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# Compatibility of Nanobiocide as Wood Preservative with Thermosetting Resin used as Adhesive for Plywood Manufacturing

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**Abstract**

*The study objective was to develop a wood preservative by nano form of Copper oxide, Zinc oxide and Copper sulphate for wood based panel products to make the system with a lesser amount of toxicity. Wood preservatives are products used for the safeguard of wood from deterioration or damage caused by detrimental organisms (for example; fungi, moulds or pests). Nanotechnology presents a notable opportunity to boost the field of wood safeguarding through executing modern and unique metal biocides with enriched properties. Nano form of Copper oxide, Zinc oxide and Copper sulphate were made by mechanical milling in the high energy planetary ball mill with 450 rpm for 12 h. From the results achieved in this study it can be concluded among the three verified preservatives the nano form of the preservatives were well-suited with the glues as compare to their soluble forms. The result also shows the bonding quality of the plywood with satisfactory limit of acceptance.*

***Keywords:*** *Nano technology, Copper sulphate, Zinc oxide, Copper oxide, nanobiocide, wood preservation*

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## INTRODUCTION

Innovative wood preservative formulations are formulated without chromium and arsenic with the intent to lessen negative environmental effect. Nevertheless, the elimination of chromium from biocide formulations also leaves them more prone to leach. Leaching of biocides from preserved wood can negatively disturb ecosystems, mainly wetlands, and can potentially lessen the beneficial lifetime of wood and preserved wood products.

To solve the problems related to leaching and easy dispersion of the biocide nanotechnology has the potential to greatly impact the wood protection industry through the creation of nano-materials with unique properties. Nanotechnology is defined as the manipulation of materials measuring 100 nanometers or less in at least one dimension. The United States National Science Foundation defines nanoscience/nanotechnology as studies that deal with materials and systems having the key properties: 1. Dimension: at least one dimension from 1–100 nanometers (nm). 2. Process: designed with methodologies that show fundamental control over the physical and chemical attributes of molecular-scale structures. 3. Building block property: they can be combined to form larger structures[1,2] patented a nano carrier

 

system that utilizes 100 nm plastic beads embedded with biocide.

Nanotechnology is expected to be a critical driver of global economic growth and development in this century. Already, this broad multidisciplinary field is providing glimpses of exciting new capabilities, enabling materials, devices, and systems that can be examined, engineered, and fabricated at the nano scale. Nano-sized particles of metal (such as; copper or zinc) are one example of new materials that may possess biological, physical, or chemical properties that are completely different than larger particles of the same metal. Enhanced antimicrobial properties for a nano-metal could be useful in development of a new biocide or co-biocide. Their small size may alter wood treatability properties such as; penetration and biocide distribution.

In the present study, mechanical milling method was employed to make nanobiocide. Because, mechanical milling/alloying (MM/MA) is a prevalent method to make nanocrystalline materials because of its simplicity and capability to mix the materials uniformly in the intimate atomic level, simply produce tonnage quantity to fundamentally all classes of materials[3].

The significant criteria before selecting any wood preservative chemical are its compatibility with the glue.

Therefore, in the current study an effort was made to assess the compatibility of the developed nano biocide with the glue in Indian condition.

## MATERIALS AND METHODS

The experiment was carried out at laboratory of Indian Plywood Industries Research & Training Institute (IPIRTI), Bangalore, Karnataka.

### Chemicals

Laboratory grade Copper oxide, Zinc oxide and Copper sulphate were purchased from the market.

### Synthesis of Nanobiocide

In planetary ball mill a few hundred grams of the powder can be milled at a time. The planetary ball mill owes its name to the planet-like movement of its vials. These are arranged on a rotating support disk and a special drive mechanism causes them to rotate around their own axes. The centrifugal force produced by the vials 12 rotating around their own axes and that produced by the rotating support disk both act on the vial contents, consisting of material to be ground and the grinding balls. Since the vials and the supporting disk rotate in opposite directions, the centrifugal forces alternately act in like and opposite directions. This causes the grinding balls to run down the inside wall of the vial the friction effect, followed by the material being ground and grinding balls lifting of and travelling freely through the inner chamber of the vial and colliding against the opposing inside wall the impact effect.

Nano form of Copper oxide, Zinc oxide and Copper sulphate were made by mechanical milling in the high energy planetary ball mill with 450 rpm for 12 h. Zirconium balls (0.5 and 1 mm) were used for grinding. The periodical intervals were kept for two hours[4].

