



## Finishing Properties of Poly Urethane Coating on Bleached and Ammonia Fumigated Mango Wood Surface

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### Authors' contributions

This work was carried out in collaboration among all authors. Author SP designed the study, performed the statistical analysis, wrote the protocol, author SR wrote the first draft of the manuscript and author GS managed the analyses of the study. Authors SG and VSKK managed the literature searches. All authors read and approved the final manuscript.

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### ABSTRACT

**Aims:** The impact of bleaching chemicals on the gloss and film thicknesses of poly urethane (PU) coated surface of mango wood (*Mangifera indica*) with ammonia fumigation and an exposure towards sunlight was investigated

**Study Design:** Thirty six wood samples of size 10.6 cm (length) X 7.62 cm (width) were prepared from 2.5 cm thick kiln dried mango wood (*Mangifera indica*). Specimens were divided into six groups, each group having 6 samples for the study.

**Place and Duration of Study:** The experiment was carried out in year 2016 at the Laboratory of Forest Product Division, Forest Research Institute, Dehradun, Uttarakhand, India.

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**Methodology:** All the samples were sanded with 80 grit size sand paper and coated with poly urethane. Two chemicals were used for bleaching purpose like an aqueous solution of oxalic acid ( $H_2C_2O_4$ ) was prepared with 30% concentration (by mixing 42.9 g of the solute in 100 ml of hot water) and a commercially available Hydrogen peroxide ( $H_2O_2$ ) was used as such (30%). For the purpose of bleaching, these chemicals were applied on to the sanded surfaces using brush at room temperature. The bleached sample surfaces were allowed to dry before proceeding to the next step. The PU (Poly Urethane) coated samples were treated with ammonia fumigation before and after bleached with the two chemicals. Ammonia fumigation was carried out in a fumigation chamber for 24 hours for all the samples (except  $T_1$ ).

**Results:** On exposure to natural sunlight for 60 hours, all the samples showed reduction in film thickness in PU coating but in a wide range of 2.8 % to 11.4%. The highest loss of coating thickness was shown by samples which were neither fumigated nor bleached. Among the fumigated samples, those bleached with oxalic acid resulted in high film thickness loss. Samples bleached with hydrogen peroxide after ammonia fumigation resulted in least film thickness reduction. Both ammonia fumigation and bleaching in general brought down the original gloss of poly urethane coating. The gloss value reduced as expected on exposure to sunlight. Bleaching by hydrogen peroxide prior to ammonia fumigation resulted in highest loss in gloss

**Conclusion:** The un-fumigated and unbleached surface resulted in minimum gloss reduction due to long exposure to sunlight.

*Keywords: Film thickness; gloss; hydrogen peroxide; oxalic acid.*

## 1. INTRODUCTION

There is a distinct difference in colour of various wood species. The variation of natural colour in wood is due to the presence of chemical substances in the heartwood. In wooden furniture, colour is one of the most important aesthetic aspects. The colour of wooden furniture should suit the other aesthetic items in a room. The natural colour of wood may not always achieve the desired aesthetics. To achieve the desired furniture colour, the choice is generally limited to colour in resemblance with or darker than the natural colour of the wood. Painting or bleaching of the wood/furniture is adopted to overcome this situation [1]. Each of wood species has its own variation in colour, texture and grain pattern. Usually, heartwood is darker than sapwood for most species. One way of overcoming this colour difference is through bleaching the wood before finishing.

The finishing of wood plays an important role towards the protection of colour in wood. The finishing liquid when applied to the wood surface the appearance of wood is transformed as it highlights the colour and figure in wood surface. Different finishing liquid can be used to protect the wood from dirt and moisture like shellac, wax, poly urethane, varnish etc. To gain the desired colour in the wood surface and to clean the wood before another colour application, bleaching is also an unavoidable option.

Bleaching is the removal of colour pigments in the structure of wood using various bleaching

chemicals and it is a good technique for removing stain also. Different types of stains require different bleaching techniques. The abrasive materials, such as sandpaper is generally used to remove the old finishes, but due to the use of sandpaper the patina (aged look) of the wood gets destroyed, and edges may be rounded off, designs may get flatten and scratches may appear on to the wood surface. Hence Sandpaper should not be preferred to remove the old finish; instead bleaching of wood would be more helpful in this case [2].

