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Development of Commercial Wood Preservatives

Efficacy, Environmental, and Health Issues

EDITED BY
Tor P. Schultz, Holger Militz, Michael H. Freeman,
Barry Goodell, and Darrel D. Nicholas

Wood Preservative Formulation Development and Systems: Organic and Inorganic Based Systems

Mike H. Freeman, Independent Wood Scientist
7421 Hunters Tree Cove, Memphis, TN 38125,
e-mail: wooddoc@aol.com

Wood preservatives lengthen the useful service life of valuable biologically-based building materials, thereby saving the consumers money and time, and minimizing the effects of deforestation and unnecessary consumption of perishable goods. The formulation of a wood preservative can greatly impact its performance, simplify application, and affect the materials employed to apply the system and construct the final treated wood product. This chapter discusses the formulation systems used for many wood preservation applications such as pressure treatment, anti-sapstain, general / DIY (homeowner applied) preservatives, millwork/joinery systems, and remedial treatments. Specific examples are given that have impacted the performance, efficacy, and ease of usage of both organic and inorganic-based systems. Use of inert ingredients as formulation aids is also briefly discussed.

Introduction

The efficacy of any pesticide, including wood preservatives, can be greatly affected by its formulation into a commercial product. Formulations play significant roles in how a biocide is available for both fungal and insect control as well as affecting the treated wood's aesthetic and physical properties including preservative leaching.
In general, wood preservative formulations contain actives that provide antifungal and/or insecticidal properties. In some cases blends of fungicides and insecticides or a single compound which is active against both fungi and insects may be employed, while in other cases activity against only decay fungi or insects is required.

Essentially all wood preservatives employ a liquid carrier as the solvent. For lumber and timbers destined for the exterior residential market, water is the preferred solvent for the actives. Most residential preservatives currently used in North America are water borne copper-rich systems, where additional amines or ammonia are used to dissolve the copper containing preservative and minimize corrosion in the treating plant. It is expected that at some point in the future totally organic systems that employ water insoluble agrochemicals will be required for exterior residential applications. For these systems the active will likely be formulated in water using sophisticated systems such as an emulsion or nanodispersion. Some millwork systems employ light organic solvents, but waterborne systems are growing more predominate. For treated wood products used in the industrial sector, except for the waterborne chromated copper arsenate (CCA) system the organic or organometallic actives are dissolved in petroleum oil solvents, where the oils often provide some additional protection to the treated wood. The few exceptions of non-liquid carrier preservatives include the liquid creosote where the active is the carrier, a few solid preservatives such as zinc borate employed for in-process treatment of wood composites, and solid rods for remedial treatment of in-service wood.

A variety of additives are also used in wood preservative formulations. The most widely used are paraffin based water repellents that are incorporated directly into water borne treatments as emulsions or dispersions. Corrosion inhibitors, surfactants, dispersants, stabilizers, colorants, and other performance enhancers are also used but typically these types of additives are in small amounts.

This chapter reviews formulation insights including current solvents and biocides, and formulation additives for many wood preservative systems. Included in this overview will be current policies, practices, biocides, additives and solvents employed, the author's personal experience in formulating many of these preservative systems and a historical review. Although all segments of the wood preservative market will be discussed, the sections are arranged in the approximate market size: pressure treating chemicals, anti-sapstain systems, millwork/joinery products, general preservative systems, and remedially treatment chemicals.

Pressure Treating Preservative Systems

Pressure Treating systems are the major wood preservatives, and have been employed to preserve wood since 1838 when John Bethel first patented the use of creosote for full cell treating of products such as railroad ties and timbers. Pressure treating chemical sales in the United States in 2006 alone exceeded $1 billion just for the water borne products, predominately inorganic copper carbonate and borax based biocides. Other pressure treating chemicals include organic systems such as pentachlorophenol in oil, creosote, and creosote-petroleum systems. Interestingly, the wood preservatives used in the pressure treating arena amount to 75% of the total poundage of pesticides used in North America.

The typical goal for pressure treating systems is to have an easy-to-employ system that will penetrate most wood species to protect the sapwood from decay and termites. Pressure treated wood preservatives must also be reasonably inexpensive or of good value for the money, easy to analyze in both solution and treated wood, and safe for all producers and users.

