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UV Blocking Efficiency of Organic Solvent Borne and Water Borne Polyurethane Wood Coatings with Nano ZnO Dispersion

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Abstract—*Wood is a lingo-cellulosic organic material with various applications for interior and exterior purposes. Being organic, it is prone to get weathered by environmental conditions in exterior applications. Weathering of wood surface by photo-oxidation is catalysed by ultraviolet (UV) radiations received from the sun and it leads to degradation of lignin causing photo-yellowing of the surface. Wood finishing is a primary function to embellish the appearance of wooden articles as well as to protect the surface from the effect of the environment. Polyurethane (PU) wood coatings are the most commonly used commercial wood finishes. Though solvent based PU wood coatings are prevalent, being volatile organic compounds (VOC) emitters, they are considered as hazards to environment and human health. Due to strict environmental legislations, trend is shifting towards the use of water borne PU coatings. A study was conducted to determine the efficiency of organic solvent borne and water borne polyurethane wood coatings in blocking UV radiations. Samples of Populus deltoides coated with these two compositions of PU were exposed to UV in an accelerated UV chamber at an elevated temperature of 60°C. Effect on the surface colour due to radiations was studied using CIElab color space model. Poor performance of the coatings was observed against UV radiations. Nano dispersion of ZnO in Propylene glycol was blended with both the coatings to enhance its UV resistant properties. The results showed that change in colour of the coated surface due to degradation of lignin complex by UV was three times to that in case of nano PU coated samples. Nano ZnO dispersed PU coatings acted as UV stabilizers and showed high performance in reducing the UV degradation of wood surface. They were found to be about 75% efficient in blocking the UV radiation and preventing wood substrate from its adverse effects.*

Keywords*: CIElab, Photo-oxidation, Photo-yellowing, Polyurethane, UV radiation, Weathering, ZnO dispersion.*

1. INTRODUCTION

Finishing of wood provides long term benefits to the article. It may change the appearance but retains the same rustic beauty of the article. Finishes like wax, shellac, oil varnishes, water based finishes have different abilities of protection, ease of application, durability and aesthetics. No single finish excels in all these aspects. Wood workers and furniture makers classify most finishes in one of the five groups: Penetrating finish, surface finish, evaporative finish, reactive finish, coalescing finish.

Among the most common wood coatings, polyurethane (PU) is hard, abrasion-resistant and durable, and is known to act as a good moisture barrier for wood based products (Poaty *et al*., 2013). Polyurethene coatings have numerous benefits which includes good mechanical strength and adhesion as well as ease of multiple coating layers (Carter, 2012). Organic solvent has traditionally been an important constituent of PU coatings – contributing to their smooth, glossy and durable finish. Polyurethane coatings comprise of about 30% petroleum derived resins (generally poly isocyanates which produces the film) and 45 – 65% of organic solvents like toluene, xylene etc which dissolve the resins. Solvent has –OH ions which react with isocyanates of resins and produce urethane.

R-N=C=O + R'-OH -----→ R-NH-C=O-R'

Polyisocyanate Polygol Polyurethane

Phenolic solvents used are Volatile organic compounds (VOC) emitters. They make this coating hazardous for environment and human health.

The aim of environmental legislations is to reduce emissions of harmful volatile organic compounds (VOCs) from these products into the environment. The two main strategies being used by paint manufacturers to reduce VOC levels in paint are increasing the proportion of solids while retaining organic solvents at a lower level, or moving to water-borne systems.

Water-borne Polyurethane dispersions (PUDs) are a rapidly growing segment of the polyurethane coating industry due to environmental legislations such as the clean air act and also due to technological advances that has made them an effective substitute for the solvent-based analogs. In water based PU coatings, phenolic solvents are reduced to 15-20% and the rest is replaced by water as solvent. Since water also has hydroxyl groups, they can react with isocyanates to produce urethane without releasing VOC's. They are versatile and environment friendly coating materials that are available in a wide range of hardness and solid content. Their zero to low volatile organic content facilitates their formulation into a compliant coating for many different substrates.

