IRG/WP 07-30422

THE INTERNATIONAL RESEARCH GROUP ON WOOD PROTECTION

Section 3 **Wood Protecting Chemicals**

Wood Protection by Commercial Silver Formulations against Eastern Subterranean Termites

Frederick Green III and Rachel Ann Arango
USDA Forest Service
Forest Products Laboratory
Madison, Wisconsin 53726
USA

Paper prepared for the 38th Annual Meeting
Jackson Lake Lodge, Wyoming, USA
20-24 May 2007

IRG SECRETARIAT
Box 5609
SE-114 86 Stockholm
Sweden
www.irg-wp.com

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Frederick Green III[1] and Rachel Ann Arango[2]

[1]USDA Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, Wisconsin 53726-2398, USA, Research Microbiologist, fgreen@fs.fed.us

[2]USDA Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, Wisconsin 53726-2398, USA, Biological Laboratory Technician, rarango@fs.fed.us

ABSTRACT

The scope of this paper is to compare commercial formulations of aqueous products containing silver for their ability to prevent termite damage by Eastern subterranean termites in a no-choice laboratory test. Five commercial products were tested in order to explore a broad range of formulation and silver forms: colloidal, ionic and nano-particles. Southern pine wood blocks were dip treated in each solution for 30 seconds, dried and weighed. No-choice tests were run for 4 weeks at 26ºC and 85% RH. Mortality and visual ratings were recorded at the end of the test period. For comparison, some formulations were compared or combined with additives, eg NHA at .33%, with and without silver. Formulations varied in viscosity from aqueous dispersions to slurries. Results showed several formulations to have excellent capacity to limit termite feeding and wood mass loss during the 4 week test: silver dispersion, zinc nanoparticles plus silver and silver protein plus NHA. It is not clear if silver is the primary active component in all these formulations. Nevertheless, silver is not likely to be a stand-alone treatment for control of termite damage but may make an important additive for paints and preservatives.

Keywords: termite damage, *Reticulitermes flavipes* (Kollar), commercial silver formulations

1. INTRODUCTION

Silver, a naturally occurring element in the environment, has had a long history of antimicrobial properties. Silver formulations are finding use in disinfectants, dishwashers, refrigerators, toilet seats, washing machine tubs, shoe inserts, medical catheter implants and other medical and antibiotic uses. In recent years a range of wound dressings have been marketed containing slow release Ag compounds. (Silver *et al* 2006) One website touts the many uses of silver:

> Welcome to the most comprehensive and objective source of information on ***isolated silver colloids and ionic silver solutions*** in the world! Silver Medicine.org is a not-for-profit venture based out of Las Vegas, Nevada, organized to provide the public with accurate and comprehensive information and research about "isolated" ionic silver and particle silver (positively charged *silver ions* and clusters of negatively charged, minute *silver particles*) as used in allopathic and alternative medicine. Silver is antiseptic, has proven antibacterial properties and is antimicrobial. Silvermedicine.org has been organized to provide comprehensive information from the knowledge-base of researchers across the globe; however, we are not able to answer specific health queries or address any specific medical case, recommend dosage levels, or otherwise prescribe or recommend silver use for any condition. Silvermedicine.org is not affiliated with any organization, which markets colloidal silver or generators.

In a groundbreaking study, the Journal of Nanotechnology has published a study that found silver nanoparticles kills HIV-1 and is likely to kill virtually any other virus. The study, which was conducted by the University of Texas and Mexico University, is the first medical study to ever explore the benefits of silver nanoparticles, according to Physorg: (Elechiguerra et.al 2005). After incubating the HIV-1 virus at 37ºC, the silver particles killed 100% of the virus within 3 hours for all three methods. Already used as a topical antibiotic in the medical industry, silver may now come under consideration as an alternative to drugs when it comes to fighting previously untreatable viruses such as the Tamiflu resistant avian influenza.