The typical commodities which are pressure treated include lumber, timbers, utility poles, cross ties, piling, fence posts, fence boards, and plywood. The American Wood-Preservers' Association (AWPA) Use Categories UC1 to UC5 list over 500 various commodities which may be commercially pressure treated. In addition to wood preservation, many fire retardant chemicals are pressure treated into wood to hinder burning, glowing or flaming/cindering.

Pressure treating biocides fall into two categories. The restricted use pesticides (RUPs) are generally biocides where use at the treatment plants presents certain risks that require special knowledge for addressing so the operator must be licensed. Among the RUPs are chromated (CCA) and ammoniacal zinc copper arsenate (ACZA), other inorganic arsenicals, pentachlorophenol and creosote. The general use pesticides such as alkaline copper quat (ACQ), copper azole (CA), oxine copper, borax or DOT, and oil or water borne copper naphthenate are not considered as risky and no special use precautions are made with these systems.

Pressure treating chemicals can be further broken down into three dominate sub-categories: organic, metallic and organo-metallic systems. Organic biocides and solvents used for pressure treating for industrial applications in the USA include pentachlorophenol dissolved in AWPA P9 Type A oil or in mineral spirits and creosote either used as a stand alone AWPA P1/P13 creosote or creosote dissolved 50/50 in petroleum oils. The oils range from slurry oils to #5/#6 oils to Bunker C oils/slurry oils or HEGO oils and the resulting treatment solutiuon systems is called creosote - petroleum solutions. The metallic or organometallic systems include CCA, ACZA, ACQ (alkaline copper quat), and CA (copper azole), which are all water borne, copper naphthenate which is both water and oil borne, the water borne inorganic borates (predominately DOT), oxine copper which is difficult to formulate but available in both oil and water borne systems, and various non-biocidal water borne fire retardant formulations that contain borates, bromine, or nitrogen- and/or phosphorus containing compounds.

Solvent Differentiation in Pressure Treating

Water Borne Systems

Most of the pressure treated systems in the United States today are water borne systems, and essentially all treated lumber used for residential exterior applications, the largest market, are water borne. The two systems in largest use, ACQ and CA, are based on copper with a small amount of an organic co-biocide to control copper tolerant fungi. Copper is the cheapest biocide per pound available today with the copper solubilized by employing amines, ammonia or a combination of these. (In addition there are acidic systems such as CCA and Acid Copper Chromate.) However, the added nitrogen stimulates mold growth on the treated wood which has to be further reduced by including a moldicide, typically an isothiazolinone (ITA), to the water based amine or ammonia system. The author and Pascal Kamdem of Michigan State University have recently experimented with tertiary and secondary amines and other solubilizers to minimize the use of moldicides such as isothiazolinones which are known skin sensitizers.

The ammonia formulated copper systems have some advantages in that they will partially penetrate the heartwood of pines and the sapwood of refractory species such as Douglas fir. These systems are extremely effective penetrants. Ammonia formulated systems do have residual odor thus minimizing their interior use until the ammonia is thoroughly evaporated from the treated wood product, and some mold growth occurs on the treated wood since ammonia also contains high percentages of nitrogen. There is also some splotching of the treated wood, due to the d9 co-ordination complex turning from a bright blue to a light green after water/ammonia has evaporated from the system and is re-wetted either by rain water or liquid spillage onto the treated wood. Fixation is usually considered complete after the ammonia evaporates or volatizes from the treated wood. These ammonia systems are usually needed for biocide penetration in almost all Douglas fir treatments with the exception of Copper Xyligen and water borne copper naphthenate, which appear to treat Douglas fir well without ammonia.

All the major wood preservative suppliers in North America also offer water borne formulation that consists of a copper-based preservative with a wax added for water repellency. The wax is emulsified and provides enhanced dimensional stability for lumber for exterior above ground applications such as decking. This benign additive is very economical, safe, and also lessens the decay potential of wood and reduces biocide leaching.

Nano-particles or micronized systems are actively being used in wood preservation today, especially for copper based systems where the copper, usually basic copper carbonate, is micronized or reduced to nano-particle size of 0.2 microns or less. These are usually coupled with a co-biocide such as an azole or quat. These micronized systems offer many advantages over the alkaline based systems which use monoethanolamine (MEA) or ammonia to solubilize/chelate the copper including reduced corrosion of treating plant equipment and metal fasteners for building the final product such as decks or fences, reduced mold growth on the treated wood and less copper leaching. For example, recent tests have shown that micronized copper leaches ten times less that amine solubilized systems and have at least one-tenth of the corrosion to mild steel fasteners and virtually no corrosion to hot dipped galvanized fasteners.

