of spruce wood in outdoor conditions, additional protection should be applied (Irbe et al. 2012).

MATERIALS

Norway spruce (*Picea abies* L.) wood in the form of five boards from different trees was used for the research. The material was obtained from a wood depot in Siedlce (Poland). The material was free from wood defects such as cracks or resin pockets. Two of the acquired boards showed clear signs of blue stain in the form of light gray streaks. One of the boards was characterized by the presence of reactive wood, which covered half of the width along the entire length of the board. This choice was intentional to verify whether the applied an aqueous solution of iron (II) sulfate allows for equalizing color differences for boards that exhibit such defects, and thus whether it enables increasing the applicability of the material by reducing the visibility of defects that lower the aesthetics of wood.

Each of the boards was planed, sanded, and cut into samples with dimensions of 10x10 cm. A total of 45 samples were obtained, then the samples were divided into groups in such a way that each group represented the material acquired for the research in full (wood with signs of blue stain, defect-free wood, samples with reactive wood). The prepared samples for the research were stored without access to light to avoid the influence of any light color changes in the wood prior to the staining tests (approx. 20°C, 55% RH).

METHODS

Iron (II) sulphate was purchased from Chempur, Poland. The solutions were prepared in the laboratory using demineralized water. Aqueous solutions of iron (II) sulfate were prepared at concentrations of 1%, 2%, and 3% (mass ratio). A single layer of the solutions was applied to one of the wide surfaces of the samples using a brush. Then the samples were placed on a flat surface and left to dry. During the first month, the sets were stored on the flat surface in a room with diffused sunlight. As part of this study, natural weathering of wood was conducted. Natural weathering involved exposing the wood to outdoor conditions in class 3 usage according to the guidelines outlined in the PN-EN 335:2013-07 standard. The outdoor aging process took place from July 25, 2022, to September 11, 2022, in an experimental field near Siedlce (52°08'18" N, 22°12'43" E). During the field tests (location in full insolation), the air temperature ranged from 2°C (September, nighttime) to 31°C, with a total precipitation of approximately 104 $mm \cdot m^{-2}$. The average daily solar radiation was around 490 $W \cdot m^{-2}$ (data obtained from the Meteo Siedlce station at https://siedlce.meteo.com.pl/hist.pl). The samples were grouped according to concentration variants and placed on separate grids, allowing free airflow, at a height of approximately 1 meter above the ground.

The assessment of the impact of treatment with iron sulphate solutions was based on color of wood surface measurements. The color was examined using a spectrophotometer (Erichsen Spectromaster 565-D) in the CIELab color space. The measurements were conducted after planing the surface of the samples, one day, one week, and one month after the application of the solution, as well as after natural weathering. Five measurements were taken on each of the tested samples - a total of at least 50 measurements per treatment variant. During the measurements, the values of three parameters describing color: L* (the lightness from black to white), a* (the coordinates between green and red), and b* (the coordinates between blue and yellow) were determined. Calculations were performed to determine the total color change (ΔE*) based on the averaged values for each concentration according to the recommendations of the PN-ISO 7724-3:2003 standard. When calculating the differences in L*, a*, and b* values during the internal exposure, reference was made to measurements of freshly planed wood. The differences after 7 weeks of weathering were compared to measurements taken after one month of internal exposure.

Data was analyzed and provided as the mean ± standard deviation. In order to determine and compare the significance of the influence of iron (II) sulfate solution and its concentration on the changes in wood color parameters, a one-way analysis of variance (ANOVA) was conducted at a significance level of 0,05. Statistical analysis of the test results was carried out using Statistica v. 13 software (TIBCO Software Inc., CA, USA). The calculations were performed using the Microsoft Excel program.

RESULTS

As a result of the application of an aqueous solution of iron (II) sulphate to the surface of spruce wood, the color of the wood changed – became grayish as the iron ions reacted with gallic acid to ferrous gallate, which subsequently oxidized to a dark ferric pyrogallate complex (Krekel

1999, Hundhausen, et al. 2020). The surface of the wood after a week was characterized by uneven staining, areas of a blue, gray color were formed. After a month of exposure, the color of the surface of the samples became even, although areas of more intense staining are still visible - the presence of intricate fibers was visible, which may contribute to the color change in a different way than wood with a straight grain arrangement. No effect of the presence of blue stain on the color changes of wood treated with iron (II) sulphate solution was observed. Blue stain became less visible due to the graying of the entire surface. Changes in the color of reaction wood under the influence of iron (II) sulphate were uniform, the surface became gray as in the case of wood without defects.

