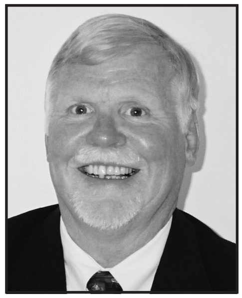
What's New? Pros and Cons of Future Preservative Systems



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Abstract

Over the past several years, there have been significant changes in the general wood preservative market. For ground contact uses, copper-based systems have replaced the chromated copper arsenate (CCA) product used for many years but there were corrosion and mold issues – now resolved – during the initial phases of the transition. Similarly, other products based on borates, silicates, or organics have been introduced for above-ground uses with some hints of ground contact uses to come. Even more radical is that non-traditional systems have been introduced such as the barrier preservative systems. The various attributes and availability of all of these products will be discussed from the utility or user perspective.

The Past

Before we delve into the future, it is instructive to briefly review our past. In 1838, John Bethell patented the use of creosote for preserving wood members and this started the wood preservation industry as we know it today. Creosote was essentially the only preservative until various "new" formulations came along in the 1930s and 1940s. There was a continued evolution of preservative systems, and **Table 1** lists some well-known systems and the time period for their introduction.

Perhaps more important though is the consideration of when the various preservative systems became standardized. As shown in **Figure 1**, there is a time lag that has approached an asymptotic value of several years between the original introduction of a system to its full ac-

Table 1. ~ *Preservative introduction dates.*

Preservative	Introduction
Creosote	1831
Copper naphthenate	1899
Acid copper chromate (ACC)	1928
Flour-chrome-arsenic-phenol (FCAP)	1930s
Chromated copper arsenate (CCA)	1938
Ammonaical copper arsenate (ACA)	1939
Ammonaical copper zinc arsenate (ACZA)	1980s
Alkaline copper quat	1990s
Copper azole	1990s

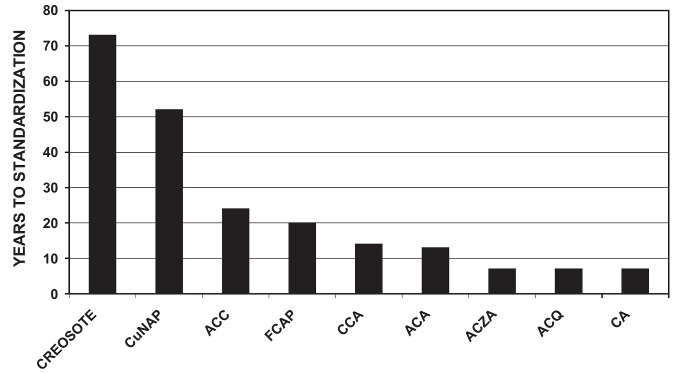

Figure 1. ~ *Time lag from introduction to standardization.*

ceptance in the American Wood-Preservers' Association (AWPA). As an aside, it should be noted that it took our predecessors some 70 years to standardize creosote largely because the AWPA was not formed until 1904. The important issue is that there is a minimum time lag of several years – regardless of the formulation or biocide – from when a system is first developed to when it becomes accepted for standardization.

The Present

Currently, the wood preservative industry is clearly split into two segments: one serving residential markets and the second serving industrial markets. Although our focus will be on the industrial segment, some consideration must be given to the residential segment.

Residential Segment

Until the voluntary withdrawal of copper chromium arsenate (CCA) in 2004, the residential market was essentially all CCA. Now, two systems, alkaline copper quat (ACQ) and copper azole (CA), have replaced CCA. The Southern Forest Products Association (SFPA) notes that some 70 percent of all treated lumber is southern pine while 86 percent of all treated lumber and timbers is southern pine. In the reverse perspective, some 44 percent of all southern pine produced is treated which is about 7.6 billion board feet annually.