Totally organic systems that contain water insoluble organic biocides for exterior residential applications will likely be formulated using nano particles dispersed in water or emulsion systems. Some of these systems are already available in Europe and similar systems are being developed for the likely future requirement for total organic systems for the residential North America market.

Interestingly, micronized systems are not new to wood preservation. This author personally started investigating micronized systems in 1988 when the author found that oxine copper dissolved in dodecylbenzene sulphonic acid and then neutralized with borax or other borates would form a pearlescent non-settling compound. This compound, when investigated either by a Coulter Counter or a laser light scattering device, had sub-micron particle sizes and was able to penetrate wood using normal pressure treating cycles such as Rueping, Lowry, Bethell and modified full cell processes. In addition, the author found that the two component wood treating system known as CDDC or Kodiak formed a water insoluble brown complex from either copper sulfate or copper amines as the copper source and sodium dimethyl dithiocarbamate (SDDC). This water insoluble complex also had a sub-micron particle size but would settle. The author investigated passing this material through devices such as tissue homogenizers and attrition mills (attritors) to further reduce the particle size. Adding anti-caking and anti-settling compounds resulted in an effective pressure wood preservative. Chlorothalonil was also investigated since it was commonly micronized for the agricultural industry to give a particle size ranging from less than 0.1 micron to approximately 100 microns. Treating wood with formulations of chlorothalonil ground to commercial agricultural size, however, only resulted in limited penetration in southern pine due to blockages caused by the larger particles.

Today roughly fifty-five percent of the industry utilizes micronized copper instead of amine based systems to produce pressure treated wood. The predominate species is southern pine but other species include Ponderosa and Radiata pines and incised Hem-fir.

Oil Borne Systems

Typically, organic and organo-metallic systems use AWPA P9 Type a Oil (#2 Fuel Oil), AWPA P9 Type C solvent (mineral spirits or VM & P Naptha), Number Six Fuel Oil or Bunker C Oil, or specialty organic solvents. Oil or solvent borne systems are usually used for industrial products where exudates and odor are not as much a problem as in the residential market. In addition, heavy oils enhance the efficacy of the actives. Creosote is often a stand alone (no solvent carrier) wood preservative.
For organics, creosote is used mainly for railroad crossties and certain regional markets of utility poles and piling. However the dominant utility pole treatment is pentachlorophenol in oil. The author has spent over two decades doing specialty formulations of pentachlorophenol type systems for this market. These are usually based on carbonyl compounds such as ketones or ketone byproducts and water insoluble alcohols such as kettle bottoms or still bottoms from the production of 2-ethylhexanol. In addition, pentachlorophenol is readily soluble in still bottoms and kettle bottoms of cyclohexanone as well as MiBK so that 40% to 50% concentrates can be produced, shipped to the pressure treater and then further diluted with Number Two Fuel Oil, P9 Type a Oil, or equivalent.

Pressure Treating Problems

There are certain problems which must be addressed with all pressure treating chemicals including oil borne solutions. If not correctly formulated the solutions can entrain wood sawdust, wood sugars, and inorganic debris which can cause sludging and/or emulsion formation. Also, particles in the solution will hinder penetration, leaving the untreated sapwood prone to decay. Additionally, the solubility of the biocide in the carrier system must be maintained. If the biocide is a crystalline product such as pentachlorophenol, it can recrystallize out of solution leaving the treated wood susceptible to attack. Thus, complete solubility of any biocide in the system is essential even though most organic biocides can not penetrate the wood cell wall. In addition, treating solutions must be relatively stable with continued re-use or penetration problems may occur with the treated wood. Problems that have occurred with water borne copper systems, including those which utilize a secondary biocide as an emulsion additive, include selective absorption, solution stability, penetration problems, and sludging/particle growth problems.

Anti-Sapstain Systems

Anti-Sapstain systems have been around for three to five thousand years. There is historical evidence that Egyptians used powered Natrum to prevent mold growth and stain organisms from infecting sheets of papyrus. In the Shang Dynasty in China some thirty five hundred years ago workers employed wood ash dissolved in water to prevent mold and mildew growth on wood for chopsticks. The goal in any anti-sapstain and mold control system is to prevent sapstain and mold organisms (fungi) from discovering and infecting green or unseasoned wood. Anti-sapstain chemicals often called prophylactic coatings.