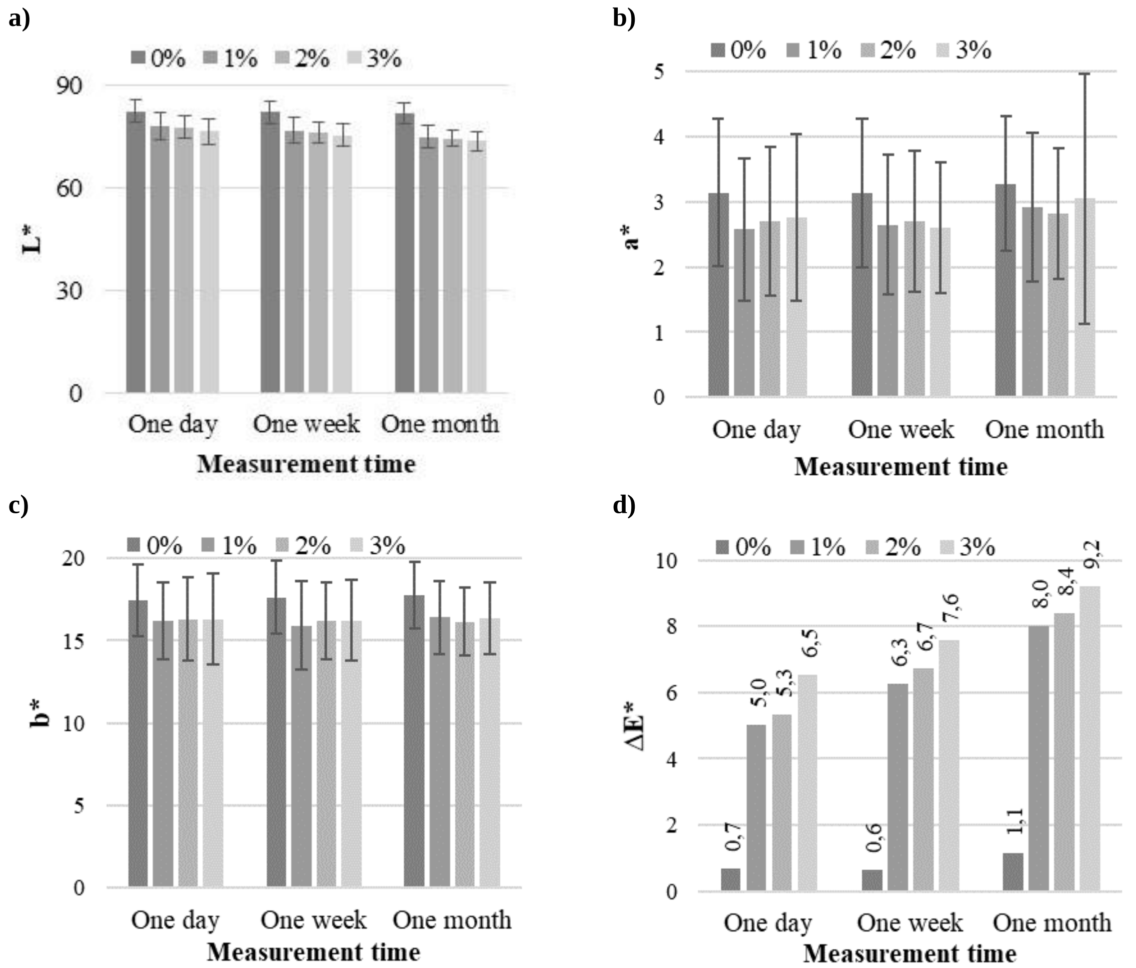

Figure 1. Coordinates of CIE Lab color system for individual variants (means and standard deviations in tentacles): a) L*, b) a*, c) b*, d) ΔE*

Table 1. The results of the one-factor analysis of variance for the color parameters measured the day after the application of the iron (II) sulphate solution

Parameter	Factor	Sum of squares	Mean sum of squares	Fisher's F-test	Significance level p
L*	Iron (II) sulphate	1360,77	453,59	36,112	0,000000
	Solution concentration	53,56	26,78	2,007	0,137920
a*	Iron (II) sulphate	12,71	4,24	3,149	0,025806
	Solution concentration	0,184	0,092	0,067	0,935228
b*	Iron (II) sulphate	84,64	28,21	4,749	0,003112
	Solution concentration	0,202	0,101	0,016	0,984603

* - significant at the 0.05 level.

