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Dispersed Copper Azole for Refractory Species

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Introduction

Dispersed copper formulations have been commercially available for over two years and have taken a major share of the market in the United States. These treatments are well suited for easy to treat species such as southern yellow pine. Due to their particulate nature, penetration of refractory species such as Hem-Fir, Douglas-fir, and SPF has had mixed results. This paper discusses work currently being undertaken by Arch Wood Protection to overcome issues with refractory species penetration in an effort to provide a quality treated wood product with dispersed copper azole.

Dispersed System Basics

The primary difference between soluble and dispersed copper formulations is the form of copper. Instead of copper being dissolved by amine it is in a particulate form and dispersed or suspended in the treating solution. Suspension agents are added to keep the particles from agglomerating and increase the time it takes for them to settle. In dispersed systems, the particles are small enough that physical and surface chemistries can have an impact on their properties. It is well known that particle size and geometry of the particle also affects penetration.

Concentrates from these systems can be easily recognized by differences in color of the concentrate, work tank solution, and treated wood. The dissolved, amine copper systems such as CA-B, CA-C, and ACQ are dark blue in color whereas dispersed basic copper carbonate systems such as µCA-B, µCA-C, and MCQ are more azure in color. Wood treated with dissolved copper systems result in a traditional treated wood green color whereas the dispersed copper systems result in little color to a light green shade.

In developing and formulating dispersed products, concerns can be categorized into three major groups: formulation, generation of particulates, and treating variables. Formulation is the most difficult and depends on final attributes desired. Particles have a tendency to settle, agglomerate, and accumulate at the bottom of the container. The formulator must develop a system that will maintain particle suspension for a sufficient time period. There are thousands of dispersants to choose from, each with its own attributes. The challenge is finding the correct match for the specific combination of components and chemistries involved.. Physical proprieties of the treating solution also present a challenge with respect to the size of the particulates, solution rheology, and interaction with any additives that may be included.

Generation of the particulates is an interesting science in itself. Grinding is currently the most common method for producing particles. Grinding is accomplished by passing a mixture of the desired solid copper compound, such as basic copper carbonate, and dispersant through a rotating bead mill. The mixture interacts physically with the beads which break the particles as they pass through the mill. During sequential passes through the mill the copper is broken into smaller particles. There are a number of equipment manufacturers with patented methods of keeping the beads interacting with the particulate solution without occluding a very fine screen. The screen's function is to allow the mixture to pass while retaining the beads in the mill's grinding chamber.

The composition of the mixture, characteristics of the grinding process, and number of passes through the mill determine the particle size distribution of the mixture. The primary objectives of the milling are to produce a suitable particle size distribution with suitable stability for wood treatment while minimizing grinding time (to maximize capacity).

Particle size plays a dominate role in the ability of the copper to penetrate and provide the distribution needed for protection of the wood. Particle size measurement is therefore an important part of determining the quality of the milled formulation. Particle size analyzers commonly use one of three methods: dynamic light scattering, laser light scattering, and sedimentation. Results from measuring the same material on the different types of machines will results in different particle size distributions. This may be important when trying to understand the physical properties of a formulation or when describing the formulation to outside agencies. The EPA is interested in properties of materials that can be classified as nano materials. A nano particle is generally classified as a particle less than 100 nm. However, there is not an official definition for nano-materials, i.e. when a material contains both nano particles and particles above 100 nm. It has been suggested, but not officially defined, that a nano material is one that contains more than 10% of its particles less than 100 nm. With considerable variation from the method of particle size analysis, it will be important to describe how the particles were measured.

Wood treatment objectives include uniform distribution within the treatable portion of the wood and penetration of the cell wall. Uniform distribution is achieved when a pressure differential moves treating solution through longitudinal trachieds and rays, traveling from one cell lumen to another and through the pit structures. In species such as southern yellow pine these pathways are relatively open and easily penetrated in the sapwood region but occluded in the heartwood region. In refractory species such as red pine, hem-fir, SPF, and Douglas-fir these paths are much smaller and often occluded making them very difficult to penetrate with treating solution and achieve an even distribution in the wood. In many refractory species where heartwood cannot be readily differentiated from sapwood, penetration of and distribution in the outer shell is all that is required. Incising is often needed to accomplish this penetration.