Almost all biocides employed are dissolved or dispersed in water and applied to green lumber before air- or kiln-drying. Depending upon the application method, many different avenues of formulating an anti-sapstain chemical exist. Briefly, application methods include use of dip tanks either as bulk or inline dip tanks, spray booths which may be sprayed either laterally or inline, flood coaters and electrostatic spray coating.

In dip tank application, the volume of water is anywhere from fifty to two hundred times the level of the anti-sapstain concentrate for the anti-sapstain biocide. This allows for solutions of efficacious molecules to be applied to a relatively high surface area of green wood. In bulk dip tanks, typically the logs have been cut into board length material or flitches or veneers and are stacked on an automated lowering and raising device like a forklift mechanism and dipped for anywhere from thirty seconds to three minutes into a large volume tank which has the overflow capacity to hold both the lumber and the treating solution. Inline dip tanks take the wood that is coming linearly or laterally from the sawmill and, before further machining, quickly dip the material into an aqueous solution of the biocide dispersed or solubilized in water.

Spray booths, either lateral or inline, are exactly as defined by the term. In these applications dispersions or true solutions of biocides in water are sprayed as an ultra-fine mist onto all six surfaces of the board before it is dried. Flood coaters, typically called rain shower booths, have been used for years but are now falling out of favor due to environmental exposure to workers. Flood coaters basically applied the diluted anti-sapstain chemical in a ribbon-like feed where the wood was passed under the flood coater and coated on all four large surface sides with some ingrain coating as well. Electrostatic coverage usually involves first coating the wood with an ionic compound or solution so that the wood surface could carry a charge, or if the wood has sufficient moisture content charging the surface of the wood and then putting a counter ionic charge on the spray solution to allow coverage of the wood surface regardless of the application angle from any spray head.

Today’s anti-sapstain preservative systems are predominately water soluble or water dispersible concentrates. The pH of today’s systems can range from neutral to acidic or alkaline. Alkaline systems have typically been employed in the past to minimize iron stain due to iron contacting the green wood and later forming iron tannate complexes, as well as minimizing corrosion in the mild steel used to manufacture anti-sapstain application equipment.

Solvents

Water is the dominant solvent in use today due to economic and safety reasons and ease of application. In addition to water, there can be water dispersible co-solvents, cationic or anionic emulsifiers, alcohols, glycols, esters, and dispersing agents.

Biocides

Historically mercuric compounds, toxic to both man and fungi, launched the “modern” anti-sapstain work some 200 years ago. These mercury formulations included water soluble salts, usually phenol mercuric acetate or phenol mercuric lactate, with a lignosulphonate emulsifier and a co-solvent.

In the 1930s the chlorophenate compounds developed for wood preservation gained prominence for mold and stain control. Furthermore, synergism was found when chlorophenates were combined with borates. These systems also minimized iron stain on the wood, prevented corrosion in mild steel dip tanks and resulted in greater efficacy against decay organisms. Additionally, the small amount of free chlorine in the

chlorophenate systems acted as a wood surface bleaching agent making the wood surface “brighter” to enhance the appeal of the treated wood. The only problem was that some Cepheloascus fungi were tolerant, but it was found that adding a trace of a mercuric compound to the chlorophenate formulation controlled the complete spectrum of mold and stain organisms.
Chlorophenates, however, began to be reviewed in the 1980s due to the negative publicity concerning compounds such as agent orange and other phenoxy herbicides. New biocides for the anti-sapstain began to replace the chlorophenates which had been used for over half a century.

The first launch into non-chlorophenate anti-sapstain control was based on oxine copper (copper-8-quinolinolate, or copper-8 or Cu-8). Patents were granted worldwide for the use of oxine copper dissolved in dodecylbenzene sulphonic acid (DDBSA). Work by West and Nagel and others found that oxine copper dissolved in DDBSA was a very robust and effective system for anti-sapstain control. Formulations based on this technology still exist today.

Further work on non-metallic systems included the investigation of quaternary ammonium compounds (quats) and carbamates. Included in these is a formulation known as NP-1 that is a mixture of IPBC and DDAC (3-iodo-2-propynyl butyl carbamate and didodecyldimethylammonium chloride). Additional investigation into phenolic based compounds included uses of OPP (ortho-phenoxy phenol) and Sodium OPP, commonly referred to Dowicide 1 and Dowicide A. These phenolic formulations have certain side effects which limit their use even though they are effective biocides.