The average values of the L* parameter determined on the day, week and month after treatment were shown in Fig. 1. As a result of treatment with iron II sulphate, the wood darkened. The concentration of the solution had no effect on the amount of darkening (Tab.1). The greatest change took place 24 hours after application of the solution, the further passage of time caused gradual but smaller changes in the L* value. Hundhausen et al. (2020) in their studies showed that spruce samples darkened slightly immediately after the application of the iron (II) sulfate solution and exposure to light caused a grayish color change and further darkening of the wood surface. With increasing concentration, the brightness values decrease, however, the differences between the tested concentrations were small and insignificant. Similar conclusion was made by Jankowska and Kwiatkowski (2022) who tested European oak wood.

The comparison of changes in lightness (ΔL*) between wood with blue stain, reactive wood and wood without defects is shown in Fig. 2. Clearly greater changes in lightness of samples treated with iron (II) sulphate were observed in all groups. This means that defects such as blue stain or reaction wood do not affect the size of wood color changes. The greatest difference between the applied concentrations of iron (II) sulphate solution was found for reaction wood.

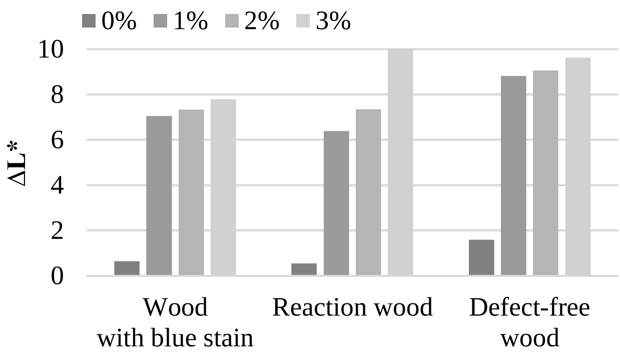

Figure 2. Comparison of changes in lightness (ΔL*) for different variants of the research material

The treated samples showed lower average a* values, i.e. a color closer to green than the control samples. The presence of reaction wood with a color closer to red, i.e. with a higher value of the a* parameter, had a large impact on the variability of the results. The reason for the increased values of the a* parameter one month after painting may be the effect of light. In a study by Muller et al. (2003) on spruce wood showed a slight initial decrease and a subsequent slight increase in the value of the a* parameter with increasing exposure time. The samples with the solutions applied showed lower mean b* values than the control samples. These differences are statistically significant (Tab.1). This means a color change towards blue. As in the case of the L* and a* parameters, the greatest change was observed 24 hours after the application of the iron (II) sulphate solution. Measurements performed one week and one month after application showed a slight increase in average b* values. It can be speculated that the lack of major changes is due to the large diffusion of sunlight entering the room where the samples were kept. Spruce wood (*Picea excelsa* L.) exposed to UV irradiation, mimicking the natural exposure of wood to sunlight, showed an increase in the b* value with increased exposure time (Müller et al. 2003). There were no significant differences in a* and b* values between the concentrations tested (Tab. 1).

The greatest change in the total color change of ΔE* took place the day after painting, the further passage of time caused a gradual increase of ΔE* (Fig. 1). The change in wood color under the influence of iron (II) sulphate probably occurs as a result of iron oxidation by free radicals formed during the photolysis of lignin ether bonds (Hundhausen et al. 2020). The concentration of the iron (II) sulphate solution had little effect on the overall color change. The samples treated with the 3% solution showed the greatest differences.

The wood has been naturally weathered for seven weeks. At that time, they were exposed to strong solar radiation, especially during the first month of exposure. There was frequent and heavy rainfall during the last week of exposition. After 4 weeks of outdoor exposure, grayish spots were seen on the control samples. Such local changes were not observed on wood treated with iron (II) sulphate solution before weathering, which may mean that the application of the preparation on wood before external exposure allows for a uniform change in surface color. Late wood changed color to a more pronounced orange-brown. Most likely, this is due to the action of UV rays, which cause the photolysis of lignin, changing the wood color (Müller et al. 2003). The color of wood with blue stain treated with iron (II) sulphate solution became even after the weathering. The previously visible light gray streaks of blue stain were not noticeable.

