

Chemical Bleaching of Wood and Its Aging

An Investigation of Mahogany, Walnut, Rosewood, Padauk and Purpleheart

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ABSTRACT

This paper investigates chemical bleaching of wood and its ageing to make specie specific recommendations on which bleaching solutions to use when color adjusting veneer for furniture restoration. In more detail, chemical bleaching of European walnut (*Juglans regia*), Rio rosewood (*Dalbergia nigra*), purpleheart (*Peltogyne spp.*), Honduras mahogany (*Swietenia macrophylla*) and padauk (*Pterocarpus spp.*) has been investigated using eleven different bleaching solutions. Both oxidative (e.g. hydrogen peroxide and potassium permanganate) and reductive (e.g. oxalic acid and sodium bisulfite) solutions have been used. Furthermore, to investigate aging of the bleached surfaces they were subjected to sunlight behind a glass window until a change in Blue Wool Scale 3 was obtained. Visual examination has been used to rank the color change after the chemical bleaching and the sun light exposure experiment. A small color change after the sun light exposure experiment indicates a high degree of lightfastness and is preferred for long term stability when restoring furniture. The results show that the wood species react in different ways to the investigated bleach solutions and to sun light exposure. It can also be noted that all investigated solutions were not suitable for all wood species. Moreover, the sun light exposure experiment identified effective bleach solutions that gave an unacceptable low lightfastness for mahogany and padauk after chemical bleaching. Based on the chemical bleaching and sun light exposure results, preferred bleaching solutions are recommended for the investigated wood species.

Front page. The investigated wood species after chemical bleaching, with unbleached references to the left.

SVENSK SAMMANFATTNING

En vanlig restaureringsuppgift är att ställvis ersätta borttappat träfaner på en möbel. Originalfaneret har blekts med tiden, varför det nya faneret ofta är för färgstarkt och färgen behöver reduceras. När vi upplever en bit padouk som intensivt röd eller amarant som lila, beror det på att det i träet finns ämnen som tar upp energi motsvarande energin i våglängder av synligt ljus. När ämnena absorberar en del av det synliga ljuset registrerar våra näthinnor att de saknas, vilket tolkas som en färg av vår hjärna. De ämnen som absorberar synligt ljus kan brytas ner av solljus över längre tid eller på några minuter genom tillförseln av ett oxidations- eller reduktionsmedel.

I mitt examensarbete undersöker jag hur olika oxidations- och reduktionsmedel bleker olika träslag. Jag har valt att undersöka hondurasmahogny, europeisk valnöt, brasiliansk jakaranda, padouk och amarant, då det är träslag som ofta behöver blekas när de används i kompletteringar. Vidare undersöker jag hur den genom blekning erhållna färgen i träet i sin tur påverkas av solljus. Detta är viktigt för att förstå hur de restaurerade delarna på möbelen kommer att åldras. De viktigaste resultaten sammanfattas nedan:

- Valnöt, jakaranda och amarant reagerade på liknande sätt vid kemisk blekning med de i studien använda lösningarna. De blekas mest av natriumhydroxid och salter med väteperoxid.
- Mahogny och padouk reagerade på liknande sätt vid kemisk blekning. De blektes mest, med ett jämnt resultat, av väteperoxid med natriumhydroxid eller ammoniak.
- Oxidationsmedel blekte effektivare än reduktionsmedel.
- Enbart väteperoxid gjorde jakaranda mörkare.
- En hög ammoniakkoncentration gav blekare resultat än en låg på alla träslag utom amarant.
- Valnöt var mest ljusäkt av de undersökta träslagen.
- Majoriteten av mahognyproverna mörknade av solljusexponeringen.
- Jakaranda och padouk blektes av solljusexponeringen.
- Flertalet amarantprover mörknade och ett mindre antal blektes av solljusexponeringen.
- Solljusexperimentet identifierade blekningslösningar som gav oacceptabelt låg ljusäktethet på mahogny och padouk.

För effektiv blekning och godtagbar ljusäktethet rekommenderas följande lösningar för respektive träslag. Välj lösning beroende på önskad blekningsgrad (se Tabell 2 sid 10).

- Mahogny: väteperoxid, oxalsyra eller kaliumpermanganat och natriumbisulfit.
- Valnöt: väteperoxid med eller utan ammoniak, väteperoxid och natriumhydroxid med eller utan salter eller natriumbisulfit och oxalsyra.
- Jakaranda: väteperoxid med ammoniak, oxalsyra, väteperoxid och natriumhydroxid med eller utan salter, natriumbisulfit och oxalsyra eller kaliumpermanganat och natriumbisulfit.
- Padouk: natriumhydroxid, natriumsilikat och kalciumhydroxid följt av väteperoxid.
- Amarant: väteperoxid med eller utan ammoniak, väteperoxid och natriumhydroxid med eller utan salter eller kaliumpermanganat och natriumbisulfit.

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1. INTRODUCTION

In most species, heartwood has a darker color than sapwood. The spontaneously occurring transition of sapwood into heartwood is accompanied by the loss of its physiological activity and the formation of various secondary metabolites with darker color [1]. The color of wood depends on the specie's absorption and reflection of light, which is largely determined by its chemical components. Wood consists mainly of cellulose, hemicellulose and lignin. Cellulose and hemicellulose do not absorb visible light. It is assumed that lignin absorbs wavelengths below 500 nm, but many woods absorb light above 500 nm. The latter is attributed to phenolic substances such as flavonoids, lignin, tannin and quinine [1]. **Figure 1** shows an example of the chemical structure of a phenolic substance. It is the electrons in the conjugated double bonds (marked in **Figure 1**) in these structures that are responsible for colors [2]. In short, conjugated double bonds allow the atoms in the molecule to share electrons.

The reason for color is that when a molecule absorbs light it absorbs energy and goes to a state of higher energy than it had before. The energy difference between the normal state and the excited (more energetic) state is fixed. This energy difference in conjugated double bonds is equal to the energy of visible light and therefore some wavelengths of visible light will be absorbed. If all wavelengths are equally reflected by an object it appears white and if they are completely absorbed as black. If the reflected light is deficient in some wavelengths, because of absorption by conjugated double bonds, the eye and brain interpret the remainder as a particular color [2].

The phenolic substances can be both high-molecular-weight pigments that are insoluble in solvents, or low-molecular-weight pigments [1]. The latter can be extracted in solvents and are hence commonly referred to as extractives. It can be noted, that the color of a wood specie is most likely due to several colored substances, i.e. several substances with its own conjugated double bonds. The different colored substances have different chemical reactions when they age or are exposed to light as is described below.