Natural wood, being a biological material, undergoes rapid degradation by ultraviolet (UV) radiations and other environmental factors under outdoor exposure, known as weathering. Ultraviolet (UV) radiation in sunlight catalyzes photo-degradation of organic materials exacerbated by moisture, temperature change, freeze–thaw cycles, abrasion by windblown particles, and growth of microorganisms. Degradation occurs near the surface of wood, wood products, and finishes. Lignin, that constitutes about 15–36% of total weight of wood, contain chromophores that can readily absorb UV radiations. Cellulose and hemicellulose are less prone to direct radiation damage. Therefore, light induced degradation primarily occurs in lignin.

Several methods to reduce wood polymer degradation and hence improve polymer stability have relied on the inclusion of additives and/or fillers, such as thermal stabilizers or UV stabilizers. It is well known that zinc oxide (ZnO) nanoparticles are safe materials with UV absorption capabilities. ZnO particles have been used as a UV absorber in sunscreen and cosmetic applications. Thus they could be used as a UV stabilizer for polymers. Dispersion of ZnO nanoparticles in Propylene Glycol and PU coatings restricted the colour changes and photodegradation of wood polymers (Pandey et al., 2012).

Against this background, performances of organic solvent borne and water borne polyurethane wood coatings were studied. Attempts were made in this work to enhance their UV stabilization by dispersion of nano particles in the coatings.

2. MATERIALS AND METHODS

A plank of *Populus deltoides* was flat sawn from the sapwood section and was seasoned to 10% moisture content level. After sanding the surfaces, defect free specimens of size 15X7.5X0.5 cm^3 were prepared. These cuboidal specimens were hand sanded with fine grit sand paper of 120 grit size to prepare the surface for coating. Total 20 defect free samples were taken for the experiment.

Preparation of zinc oxide nano dispersion

20% concentration dispersion of nano ZnO was prepared by mixing 80gm of nanoparticles of ZnO in 400 ml of Propylene Glycol (PG). Then it was mechanically stirred for 20 minutes to get a homogenous solution. The obtained homogenous mixture was then ultrasonicated for 1 hour. The prepared solution was then kept in bottle for further use in experiment. After pre-finishing operations, 5 samples were coated with water borne PU and 5 with organic solvent borne PU. Three coats were applied on each sample. The nano ZnO dispersion was mixed with the coatings in such a ratio that the resultant nano coating has 2% concentration of ZnO. Remaining 10 samples were coated with this nano coating (5 with nano water borne PU and 5 with nano organic solvent borne PU).

UV Exposure and Colour Measurement

The colour quantification of coated wood samples was done using CIElab space method by colorimeter prior to exposure of samples to the UV radiations. The samples were then exposed to UV in an accelerated UV chamber with a constant intensity of 0.68 W/m^2 at an elevated temperature of 60^0C. The exposure was continued for 250 hours and periodic colour measurements were taken to observe the weathering of wood caused by the UV radiations. The colour changes were measured using a Hunter lab spectrocolorimeter (Lab scan XE model colourimeter equipped with Xenon flash lamp source, 10° standard observer, D65 standard illuminant). The method adopted was CIE L*, a*, b* where, the three parameters viz. lightness index (L*) and the chromaticity coordinates of redness (a*) and yellowness (b*) were measured on each specimen before and after exposure. Colour parameters were measured at six different locations for each samples and mean values and standard deviations were calculated (Nair et al.,2018). The changes in the parameters (ΔL*, Δa* and Δb*) due to exposure were calculated. The total colour change, ΔE*, as a function of the exposure time was calculated as

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$$

Where,

ΔL* = Change in brightness (+ L = white, -L = black)

Δa* = Change in red coordinate (+ a indicates red, -a indicates green)

Δb* = Change in yellow coordinate (+ b indicates yellow,-b indicates blue).

The values of ΔE* thus obtained were used as an indicator of degree of weathering caused by UV exposure.

3. RESULTS AND DISCUSSION

UV resistance of water borne PU wood coatings

Colour coordinates i.e. L*, a* and b* of the water borne PU coated samples were recorded and the values were averaged for each coordinate. To observe the degradation caused by UV, surface colour measurements were taken using CIElab colour space at regular intervals during the exposure and change in colour coordinates was evaluated. Table 1 shows the mean values of **Δ**L*, **Δ**a*, **Δ**b* coordinates and net colour change (**ΔE)** due to surface weathering of poplar wood coated

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with water borne PU at different time intervals of UV exposure.