Bleaches often contribute to good quality and lasting finishes. Specialty bleaches are available for removal of iron stains, mineral streaks, fungus discoloration and chemical stains. Furniture is usually bleached to obtain lighter, brighter and clearer finishes [3]. Another important reason for bleaching is, to improve surface characteristics for adsorption of finishes [4]. Bleaching is also employed for changing the properties of wood surfaces before coating in order to reduce their photo yellowing [5].

Normally when wood is exposed to outdoor conditions, there is a drastic reduction in its hardness and glossiness. However this effect has been observed to be reversed with bleaching after exposure to outdoor conditions [6]. The bleaching of surface can be used for the restoration of wooden materials exposed to outdoor conditions but different wood species respond differently to bleaching [7]. Kristiansson, [8] explains that during bleaching of wood with

chemicals, the breaking of conjugated double bonds in the compounds is responsible for the colour changes that result. Chemical wood bleaching can be carried out either by oxidation (the loss of electrons) or by reduction (the addition of electrons).

Mango (*Mangifera indica*) wood is a popular commercial manufacturing material and growing in popularity amongst designers, manufacturers and consumers. The reasons behind its popularity are numerous, but the most important factor is its sustainability in availability. The density variations seem to be irrelevant with respect to the possible impact on mechanical properties of ammonia treated wood. However, stiffness and strength losses were in the range of 6 to 15%, which is negligible with respect to common solid wood applications. It is in this context that a preliminary study on this wood surface was taken up using an oxidative (hydrogen peroxide) and a reductive chemical (oxalic acid).

## 2. MATERIALS AND METHODS

Thirty six wood samples of size 10.6 cm (length) X 7.62 cm (width) were prepared from 2.5 cm thick kiln dried mango wood (*Mangifera indica*). Specimens were divided into six groups, each group having 6 samples. All the samples were sanded on one surface using 80 grit size sand paper on a belt sander.

An aqueous solution of oxalic acid ( $H_2C_2O_4$ ) was prepared with 30% concentration (by mixing 42.9g of the solute in 100ml of hot water). A commercially available Hydrogen peroxide ( $H_2O_2$ ) was used as such (30%). For the purpose of bleaching, these chemicals were applied on to the sanded surfaces using brush at room temperature. The bleached sample surfaces were allowed to dry before proceeding to the next step. Ammonia fumigation was carried out in a fumigation chamber for 24 hours for all the fumigated samples (except  $T_1$ ). The steps of treatments given to the samples are detailed in Table 1.

The 12 samples in groups NF and AF ( $T_1$  and  $T_2$ ) were not given any bleaching treatments. The 12 samples in  $T_3$  and  $T_4$  (HPAF and OAAF) were ammonia fumigated after the bleaching treatment. The rest of the 12 samples in  $T_5$  and  $T_6$  (AFHP and AFOA) were given the bleaching treatment after ammonia fumigation.

All the samples were given light sanding using 320 grit sand paper prior to coating with

Polyurethane (PU). In all cases, two coats of PU were applied on to the surfaces using muslin cloth. Enough time was given for the first coat to dry before applying the second coat.

After the coats dried, initial gloss (IG) was measured with the help of a tri-Micro gloss meter [9] using the EN ISO 2813 (1999) standards, a 60° light beam angle was used [10]. A total of 3 random gloss readings were taken on each sample so that for each treatment, there were 18 (6x3) readings. In a similar manner, 18 random readings of the initial film thicknesses (IFT) also were recorded using a film thickness gauge [11]. The samples were then exposed to natural sunlight for following hours 6 h to 60 h. The gloss readings were measured after every 6 h of exposure as explained above. The final film thicknesses (FFT) were recorded after 60 h of natural sunlight exposure as was done initially. The sunlight exposure took 10 days. Thus there were 18 gloss readings and 18 film thickness readings were available for each treatment and for each time they were recorded.

Reduction in Film thickness and gloss were calculated as % with respect to their corresponding initial values.

Gloss reduction (GR) = IG – FG

Gloss reduction percentage (GR%) =  $\frac{GR}{IG} * 100$

Where IG is the initial gloss and FG is the final gloss

Film Thickness reduction (FTR) = IFT – FFT

Film Thickness reduction percentage (FTR%) =  $\frac{FTR}{IFT} * 100$

Where IFT is the initial Film Thickness and FFT is the final Film Thickness

Statistical analyses were carried out using SPSS software.