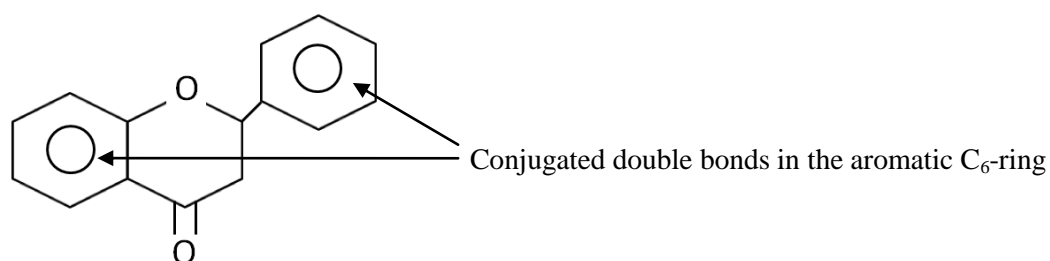


Figure 1. An example of a phenolic compound, in this case a flavonoid [3].

All wood species change color with light radiation, but the rate and the change in color varies. Moreover, wood species react differently to light of different wavelengths. Wood aged indoors is affected only by visible light, since very little UV radiation can penetrate common window glass [4]. In general, photo-induced discoloration of wood can be classified into five groups: darkening only, darkening and then fading, darkening-fading-darkening, fading only, and fading and then darkening [1]. In wood an intensive discoloration at the initial stage of light

exposure is often attributed to reactions with extractives. This is an example of the difference in chemistry of the colored substances.

Discoloration by light, or photo-oxidation, is a surface phenomenon that occurs down to about 250 μm into the wood. Light starts a sequential free radical chain reaction commonly using oxygen radicals. The oxygen can come from air or compounds in the wood. The free radicals can migrate in to the wood and cause discoloration deeper than light can penetrate; visible light can penetrate up to 200 μm and UV light 75 μm into wood. The oxygen radicals reacts with the conjugated double bonds and thus breaks the molecules responsible for color. Furthermore, the rate of photo-discoloration is affected by water content and is enhanced by metal ions in the wood.

A frequent task for furniture conservators is to add new veneer were original old veneer partially has been lost. Veneer on old furniture has commonly been discolored by light. Therefore, the color of the new replacement veneer has to be adjusted to match the old veneer. This is commonly done by chemical bleaching, sometimes followed by color dyeing since some colors may fade more than others over time.

Bleaching wood with chemicals aims at breaking the conjugated double bonds in the compounds responsible for the color. This means that not all double bonds must be broken, but the sharing of the electrons between the atoms must cease. This interrupts the absorption of visible light and thus removes the color. Chemical wood bleaching can be done either by oxidation (the loss of electrons) or by reduction (the addition of electrons). **Figure 2** shows two schematic reactions for this. A commonly used oxidation bleach in furniture conservation is hydrogen peroxide; an example of a reduction bleach is sodium bisulfite. In general, stains and dyes are considered to respond more to oxidative bleaching [2].

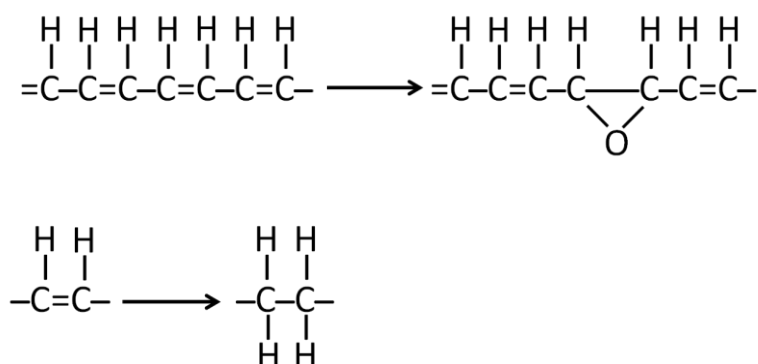


Figure 2. Schematic reactions of oxidation (upper) and reduction (lower) of colored compounds with conjugated double bonds in wood.

This study investigates chemical bleaching of five different wood species using eleven different chemical solutions (both oxidation and reducing agents and combinations thereof). Furthermore, the bleached wood species are partially exposed to sun light to investigate indoors aging of the bleached wood surfaces.

2. EXPERIMENTAL

Five wood species were selected for this study: European walnut (*Juglans regia*), Rio rosewood (*Dalbergia nigra*), purpleheart (*Peltogyne spp.*), Honduras mahogany (*Swietenia macrophylla*) and padauk (*Pterocarpus spp.*). The wood samples were examined macro- and microscopically to determine the specie. 12 heartwood samples were taken within an adjacent area of a log of each specie - one for each of the 11 test bleach solutions and a 12th as reference. The samples measured 5 x 32 x 80 mm³ (*T x W x L*). The samples were prepared using a band saw, a jointer and a thickness planer. The samples were photographed and to ensure correct colour documentation a gray card was used. The samples were stored in a dark box until commencing the bleaching test.

The chemicals and deionized water used were purchased from Fisher Scientific. The test bleach solutions were prepared as shown in **Table 1**. The rationale for including the various solutions in this investigation is also summarized in **Table 1**. All water used was deionized.

The bleaching tests were performed at ambient temperature of $20 \pm 0,5$ °C and relative humidity 28 %. The solutions were evenly applied to the samples using brushes. Each solution was applied to the five different wood species. The samples were afterwards rinsed thoroughly with deionizer water until pH of the rinse water was confirmed to be pH neutral (pH=7) using pH indicator strips pH 0-14 Universal from Merck. Several solutions, for example no 7 and 8, required significant amounts of rinsing to reach pH neutrality. The samples were left to dry in air after rinsing. The samples were visually ranked in terms of most bleached. Visual ranking was used, since this is how a replaced veneer piece on a restored furniture will be scrutinized. The result was documented by photography using a grey card as colour reference. It can be noted that reference [5] recommends using acetic acid to neutralize hydroxide and hydrogen peroxide after bleaching. It was decided not to use acetic acid to neutralize hydroxide in this investigation, due to the following rationales (i) the amount of acid required to reach pH neutrality is unknown and it is therefore more likely that you end up with excess acid or base and (ii) wood is porous, which makes neutralization difficult as acid and base molecules may be trapped in various pores and not react with each other as intended.

Furthermore, the samples were used for an aging study to investigate the impact of sunlight on the bleached wood samples. The Blue Wool Scale method was used as a reference to quantify the amount of sun radiation. Approximately half of the bleached wood surface was covered with aluminum foil as an none exposed reference. The sun light exposure experiment was carried out behind a window facing south until a change in Blue Wool Scale number 3 was noticed (the duration was 32 days in April - May in Stockholm, Sweden). This corresponds to approximately 3600 lux hours of exposure. Exposure to average indirect indoor lighting (120 to 180 lux) for 12 hours a day equals from 503 to 790 lux hours each year [6]. This corresponds to an estimated 4,5 to 6,8 years indirect indoor lighting exposure before the same change in colour as in this experiment would be noticed.