A clear decrease in the average values of the L* parameter of the samples subjected to the aging process was observed. This is in line with what Hundhausen et al. (2020), namely a significant decrease in the L* value, especially in the first weeks of weathering, which means darkening of the wood surface. The greatest changes were noted for samples treated with a 2% and 3% solution, the smallest change was shown for samples with a 1% solution. Both the impact of the iron (II) sulphate solution and its concentration have a significant impact on the brightness of the wood surface after weathering (Tab. 2). The statistical analysis shows that the parameters a* and b* measured after weathering depend on the impact of the iron (II) sulphate solution, while the concentration of the solution has no significant effect on their values.

Table 2. The results of the one-factor analysis of variance for the color parameters measured the day after the weathering process

Parameter	Factor	Sum of squares	Mean sum of squares	Fisher's F-test	Significance level p
L*	Iron (II) sulphate	1650,19	550,06	66,132	0,000000
	Solution concentration	410,57	205,29	21,796	0,000000
a*	Iron (II) sulphate	25,72	8,58	7,261	0,000186
	Solution concentration	7,11	3,55	2,935	0,059266
b*	Iron (II) sulphate	77,58	25,86	5,515	0,001514
	Solution concentration	29,49	14,74	3,080	0,051799

* - significant at the 0.05 level.

The highest total color change (ΔE*) was shown by samples with a 3% solution applied (Tab. 3). A surprising result is the lower ΔE* value of the samples painted with the 1% solution than the control samples. It can be concluded that the application of a solution with a concentration of 1% to the surface of wood reduces the range of changes in the color of spruce wood during exposure to the external environment.

Table 3. Differences in the average values of the parameters L*, a*, b* and the total color change (ΔE*) related to measurements after one month indoor exposure

Solution concentration	ΔL*	Δa*	Δb*	ΔE*
0%	-15,7	2,4	-0,7	16,5
1%	-13,5	2,1	-0,4	15,7
2%	-17,7	1,9	-0,5	19,5
3%	-17,9	1,3	-1,7	19,8

CONLUSIONS

On the basis of the conducted research on the change of the color of Norway spruce (*Picea abies* L.) wood under the influence of an aqueous solution of iron (II) sulphate of various concentrations, the following conclusions were formulated:

1. An aqueous solution of iron (II) sulphate changes the color of Norway spruce (Picea abies L.) wood to gray.
2. The greatest color change occurs shortly after application of the solution, with further time it causes gradual but slower changes in the color of the wood surface.
3. The concentration of the iron (II) sulphate solution does not affect the extent of the color change of the wood surface. Thus the use of solutions with concentrations higher than 1% seems to be unproductive.
4. Under the influence of natural aging, the surface color of spruce wood changes significantly. The two- and three-percent iron sulfate-treated samples showed greater changes than the control samples. Samples with a 1% solution achieved lower color change values than controls, which may be a topic for future research.
5. Modifying the surface of blue stained wood with a solution of iron (II) sulphate can be used as a method of reducing the visibility of this defect.

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Streszczenie: *Oddziaływanie siarczanu żelaza (II) na barwę drewna świerku pospolitego* Praca przedstawia wyniki badań zmiany barwy drewna świerku pospolitego (*Picea abies* L.) pod wpływem działania wodnego roztworu siarczanu żelaza (II) o trzech różnych stężeniach – 1%, 2%, 3%. Ocenę zmian barwy wykonano w oparciu o wyniki obserwacji makroskopowych jak również przeprowadzono pomiary parametrów barwy oraz ich zmiany w oparciu o przestrzeń barw CIELab. Celem określenia trwałości barwy powierzchni drewna traktowanego roztworem siarczanu żelaza (II) przeprowadzono naturalne starzenia w środowisku zewnętrznym.
Na podstawie przeprowadzonych badań wykazano, że siarczan żelaza (II) powoduje szarzenie drewna świerku pospolitego. Stwierdzono, że stężenie roztworu nie ma wpływu na zmiany barwy. Modyfikacja powierzchni drewna objętego sinizną za pomocą roztworu siarczanu żelaza (II), może być zastosowana jako metoda niwelowania widoczności tej wady. W wyniku ekspozycji drewna w środowisku zewnętrznym przez okres 7 tygodni powierzchnia drewna uległa wyraźnemu wybarwieniu, przy czym największą różnicę wykazały próbki modyfikowane roztworem 3%.

Słowa kluczowe: świerk pospolity, *Picea abies* L., siarczan żelaza, starzenie drewna

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