Additional work into the investigation of mold and mildew control for lumber, based on testing of fungicides for the leather and pulp and paper industries by Stanley Buckman, included formulations based on TCMTB and MBT (2-(thiocyanomethylthio) benzothiazole and methylene bis-thiocyanate). These formulations, although extremely robust, had certain negative implications concerning worker exposure such as dermal and eye irritation.

Studies in America, New Zealand and Australia also found that certain co-biocide combinations, including those of oxine copper and carbendizim, or oxine copper and chrolothalonil (CTL), proved to be synergistic and very effective anti-sapstain and mold control combinations. These products are currently marketed under the trade names Nexgen and Hylite Extra, respectively. Additionally, a formulation innovation by West, Freeman and Accampo dissolved certain biocides in high concentrations in amine phosphonate systems. These amine phosphate systems, currently called The StaBrite System, could dissolve biocides such as IPBC, and the azoles azaconazole, propiconazole, and tebuconazole. The largest commercial system is the StaBrite P System, a formulation of IPBC in the patented amine phosphonate carrier. It was later discovered that the amine phosphonate carrier system was also an excellent bleaching compound for the surface of the wood to give a brighter appearance and greater appeal as well as inhibited corrosion with the mild steel dip tanks and removed saw marks and iron tannate stains from the wood surface. Additional patents were given for the amine phosphonate system as a hard surface cleaning agent, very similar to the patents issued for quaternary ammonium compounds for the same application.

The leading biocide formulations in today’s anti-sapstain market include NexGen (MBT and CTL), NP-1 (IPBC and DDAC), Busan 1009 (TCMTB (2-(thiocyanomethylthio) benzothiazole, also called Busan 30) and MBT (methylene bis-thiocyanate)), MicoStat P (propiconazole and DDAC), BriteWood XL, BriteWood S, BriteWood P, and a new entry called Bazooka. In addition, new environmentally formulations launched in the last 24 months include formulations of sterol inhibitor-based chemicals that usually employ propiconazole or propiconazole/tebuconazole/IPBC combinations such as Premier and Anti Blu XP. Additionally in North America, particularly Canada, formulations of sodium carbonate mixed with borax and marketed under the name F2 have market niches where environmental concern for water run off from the treated wood and worker exposure give it a semi-permanent market position.

To recap, the biocides used in anti-sapstains are:

- Oxine Copper
- IPBC
- DDAC
- Isothiazilines
- TCMTB/Busan 30
- MBT
- CTL
- Propiconazole
- Tebuconazole
- OPP
- NaOPP
- Borax
- Sodium Carbonate

Formulation Additives

Formulation additives are typically used to add a particular trait or physical property to the biocide system to mitigate effects of the primary biocide system on operating equipment, enhance the efficacy of the actives, or improve the wood properties such as brightness and color. Borax, the historical anti-sapstain additive, is typically used to make the system alkaline to prevent iron stain from occurring on the wood, darkening of the heartwood, particularly in Douglas fir, and minimize corrosion to the mild steel equipment used in the treating process.
Substituted phosphonic acids began to gain wide appeal in the early 1990s when it was found that these products were inexpensive and would chelate iron and iron compounds into colorless or white coordination complexes which would not stain or discolor the wood. These substituted phosphonic acids chelated the iron from the solution and, when the phosphate content was high enough, would actually act to brighten the surface.

Emulsifiers and dispersants keep active ingredients concentration uniform and dispersed in both the concentrate and the ready-to-use (RTU) solutions. These emulsifiers and dispersants, historically based on both anionic and cationic compounds which lead to selective absorption of the biocide on the wood, are now sometime coupled with other chemical formulation additives which include distinct surface active ingredients to prevent hard cake settling in dip tanks and ensuring uniform distribution of the biocide on the wood surface.

Although not considered an anti-sapstain organism, insect attack, especially to hardwoods, is of growing concern. It is known that insect movement can lead to the spread of sap and mold fungi from lumber piece to lumber piece or stack to stack. Therefore insecticides have been added to anti-sapstain formulations to prevent attack and infestation by Lyctid, Anoobiid. and Ambrosia Beetles and termites for over 70 years. Historically, the largest insecticide used for this purpose was Lindane (gamma hexachlorobenzene). Today's market includes other insecticides such as Chloropyrifos, Imidicloprid, and Permethrin.

