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Wood Protecting Chemicals

Field Stake Tests with Copper-based Preservatives

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Abstract

The performance of field test stakes derived from commercially produced ground contact retention copper quat preservatives based on either soluble copper complexed with ethanolamine, or from a water-based suspension of particulate micronized copper compounds, as well as untreated southern yellow pine controls, is compared at two decay test sites. After less than one year in field test some of the untreated controls at both test sites showed severe fungal deterioration. Stakes treated with the soluble copper preservative are unattacked, while those treated with the particulate micronized copper preservative are showing varying degrees of decay, which in some cases is severe or complete. Possible reasons for the performance differences observed are discussed.

Keywords

Copper, preservatives, soluble, particulate, micronized, field, stake, mode of action

Introduction

Wood preservatives based on copper have had a long history of commercial use (Nicholas et al 1997). Three general types of product can be recognized, the systems containing chromium as a corrosion inhibitor, fixation agent and co-biocide, as exemplified by chromated copper arsenate (CCA), the copper complexes such as copper naphthenate, and the water-based copper preservative systems containing a nitrogen base as a solubilizer, fixation agent and corrosion inhibitor, as in the case of ammoniacal copper arsenate (ACA), ammoniacal copper zinc arsenate (ACZA), ammoniacal copper citrate, copper azole (CA), copper HDO and alkaline copper quat (ACQ). These latter systems used ammonia or amines to solubilize and stabilize the copper in solution and to provide penetration throughout the wood structure and

interactions with the wood components. Such systems have been used since the mid-1930s in the United States. The active copper components of such systems provide most of the performance characteristics of the preservatives, with the secondary biocides being important in protecting the treated wood against some copper tolerant fungi, and also to some degree against termites. While “fixed” to a large degree within the wood structure, the highly fungicidal alkaline copper component appears to retain some degree of mobility which leads to some increase in corrosion profile with some fasteners, and also a non-zero leaching profile (Zhang, 2000). Long term field and service performance of such alkaline copper preservatives in in-ground applications has been excellent.

In recent years several products have been developed which use the same copper and co-biocide components as some of the alkaline copper systems mentioned above, but use solid particulate copper compounds (usually copper carbonate) suspended in water rather than the water soluble copper complexes based on copper and amine or ammonia. Initial reports in the patent literature suggest such developments first occurred during 2001. The patent literature also suggests that particle size of the “micronized” copper component is important, and a mean particle size in the region of 190 nm is described as being optimal. Smaller size would increase leachability and potentially bring health issues related to nano-particles, while larger particle sizes would be detrimental to the treatment of even the highly permeable pine species which are currently practicable to treat.

Examples of such products appeared on the market in 2006 but little long term technical information was publicly available on such products. Currently, there are no scientific publications that include long term field stake data for the micronized copper preservative systems. Two papers at the IRG meeting in 2007 looked at copper distribution in the wood and across the cell wall (Matsunaga et al. 2007, Archer, unpublished) while another report circulated around that time looked at macro-distribution (Detter-Hoskin) One study did not find any copper in the cell wall while the other found low levels of copper which the authors ascribed to the presence of small amounts of soluble copper. The macrodistribution study found variable distribution within the wood structure.

Little field performance data has been made available, although in presentations it has been stated that one MCQ preservative performed as well as the amine copper systems at the Austin Carey test site in Gainesville, FL, in a ground contact stake tests.

In our earlier work we expressed concern as to whether the absence of cell wall penetration of the copper preservative component would lead to failure from soft rot in service (Hulme, 1977). In discussion of this work, this concern was verbally refuted although data was not available at that time. At that time we did not consider basidiomycetes fungi to be an issue as available soil block data was said to support efficacy claims in this regard. At that time the assumption was made that the apparent presence of insoluble copper particles on the lumen surfaces would perhaps inhibit such fungal attack.

Within Viance questions arose as to whether our technical concerns in regards to the likely long term performance were valid, especially when some large wood treaters, and one or two large retailers were promoting such products. In order to address such concerns, and lacking available literature on the performance of particulate copper systems in comparison with solubilized copper systems such as ACQ and CuAz, we embarked on a study using commercially available materials from reputable wood treating companies, with treatment chemicals supplied to those treaters by organizations other than Viance. The research project was designed to provide, as closely as possible, treated materials that were representative of the products being marketed.