The degree of color change after sun light exposure was visually graded in four groups: none, minor, intermediate and major. Again, visual grading was used, since this is how a replaced veneer piece on a restored furniture will be scrutinized. The results were documented by photography using a grey card as colour reference. All photos of the samples in this report were color adjusted using the gray card in Adobe Photoshop CS5. A small color change after the sun light exposure experiment indicates a high degree of lightfastness and is preferred to use for long term stability. Therefore, it is recommended to use chemical solutions for bleaching for which the color change on the studied wood samples after sun light exposure were graded as none, minor or intermediate.

Table 1. The investigated bleach solutions, its preparation, application, rationale and proposed mechanism.

No.	Bleach Solution	Preparation of 100 ml	Technique of application	Rationale	Proposed mechanism
1.	35 % H ₂ O ₂	Hydrogen peroxide used fresh as received. H ₂ O ₂ decomposes in air.	Even coat applied and let to dry for 30 min.	Commonly used by conservators in Sweden.	H ₂ O ₂ is an oxidation bleaching substance. Reaction formula: 2H ₂ O ₂ → 2H ₂ O + O ₂ [7]
2.	35 % H ₂ O ₂	Hydrogen peroxide used fresh as received.	Even coat applied and heated with hot air gun.	Used by conservators at Rijksmuseum in Amsterdam.	
3.	34,65 % H ₂ O ₂ 0,35 % NH ₄	99 ml 35 % hydrogen peroxide and 1 ml 35 % ammonia. Closing container with H ₂ O ₂ and NH ₄ mixture may cause it to explode.	Mixed to one solution, even coat applied and let to dry for 30 min.	Commonly used by conservators in Sweden.	H ₂ O ₂ is an oxidation bleaching substance. Reaction formula: 2H ₂ O ₂ → 2H ₂ O + O ₂ . This reaction is catalyzed by hydroxide ions, OH ⁻ [6]. NH ₃ produces OH ⁻ thru the following equilibrium: NH ₃ + H ₂ O ↔ NH ₄ ⁺ + OH ⁻ [7]
4.	17,5 % H ₂ O ₂ 17,5 % NH ₄	50 ml hydrogen peroxide and 50 ml ammonia. Closing container with H ₂ O ₂ and NH ₄ mixture may cause it to explode.	Applied as in bleach no 3.	Used by some conservators in Sweden.	
5.	1,44 M C ₂ O ₂ (OH) ₂ in water	13,0 g oxalic acid in 100 ml water. Can be prepared in advance.	Applied as in bleach no 3.	Commonly used by conservators in Sweden.	Oxalic acid is a reducing bleaching agent.
6.	2,66 M C ₂ O ₂ (OH) ₂ in denatured alcohol	24,0 g oxalic acid in 100 ml denatured alcohol. Can be prepared in advance.	Applied as in bleach no 3.	Suggested to give stronger bleaching action than no 5 [8].	
7.	a 1,25 M NaOH	5,0 g sodium hydroxide in 100 ml water. Can be prepared in advance; store in a plastic container as it etches glass.	a-solution applied and let to dry 30 min. b-solution applied and let to dry for 30 min.	Claimed to be strong and effective [8].	OH ⁻ catalyses the reaction of H ₂ O ₂ : 2H ₂ O ₂ → 2H ₂ O + O ₂ Likely the ion HO ₂ ⁻ is formed as an intermediate reactant [7].
	b 35 % H ₂ O ₂	Hydrogen peroxide used fresh as received.			

No.		Bleach Solution	Preparation of 100 ml	Technique of application	Rationale	Proposed mechanism
8.	a	3,30 M NaOH 0,03 M Na ₂ SiO ₃ 0,10 M Ca(OH) ₂	13,18 g sodium hydroxide, 0,75 g sodium silicate, 0,75 g calcium hydroxide in 100 ml water. Can be prepared in advance; store in a plastic container as it etches glass. Avoid contact with acids, Na ₂ SiO ₃ forms a gel like substance.	Applied as in bleach no 7.	Bleach strength claimed to be better controlled than in no 7 bleach [8].	OH ⁻ catalyses the reaction of H ₂ O ₂ : 2H ₂ O ₂ → 2H ₂ O + O ₂ [7] Silicate enhances bleaching with hydrogen peroxide and magnesium sulphate (Epsom salt) stabilizes hydrogen peroxide increasing the bleaching [9].
	b	35 % H ₂ O ₂	Hydrogen peroxide used fresh as received.			
9.	a	4,29 M NaOH	15,0 g sodium hydroxide in 87,5 ml water. Can be prepared in advance.	b-solution carefully added to a-solution, applied and let to dry 30 min. c-solution applied and let to dry for 30 min.	Epsom salt is claimed to help stabilize peroxide in wood with high mineral content, thereby giving greater effectiveness than other peroxide caustic bleaches [8].	
	b	4,48 M MgSO ₄	6,74 g Epsom salt in 12,5ml water. Can be prepared in advance.			
	c	35 % H ₂ O ₂	Hydrogen peroxide used fresh as received.			
10.	a	0,43 M NaHSO ₃	4,5 g sodium bisulfite in 100 ml water.	Applied as in bleach no 7.	Shop bleach for walnut that is claimed to be less powerful than no 7 bleach [8].	NaHSO ₃ and oxalic acid are reducing agents.
	b	0,67 M C ₂ O ₂ (OH) ₂	6,0 g oxalic acid in 100 ml water. Can be prepared in advance.			
11.	a	0,05 M KMnO ₄	0,75 g potassium permanganate in 100 ml water.	a-solution applied. While still wet, b-solution applied and let to dry for 30 min.	Claimed to be a specialty bleach for European walnut [8].	KMnO ₄ is an oxidizing agent. NaHSO ₃ is a reducing agent.
	b	0,22 M NaHSO ₃	2,25 g sodium bisulfite in 100 ml water.			

3. RESULTS AND DISCUSSION

3.1 CHEMICAL BLEACHING INVESTIGATION

The effectiveness of the different bleach solutions on the wood species are presented in **Table 2**. The results are presented and discussed per wood specie and general observations regarding the different bleach solutions are summarized last in this section.

Table 2. The amount of bleaching of the different solutions on the wood samples. Ranked visually from least to most bleached. Bleach solutions with unsuitable result are marked with grey boxes.