## 3. RESULTS AND DISCUSSIONS

The bleaching treatments had some visual effects on this surface. The colour changed to yellow in case of hydrogen peroxide and little pinkish in case of oxalic acid. Bleaching of Pine wood with NaOH and  $H_2O_2$  has been reported to cause yellowing and increased red value due to a commercial bleaching agent containing oxalic acid and ethyl alcohol [10]. The Oxalic acid

bleached sample also had some white patches on their surfaces. Wood carbohydrates are probably all white. In bleaching process, first darkening of the wood occurs followed by the leaching out of extracts, and simultaneous extraction with evolution of gas [12].

### 3.1 The Effect of Bleaching on the Film Thickness (FT)

Initial mean film thicknesses (IFT) of the coatings varied from 34µm to 36µm. The important observation is that these thickness values due to two coats of PU achieved on *M. indica* is far less than the value (54.9 µm) reported for *Dalbergia sissoo* [11]. The thickness obtained with two coats of an acrylic varnish containing PU on the surface of pine was even more (66.5 µm) which was attributed to the greater volume of voids in pine [13]. Film thickness achieved is not only the coating's property but is a combined effect of coating and wood substrate on which it is applied. Though, the mean IFT achieved did not vary much on the six sets of samples, the individual values were analyzed through one-way ANOVA which confirmed that the means actually differ significantly ( $p < 0.001$ ). Hence, To investigate the actual pattern, Duncan's subsets were formed with the Initial thickness values 34. Duncan's subsets were formed with the IFT values which are shown in Table 2.

The table distributes the initial FT values into three subgroups. It also shows that the thickest film formation is on the sample surfaces

bleached with hydrogen peroxide irrespective of the fumigation. The other bleaching agent has resulted in 34 µm -35 µm film thicknesses which are significantly lower than that obtained on the surfaces bleached with H<sub>2</sub>O<sub>2</sub>. A study on time dependent bleaching by H<sub>2</sub>O<sub>2</sub> of basswood (*Tilia*) has shown decreases in cellulose, hemicellulose, and lignin content [14]. Moreover, the initial surface roughness and the type of wood substrate always influence the film formation [15]. Thus, a surface modification leading to formation of thicker coats on H<sub>2</sub>O<sub>2</sub> bleached surfaces can be expected.

It was found that 60 hours of exposure to natural sunlight resulted in measurable reduction in film thicknesses in each case. The mean values of the final film thicknesses (FFT) ranged between 31 µm and 35µm. All the individual FFT values also were analyzed using one-way ANOVA which again indicated significant differences ( $p < 0.001$ ). As in the case of IFT, these final values also were tested through Duncan's homogeneity, and the subsets obtained are given in Table 3.

Unlike in the case of initial FT the final FT is found to be distributed and is grouped into five subsets. This indicates different levels of effect due to sun exposure of the coated surfaces. The final film thickness reduces in all cases. Samples first ammonia fumigated and then bleached with hydrogen peroxide showed the highest film thickness of 35µm. These samples have probably not lost much of its initial coat thickness

**Table 1. Treatments given to the six groups of samples prior to PU coating**

Treatment	Sample Group name	Step 1	Step 2
T <sub>1</sub>	NF	-	-
T <sub>2</sub>	AF	Ammonia fumigation	-
T <sub>3</sub>	HPAF	Bleaching by H <sub>2</sub> O <sub>2</sub>	Ammonia fumigation
T <sub>4</sub>	OAAF	Bleaching by Oxalic acid	Ammonia fumigation
T <sub>5</sub>	AFHP	Ammonia fumigation	Bleaching by H <sub>2</sub> O <sub>2</sub>
T <sub>6</sub>	AFOA	Ammonia fumigation	Bleaching by Oxalic acid

**Table 2. Duncan's subsets for Initial film thickness of different sets**

Sample Set	Number of readings	Subsets of IFT (µm)		
		1	2	3
AFOA	18	34		
AF	18	35	35	
NF	18	35	35	
OAAF	18		35	
HPAF	18			36
AFHP	18			36
Sig.		0.275	0.275	0.907