Water repellents have been added to Anti-Sapstain chemical formulation to minimize checking and splitting while the wood was drying or seasoning, which further made the anti-sapstain chemicals more effective by not opening up untreated wood to new exposure sites.

New systems now generally contain a diffusible biocide plus a biocide that stays on the wood surface. These new systems are compatible with currently available insecticides, are stable in solution and the biocide concentration is easy to analyze both on the wood and in solution. In addition, new biocides can be easily detected on the wood surface by employing a presence indicator that can be sprayed or applied to the wood surface. The products in today's market provide cost effective, efficient, and safe yet effective and efficacious protection against stain and mold organism's infestation to green wood prior to seasoning. Although formulation improvements continue in the anti-sapstain market, the biocides will likely continue to be agricultural fungicides which have broad spectrum effectiveness and an extensive environmental data package.

Millwork and Joinery Systems

The principal goal in millwork and joinery systems is to deliver an active fungicide, or active fungicide and insecticide combination along with a water repellent to give surface mold, decay and insect protection and provide excellent water repellency and dimensional stability to the product. The secondary goal of a millwork or joinery system is surface preparation for future coating, staining, or cladding.
Historically, millwork systems used 5% pentachlorophenol (also called penta) in mineral spirits with additional wax, or mercurial compounds which were oil or mineral spirits soluble, with these systems employed for 70 years. However, concern arose for use of pentachlorophenol in this application during the US EPA RPAR Hearings of the late 1970s and the early 1980s, and mercury derivatives were also restricted. Additional work led to tributyltin oxide (TBTO) and tributyltin naphthenate some three decades ago, and although use of these compounds has greatly reduced they still maintain some market share. Following the conversion of pentachlorophenol from a general use to a restricted use pesticide in the late 1980s, millwork and joinery manufacturers decided that they would prefer to employ a general use pesticide rather then to obtain Certified Applicator licenses through Certified Applicator Training. This forced the chemical formulators to look at non-chlorophenate systems.

Biocides

Millwork biocides currently employed include:

- IPBC
- Oxine Copper

- Propiconazole
- Tebuconazole
- TBTO
- TCMTB
- Chlorpyrifos
- Permethrin
- Imidicloprid
- Bifenthrin

Since many of today's fungicides are non-insecticidal, an insecticide must be added to millwork systems to prevent insect attack. These include Lindane, Bifenthrin, Chloropyrifos, Permethrin, Pyrethrums, and Imidicloprid. Historically, Dieldrin, Aldrin, Chlordane, and Esfenvalerate have also been used. Recent studies on the insecticide compound Bifenthrin continue to show promise as this molecule is active at dosage rates 100-1000 times less than other insecticides in the same generic class.
The fungicide and insecticide combinations currently used are soluble or easily dispersible in mineral based systems, or can easily be converted to a water dispersible or water emulsifiable system through the use of co-solvents and emulsifiers. Of the 64 plants in North America currently treating with millwork preservative systems, IPBC is the major biocide employed for millwork. Sold under a wide variety names such as Wood Life, Mitrol IPBC, and DAP Ready-to-Use, IPBC has replaced 90% of the market that was formally pentachlorophenol and new formulations of IPBC and co-biocides continue to emerge. For example, a new formulation containing IPBC coupled with propiconazole and tebuconazole in a mineral based system that contains paraffin wax is marketed under the name Wood Life 111. Wood Life 111 takes advantage of the synergism between propiconazole and tebuconazole by adding them to the broad spectrum of decay protection of IPBC. Although IPBC will break down into iodine-based compounds under high heat or alkaline conditions, such as those typically those found in cladding operations, studies have found that the azole compounds in these multi-biocide systems remain effective.

Solvents

The major solvent currently used for millwork and joinery systems continues to be mineral spirits. Although over half a dozen different versions of mineral spirits are available, by far the largest is Rule 66, a low odor mineral spirits where the aromatic content is 2% or less. For millwork manufactures who want to quickly evaporate the solvent from the system, the mineral spirits can be readily replaced by VM & P Naphtha (Lacolene). Some millwork preservative systems employ water as the carrier and include wax for dimensional stability and block co-polymers to further give the wood dimensional stability and minimal grain raising during the application and re-drying process.