Wood specie	Bleach solution number										
	Least bleached					Most bleached					
Mahogany	10 ^{a)}	2	1	6	5	11	3	4	7	8 ^{b)}	9 ^{b)}
Walnut	11 ^{a)}	5 ^{a)}	6 ^{a)}	1	10	2	3	7	4	9	8
Rosewood	1 ^{a)}	6 ^{a)}	2 ^{a)}	5	10	11	3	4	7	8	9
Padauk	6 ^{a)}	10 ^{a)}	5 ^{a)}	11	2	1	3	4	7	9 ^{c)}	8
Purpleheart	11	10 ^{d)}	5 ^{d)}	6 ^{d)}	2	1	4	3	7	9	8

Unsuitable due to:

- a) Darker than reference
- b) Uneven and red streaks
- c) Uneven
- d) Pink

3.1.1 Mahogany

The bleached mahogany samples ordered in increasing degree of bleaching together with the unbleached reference (left) are shown in **Figure 3**. Hydrogen peroxide with either sodium hydroxide or 50% ammonia (no 7, 4) gave the most bleached even result. Reducing the amount of ammonia (no 3) reduced the amount of bleaching. A moderate bleaching was accomplished by potassium permanganate followed by sodium bisulfite (no 11) and both oxalic acid in water and alcohol (no 5, 6). Least bleaching was accomplished by hydrogen peroxide (no 1, 2). It can be noted that heating the hydrogen peroxide with a hot air gun gave less bleaching than air drying. The following bleach solutions are not recommended for mahogany: oxalic acid with sodium bisulfite (no 10) that gave a darker mahogany and hydrogen peroxide with sodium hydroxide and salts (no 8, 9) that gave an uneven and red streaked result.

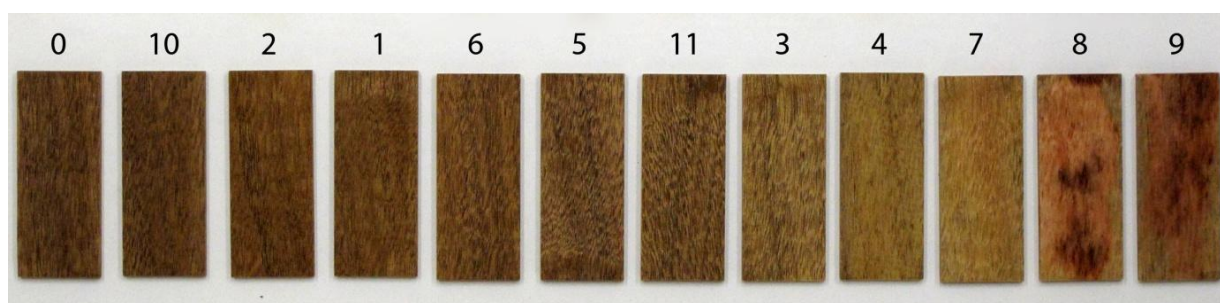


Figure 3. The bleached mahogany samples ordered from least bleached to most bleached together with the unbleached reference (left).

3.1.2 Walnut

The bleached walnut samples ordered in increasing degree of bleaching together with the unbleached reference (left) are shown in **Figure 4**. Hydrogen peroxide with sodium hydroxide and salts (no 8, 9) bleached walnut the most. This was followed by hydrogen peroxide with ammonia (no 3, 4) and sodium hydroxide (no 7), respectively, which in turn was followed by hydrogen peroxide (no 1, 2) and oxalic acid with sodium bisulfite (no 10). For walnut, heating the hydrogen peroxide with a hot air gun increased the amount of bleaching compared to air drying. Solution 7 should be a more effective bleaching solution than no 10 for walnut according to reference [8], which was supported by this study. The following bleach solutions are not recommended for bleaching walnut as they gave a darker colour: oxalic acid in water or alcohol (no 5, 6) and potassium permanganate followed by sodium bisulfite (no 11).

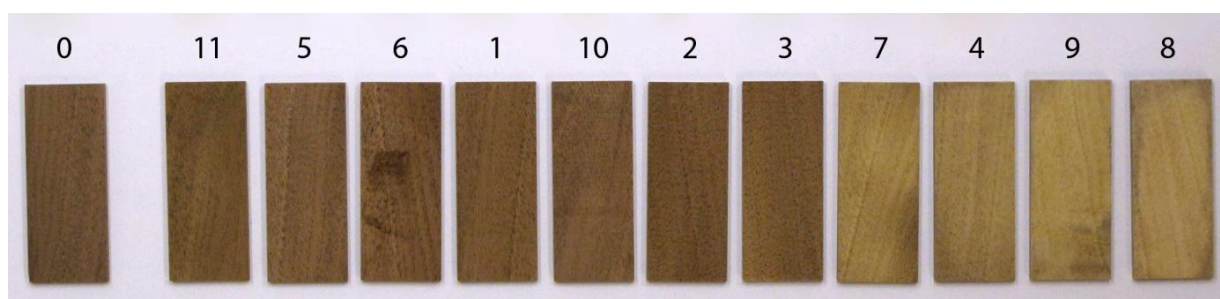


Figure 4. The bleached walnut samples ordered from least bleached to most bleached together with the unbleached reference (left).

3.1.3 Rosewood

The bleached rosewood samples ordered in increasing degree of bleaching together with the unbleached reference (left) are shown in **Figure 5**. Rosewood reacted similar to walnut with the bleaching solutions, except for treatment with hydrogen peroxide alone. Hydrogen peroxide with sodium hydroxide and salts (no 8, 9) bleached rosewood the most. This was followed by hydrogen peroxide with sodium hydroxide (no 7) and ammonia (no 3, 4), which in turn was followed by potassium permanganate with sodium bisulfite (no 11) and oxalic acid with sodium bisulfite (no 10) and oxalic acid in water (no 5). An interesting observation is also that black streaks in the rosewood were also successfully bleached by solutions no 3, 4 and 7-9; this was not the case for the other bleach solutions. The following bleach solutions

are not recommended for bleaching rosewood as they gave a darker colour: hydrogen peroxide (no 1, 2) and oxalic acid in alcohol (no 6).

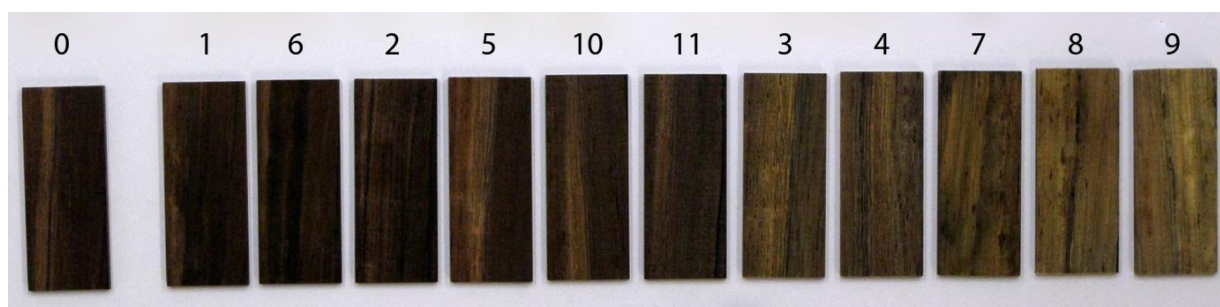


Figure 5. The bleached rosewood samples ordered from least bleached to most bleached together with the unbleached reference (left).