Methods

Test Materials

Southern yellow pine 4 x 4 x 8 foot long posts treated to retentions of 0.40 pcf (6.4 kg/m³) with either alkaline copper quat (ACQ-D) or Micronized Copper Quat (MCQ) were procured from local retailers in the Charlotte, NC area. A total of seven posts were obtained for each treatment. The ACQ material was purchased from one retailer and the MCQ material was purchased from another retailer. All material and identifying tags were photographed and recorded.

Test Sample preparation for ground contact field tests

Before cutting the materials into test samples, each post was cross-cut into four foot (1200mm) lengths and then thin cross-section wafers were cut from the center zone of each post. One set of these wafers was sprayed with a heartwood indicator and also a copper penetration indicator in order to visualize the preservative penetration patterns, which were quite uniform throughout the sapwood zones of the posts. Photographic records were made of this work. The treated portion - excluding the untreated heartwood areas - of another set of these wafers representing all of the posts was analyzed for the preservative components (CuO and DDACarbonate). The results of these analyses are shown in Table 1. In addition to the composite analysis of the cross section from each post, a corner section cross sectional wafer from each of the posts measuring 30mm square was divided into 15 mm quadrants for chemical analysis. Each of these quadrants, labeled A, B, C, D, was representative of the individual stakes cut from each post (Fig. 1). A composite sample was made from each of these quadrants and analyzed for CuO. The results of these analyses are shown in Table 1.

For the analyses, the cross sections of the posts were cut so that no heartwood was present for the analysis. Two cross section pieces were cut and ground together to form one homogeneous sample for each post. The wood was ground through a 30-mesh screen, then dried and evaluated for copper on the ASOMA X-ray fluorescence analyzer and quat by a Mettler-Toledo auto-titration system.

The groups of ACQ and MCQ materials were machined to provide groups of stakes representing the commercial ground contact retention treatment derived from each mother post. The stakes were cut from the outside corner zones of the posts. Heartwood zones were avoided while knots were avoided as far as practical. The mother board information was recorded and distribution of the stakes from each mother board was evenly distributed among the various test sites and test types. Metal barcode information for each site/test was recorded and correlated with the original mother board analytical information. In addition, 120 (30 x 30 x 450mm) stakes were cut from untreated southern yellow pine boards to serve as controls.

Field Stake Tests

The ground contact field decay tests reported in this paper installed during the first half of 2007 are shown below:

Tanegashima

Ground contact stake test: 20 stakes each of ACQ-D and MCQ, and 20 untreated control stakes.

Hilo (Keaau decay site 1)

Ground contact stake test: 10 stakes each of ACQ-D and MCQ, and 10 untreated control stakes.

Installation of Stake Tests

The stakes were installed randomly in rows to a depth of no more than half their length at test sites near Hilo, HI and in Kagoshima Prefecture, Japan. The Hilo test site is an open field with a rich loam soil type, while the Tanegashima site is an open canopy site on a light loam soil. Average rainfall in Hilo is approximately 3250mm while the Kagoshima prefecture site has an average rainfall of approximately 2100mm.

Results

Chemical Analyses

As mentioned above extensive chemical analyses were carried out at various stages of the work. The results of work carried out during the preparation of the materials is summarized in Table 1 below. This data shows that both preservative systems show similar variations in preservative retention from post to post and within the posts as shown in the quadrant analyses. There are no obvious differences or deficiencies seen in either preservative treatment for either copper or quat retention and distribution in the materials used. The MCQ posts tended to be more tightly targeted around the required retention for the commercial treatment, and but the distribution of both

preservative system and their components was within the accepted range and in these materials. No remarkable trends were discernible between or within the systems and materials used that would indicate the results obtained in the field exposures. The analytical data for the posts indicates that the ACQ treated posts were treated in accordance with AWPA standards (there is presently no AWPA standard for MCQ) and that the MCQ were treated equivalently to that expected for these active ingredients in the AWPA standards. There is some variation in preservative retentions of the different posts, but this is normal for commercial treatments.

Table 1.