**Table 3. Duncan's subsets for final film thickness of different sets**

Sample Set	Number of readings	Subsets of FFT ( $\mu\text{m}$ )				
		1	2	3	4	5
NF	18	31				
AFOA	18	31	31			
AF	18		32			
OAAF	18			33	33	
HPAF	18				34	
AFHP	18					35
Sig.		0.243	0.206	0.284	0.099	1.000

which was 36  $\mu\text{m}$ . Here again the surfaces bleached with H<sub>2</sub>O<sub>2</sub> have retained the highest thicknesses of the PU coat. However, unlike in IFT, the FFT of H<sub>2</sub>O<sub>2</sub> bleached samples which were ammonia fumigated before bleaching stands out with 35  $\mu\text{m}$  (against 36  $\mu\text{m}$  before exposure). The behavior of the other bleaching agent (OA) looks to be quite interesting. Bleaching with OA after ammonia fumigation (AFOA) has resulted in least film thickness before and after sun exposure. Another interesting observation is that PU on un-bleached surface has considerably lost its film thickness due to natural exposure (from 35  $\mu\text{m}$  to 31  $\mu\text{m}$ ).

Having looked at the initial and final coating thicknesses, it would be interesting to see the extent of reduction in FT due to natural sun-exposure. Fig. 1 shows the reduction percentages in film thickness of PU coating compared to the initial values after the sunlight exposure calculated as described in the methodology section.

As seen from Fig. 1, the highest reduction percentage of 11.4% is observed in unbleached and un-fumigated PU coated surfaces followed by those bleached with OA after ammonia fumigation and the unbleached fumigated samples. The least reduction of 2.8% is found with samples ammonia fumigated and then bleached with hydrogen peroxide. Different rates of depletion of polymer coatings are reported to be linked to surface or bulk driven photo-chemical erosion. The initial rate of material erosion is reported to be constant and non-specific to two polymers studied by Melo *et al.* [16]. According to Tator [17], polyurethane resins are transparent to short wave UV radiations and they allow them to pass through with very little molecular absorption. Kim *et al.* [18] reported that long term natural weathering on historical monuments degraded the lignin linearly from the surface. Thus, the major degradation is caused to the wood surface underneath the polyurethane coat which affects the stability of coating film over it.

However, except for one case (HPAFPU), all the bleached samples seem to lose thickness of the PU coating to a lesser extent (2.8 to 8.8%). It is to note that all sets of samples which showed more than 8.6 % FTR resulted in lowest final film thicknesses of 31  $\mu\text{m}$  – 32 $\mu\text{m}$  (Table 3). The least reduction of 2.8 % is found with samples ammonia fumigated and then bleached with hydrogen peroxide. This set of samples indeed had the thickest (35 $\mu\text{m}$ ) coating after 60 hrs of sunlight exposure. Uysal *et al.* [4] reported that Scots pine surface bleached with NaOH+H<sub>2</sub>O<sub>2</sub> solution resulted in hardest varnish layer.

Thus we can see from the studies on film thickness that bleaching with hydrogen peroxide results in higher film thickness and lesser coating material loss for PU due to natural sun exposure.

### 3.2 The Effect of Bleaching and Sunlight Exposure on the Gloss

Gloss is the result of specular reflection where the reflecting surface is expected to be very smooth and mirror-like [19]. The initial gloss (IG) values were analyzed through one-way ANOVA and it was found that large and significant variations exist between them ( $p < 0.001$ ).

Duncan's homogeneity test (given in Table 4) grouped the IG values into five subsets with the PU coating on unbleached surface showing highest value of 63.4 GU. This value is very close to that reported (62.2) GU for PU clear varnish on poplar surface [20]. However, a gloss value of 90.3 GU on has been reported for PU on *M. dubia* substrate but with four consecutive coatings [9]. In this context, it is pertinent to note that the third coat was reported to be critical in sudden increase in gloss for film forming wood finish on the substrate of mango wood itself [21].

All other surfaces in the present study including unbleached and fumigated ones showed considerably lower initial gloss values ranging

from 31.4 GU for AFHP to 48.6 GU for HPAF (Table 4). The fact that ammonia fumigation of wood samples reduces the surface gloss is already reported [20]. They reported a 22 % reduction in the surface gloss of uncoated poplar samples after 72 hours of ammonia fumigation. A mild change in colour has been reported for mango wood surface itself due to 24 h of ammonia fumigation [22]. In a study on ammonia fuming, it was reported that hardwoods show larger colour changes than softer ones [23]. It

was found by them that the tannin content was reduced due to fumigation in oak and spruce wood samples. The change in colour (usually darkening) of the wood due to fumigation, helps in reduction of gloss of the coating also. Thus, the lower gloss values shown by bleached and unbleached but fumigated samples stands vindicated. Fig.2 displays the gloss values of ammonia fumigated (AF) and unfumigated (NF) samples coated with PU at different sun-exposure times.