3.1.4 Padauk

The bleached padauk samples ordered in increasing degree of bleaching together with the unbleached reference (left) are shown in **Figure 6**. Padauk reacted similar to mahogany with the most effective bleach solutions (no 3-4, 7-9). Hydrogen peroxide with sodium hydroxide and salts (no 8) gave the most bleached, but somewhat uneven, result. Hydrogen peroxide with either sodium hydroxide or 50% ammonia (no 4, 7) gave the most bleached even result. Reducing the amount of ammonia (no 3) reduced the amount of bleaching. A moderate bleaching was accomplished by using hydrogen peroxide alone (no 1, 2). It can be noted that heating the hydrogen peroxide with a hot air gun gave less bleaching than air drying. The smallest amount of bleaching was accomplished by potassium permanganate followed by sodium bisulfite (no 11). The following bleach solutions are not recommended for bleaching padauk: all solutions with oxalic acid (no 5, 6 and 10) as they gave a darker color and hydrogen peroxide with Epsom salt (no 9) as it gave an uneven result.

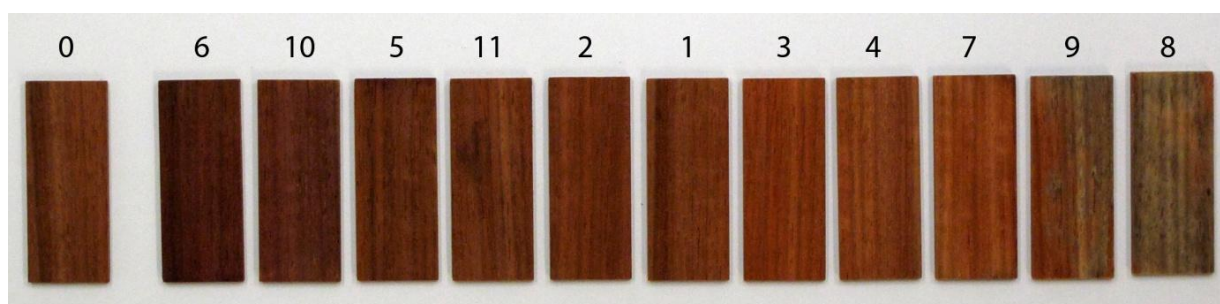


Figure 6. The bleached padauk samples ordered from least bleached to most bleached together with the unbleached reference (left).

3.1.5 Purpleheart

The bleached purpleheart samples ordered in increasing degree of bleaching together with the unbleached reference (left) are shown in **Figure 7**. Purpleheart reacted similar to walnut and rosewood for the solutions that bleached it the most (no 3,4 and 7-9). Hydrogen peroxide with sodium hydroxide and salts (no 8, 9) bleached purpleheart the most. This was followed by hydrogen peroxide with sodium hydroxide (no 7) and ammonia (no 3,4). It can be noted that a

higher concentration of ammonia (no 4) gave less bleaching than a lower concentration ammonia (no 3). A moderate bleaching was accomplished by hydrogen peroxide and again heating with a hot air gun reduced the bleaching of hydrogen peroxide (no 1, 2). The smallest amount of bleaching was accomplished by potassium permanganate followed by sodium bisulfite (no 11). The following bleach solutions are not recommended for bleaching purpleheart as they gave a pink colour: all solutions with oxalic acid (no 5, 6 and 10).



Figure 7. The bleached purpleheart samples ordered from least bleached to most bleached together with the unbleached reference (left).

3.1.6 General observations for the different bleach solutions

Table 3 shows the bleach solutions colored to illustrate similarities in solution chemistries and bleaching mechanisms.

Table 3. Same as table 2, with the addition that bleach solutions with similar chemistries and mechanisms are given the same color.

Wood specie	Bleach solution number										
	Least bleached					Most bleached					
Mahogany	10 ^{a)}	2	1	6	5	11	3	4	7	8 ^{b)}	9 ^{b)}
Walnut	11 ^{a)}	5 ^{a)}	6 ^{a)}	1	10	2	3	7	4	9	8
Rosewood	1 ^{a)}	6 ^{a)}	2 ^{a)}	5	10	11	3	4	7	8	9
Padauk	6 ^{a)}	10 ^{a)}	5 ^{a)}	11	2	1	3	4	7	9 ^{c)}	8
Purpleheart	11	10 ^{d)}	5 ^{d)}	6 ^{d)}	2	1	4	3	7	9	8

Unsuitable due to: ^{a)} Darker than reference. ^{b)} Uneven and red streaks. ^{c)} Uneven. ^{d)} Pink.

	Hydrogen peroxide with sodium hydroxide and salts – oxidation bleach.
	Hydrogen peroxide with sodium hydroxide or ammonia – oxidation bleach.
	Hydrogen peroxide (air and hot air gun drying) – oxidation bleach.
	Oxalic acid – reduction bleach.
	Permanganate followed by bisulfite - oxidation bleach then reduction bleach.

General observations regarding the different bleach solutions are summarized below:

- Oxidation bleaches (no 1-4 and 7-9) were more effective than reduction bleaches (no 5-6 and 10).
- Sodium hydroxide with salts (sodium silicate with calcium hydroxide and Epsom salt, respectively) followed by hydrogen peroxide (no 8, 9) were the most effective bleach solutions for all investigated wood species, but gave uneven results on mahogany and padauk.
- Hydrogen peroxide with sodium hydroxide or ammonia (no 7, 4 and 3) gave the 2nd most bleached woods and even surfaces on all wood species.
- Hydrogen peroxide alone (no 1, 2) gave rosewood a darker colour.
- Drying hydrogen peroxide with a hot air gun reduced the bleaching effect for all investigated wood species except walnut.
- A higher ammonia concentration (no 4 in comparison to no 3) gave a stronger bleach on all wood species except purpleheart.
- The bleaching effect of oxalic acid (no 5, 6 and 10) depended on the wood specie.
- Oxalic acid in denatured alcohol (no 6) is claimed to be more effective than in water (no 5) in reference [8]. This was only true for walnut, but not the other investigated wood species.
- This study supports the claim in reference [8] that hydrogen peroxide after a sodium hydroxide treatment is a strong and effective bleaching agent.
- Epsom salt is claimed to help stabilize peroxide and give a greater effectiveness compared to other peroxide caustic bleaches [8]. This was true for all investigated wood species in this study.
- The bleach strengths is claimed to be better controlled in solution no 8 than in no 7 [8]. These results did not support that; rather was the bleach strengths of no 8 stronger than 7.
- Solution no 10 is claimed to be less powerful than number 7 [8], which was supported by this study.
- Solution no 11 is claimed to be a specialty bleach for European walnut [8]. However, this solution did not bleach the walnut in this study.