Chemical analysis results of treated materials including results for the 15mm square quadrants removed from the zone where the stakes were cut from the posts and the results of cross sectional samples of the treated areas for each of the posts used in the study.

Analysis of Quadrants

Cross section analysis

		%CuO						Post	Treatment							
		A	B	C	D	Avg.	Number	Type	%CuO	%DDAC	%Total	CuO pcf	DDAC pcf	Total pcf	Ratio	
ACQ	1	2.362	1.818	1.986	0.922	1.77	1	ACQ	0.92	0.53	1.45	0.29	0.17	0.46	1.74	
	2	1.216	0.899	0.975	0.616	0.93	2		0.94	0.71	1.65	0.30	0.23	0.53	1.32	
	3	1.199	0.962	1.141	0.778	1.02	3		0.94	0.45	1.39	0.30	0.14	0.44	2.09	
	4	2.123	1.638	2.021	0.852	1.66	4		1.04	0.58	1.62	0.33	0.19	0.52	1.79	
	5	1.065	0.927	0.844	0.570	0.85	5		0.88	0.51	1.39	0.28	0.16	0.44	1.73	
	6	1.416	1.367	0.935	0.733	1.11	6		0.97	0.61	1.58	0.31	0.20	0.51	1.59	
	7	0.998	0.775	0.876	0.458	0.78	7		0.76	0.46	1.22	0.24	0.15	0.39	1.65	
MCQ	8	1.107	1.350	1.787	1.974	1.55	8	MCQ	0.75	0.50	1.25	0.24	0.16	0.40	1.50	
	9	0.882	0.724	0.922	0.658	0.80	9		0.81	0.48	1.29	0.26	0.15	0.41	1.69	
	10	0.822	0.865	0.765	0.486	0.73	10		0.80	0.55	1.35	0.26	0.18	0.43	1.45	
	11	0.525	0.505	0.533	0.545	0.53	11		0.68	0.45	1.13	0.22	0.14	0.36	1.51	
	12	0.790	0.640	0.583	0.482	0.62	12		0.68	0.59	1.27	0.22	0.19	0.41	1.15	
	13	0.918	0.749	0.784	0.399	0.71	13		0.86	0.58	1.44	0.28	0.19	0.46	1.48	
	14	0.709	0.623	0.691	0.672	0.67	14		0.59	0.40	0.99	0.19	0.13	0.32	1.48	

Biscuits of the cross-section of each individual stake exposed in Tanegashima were cut 10mm from the top of each stake. Copper analysis was performed on all the cross sections in order to gain the better idea of the treatment levels in the testing stakes. Again the heartwood and copper indicators were sprayed on the cross sections of each stake and they showed no heartwood presented in the stakes and all the stakes appeared fully penetrated with copper for both treatment types. The copper analysis results are shown in Table 2 below and the results show that the individual stakes have similar or higher retentions of preservatives than the whole post cross section analysis data and are well within the targeted retention levels.

Table 2.

Copper retentions of cross sectional samples removed from the stakes installed in Tanegashima.

Stake No.	% CuO	Stake No.	%CuO
S58	0.832	P78	0.774
S59	0.758	P79	0.837
S60	0.693	P80	0.746
S61	0.807	P81	0.800.
S62	0.796	P82	0.719
S63	0.766	P83	0.808
S64	0.862	P84	0.805
S65	0.803	P85	0.764
S66	0.783	P86	0.800
S67	-	P87	0.918
S68	0.736	P88	0.856
S69	0.722	P89	0.776
S70	0.740	P90	0.782
S71	0.786	P91	0.769
S72	0.855	P92	0.805
S73	0.785	P93	0.799
S74	0.727	P94	0.724
S75	0.787	P95	0.775
S76	0.772	P96	0.886
S77	0.820	P97	0.845

During the recent field test inspection in Japan carried out early in 2008, one of the stakes was removed from the test due to failure from decay. This stake was recovered for further chemical analyses. The stake was subsequently sawn above the exposed groundline and the cut cross-section was sprayed with heartwood indicator and also copper penetration indicator. These visualizations showed that the stake was a sapwood stake with no heartwood and had been fully penetrated by the preservative during the treatment process.