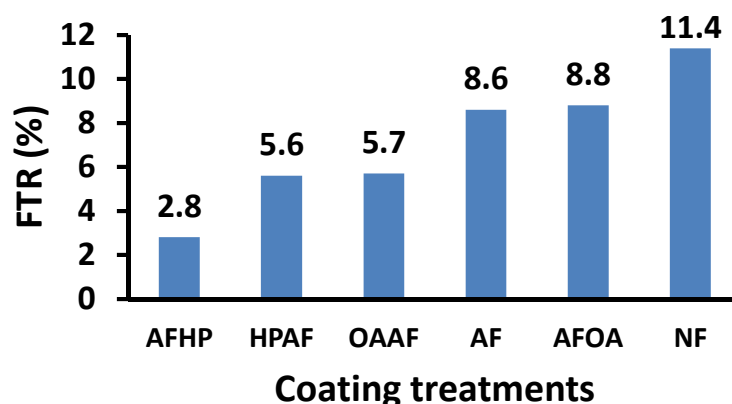


Fig. 1. Reduction (%) in film thicknesses of PU coating on different surfaces

Table 4. Duncan’s subsets for Initial Gloss of different sets

Sample Set	Number of readings	Subsets of IG (GU)				
		1	2	3	4	5
AFHP	18	31.4				
AFOA	18	33.8	33.8			
OAAF	18		38.9	38.9		
AF	18			43.8	43.8	
HPAF	18				48.6	
NF	18					63.4
Sig.		0.358	0.061	0.066	0.070	1.000

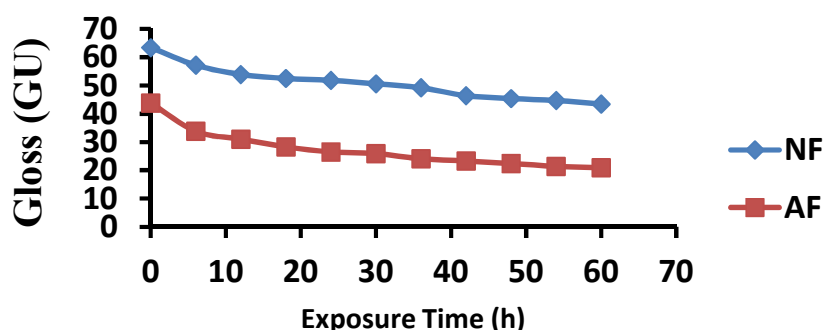


Fig. 2. Gloss values of ammonia fumigated and un-fumigated samples

From Fig. 2, it is evident that pattern of loss in gloss with time is almost similar in both fumigated and un-fumigated samples. This reduction of gloss after fumigation can be due to the tannin content of wood [24]. The initial gloss value of un-fumigated samples falls in the gloss category (50-85 GU) [25]. That of AF falls in the semi-gloss or satin category initially. Let us now have a look at the behavior of the bleaching agents on the gloss values at different times. Fig. 3 shows the pattern of gloss reduction at different times for bleached samples where fumigation was employed post-bleaching.

From the graph it is very clear that the two bleaching agent behave differently. The ones

bleached with oxalic acid seem to rather not affect the gloss values appreciably. In both AF and OAAF cases, the gloss reduction due to natural sun-exposure is gradual. However, glosses of the ones bleached with peroxide reduce drastically up to 12 hours and then the reduction becomes gradual. Bleaching with peroxide seems to augment the reduction in gloss caused by ammonia fumigation. Probably, the wood species has reacted differently with the two types of bleaching agents [26].

Fig. 2 shows the pattern of gloss reduction at different times for bleached samples where fumigation was employed prior to bleaching.