3.2 SUN LIGHT EXPOSURE INVESTIGATION

3.2.1 References

The Blue Wool Scale samples after sun light exposure are shown in **Figure 8**. The reference wood samples (not chemically bleached) are also shown in **Figure 8**. The results show that mahogany was darkened, while walnut remained unchanged and purpleheart, rosewood and padauk were bleached by the sun light exposure. Thus, walnut had the highest lightfastness in this study. Padauk changed the most in this study; it lost all its red color component and turned brown. The purple color component was reduced in purpleheart.



Figure 8. The Blue Wool Scale samples (upper) and the by chemicals unbleached wood references (bottom) after sun light exposure. The upper parts of the samples have been exposed to sun light.


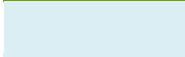





The change in color of the chemically bleached wood samples and the references after sun light exposure are summarized in **Table 4**. The degree of color change after sun light exposure was visually graded in four groups: none, minor, intermediate and major. A small color change after the sun light exposure experiment indicates a high degree of lightfastness and is preferred to use for long term stability. Therefore, it is recommended to use chemical

solutions for bleaching for which the color change on the studied wood samples after sun light exposure were graded as none, minor or intermediate.

Table 4. The sensitivity to sun light exposure of the chemically bleached wood samples together with references is presented with colors.

Wood specie	Sun light exposure results (numbers refers to bleach solution)											
	Ref	Chemically: Least bleached						Most bleached				
Mahogany	N/A	10 ^{a)}	2	1	6	5	11	3	4	7	8 ^{b)}	9 ^{b)}
Walnut	N/A	11 ^{a)}	5 ^{a)}	6 ^{a)}	1	10	2	3	7	4	9	8
Rosewood	N/A	1 ^{a)}	6 ^{a)}	2 ^{a)}	5	10	11	3	4	7	8	9
Padauk	N/A	6 ^{a)}	10 ^{a)}	5 ^{a)}	11	2	1	3	4	7	9 ^{c)}	8 ^{d)}
Purpleheart	N/A	11	10 ^{e)}	5 ^{e)}	6 ^{e)}	2	1	4	3	7	9	8

Unsuitable due to: ^{a)} Darker than reference. ^{b)} Uneven and red streaks. ^{c)} Uneven. ^{d)} Pink.

	none
	minor bleached
	intermediate bleached
	major bleached
	minor darkened
	intermediate darkened
	major darkened

The results are presented and discussed per wood specie below.

3.2.2 Mahogany

The mahogany samples after sun light exposure are shown in **Figure 9**. All samples, except the once bleached with solutions no 8 and 9, darkened to a similar color (see **Table 4**). Samples treated with no 8 and 9 were instead bleached, the red color component was reduced and the color remained uneven. There was no correlation between lightfastness and degree of chemical bleaching for mahogany. Based on the results after chemical bleaching, solutions no 1-7 and 11 were found to be suitable for bleaching mahogany. Combined with the advice to use solutions that showed none to intermediate color change after sun light exposure the following recommendation can be made: *It is recommended to bleach mahogany with hydrogen peroxide dried in air or with a hot air gun (no 1, 2) or oxalic acid in water or denatured alcohol (no 5, 6) or potassium permanganate followed by sodium bisulfite (no 11).* Thus, three bleach solutions were excluded from being recommended for use on mahogany after the sun light exposure experiment.

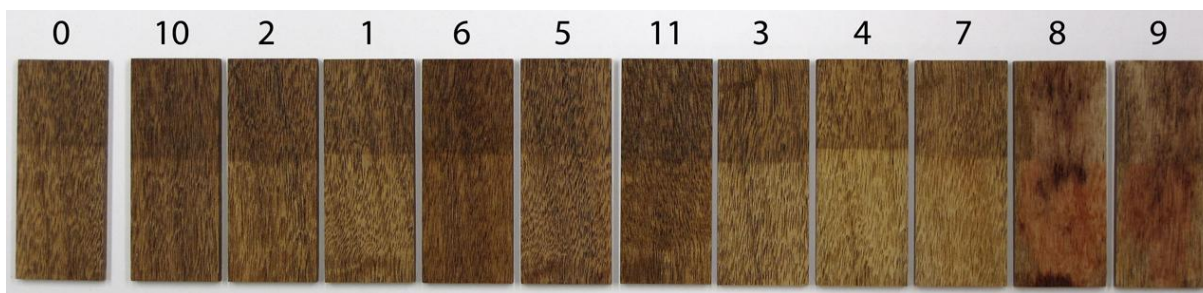


Figure 9. The bleached mahogany samples after sun light exposure ordered from chemically least bleached to most bleached, together with the unbleached reference (left). The upper parts of the samples have been exposed to sun light.

3.2.3 Walnut

The walnut samples after sun light exposure are shown in **Figure 10**. Walnut was least affected by sun light exposure and thus had the highest lightfastness in this study. There was no visible change of the reference or the samples bleached with hydrogen peroxide and ammonia (no 3, 4) or hydrogen peroxide with sodium hydroxide and Epsom salt (no 9). The rest of the samples showed a minor bleach (see **Table 4**). There was no correlation between lightfastness and degree of chemical bleaching for walnut; same as mahogany. Based on the results after chemical bleaching, solutions no 1-4 and 7-10 were found to be suitable for bleaching walnut. Combined with the advice to use solutions that showed none to intermediate color change after sun light exposure the following recommendation can be made: *It is recommended to bleach walnut with hydrogen peroxide alone or with ammonia (no 1-4) or hydrogen peroxide with sodium hydroxide alone or with salts (no 7-9) or with sodium bisulfite followed by oxalic acid (no 10)*. Thus, no bleach solution was excluded from being recommended for use on walnut after the sun light exposure experiment.



Figure 10. The bleached walnut samples after sun light exposure ordered from chemically least bleached to most bleached, together with the unbleached reference (left). The upper parts of the samples have been exposed to sun light.

3.2.4 Rosewood

The rosewood samples after sun light exposure are shown in **Figure 11**. The color of the most chemically bleached sample was not changed, whereas all the other rosewood samples were bleached by the sun light exposure. The degree of sun bleaching ranged from minor to major (see **Table 4**). There was a correlation between lightfastness and degree of chemical bleaching for rosewood; a more chemically bleached surface was more lightfast. Based on the results after chemical bleaching, solutions no 3-5 and 7-11 were found to be suitable for

bleaching rosewood. Combined with the advice to use solutions that showed none to intermediate color change after sun light exposure the following recommendation can be made: *It is recommended to bleach rosewood with hydrogen peroxide with ammonia (no 3, 4) or oxalic acid in water (no 5) or hydrogen peroxide with sodium hydroxide alone or with salts (no 7-9) or with sodium bisulfite followed by oxalic acid (no 10) or potassium permanganate followed by sodium bisulfite (no 11).* Thus, no bleach solution was excluded from being recommended for use on rosewood after the sun light exposure experiment.