Since the decay occurred in almost the entire cross section except for 3-5mm on two sides, chemical analysis was carried out for two samples: one from the one (5mm) of the two apparently undecayed sides and the other for all the area where decay occurred. The samples were obtained from the portion of stakes right above the ground line. The results of the analysis of the cross section of the original 4x4 post

which the stake was cut from and the two sections from the decayed stake were found to be 5.0 kg/m^3 and 8.28 kg/m^3 . The weighted average retention for this stake is 6.14 kg/m^3 , close to that of the targeted retention of 6.4 kg/m^3 . The requisite retention of quat (DDACarbonate) was present in the treated area.

These retentions may also be compared with the recent introduction into the U.S. marketplace of the revised ground contact retention for MCQ in southern pine of 0.34pcf (5.44 kg/m^3), as CuO plus DDAC (2:1). It should be noted that other particulate copper systems have been introduced recently for the treatment of southern yellow pine with ground contact retentions of 0.14pcf (2.2 kg/m^3 Cu and 0.086 kg/m^3 triazole) and 0.17pcf (2.72 kg/m^3) (2.62 kg/m^3 Cu and 0.104 kg/m^3 triazole). While this study does not address any potential differences in ground contact performance that different secondary biocides may impart, the use of lowered copper retentions with particulate copper preservatives may merit further extensive ground contact testing.

Field Stake Inspections

The results from the inspection of the field stakes installed in Japan are presented in Table 3. From this data it is apparent that this is an aggressive test site, with many of the untreated controls and MCQ treated wood stakes showing considerable decay after nine months' exposure. It is also apparent from this data that the ACQ treated stakes are performing very well, with none of the stakes showing evidence of decay.

Table 3.

Decay ratings for field stakes after nine months' exposure in Tanegashima, Japan.

ACQ			MCQ			Untreated		
Stake No.	Retn. (pcf) ¹	Rating ²	Stake No.	Retn. (pcf) ¹	Rating ²	Stake No.	Retn. (pcf) ¹	Rating ²
S58	0.46	10	P78	0.40	9	U79	0	8
S59	0.46	10	P79	0.40	10	U80	0	0
S60	0.46	10	P80	0.40	10	U81	0	0
S61	0.53	10	P81	0.41	10	U82	0	0
S62	0.53	10	P82	0.41	10	U83	0	7
S63	0.53	10	P83	0.41	8	U84	0	0
S64	0.44	10	P84	0.43	4	U85	0	10
S65	0.44	10	P85	0.43	10	U86	0	9
S66	0.44	10	P86	0.43	10	U87	0	0
S67	0.52	10	P87	0.36	6	U88	0	8
S68	0.52	10	P88	0.36	9	U89	0	0
S69	0.52	10	P89	0.36	9	U90	0	8
S70	0.44	10	P90	0.41	4	U91	0	10
S71	0.44	10	P91	0.41	10	U92	0	4
S72	0.44	10	P92	0.41	10	U93	0	0
S73	0.51	10	P93	0.46	10	U94	0	0
S74	0.51	10	P94	0.46	7	U95	0	0
S75	0.51	10	P95	0.46	4	U96	0	9
S76	0.39	10	P96	0.32	0	U97	0	7
S77	0.39	10	P97	0.32	7			
Mean % soundness		100			78.5			42.1

¹ Average preservative retention for cross sectional treated area for the post that the stakes were cut from.

² Stakes were rated in accordance with AWPA Standard E7 with 10 denoting sound and 0 denoting failure.

Inspection results for the stakes exposed at the Hilo test site are presented in Table 4. From this data it is apparent that most of the control samples are showing evidence of decay, indicating that the test site has a high level of decay potential. For the MCQ treated samples, two stakes have minor amounts of decay established and two show evidence of suspected decay. In contrast the ACQ treated stakes were all sound.

Table 4.

Decay ratings for field stakes after ten months' exposure in Hilo, HI.