Within the medical field, an area that has been largely unexplored is the interaction of metal nanoparticles with viruses. This work has demonstrated that silver nanoparticles undergo a size-dependent interaction with HIV-1, with nanoparticles exclusively in the range of 1–10 nm attached to the virus. The regular spatial arrangement of the attached nanoparticles, the center-to-center distance between nanoparticles, and the fact that the exposed sulfur-bearing residues of the glycoprotein knobs would be attractive sites for nanoparticle interaction suggest that silver nanoparticles interact with the HIV-1 virus via preferential binding to the gp120 glycoprotein knobs. Due to this interaction, silver nanoparticles inhibit the virus from binding to host cells, as demonstrated in vitro. (Elechiguerra *et al* 2005)

The interaction of nanoparticles with biomolecules and microorganisms is an expanding field of research. Recently there has been an interest in silver formulations as wood preservatives (Green *et al* 2004, Ellis 2007). In a preliminary study ionic salts were examined for their effect on decay fungi, termites and mould fungi (Dorau *et al* 2004). Although some protection was afforded to damage by *R. flavipes*, it was thought to reside primarily in the silver anions eg: Br, Cl, I, S_20_3. The objective of this study was to test commercial silver-containing formulations using colloidal, ionic or true nano-sized particles as wood preservatives against termite damage by *Reticulitermes flavipes* (Kollar) on southern yellow pine specimens.

2. EXPERIMENTAL METHODS:

2.1 No-choice test

Test samples of southern pine sapwood (25 x 25 x 5 mm) were dip treated in aqueous solutions for 30 seconds, air dried and placed in the bottoms of an acrylic cylindrical containers (90mm in diameter and 60mm in height) with one gram of *R. flavipes* collected at Janesville, WI. Dishes were maintained at 27ºC and 85% RH for a period of 4 weeks following the methods of AWPA E 1-97 (AWPA 2006). At the end of the test, samples were air dried and weighed to determine mass loss (n=5).

2.1.1 Formulations used:

Mild Silver Protein (0.62%) –Colloidal: AgNO3 plus BSA (1310 ppm silver; Argyrol)
N'N-hydroxynaphthalamide (NHA) –0.33% aqueous
1% AgCl/TiO_2 Matrix -Ionic 1 % dispersion; 1200 ppm Ag plus 3700 ppm Ti
0.5% ZnO (nano) (+/- Ag) –Nanoparticles, 20 nm in diameter, dispersion (7921 ppm Zn)
Ag -Zeolite (+/- Cu) –6000 ppm Ag, 5000 ppm Cu, 13000 ppm Al (slurry/coating)
Copper Citrate (1.2%) –1:10 dilution from aqueous stock
40 nm Ag Ethlene-glycol –nano silver 9320 ppm Ag
0.5% CuO (nano) –Nanoparticles: CuO (no silver), dispersion (7970 ppm Cu)
Colloidal Silver (2 ppm) –silver particles, non-ionic (Marketed, consumable product)

3. RESULTS AND DISCUSSION

Table 1: Results of termite test

TREATMENT (N=5)	MASS LOSS (% +/- SD)	MORTALITY (%)	VISUAL RATING (0-10)
Mild Silver Protein (0.62%) + NHA (0.33%)	4.7 (4.2)	0	6.4
1% AgCl/TiO_2 Matrix	5.0 (1.9)	90	9.4
0.5% ZnO (nano) + Ag	8.6 (1.9)	76	7.6
Ag Zn-Zeolite (- Cu)	8.6 (1.5)	20	9.2
Copper Citrate (1.2%)	10.0 (2.5)	0	7.8
0.5% ZnO (nano)	10.1 (4.4)	70	7.2
40 nm Ag Et-glycol	11.9 (6.4)	0	5.6
Ag Zn-Zeolite (+ Cu)	13.7 (2.3)	0	8.0
Mild Silver Protein (0.62%)	23.8 (3.0)	0	0.8
0.5% CuO (nano)	29.7 (14.8)	0	0
Colloidal Silver (2 ppm)	30.3 (8.8)	0	0
SYP Control	34.2 (9.5)	0	0