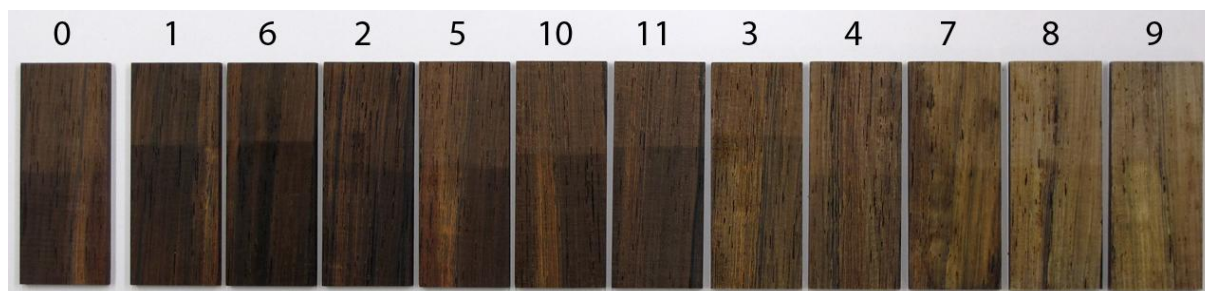


Figure 11. The bleached rosewood samples after sun light exposure ordered from chemically least bleached to most bleached, together with the unbleached reference (left). The upper parts of the samples have been exposed to sun light.

3.2.5 Padauk

The padauk samples after sun light exposure are shown in **Figure 12**. The red color component had vanished in all samples after sun light exposure. This shows that sun light can be used to remove remaining red color components in padauk after chemical bleaching. The degree of sun bleaching in the samples ranged from intermediate (samples treated with solution no 8, 9) to major (all other samples; see **Table 4**). In samples 8 and 9 there was least red color remaining after the chemical bleaching and here bleaching of the wood besides reduction in the red color could be observed. There was a correlation between lightfastness and degree of chemical bleaching for padauk; as for rosewood a more chemically bleached surface was more lightfast. Based on the results after chemical bleaching, solutions no 1-4 and 7-9 were found to be suitable for bleaching padauk. Combined with the advice to use solutions that showed none to intermediate color change after sun light exposure the following recommendation can be made: *It is recommended to bleach padauk with hydrogen peroxide after treatment with sodium hydroxide, silicate and calcium hydroxide (no 8).* Thus, several bleach solutions were excluded from being recommended for use on padauk after the sun light exposure experiment. However, the results also suggest that a short sun light exposure (estimated to about 2 weeks) removes the red color component and thus more bleaching solutions could be appropriate to use.

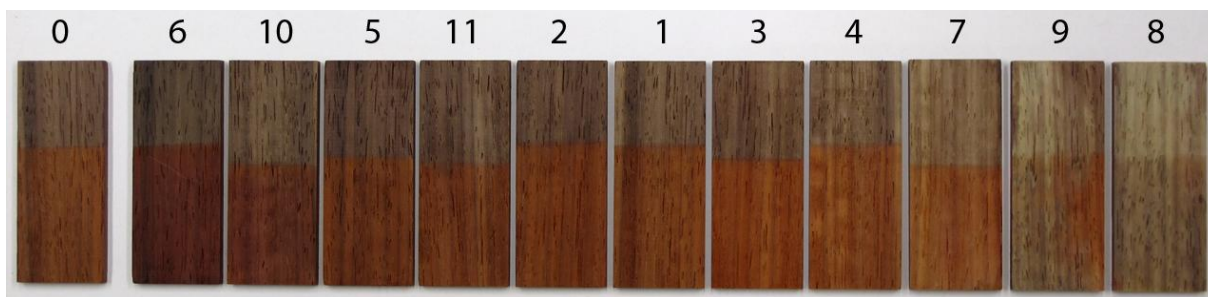


Figure 12. The bleached padauk samples after sun light exposure ordered from chemically least bleached to most bleached, together with the unbleached reference (left). The upper parts of the samples have been exposed to sun light.

3.2.6 Purpleheart

The purpleheart samples after sun light exposure are shown in **Figure 13**. The degree of color change ranged from intermediate to major bleached and minor to intermediate darkened (see **Table 4**). An overall observation is that all samples (except samples treated with solutions no 8, 9) were similar in color after sun light exposure. For example, sample 1 and 10 could not be distinguished from another. In more detail, purple and pink colors tones were reduced in the reference and samples treated with solutions no 5, 6, 10 and 11 after sun light exposure. Instead, the purple color tone had increased in samples treated with solution 1-4 and 7-9; although to a lesser extent for samples treated with solution no 8 and 9. There was a trend towards a correlation between lightfastness and degree of chemical bleaching for purpleheart, however it was not strict as for rosewood and padauk. Based on the results after chemical bleaching, solutions no 1-4, 7-9 and 11 were found to be suitable for bleaching purpleheart. Combined with the advice to use solutions that showed none to intermediate color change after sun light exposure the following recommendation can be made: *It is recommended to bleach purpleheart with hydrogen peroxide alone or with ammonia (no 1-4) or hydrogen peroxide with sodium hydroxide alone or with salts (no 7-9) or with potassium permanganate followed by sodium bisulfite (no 11)*. Thus, no bleach solution were excluded from being recommended for use on purpleheart after the sun light exposure experiment.

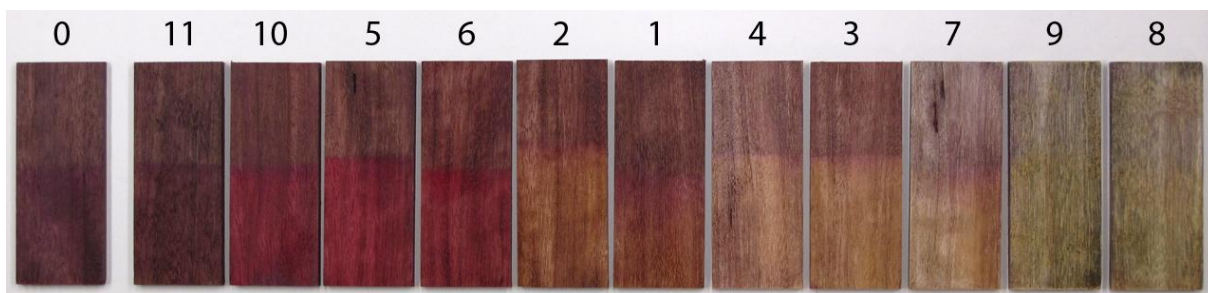


Figure 13. The bleached purpleheart samples after sun light exposure ordered from chemically least bleached to most bleached, together with the unbleached reference (left). The upper parts of the samples have been exposed to sun light.