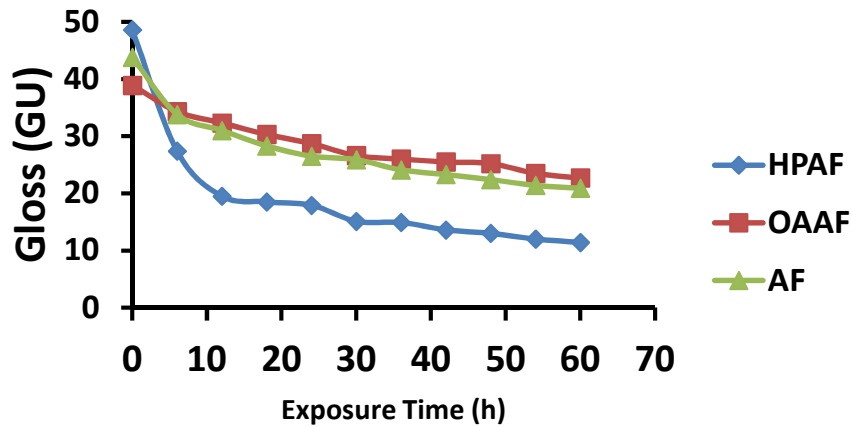


Fig. 3. Gloss values of ammonia fumigated and Post-bleaching fumigated samples

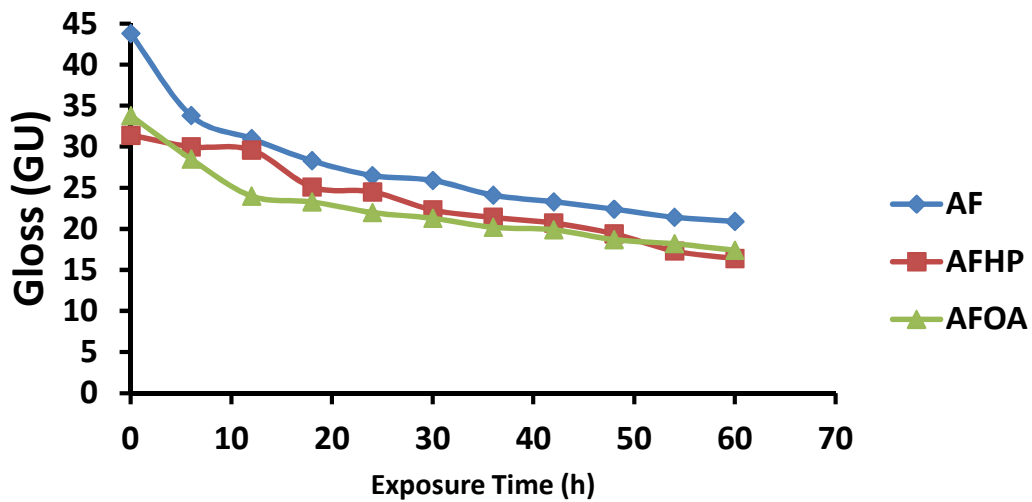


Fig. 4. Gloss values of ammonia fumigated and Post-fumigated bleached samples

In this case, the bleaching by either chemical seems to have reduced the gloss values almost similarly. The reaction of ammonia vapour prior to bleaching seems to have over-ridden the differences in the bleaching technique as far as reduction on gloss of the coated surface is concerned.

It was already seen that the un-fumigated surface showed the highest gloss. As discussed above ammonia fumigation brought down the gloss. Hence, the gloss values of all the bleached samples (fumigated prior or post bleaching) were analyzed using one-way ANOVA. The analysis showed some interesting differences ( $p < 0.001$ ) in the gloss patterns which are shown as Duncan's subsets for five different exposure times in Table 5.

Table 5 presents some interesting observations. The highest gloss initially was for HPAF samples. As seen in Fig. 2 this had a sharp loss in the

initial exposure itself and thereafter it has consistently registered the lowest gloss values. On the other hand, OAAF which had the second highest gloss initially has consistently maintained high gloss throughout the exposure. This is also illustrated in Fig 2. Except for a brief period between 12 and 24 hours, the gloss values were always grouped into three subsets. It can be concluded that if one is adopting bleaching and ammonia fumigation together, bleaching with oxalic acid before fumigation is helpful in gloss retention of the PU coating in the products service life. If hydrogen peroxide is used for bleaching, fumigation before bleaching is beneficial in retaining a shiny surface as the product is exposed to sunlight. According to Kilic and Hafizoglu, [27] when wood material is exposed to external conditions, it becomes deformed or structurally degraded. This will have an implication of the coated surface also. Having looked at the gloss values at different times, let us now take a look at the gloss reductions.