Once the treating solution is well distributed it is important for some copper to enter the cell wall to protect against soft rot fungi. Questions have been raised concerning the ability of dispersed copper to enter the cell wall due to its particulate nature. In an effort to determine existence of copper in the cell wall, treated samples of southern yellow pine treated with CA-C and µCA-C were sent to Dr. Jeffrey Morrell at Oregon State University and Dr. Robert Hanna at SUNY-ESF. Dr. Morrell used a scanning electron microscope equipped with energy dispersive x-ray analysis capabilities (SEM/EDXA) to "map" copper across cell walls. Dr. Hanna analyzed the cell walls of these samples for presence of copper using a Scanning Electron Microscope equipped with Energy Dispersive Spectroscopy (EDAX) capabilities. Dr. Hanna's technique is based on focusing an electron beam on a specific point in the cell wall. The beam penetrates the cell wall then expands in a tear-drop shaped form which is analyzed. The analysis provides an X-ray spectrum for metals with a specific peak for copper. Results from these studies have proven that when a dispersed copper treating solution is well distributed in the wood and cell lumen, copper enters the cell wall. Soft rot tests with comparisons between amine Cu systems and µCA-C have confirmed efficacy of this material.

Arch Wood Protection has thoroughly evaluated the efficacy of our µCA-C (dispersed) compared to CA-C (dissolved in amine) and demonstrated similar efficacy, cell wall penetration, and ancillary properties for both above ground and ground contact service. Using AWPA testing standards µCA-C has shown effectiveness against attack by brown rot, white rot, soft rot, and termites. As an added benefit, µCA-C has much lower leaching which will provide more copper to protect the wood throughout its useful life. Long term AWPA standardized field tests are in progress in a number of global locations. Arch Wood Protection has the confidence to offer this product with the same warranty as its other preservative systems.

Work with Canadian Refractory Species

Dispersed copper products have been shown to be well distributed in treated southern yellow pine; however, to date this has not been consistent for refractory species. Work is still needed in this area, but significant progress has been made. Arch Wood Protection has been working to provide a commercially viable dispersed formulation for red pine, ponderosa pine, western hemlock, hemlock-true firs, Douglas-fir, European species, and Asian species.

In work done on these species by understanding a number of variables discussed above we have had success in providing proper shell penetration for incised hem-fir and SPF lumber. Douglas-fir has been more of a challenge. Without the use of ammonia, variable results for Douglas-fir have been achieved.

In an effort to prepare for commercial treatment in Canada, 10 charges each for Canadian 4x4 red pine, 4x4 hem-fir, 2x8 western SPF, and 2x6 eastern SPF were treated with µCA-B in the Arch Technical Center in Conley, GA. Five charges of each species were treated to requirements of both the CSA commercial and residential standards. All charges were 3rd party inspected to determine a pass/fail rating by sampling 20 cores per charge. Results from these tests showed that all charges treated to residential standards passed. Red Pine passed the commercial standard, however, both of the SPF species groups had one charge each below 80% (70% and 75%), and the hem-fir had 3 below 80% (60%, 70%, and 75%).

In the United States, the Arch µCA-C dispersed copper product has been issued a code evaluation report for southern yellow pine lumber and plywood, red pine, ponderosa pine, hem-fir, western hemlock, and Douglas-fir plywood. Our treaters who have 3rd party inspection are currently treating southern yellow pine lumber and plywood, red pine, and ponderosa pine.

Arch continues work to improve dispersed copper products for refractory species. The variables, that are not related to the product formulation, that influence the quality of refractory species treatment include species and plant variability, which are difficult to bring into a research center. To test our products in the "real world" a mobile treating cylinder is being used for trials at selected treating plants. This enables each plant to assess treatability of refractory species from the numerous mills from which it sources white lumber. Initial trials are currently being held in the Pacific Northwest and California on hem-fir.

Conclusions

Refractory species are more challenging with respect to penetration and distribution of dispersed copper treatments. However, these species can be successfully treated by developing appropriate formulations, selectively sourcing white lumber, and using appropriate treating methods. Ultimately quality and consistency of treatment must be proven by achieving conforming treating results in actual treating plant conditions.