4. CONCLUSIONS

The investigated wood species reacted in different ways with the bleach solutions in this study, although similarities for effective bleach solutions could be found. Exposing the chemically bleached wood samples and references to sun light behind a glass window showed that color change depended on the wood specie and for some wood species also on the chemical bleach solution used. The key findings are summarized below:

- Walnut, rosewood and purpleheart reacted similarly to chemical bleaching when using the solutions investigated in this study. They were most bleached by hydrogen peroxide bleaches with sodium hydroxide and salts (no 8,9).
- Mahogany and padauk reacted similarly to chemical bleaching and were most even bleached by hydrogen peroxide with sodium hydroxide or ammonia (no 3,4 and 7).
- Hydrogen peroxide with sodium hydroxide or ammonia (no 3,4 and 7) gave the 2nd most bleached woods and even surfaces on all investigated wood species.
- Oxidation bleaches were more effective than reduction bleaches.
- Hydrogen peroxide alone (no 1, 2) is not suitable for bleaching rosewood as it gave rosewood a darker colour.
- Drying hydrogen peroxide with a hot air gun reduced the bleaching effect for all investigated wood species except walnut.
- A higher ammonia concentration (no 4 in comparison to no 3) gave a stronger bleach on all wood species except purpleheart.
- Oxalic acid in water was only a suitable bleach solution for mahogany and rosewood.
- Walnut showed the highest lightfastness in this study; the reference and chemically bleached samples were none to minor bleached.
- A majority of the investigated mahogany samples were darkened by sun light exposure.
- Rosewood and padauk were bleached by the sun light exposure.
- The purpleheart samples obtained a similar color after sun light exposure; the chemically most bleach sample darkened and the chemically least bleach samples were bleached by the sun light exposure.
- There was a correlation between lightfastness and degree of chemical bleaching, i.e. a more chemically bleached surface was more lightfast, for rosewood and padauk. Purpleheart showed a similar trend. There was no such correlation for walnut and mahogany.
- The sun light exposure experiment identified effective bleach solutions that gave an unacceptable low lightfastness on the end result of mahogany and padauk.

For effective bleaching and an acceptable lightfast result it is recommended to bleach:

- **Mahogany** with hydrogen peroxide dried in air or with a hot air gun (no 1,2) or oxalic acid in water or denatured alcohol (no 5, 6) or potassium permanganate followed by sodium bisulfite (no 11).

- **Walnut** with hydrogen peroxide alone or with ammonia (no 1-4) or hydrogen peroxide with sodium hydroxide alone or with salts (no 7-9) or with sodium bisulfite followed by oxalic acid (no 10).
- **Rosewood** with hydrogen peroxide with ammonia (no 3,4) or oxalic acid in water (no 5) or hydrogen peroxide with sodium hydroxide alone or with salts (no 7-9) or with sodium bisulfite followed by oxalic acid (no 10) or potassium permanganate and sodium bisulfite (no 11).
- **Padauk** with hydrogen peroxide after treatment with sodium hydroxide, silicate and calcium hydroxide (no 8).
- **Purpleheart** with hydrogen peroxide alone or with ammonia (no 1-4) or hydrogen peroxide with sodium hydroxide alone or with salts (no 7-9) or with potassium permanganate and sodium bisulfite (no 11).

5. FUTURE WORK

This paper investigates chemical bleaching and its ageing aiming at understanding how veneer pieces used in furniture restoration will change over time. It would be interesting to also investigate aging of wood after chemical bleaching in combination with:

- staining wood with dye, e.g. Herdins bets commonly used by Swedish furniture conservators.
- surface treatments like shellac.

For example, interesting questions regarding aging and color change of chemically bleached and dyed wood are: What light induced color change is due to chemical bleaching and what is due to changes in the dye? Does dye absorb light and prevent bleaching of wood further (similar to a sun lotion)? An investigation combining chemical bleaching, dye, surface treatment and aging is a significant task that would add important understanding to the aging of added veneer in furniture restoration. This investigation would benefit from using an experimental planning method, e.g. Design of Experiments [10], to reduce the number of experiments and yet obtain valid conclusions.

Moreover, it would be interesting to investigate hydroxide at other concentrations in combination with hydrogen peroxide. These can be more minor tasks. For example, investigate hydroxide:

- at low concentration similar to what is obtained by using ammonia. It is an advantage to avoid using ammonia, since it is both toxic and harmful to the environment.
- in combination with a buffer, to ensure a stable hydroxide concentration.
- at other concentration than used in this paper, e.g. test other concentrations of hydroxide together with Epsom salt.
- from other sources than NaOH and NH₃.

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7. REFERENCES

- [1] **Hon DNS, Minemura N** (2001) *Color and Discoloration*. In: Hon DNS, Shiraishi N (eds) Wood and cellulosic chemistry, 2nd edition. Marcel Dekker, pp 385-442.
- [2] **Commission, Museums & Galleries** (1992) *Science for conservators volume 2*. Routledge, pp 113-116.
- [3] **Hon DNS, Minemura N** (2001) *Chemistry of Extractives*. In: Hon DNS, Shiraishi N (eds) Wood and cellulosic chemistry, 2nd edition. Marcel Dekker, pp 218-220.
- [4] **Williams, RS** (2005) *Weathering of Wood*. In: Rowell RM (eds) Handbook of Wood Chemistry and Wood Composites. CRC Press, pp 140-142.
- [5] **Rivers S, Landrey G, Gritt S** (2003) *Conserving transparent coatings on wood*. In: Rivers S, Umney N (eds) Conservation of Furniture, pp 614-616.
- [6] **www.drb-mattech.co.uk/uv%20blue%20wool.html**. [Online] [Cited 2012 05 01]
- [7] **Hägg, Gunnar** (1989) *Allmän och oorganisk kemi*, ninth edition. Almqvist & Wiksell, pp 488, 520.
- [8] **www.fpl.fs.fed.us/documnts/fplrn/fplrn165.pdf**. This reasearch note is a slight revision of a report written in 1948 by chemical engineer Leslie E Downs. [Online] [Cited 2012 02 10]
- [9] **Burton JT** (1986) *An investigation into the Roles of Sodium Silicate and Epsom Salt in Hydrogen Peroxide Bleaching*. J of Pulp and Paper Sci 12:95-99.
- [10] **www.itl.nist.gov/div898/handbook/pri/section1/pri11.htm**. [Online] [Cited 2012 05 10]