Table 1: Colour differences of water borne PU coated samples

Sample	After 24 hrs ΔL*, Δa*, Δb* ΔE*		After 50 hrs ΔL*, Δa*, Δb* ΔE*		After 100 hrs ΔL*, Δa*, Δb* ΔE*		After 250hrs ΔL*, Δa*, Δb* ΔE*	
1	-5.0 2.6, 14.1	15.2	-7.7, 3.8, 17.9	19.8	-4.9, 3.5, 19.7	20.6	-5.3, 10.9, 22.4	25.5
2	-5.4, 3.6, 17.2	18.4	-6.3, 4.1, 19.2	20.6	-5.2, 3.5, 19.9	20.9	-4.9, 11.7, 24.1	27.2
3	-7.1, 4.2, 14.3	16.5	-8.7, 5.9, 18.7	16.5	-8.6, 5.9, 19.7	22.3	-7.9, 13.4, 24.2	28.8
4	-4.9, 3.1, 13.5	14.7	-7.1, 4.2, 14.3	16.5	-8.6, 5.9, 19.7	22.3	-4.3, 12.1, 23.3	26.6
5	-4.9, 3.1, 16.5	17.5	-4.9, 3.1, 13.5	14.7	-5.9, 4.7, 17.5	19.1	-4.3, 12.1, 23.3	26.6
Mean ΔE*		16.5		20.0		21.1		27.0

The calculated values in table 1 are indicative of the fact that there is in general, an increase in colour change with UV exposure time. The colour starts changing even after 24 hrs of exposure (colour change ranges from 14.7 to 18.4). This change keeps on increasing with the duration of exposure and reaches to a range of 25.5 to 28.8 after 250 hrs. Higher values of **Δb*** signify photo yellowing of the wood surface and inability of water borne PU coating to resist UV degradation.

Several works have revealed that nano particles of ZnO have the property to stabilize UV radiations. ZnO nanomaterials have been found to have some excellent properties like exceptional mechanical strength, antibacterial and UV absorption properties. Yadav *et al*., (2006) found the nano ZnO (2%) coated cotton fabric to have UV blocking property. About 75% of the incident UV light was absorbed due to this coating. Coatings containing ZnO nanoparticles enhanced the durability of linseed oil based paintings against UV aging in respect to colour change (*Osama et al.,2014*). To observe the efficacy of nano ZnO in water borne PU, nano water borne PU coated samples were exposed to UV for 250 hrs and the effect on colour was studied. Table 2 shows change in colour coordinates and overall colour change with exposure to UV for nano water borne coating.

Table 2: Colour differences of nano mixed water borne PU coated samples

Sample	After 24 hrs ΔL*, Δa*, Δb* ΔE*		After 50 hrs ΔL*, Δa*, Δb* ΔE*		After 100 hrs ΔL*, Δa*, Δb* ΔE*		After 250 hrs ΔL*, Δa*, Δb* ΔE*	
1	0.4, 0.9, -0.3	1.1	-0.7, 1.3, 0.0	1.4	-0.3, 0.8, 1.6	1.8	0.1, 5.8, 3.8	6.9
2	-0.3, 0.9, -1.2	1.5	-1.1, 0.9, -1.4	2.0	-0.2, 0.5, 0.1	0.5	-1.4, 5.8, 2.9	6.5
3	0.1, 0.6, 0.9	1.1	0.1, 0.5, 0.8	0.9	0.1, 0.1, 2.7	2.7	1.1, 5.1, 5.7	7.7
4	2.1, 0.1, -0.7	2.2	0.7, 0.6, 0.2	0.9	1.1, -0.01, 1.1	1.6	0.9, 5.3, 4.9	7.2
5	1.2, 0.5, -0.7	1.5	-0.1, 0.8, -0.3	0.9	-0.4, 0.8, 1.5	1.8	0.7, 5.8, 3.8	7.0
Mean ΔE*		1.5		1.2		1.7		7.0

From values in table 2 it is evident that ZnO nanoparticles have drastically reduced the colour change of wood surface due to UV exposure. Lower values of Δb* indicate slow yellowing of the coated surface due to resistance offered to the UV radiations. Upto 100 hrs of exposure, yellowing (degradation) of wood surface was almost negligible. The improvement in total colour change (**ΔE*)** due to nano addition after 250 hours of exposure is from 27.0 to 7.0 which is an improvement of 74%.