### Pot Life

Effect of addition of the chemical on pot life of the adhesive was assessed by checking the flow time of the adhesive through flow–period after eight hours of mixing the chemical preservative in the resin. Eight hours period was taken with the assumption that resin should remain usable for the entire duration of a normal production in plywood manufacturing industry.

### Glue Line Treatment of Plywood

0.5% of Copper oxide (nano form), Zinc oxide (nano form) and Copper sulphate (nano form), respectively were mixed with Phenol formaldehyde (PF) resin as glue additive on the weight of liquid resin. Control samples were prepared by adding Laboratory grade (without nano form) Copper oxide, Zinc oxide and Copper sulphate, respectively in glue. After adding the preservative chemicals in the resin, the mixture was then stirred using a mechanical stirrer at a rotation speed of 1000 rpm for thorough dispersion. Laboratory scale plywood of 4 mm was made using poplar veneer of 1.6 mm equal construction. The liquid PF resin (48% solid content) was admixed with 8% coconut shell powder as filler. The veneers were dried to a moisture content of 6–8% and then coated with above adhesive mixed. The glue coated veneer was given an open assembly time of 1½ to 2 h to attain moisture content of 12–14%. The veneers were then assembled to 4 mm thickness and loaded into the hot press. The assembly was hot pressed at a temperature of 145±5˚C with a specific pressure of 14–16 kg/cm$^2$. Curing time of thickness + 3 min was provided. The hot pressed panel was downloaded and stacked for about 24–48 h for stabilisation. The panels were then dimensioned to required size for further evaluation.

### Bond Quality

Cyclic test was carried out for the samples of size 12.5x12.5 cm as per IS:848[5] for BWP grade plywood. The samples were immersed in boiling water for 8 h and then allowed to dry at 65±2˚C for 16 h. This process was repeated for six cycles. Thereafter, knife test was done by forcibly separating the plies. Results are tabulated in Table 1.

## RESULTS AND DISCUSSION

The present study was taken up to and to assess the compatibility of nanobiocide with the glue. Nanobiocide was developed by mechanically grinding it in high energy planetary ball mill. The advantage of ball milling is it can be readily implemented commercially. It is an effective and simple technique of obtaining nano sized materials. The particle size of nanobiocide was analysed by particle size analyser. The particle size was analysed by Malvern's Zetasizer instrument at Malvern-Aimil Application centre, Bangalore and the results are as follows:

Results

| | | | Size (d.nm): | % Intensity | Width (d.n... |
|---|---|---|---|---|---|
| Z-Average (d.nm): | 447.4 | Peak 1: | 567.4 | 93.5 | 382.9 |
| PdI: | 0.372 | Peak 2: | 4797 | 6.5 | 725.9 |
| Intercept: | 0.859 | Peak 3: | 0.000 | 0.0 | 0.000 |

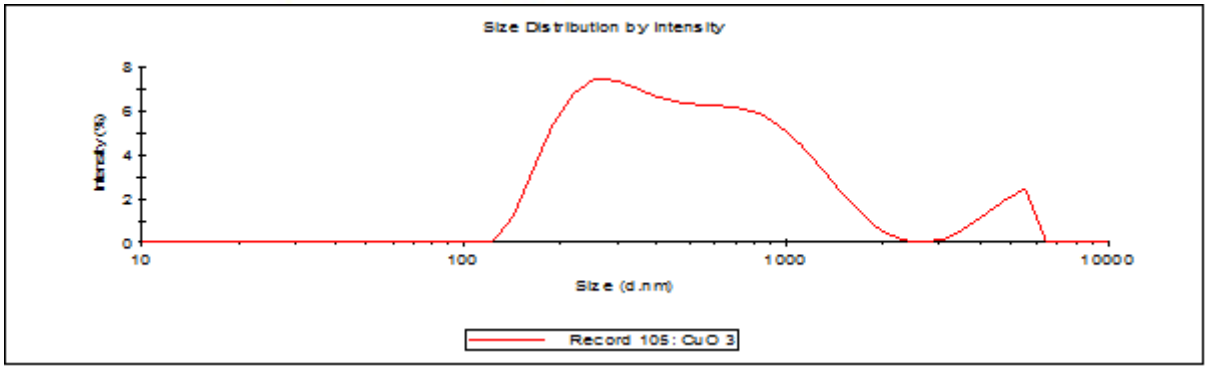


***Fig. 1:*** *Particle Size Distribution of Nanobiocide.*

From the graph shown in Figure 1, it can be seen that the most of the particles were in the range of 100 nm.