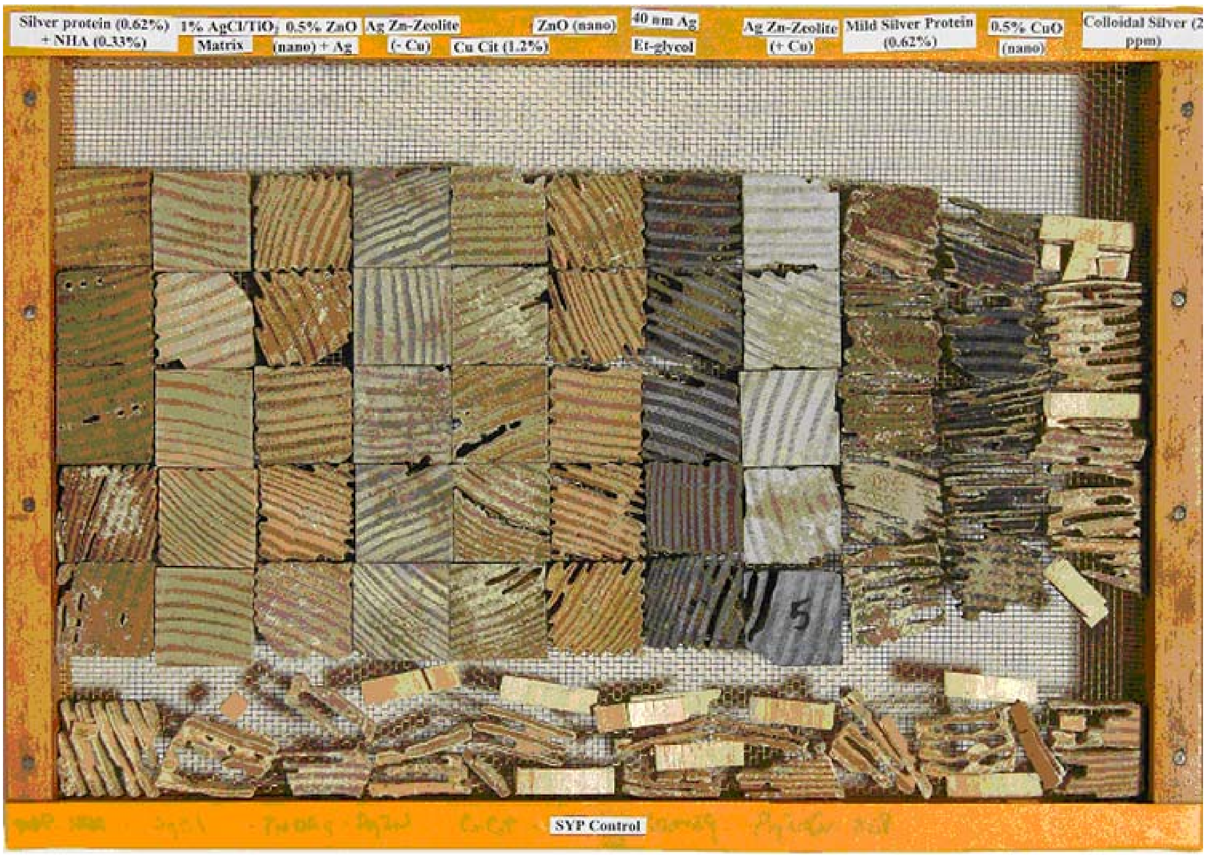

Figure 1: No-choice termite test (wood blocks are positioned left to right as Table 1 above, with controls at the bottom)

Mass losses of treated SYP wood blocks following 4 weeks incubation ranged from 5-30%. Two formulations (silver protein plus NHA & silver choride inonic dispersion) showed less that 5% mass loss, but the silver protein alone at the same concentration showed 23% mass loss indicating that the NHA, even at a low concentration (0.33%) was the more active ingredient. Previously the minimum inhibitory concentration to inhibit damage by *R. flavipes* has been shown to be 0.5% NHA (Green *et al* 1997, 2001; Arango *et al* 2006). As for the ionic AgCl dispersion, it is most likely that other active ingredients: metals, presented in measurable quantities of Al, Si and Ti, also contributed to its protection (Ximenes and Evans 2006).

Mass loss of pinewood blocks treated with nanoparticles showed mass losses of 8-30%. The best protection within this group was seen with ZnO + Ag coating. Closely behind was the ZnO alone suggesting that unless the silver concentration would be increased it doesn't appear to improve efficacy. Surprisingly, the CuO showed no protection. This may be due to charged particles reacting away from fungal hyphae? There are charges on the silver particles which could lead to either non-covalent binding or repulsion (Van Der Wall forces) interfering with the biocide. Aqueous copper citrate (1.2% AI) alone has been shown to give excellent protection at Gulfport MS in field testing over 9 years at the Harrison Experimental Forest. However, Copper citrate treated pine showed 10% mass loss in no-choice laboratory testing at FPL (Table 1). In addition, copper added to the silver chloride, titanium oxide slurry showed decreased protection from 8>>>13% mass loss. The Zn and Ag nano particle formulations performed better than copper oxide nano particles at comparable concentrations.