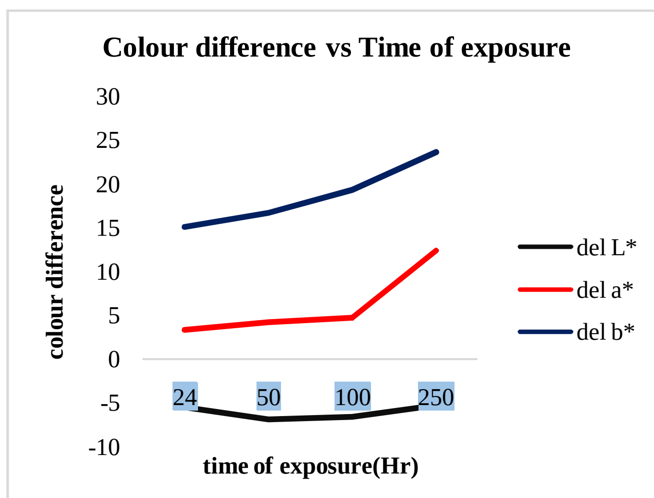

Fig. 1: Water borne PU coated samples Vs Time

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From figure 1, it can be observed that the major contributor to the change in colour is b* coordinate. The pattern of increase in **Δ**b* indicates the increase in yellowness. Contrary to this, change in L* and a* are small and almost constant till 100 hrs of exposure. Afterwards redness of the samples increases. Figure 1 confirms the yellowing of wood substrate underneath the water based PU coating as a result of lignin degradation by UV.

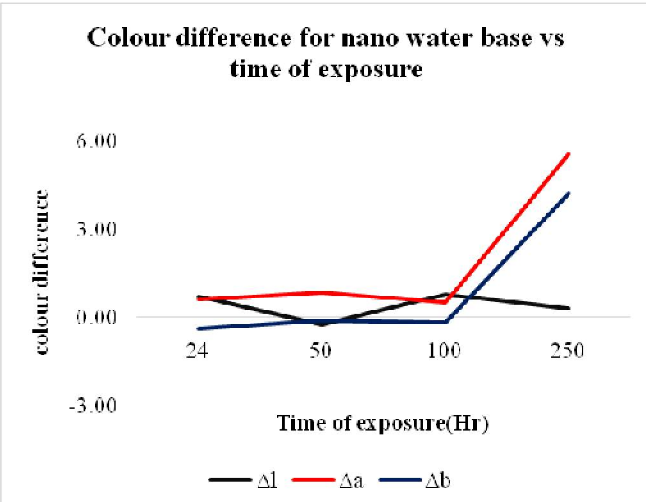


Fig. 2: Nano water PU coated samples Vs time

Figure 2 is evident of the fact that upto 100 hours of exposure changes in all the three colour coordinates are almost negligible. After 100 hrs, redness and yellowness increase but to a very less extent in comparison to that of water based PU coated samples. The graphs clearly depict the effect of ZnO nanoparticles in reducing the UV degradation of wood surface to a greater extent. Net change in colour for nano water borne PU coated samples is very small in comparison to that of water borne PU coated ones throughout. Thus, it can be concluded evidently that 2% ZnO nano dispersion in PG is effective in enhancing the UV blocking capacity of water based PU coatings.

UV resistance of organic solvent borne PU wood coatings.

The set of samples coated with organic PU were exposed to UV at elevated temperature and photo-degradation of the surface was studied. Table 3 shows the mean values of **Δ**L*, **Δ**a*, **Δ**b* coordinates and net colour change (**ΔE*)** due to surface weathering of poplar wood coated with organic solvent borne PU at different time interval of UV exposure.

Table 3: Colour differences of organic solvent borne PU coated samples

Sample	After 24 hrs ΔL*, Δa*, Δb* ΔE*		After 50 hrs ΔL*, Δa*, Δb* ΔE*		After 100 hrs ΔL*, Δa*, Δb* ΔE*		After 250hrs ΔL*, Δa*, Δb* ΔE*	
1	-9.4, 3.4, 8.4	13.1	-7.4, 3.5, 9.5	12.6	-15.4,5.7, 16.8	23.5	-18.3, 9.0, 21.1	29.3
2	-10.2, 1.8, 5.7	11.8	-8.6, 4.9, 14.8	17.8	-13.3,5.5, 10.3	17.7	-17.0, 7.3, 13.8	23.0
3	-10.1, 5.6, 14.6	18.6	-8.4, 3.7, 9.7	13.4	-14.4,5.1, 13.8	20.6	-17.3, 8.7, 20.5	28.2
4	-9.6, 3.5, 7.6	12.7	-8.7, 3.5, 10.5	14.1	-15.1,5.7, 15.6	22.4	-17.3, 8.0, 20.9	28.2
5	-9.9, 4.2, 6.4	12.5	-9.3, 4.5, 13.6	17.1	-15.0,5.2, 17.1	23.4	-18.3, 8.6, 21.2	29.2
Mean ΔE*		13.7		15.0		21.5		27.6