After adding these chemicals in the glue the most important property is the pot life study. The studies on pot life of liquid PF resin after adding the nanobiocide was observed. Addition of preservative chemical has not changed the viscosity after 8 h. The flow rate recorded after mixing the chemical in glue was 26 sec. From the results, it can be concluded that incorporation of preservative chemical into the glue has not affected the pot life of PF resin. Boiling water proof test was carried out to determine the effect of chemical on bond quality of plywood. The test was performed as per IS: 848[5]. After carrying out the cyclic test for BWP, the separation of plies at the edges and/or surface at the end of six cycles was observed. The results are given in Table 1. From Table 1, it can be observed that nanobiocides blended well in the resin and did not affect the bond quality as compared to their control (Laboratory grade) form.

***Table 1:*** *Bond Quality of Plywood.*

| **Test** | **Criteria for conformity Clauses 4 and 7.3.2 of IS: 848-2006** | **Results** | | |
|---|---|---|---|---|
| | | **Copper sulphate** | **Copper Oxide** | **Zinc Oxide** |
| BWP GRADE (Boiling Water Proof) Six cycles: Each cycle consisting of 8 h boiling in water and thereafter drying at 65 ± 20C for 16 h. | No separation of plies at the edges and/or surface at the end of six cycles.<br><br>On forcible separation of plies with knife, wood failure shall be predominant and shall be more than 75% for excellent bond and not less than 50% for pass standard. For less than 50% wood failure, the specimen shall be considered as failed. | **Contol:** No separation of plies at the edges and/or surface at the end of six cycles. On forcible separation of plies with knife, **75%** wood failure Pass Standard<br><br>**Nano:** No separation of plies at the edges and/or surface at the end of six cycles. On forcible separation of plies with knife, **85–90%** wood failure Excellent Bond | **Contol:** No separation of plies at the edges and/or surface at the end of six cycles. On forcible separation of plies with knife, **70%** wood failure Pass Standard<br><br>**Nano:** No separation of plies at the edges and/or surface at the end of six cycles. On forcible separation of plies with knife, **75–80%** wood failure<br><br>Excellent Bond | **Contol:** No separation of plies at the edges and/or surface at the end of six cycles. On forcible separation of plies with knife, **60–70%** wood failure Pass Standard<br><br>**Nano:** No separation of plies at the edges and/or surface at the end of six cycles. On forcible separation of plies with knife, **75–80%** wood failure<br><br>Excellent Bond |

In the present investigation, the particle size of nanobiocides obtained was 100 nm by milling with Zirconium balls for 12 h. These results are in consistent with the findings of Gu Wan Li *et al.*[6]. They reported that the $Cu/Ti_3SiC_2$ particle decreased rapidly with the agate milling ball and the final size obtained was 20 nm, while with the zirconium ball, the particle size obtained was 100 nm. Further they concluded that $Cu/Ti_3SiC_2$ system agate ball is suitable in the mechanical ball milling process.

The science of nanotechnology is in nascent stage. Some researchers in the foreign country studied the efficacy of nanobiocide against wood destroying

organisms. But the data for toxicity for human of that developed nanobiocide is not been well documented till date. Every technology has its advantages and disadvantages. There is discrepancy between the number of published papers that deals with the development of nano particulate material and the number of toxicity studies being done. Scientist's states that they are unaware of the problems arise from the use of nanobiocide because research has not been done[7] on this particular area. In the present study, difference in the efficacy seen between the nanobiocide and control samples was very less. Reduction in the particle size may provide better efficacy but the human health effects has to be studied thoroughly.

There are some evidence that nanoparticles may have adverse effects on the environment, human and animals. Oberdorster *et al.*[8] showed that due to high surface area to volume ratio, nanoparticles are more biologically active than other larger molecules and can enter the human body. Nanometarials gain access to our body may more readily penetrate biological membranes and access cells, tissues and organs. Nanomaterials which measures less than 70 nm can even be taken up by human cells nuclei, where they can cause major damage[9–11]. Unfortunately, the greater chemical reactivity and bioavailability of nano materials may also result in greater toxicity of nanoparticles compared to the same unit of mass of larger particles[12].

## CONCLUSION

Converting micronized particles into nano form by mechanical milling with the planetary ball mill is simple and effective method. Commercial grade nano sized biocides can be made easily by ball milling. From the cyclic bond test it is very much clear that the nanobiocides did not affect the bonding quality of the plywood. They blended well with the adhesive than their soluble counterparts (control). Further studies are needed on the assessment of toxicity of nano particles to the environment and human being which is unexplored.

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