ACQ			MCQ			Untreated		
Stake No.	Retn. (pcf) ¹	Rating ²	Stake No.	Retn. (pcf) ¹	Rating ²	Stake No.	Retn. (pcf) ¹	Rating ²
S99	0.46	10	P19	0.40	10	U99	0	9
S01	0.53	10	P21	0.41	9	U01	0	9
S03	0.53	10	P23	0.41	9.5	U03	0	6
S05	0.44	10	P25	0.43	10	U05	0	8
S07	0.52	10	P27	0.36	10	U07	0	10
S09	0.52	10	P29	0.36	10	U09	0	6
S11	0.44	10	P31	0.41	10	U11	0	6
S13	0.51	10	P33	0.46	9.5	U13	0	8
S15	0.51	10	P35	0.46	10	U15	0	10
S17	0.39	10	P37	0.32	9	U17	0	9
Mean % soundness		100			97			81

¹Average preservative retention for cross sectional treated area for the post that the stakes were cut from.

²Stakes were rated in accordance with AWPA Standard E7 with 10 denoting sound and 0 denoting failure.

It is apparent from the results obtained at these two test sites that MCQ is showing premature decay, even though the analytical data indicates that the test material was treated in accordance the 0.40pcf ground contact retention specified for ACQ-D within the AWPA standards. (Note that the MCQ posts were treated to the 0.40pcf retention approved at that time for MCQ in ground contact by the ICC-ES, and qualified by third party inspection [as is the norm in the U.S.]

Discussion

The extensive analytical work carried out as part of this study was to determine if significant chemical retention or distribution differences existed between either the two commercial treatments with the two different preservatives with the same targeted active ingredient retentions, or within the chemical retention and distributions within the stake sets. While there are differences, as is always the case, within the commercially treated wood and within the stake sets, the differences are overlapping and do not appear to be at all causal to the performance differences seen to date in the field stake tests in ground contact.

Rather, it seems more likely that the differences between the performance of ACQ- and MCQ-treated wood observed in this study seem likely to be due to efficacy differences between solubilized copper and particulate copper preservative systems. In this section we have attempted to provide reasoned explanations to address the observed results. One or more of the following factors, along with other possibilities, may be causal agents:

- The differences in surface-to-volume ratio between particulate copper compared to solubilized copper and how this impacts the oxalic acid inhibition process of copper-tolerant fungi.
- Microdistribution/retention levels of copper within the cell wall.
- Differences in the bioactivity of solubilized versus particulate copper, and possible synergistic effects of the copper and the secondary organic biocide, in protecting the wood from multiple fungal vectors.
- The moisture content of the wood in ground contact and how this impacts the solubility of copper ions from particulate copper and, consequently, any protective effect of such copper against decay fungi.
- Field test site variations with respect to soil chemistry and moisture, wood moisture, fungal species present, etc.

Little, if any, scientific information has been published on the mechanism of action of particulate copper fungicides as wood preservatives. Perhaps the most likely surrogate for this lies with the foliar copper fungicides, which are largely insoluble copper compounds sprayed on leaves or other exposed plant surfaces to protect plants from fungal attack. The mechanism of foliar copper fungicides is generally considered to be rainfall on the plants solubilizing small amounts of the copper which prevent spores from developing (Richardson, 1997a). Extrapolating this concept to wood preservatives is difficult for a couple of reasons, with the most notable being that within the wood structure actively growing fungal mycelia are present rather than spores trying to develop and survive within a limited time. Further, in some situations insufficient moisture may be present in the wood to give sufficient mobile copper to combat any fungal mycelia which are actively growing in the wood. While it is possible with particulate copper, as described previously (Matsunaga, et al. 2007), for some copper ions to be solubilized and subsequently possibly penetrate the cell wall, the amount/retention level of the solubilized copper within the cell wall may, as Evans clearly noted, be insufficient to protect against soft rot attack. Furthermore, the retention level within the cell wall may even be inadequate to protect against actively growing basidiomycetes fungi.