The circumstances surrounding the withdrawal of CCA from residential uses were that "perception outweighed reality." The use became a public relations issue and years of solid science that demonstrated the safe use of CCA were not capable of overcoming the negative publicity associated with "arsenic in the wood." Some extremists approached near hysteria on the issue, class action lawsuits were announced, and the science was lost in the background. If fact, some of the science was even turned against CCA and predictions were made that there were health risks for children playing on decks. But, and it's a big but, the children needed to play on the decks for unbelievably long times: essentially all day, every day for 15 years. In simple terms, the exposure scenarios were extremely, no unbelievably, biased against CCA, but the negative publicity won in the end. As a result, two "new" waterborne systems have replaced CCA.

One replacement consists of the alkaline copper quats. There are three formulations currently listed in AWPA standards, and these differ in the choice of solvent and the choice of the quaternary compound. The most popular is ACQ-D which uses an alkanolamine (MEA) as the solvent and DDAC as the quat. This is followed by ACQ-C which also uses MEA but ADBAC is the quat. Both of these systems are typically used with deep sapwood pines such as southern pine. On the West Coast, ACQ-B has found favor with its ammonaicial base and DDAC for treating Douglas-fir and other shallow (thin) sapwood species. The ACQs were first introduced in 1992 in the United States. They have also found use in Europe, Japan, and Australasia. They also have AWPA listings for all preservative uses except marine exposures.

The copper azole formulations, CBA-A and CA-B, are the second type of replacement formulations. These differ in that the Type A contains boric acid while the Type B does not. The amount of copper to azole is maintained at a constant ratio in both formulations. Copper azole was also introduced in 1992 and has AWPA listings for all use categories except marine exposures. The formulations are also used in Europe, Japan, and Australasia.

During the initial replacement period, it was found that there were many issues to confront. The first was the fact that on a per pound of actives basis, the replacements were about four times more costly than CCA. Obviously, this caused some cash flow difficulties as treaters sold "cheap" CCA stock and bought "expensive" new chemicals to treat new stock.

The treaters then found that the new systems were not simple "drop-in" replacements for CCA as they had believed. In many cases, water treatment plants had to be installed at significant costs. Treating cycles had to be adjusted and in general, more care needed to be given to maintain the consistency of the preservative formulation.

The presence of the amine or ammonia in the formulations also led to a new set of problems. The mold organisms that inhabit wood are typically nitrogen starved and hence limited in their growth rate. But now there was an almost unlimited source of nitrogen so some of the wood produced had significant mold growth. Increasing the moldicides resolved this problem but at an additional cost.

There were also additional concerns regarding corrosion with the new formulations. The high copper content was deemed responsible and galvanic corrosion was occurring at the metal-wood interface where oxygen was also available.

The higher copper content also was cited for the increased amounts of copper that were leaching into the environment. This factor could be an issue for aquatic toxicity in the future.

Industrial Segment

The above review suggests strongly that there will be changes forthcoming in the industrial segment as well.

Currently, creosote, pentachlorophenol, and the arsenicals CCA and ACZA dominate the industrial markets. A fourth product, copper naphthenate, is also available but each of these systems have issues.

Creosote Issues

Creosote use has been restricted in Maine for use in marine environments without a special permit and other states have introduced similar legislation. Again this is a case of perception versus reality. What follows is a quote from the Spring 2001 issue of the Lobster Bulletin[1] and gives a sense of the science versus emotion issue.