Mortality in these experiments ranged from 20% in the Ag-Zeolite coating to 90% in the 1% $AgCl/TiO_2$ matrix and ranged from 20-76% in the Zn containing formulations. In groups that had no mortality protection may have been due to repellency or avoidance rather than direct toxicity. This also implies that these are all relatively low toxicity treatments and not broad spectrum biocides when consumed.

In a previous paper on the effect of ionic silver salts on termite protection we concluded that protection was primarily provided by the counter ions (eg Cl, NO_3, Br, I,; Dorau *et al* 2004)
Taking into consideration the mass losses (4.7-13%) in the first eight treatment groups the protection afforded or damage resistance observed after only 30 seconds of dip treating using aqueous formulations, compared with un-dipped controls, results are quite promising. Full cell pressure treatment or even just vacuum impregnation would clearly limit damage even further for those low viscosity formulations. However, because these are "multicomponent" formulations it is difficult to determine the role of silver alone in protection of wood without evaluating the efficacy of each individual active ingredient.

4. CONCLUSIONS:

It is somewhat difficult to compare these formulations as to the contribution of the silver component due to variations in composition and viscosity. Some silver solutions were ionic, while others were colloidal or nano-particles. In addition, some formulations contained additional biocides, including aluminium, zinc, copper, titanium, and silicone. Silver may have contributed modestly to protection, but paired samples with and without silver gave similar protection. Surprisingly, in general, copper ions were not shown to contribute to improved protection either as nano particles (CuO) or as copper salts (CuCit). Future experiments do not seem to warrant leaching studies of silver as potential biocides to termites. ZnO nanoparticles, with and without silver coating, performed well in aqueous dispersion.

5. REFERENCES

Arango, R A, Green III, F, Hintz, K, Lebow, P, Miller R. (2006): Natural durability of tropical and native woods against termite damage by *Reticulitermes flavipes* (Kollar) *International Biodeterioration and Biodegradation* **57**, 146-150.

AWPA. (2006): Standard method for laboratory evaluation to determine resistance to subterranean termites. AWPA Method E1-97. Book of Standards. American Wood Preservers' Association, Granbury, TX. pp. 288-291.

Dorau, B, Arango, R, Green III, F. (2004): An investigation into the potential of ionic silver as a wood preservative. In: Proceedings of the 2nd Wood-Frame Housing Durability and Disaster Issues Conference ed. Forest Products Society. Las Vegas, NV, October 4-6, pp. 133-145. FPS.

Elechiguerra, J L, Burt, J L, Morones, J R, Camacho-Bragado, A, Gao, X, Lara, H H, Yacaman, M J. (2005): The interaction of silver nanoparticles with HIA-1. *Journal of Nanobiotechnology* **3**, 1-10.

Ellis, J R (2007): Silver—the next generation wood preservative. International Research Group on Wood Protection. IRG/WP 07-30419.

Green III, F, Kuster, T, Ferge, L, Highley, T (1997): Protection of southern pine from fungal decay and termite damage with N'N-napthaloylhydroxylamine (NHA). *International biodeterioration Biodegradation* **33**, 103-111.

Green III, F, Crawford, D M, Lebow, S, Yoshimura, T (2001): Relative toxicity of N'N-napthaloylhydroxylamine (NHA) against Eastern subterranean and Formosan subterranean termites in southern yellow pine. In: *Proceedings of the 2nd conference on Durability and Disaster Mitigation in Wood-Frame Housing,* Madison, Wisconsin, Forest Products Society, pp. 235-238.

Jayachandram, K, Seema S, Ellis, J. (2006): Exploratory Research on Silver Chemicals as Wood Preservatives. In Proceedings of the American Wood Preservers' Association, Austin, TX 102:61-66 AWPA, Alabama.

O'Neill, M A, Vine, G J, Beezer, A E, Bishop, A H, Hadgraft, J, Labetoulle, C, Bowler, P G. (2003): Antimicrobial properties of silver-containing wound dressings. *International Journal of Pharmacology,* Sep 16: **263**(1-2), 61-8.

Silver, S, Phung LT, Silver, G (2006): Silver biocides in burn and wound dressings and bacterial resistance to silver compounds. *Journal of Industrial Microbiology and Biotechnology*, **33**, 627-634.

Williams, A (2000): Alfred Barnes, Argyrol and art. *The Pharmaceutical Journal*, **265,** (7128), 933-934.

Ximenes, F A, Evans, P D. (2006): Protection of wood using oxy-aluminium compounds. *Forest Products Journal*, **56**, 116-122.