Some additives are included in the millwork and joinery systems. The most common is approximately 0.75% w/w of a ready-to-use solution of paraffin wax. And although many paraffin waxes are used, most common are those with an approximately 104 – 115 ºF melt point and a medium to moderate needle penetration value. Some paraffin waxes have been replaced by small quantities of microcrystalline wax or hydrophobic polymers. Other additives to interior systems include trace levels of aromatic solvents in which an effective insecticide has been added.

Additional Factors

Additional formulation developments generally involve enhancing dimensional stability and water repellency. Although water repellency may be initially thought to be quickly and easily determined by simple test methods such as contact angle of water droplets on the wood surface, other investigations found that long term swellometer tests are more informative for determining the long term dimensional stability of the treated wood product. Automated swellometers coupled with computer systems have also shown that if dimensional stability is maintained for 100 hours, typically the product will perform well in service.

Additional tests on millwork formulated systems include simple paintability tests such as the Hatch Mark Test and analytical procedures for active ingredient determination for both penetration and retention, typically in the endgrain of the treated commodity. New innovations in the millwork and joinery systems include pressure treating the commodities with water based system that includes a water repellent, allowing the wood to dry and then machining the wood product to its final dimensions. Innovative work in this area has recently been incorporated by the Jeld-Wen Corporation using their Aura Last Preservative System. However, there have been some complaints of increased corrosion to metal fasteners and other metal parts used in window manufacturing. Additionally, new water based preservative compounds such as Wolman AG (or Wolman L-3), a mixture of tebuconazole, propiconazole, and imidacloprid, for above ground uses of pressure treated wood, may allow treated wood to be used in millwork and joinery applications if dried after treatment and machined into place, similar to the Aura Last System. Although millwork and joinery preservatives, often called the LOSP (Light Organic Solvent Preservative) systems in Australasia and Europe, have been around for over 100 years, research continues to improve these systems to provide longer lasting products for the homeowner in the future.

General Preservative Systems

General Preservative Systems are those wood preservatives, biocides, and insecticide formulations which are best described by their name. These products are used as 'do-it-yourself' products by home owners and small industry users. These products employ general use pesticides to ensure their availability to over-the-counter purchasers and applicators without a certified pesticide license. Typical applications include brush-on, soak, dip, and spray on systems. The goal of general wood preservative systems is to provide protection against mold, mildew, decay fungi organisms and possibly insect protection when pressure treated wood is not available or not desirable. The secondary goal is that the products be easy to apply, relatively safe to workers and homeowners, easy to clean up, and employ general use pesticides. The ability for the treated wood to be painted, i.e. have paintability and stainability, are also desirable properties.

Biocides

With the exception of inorganic borates such as DOT (disodium octaborate tetrahydrate), most of the general wood preservatives are organo-metallic complexes or organic chemicals. These include copper naphthenate, both oil and water borne, IPBC, chlorothalonil, oxine copper, Folpet, zinc naphthenate, and quaternary ammonium compounds (quats) such as DDAC.

Solvents

The most common solvent for general preservatives are mineral spirits, which is usually of the variety of Rule 66 Low Odor Mineral Spirits which has a low aromatic content to minimize worker exposure as well as odor of the treated wood product. In addition, mineral spirits plus paraffin or microcrystalline wax is often used when water repellency is desired. Other solvents include AWPA Type P9A Oil (#2 Fuel Oil or equiv.) and recently biodiesel (methyl soyate). When a drying oil is desired typically tung oil, linseed oil, or their combination is employed. Water plus either surfactants or emulsifiers are also used, sometimes with polymers or waxes to impart water repellency to the treated wood.

General preservative systems typically have a few formulation specifics which they must meet along with being efficacious. These include easy clean-up, relatively safe for any exposure, and non-phototoxic so terrestrial and non-terrestrial plants are not affected if a spill occurs. These systems should also be compatible with almost all container types and should be tested accordingly to make sure they are compatible with typical containers which a home owner would use to store these products. In addition, the product should be shelf stable and have a uniform distribution both in the concentrate and in the ready-to-use solution during storage and immediately before application.

Remedial Treatment Systems

Remedial Treatment Systems are used to arrest decay and insect attack in both untreated wood and in wood where the original preservative has been depleted to below threshold value permitting attack by insects and decay organisms. Thus, the goal of remedial treatment systems is to extend the useful service life of a treated or previously untreated wood member, with the secondary goal to stop or eliminate any current attack by fungi or insects.