Table 5. Subsets of gloss (GU) at different times of exposure

Time	0 h			12 h				48 h			60 h		
	1	2	3	1	2	3	4	1	2	3	1	2	3
HPAF			48.6	19.5				13.0			11.4		
AFHP	31.4						29.6		19.4				16.4
AFOA	33.8	33.8			24.0				18.7				17.4
OAAF		38.9						32.3		25.2			22.7
sig	0.42	0.1	1.0	1.0	1.0	1.0	1.0	1.0	0.34	1.0	1.0	0.24	1.0

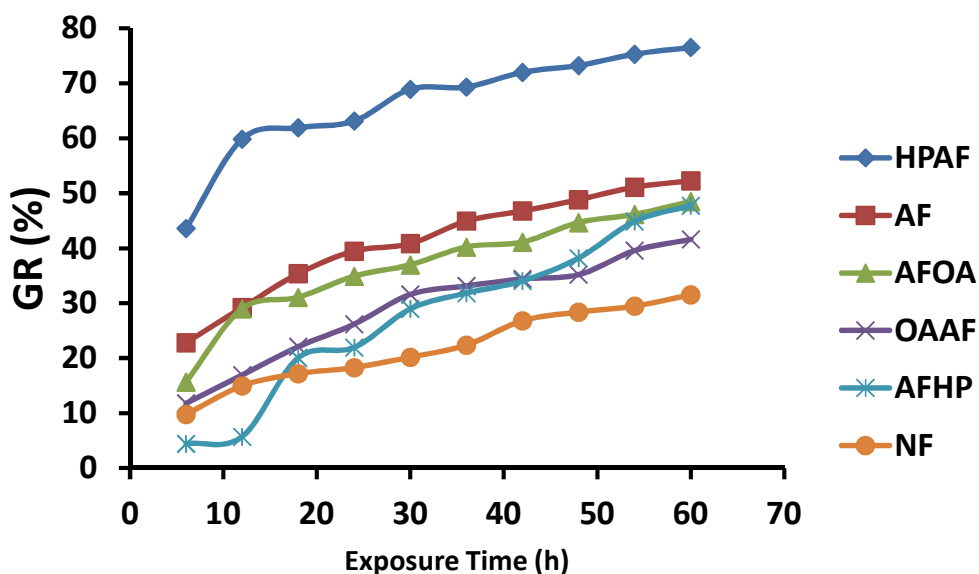


Fig. 5. Gloss reduction percentages of various samples



Fig. 5 clearly confirms the fact that bleaching by hydrogen peroxide prior to ammonia fumigation has caused the highest loss in gloss. In the case of oxalic acid, this trend is reverse. However, the difference looks to be smaller in the case of bleaching by oxalic acid. The unfumigated and unbleached surface resulted in minimum gloss reduction due to natural exposure almost throughout the experiment except during the first 12 hours. The actual values were 9.8 % after 6 h and 31.5 % after 60 h. Ghosh *et al.* [28] reported only a maximum of 15.4% of loss of gloss in PU coated Eucalyptus samples after 120h of UV exposure. In another experiment on natural weathering (including rains) on heat treated wood of *Scots pine*, the gloss of polyurethane varnish reduced in the range of 36 %– 57% where the initial glosses were in the range 88 – 97 GU [29]. High gloss retention by PU has been reported in another study also [15,30]. We can conclude that gloss values decrease in both sets of bleached samples with the time of exposure. The decrease in gloss is very high for HPAF samples (about 43 % to 76 %).

#### 4. CONCLUSIONS

The highest reduction in film thickness of PU (11.4%) is observed in unbleached un-fumigated PU coated surfaces followed by those bleached with OA after ammonia fumigation and the unbleached fumigated samples. The least reduction of 2.8 % is found with samples ammonia fumigated and then bleached with hydrogen peroxide. It can be concluded that bleaching with hydrogen peroxide results in higher film thickness and lesser coating material loss for PU due to natural sun exposure. Ammonia fumigation of the wood surface was found to reduce the gloss given by PU coating drastically. Bleaching with oxalic acid before fumigation is helpful in better gloss retention of the PU coating in natural exposure. If hydrogen peroxide is used for bleaching, fumigation before bleaching is beneficial in retaining a shiny surface as the product is exposed to sunlight.

#### DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for

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#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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