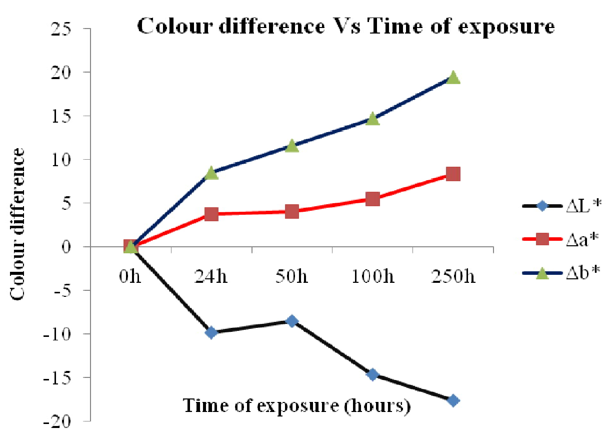
Table 3 indicates the inefficiency of organic solvent borne PU coatings in blocking UV radiations and preventing the wood surface from degradation as was the case with water borne counterpart. Colour of coated wood changes drastically with exposure to UV. Higher values of **ΔL* and Δb*** represent the darkening and yellowing of wood surface due to weathering. Table 4 shows change in colour coordinates and overall colour change with exposure to UV for nano organic solvent borne coated poplar wood.

Table 4: Colour differences of nano mixed organic solvent borne PU coated samples

Sample	After 24 hrs ΔL*, Δa*, Δb* ΔE*		After 50 hrs ΔL*, Δa*, Δb* ΔE*		After 100 hrs ΔL*, Δa*, Δb* ΔE*		After 250 hrs ΔL*, Δa*, Δb* ΔE*	
1	0.04, 0.7, 0.7	0.97	1.1, 0.1, 1.4	1.76	0.7, 0.6, 0.9	1.28	0.6, 3.8, 1.6	4.16
2	0.5, 0.04, 0.8	0.96	0.9, 0.3, 0.1	0.95	1.0, 0.3, 0.2	1.06	1.9, 3.6, 2.1	4.63
3	2.3, 0.3, 0.4	2.33	2.9, 0.4, 1.2	3.16	1.6, 0.4, 0.4	1.70	0.4, 4.9, 3.2	5.84

4	1.1, 0.3, 0.2	1.19	1.7, 0.2, 1.4	2.18	1.3, 0.5, 3.5	3.72	0.1, 7.2, 9.4	11.83
5	1.5, 0.3, 0.4	1.57	1.7, 0.2, 1.3	2.14	1.1, 0.5, 0.8	1.47	0.9, 5.6, 4.3	7.11
Mean ΔE*		1.4		2.0		1.8		6.7

From the values in table 4 it is evident that dispersion of nano ZnO in organic solvent based PU coating increases the UV stabilizing capability of the coating. The variations in colour coordinates due to UV degradation, which were very high for the samples coated with PU, got curtailed and no noticeable yellowing could be observed. The improvement in total colour change (**ΔE***) due to nano addition after 250 hours of exposure is from 27.6 to 6.7 which is an improvement of 75%. Pictorial comparison in fig 3 and fig 4 clearly demonstrates the efficacy of nano ZnO in enhancing the UV blocking capacity of organic solvent borne PU wood coatings.