The mechanism of action of wood destroying copper tolerant fungi has been studied extensively. Some studies show that such fungi gain their copper tolerance by converting active soluble copper ions into insoluble copper oxalate (Clausen et al. 2000). Other studies have shown the formation of calcium oxalate and also differences between mechanisms observed inside and outside of the wood matrix (Schilling and Jellison). It is instructive to compare the water solubility of copper oxalate and copper carbonate. Copper(II) oxalate is stated to be “Practically insoluble in water”, while copper(II) carbonate is “virtually insoluble in water” but “sol in dil acids” such as the acidic environment that can surround fungal decay mycelia (Budavari et al., The Merck Index, 11th ed, Merck and Co., 1989; Goodell 2003, Richardson 1997b). In considering the differences between copper oxalate and copper carbonate in regards to solubility and bioavailability, with wood treated with solubilized copper each copper cation is likely a separate entity. Consequently, the copper-tolerant fungi would need to spend considerable metabolic energy biosynthesizing sufficient oxalic acid to complex the relatively high levels of bioavailable copper. By contrast, with particulate copper only the copper carbonate on the surface of each particulate cluster is available to be solubilized; any copper in the interior of the particle would be

insoluble and therefore not bioactive until the surface erodes away. Furthermore, decay fungi may only need to produce sufficient oxalic acid to cover the surface of the particulate copper to prevent any of the copper in that particle from solubilizing. Assuming that each copper particle is a sphere, the number of copper atoms in that sphere is a cube function while the surface area is only a square function. Thus, the copper-tolerant fungus may only have to biosynthesize a relatively limited level of oxalic acid with wood treated with particulate copper, with energy resources thus freed up for the copper colorant fungi to expend on decay activities.

Another factor at work could be possible synergistic protective effects by the soluble copper and organic co-biocide. We have long recognized that a wide variety of microorganisms are involved in the fungal decay of wood, but recent technical advances have made us even more aware of this. Specifically, with modern DNA techniques it was recently noted that only 2% of the decay fungi that exist on wood can be isolated and grown on agar media (Kirker, 2008); the vast majority of decay fungi present were not recognized by traditional techniques. Further, wood-inhabiting but non-decay fungal and bacterial microorganisms also play a role in the decay process, and most are likely inhibited by copper ions. While we surmise that the activity or inactivity of the copper compounds in a mixed preservative system consisting of copper and other biocide component(s) may well influence the ability of secondary biocides to protect wood in ground contact from the multiple decay fungi and other involved but non-decay vectors, little data is available to directly address this issue. It would not be unreasonable to assume, however, that the combination of two biocides – both of which need to be present at some minimal level – would be more effective than the co-organic biocide and only a limited level of actively available copper.

It is generally considered that the optimum conditions for decay by basidiomycete fungi in wood products occurs when the temperature is between 10°C and 30°C and the moisture content of the wood is at or above 25% MC (but less than around 100% MC). When one considers this in the light of the mechanism of foliar copper fungicides described above, it can be postulated that it might be possible for decay to develop in wood that has sufficient moisture for fungal decay but insufficient free water to solubilize copper from the insoluble particulate copper.

A further factor of a more general nature involves the differences between ground contact performance of treated wood at different test sites. Temperature is clearly a predictable factor in decay rates, and soil moisture plays a role also, but the most significant factor is soil type and its relationship to soil moisture and how this affects the overall decay fungal pressure on any given wood product system, biocide-treated or otherwise. The two test sites used in this study were significantly different in soil type and moisture. The Hilo test site is a rich loamy soil with high rainfall and a dense grass cover that retains high moisture even being fully exposed to the sun. The Tanegashima test site has a lighter loam soil with a light forest litter cover on a well drained slope, under a light forest canopy. While stake moisture contents were not taken at either site, the general moisture content of the Hilo stakes is highly likely to often be greater than for stakes exposed at the Tanegashima test site. How this has affected the results to date has not been determined. Further, it is likely that copper-tolerant and/or soft-rot fungi are more prevalent in certain soil types than others.

It is clear from the above that one or more of a variety of explanations could explain our results. Indeed there may be further factors that we have not addressed which could be contributing to the striking differences in performance observed. We are continuing our studies using a variety of methodologies and test sites in the hope that such research will bring further clarity to our recent observations.

Conclusions

The results indicated significant differences in the performance of the two commercial copper preservative systems included in these stake tests after a very short time period. The presence of wood decay in the particulate copper treated samples after this short exposure period suggests that the use of particulate copper rather than soluble amine-complexed copper in the formulation has lead to substantially faster onset of decay than is the norm with the soluble copper formulation. Additional field stake tests are being carried out to further investigate the phenomenon and to further quantify the differences in performance seen to date. There is also considerable scope for detailed scientific investigation into the mode of action, of such particulate copper preservative systems.

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