Remedial treatment chemicals used previously include many historical biocides such as pentachlorophenol, creosote, sodium dichromate, arsenic acid, borax or boric acid, sodium fluoride, copper naphthenate, lindane, and chloropyrifos as well as fillers/carriers like clays and thixotropic (water thicking) agents. Biocides currently used include copper naphthenate, copper hydroxide, boric acid, borax, sodium fluoride, and DOT. Remedial treatment systems generally fall into four predominately large categories; Thixotropic Gels or Pastes which may be either oil or water borne, Fumigants, Solid Rods, or Liquid Injectable Systems.

By far the largest category is the Thixotropic Gels or Pastes. The most effective remedial gels/pastes contain one agent that closely adheres to the wood surface, such as the base of the utility pole where a groundline decay can occur most readily, and a second agent which diffuses deeply into the wood, possibly even into the previously untreated heartwood. Products sold in this market over the years include many of the products under the Pole Nu or the Osmoplastic name usually followed by a number or letter such as Pol Nu CuRAP 20 or Osmoplastic B, Osmoplastic F, or Osmoplastic CF. Fumigants in this area include products such as vapam (Metam Sodium) usually employed as a 32.7% water borne active ingredient concentrate, chloropicrin, sulfuryl fluoride or MITC (methyl isothiocyanate). In addition, solid rods such as IMPEL rods, FluroRods, or Cobra rods are also used as both a preventative and also as a curative in the remedial treatment arena. Rods have had some complaints against them in that they sit as a reservoir of wood preservatives until the treated wood has a high enough moisture content to dissolve the rod but that means the high moisture content can also promote and sustain decay.

In addition to solid rods there are also solid fumigants which are a sub-category of both the Fumigant Category as well as the Solid Chemicals Category. These include such new fumigants as Basimid (Dazomet) which produces methylisothiocyanate upon reaction with wood acids, as does Vapam and Mitc-Fume. Some researchers have found that the addition of an acidic copper compound, like copper sulfate, dissolved in water and co-introduced into the same application site as Basimid increases its toxicity and stoichiometric yield.

Liquid Injectable Systems are used to treat wood voids. Historically the biggest product used in this market for this application has been a product produced by Osmose called Hollow Heart. However, Hollow Heart contained significant amounts of toxic chemicals and has been replaced by a new environmentally friendly formulation called Hollow Heart CF which is a mixture of Copper Naphthenate and Sodium Fluoride. These liquid injectable systems are usually placed into wood voids after drilling the wood to determine if a void exists in the interior and injected under low pressure to fill the void to arrest decay and insect attack.

Summary and Conclusions

Wood preservative use has grown in the last 170 years into a modern, well segmented, complex and sophisticated market which extends the usable service life of wood thus saving the homeowners or other consumers' money and time while reducing harvesting and deforestation in the world. One should remember that chemical treatment costs pennies but saves dollars if the product is formulated correctly, and that toxic biocides can be safely handled if adequately formulated.

Specific goals for new wood preservative systems include good efficacy against the wide variety of oranisms that can degreade the wood product in its intended application, ease of formulating, ease of analysis in both the solution and the treated wood, good penetration into the wood, and safe for the environment, human applicators and final users. They must also have a good cost-to-benefit ratio and be economical in the long run for the producer. New wood preservative formulations now being examined are mostly based on agriculture organic biocides for employment in the large residential lumber market. These biocides are not water soluble so will have to be formulated using new formulation technologies such as nano-particle dispersion and emulsion systems. Emulsion systems recently developed do not have the faults of older emulsions such as water dispersible pentachlorophenol.

These new nano-dispersion and emulsion systems are already in the marketplace or going through the AWPA and/or the Building Codes (ICC-ES) for listing. Finally, new systems are essentially "cocktails" because many of the new agricultural chemicals being considered have a limited spectrum of activity, so biocide mixtures are used to obtain the broad fungicide and insecticide protection necessary for the long service life of treated wood. This means that formulation complexity may be increased.

Formulation is extremely complex and this chapter only provides an introduction. It is recommended that any proposed formulation change involve input by both a formulation chemist and wood preservationist, along with other professionals, to ensure that any of the many possible negative impacts will be properly addressed.

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