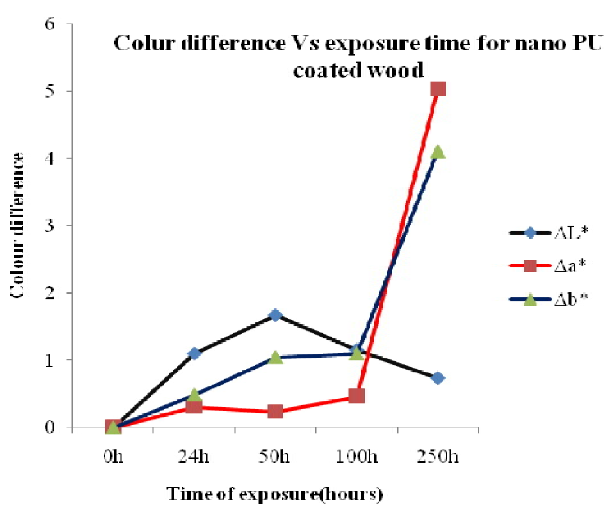


Fig. 4: Nano PU coated samples Vs time

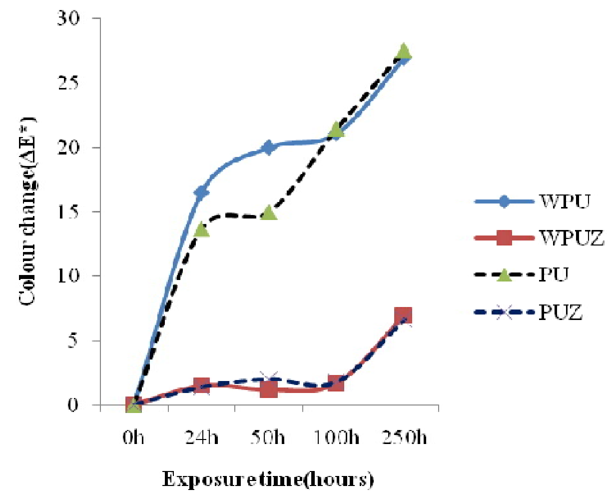


Fig. 5: Performance of different coating combinations against UV radiations

Figure 5 clearly illustrates the increased efficiency of both water borne and organic solvent borne PU coatings against UV radiations with inclusion of nano ZnO in their composition.

4. CONCLUSIONS

Both forms of polyurethane wood coatings show poor performance in blocking UV radiations. Nano ZnO dispersion in Propylene Glycol is found to be compatible with both water borne and organic solvent borne PU wood coatings.

Net change in colour for different coated surfaces are compared in fig. 5.

A significant increase in the UV blocking efficiency of both the coatings could be achieved with 2% concentration of nano ZnO. Use of coatings with ZnO dispersion resulted 75% efficiency in blocking the UV radiations and preventing wood substrate from its adverse effects.

REFERENCE

[1] Asif, A., Shi, W., Shen, X., and Nie, K. 2005. Physical and thermal properties of UV curable waterborne polyurethane dispersions incorporating hyperbranched aliphatic polyester of varying generation number. *Science of Polymer. Vol:46(24). pp. 11066-1107.*

[2] Carter, N. (2012). Scavenge moisture and cut pinholes in a trice. *European Coatings Journal, Vol:6. pp.18-21.*

[3] Nair,S., Giridhar, B.N. and K.K. Pandey (2018). UV stabilisation of wood by nano metal oxides dispersed in propylene glocol. *Journal of photochemistry and photobiology. Vol.183. pp.1-10.*

[4] Osama, M., Fekya, E., Hassanb, E.A, Fadelb, S.M, and Hassan, M.L. 2014. Use of ZnO nanoparticles for protecting oil paintings on paper support against dirt, fungal attack, and UV aging. *Journal of Cultural Heritage. Vol: 15. pp. 165–172.*

[5] Pandey,K.K., Srinivas.K., and Salla, J. 2012. Improvement of UV resistance of wood surfaces by using zinc oxide nanoparticles. *Polymer Degradation and Stability*. *Vol: 97(4). pp.592–596.*

[6] Poaty, B., Riedl, B., Blanchet, P., Blanchard, V., and Stafford, L. (2013). Improved water repellency of black spruce wood surfaces after treatment in carbon tetrafluoride plasmas. *Wood science and technology, Vol: 47(2). pp. 411-422.*

[7] Yadav, A., Prasad,V., Kathe, A.A, Raj, S., Yadav, D., Moorthy, C.S. and Vigneshwaran, N. 2006. Functional finishing in cotton fabrics using zinc oxide nanoparticles. *Bull. Mater. Sci., Vol. 29(6). pp. 641–645. © Indian Academy of Sciences.*

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