> *Maine policy-makers need to take another look at the state's approach to the use of creosote-treated timbers in coastal waters. Rules developed to implement the Natural Resources Protection Act in effect prevent the use of timber treated with creosote for marine piers and other structures. Last summer, we began to pay the price. In a single year, shipworms destroyed pilings in Belfast, Rockland, and Searsport, and an aquaculture company in the Damariscotta River had damage to its oyster-growing facilities.*
>
> *The purpose of Maine's creosote ban was apparently to prevent contamination of coastal waters by toxic PCBs. Two decades ago, some creosotes indeed contained PCBs as a contaminant. Maine's ban was a precautionary move. No cases of PCB contamination in Maine coastal waters had been traced to creosote.*
>
> *Creosote is largely insoluble in water and thus maintains its protective ability in wood that is constantly wet. "Nonbleeding" formulations are now available, but some elements are soluble. Previous research indicates that there is minimal risk to marine organisms. More study is needed to determine the extent of this risk as well as the best alternatives. Legislators need to weigh the risk against ongoing damage to structures.*

The implication is clearly that the initial reaction was in error and not justified by the science. However, no legislation repealing the ban has been forthcoming.

Creosote exposures are being reviewed as part of the reregistration process being conducted by the Environmental Protection Agency (EPA). The final document has been pending for some time and current estimates are that it will be available this fall. But, it is certain that upon its issuance, remedial treatment uses of creosote will no longer be allowed nor will the butt or thermal treatment of wood.

Further compounding the issues is the fact that currently creosote is in short supply. The uncertainty of supply has forced many utilities to evaluate alternate treatments.

Pentachlorophenol Issues

Despite a long history of safe use, the environmental demise of pentachlorophenol has long been predicted. In fact, your presenter was charged with developing a penta replacement when he started in the wood preservative industry in 1975 since it was going to be banned any day now. Some 30 years later, penta continues to be the dominant treatment for utility poles. But it is likely that there will be similar restrictions for butt and thermal treatments and for remedial products as there will be for creosote.

Arsenical Issues

Obviously, the first concern for arsenical treatments is that the negative publicity associated with their residential use will spill over into the industrial arena. That is, somehow someone will determine that risks associated with children playing on decks can apply to linemen wearing gloves and other safety equipment. Although this seems unlikely, the authors have seen other extremely unreasonable scenarios developed for litigation.

Other issues with arsenicals include pole hardness, charring, and afterglow. All of these issues can be addressed by the use of additives.

Copper Naphthenate

Despite being known for over 100 years, copper naphthenate has not become well entrenched for utility poles. This use was accepted by the AWPA in the mid-1980s but copper naphthenate has only a small share of the industrial market. Currently, about 6 percent of the wood pole market is copper naphthenate.

This is somewhat surprising in that copper naphthenate has low mammalian toxicity and is not consid-

[1] http://kodiak.asap.um.maine.edu/lobster/library/ publications/bulletin/spring2001.htm.

ered as “copper rich”. Therefore, it has low leaching of about 4 ppm in standardized tests.

The Future

Prior to discussing the future, the authors want to point out that they do not mean for the above discussion to be interpreted as demeaning to the preservatives currently used in the industrial segment. These preservatives have been safely used for decades and have performed well. They can be safely used for decades into the future presuming that science overweighs perception.

But that may not happen. There is continuing environmental pressure on heavy metals, creosote, and penta. Some European countries, notable Denmark, Norway, and Holland, have recently eliminated copper containing preservatives. (Of course, chromium-containing preservatives were eliminated years ago.) Some lawyers are still attempting to build class actions suits, and it may be that reality will lose again to the imagined threat.

In Europe now, all-organic systems are being used as replacements for oilborne treatments. These combinations of fungicides and insecticides are relatively expensive, have somewhat limited activity, and are somewhat mobile. Even with this range of issues, the all organics will be the oilborne preservatives in use in Europe in the future.

In the United States, various formulations have been introduced in recent years as replacement preservatives. These include a wide variety of chemicals and approaches to preservative performance. In fact, one or the other of the authors has worked on the development of essentially all of these systems.

For the waterborne treatment of wood, many of the “new” preservatives are similar to those already in use:

- Borate-based systems with significantly reduced leaching characteristics are being developed by several organizations.
- Additional uncomplexed copper systems such as copper azole or ACQ with new co-biocides are being proposed
- Complexed metal-based systems such as waterborne copper naphthenate, oxine copper, and copper xyligen are finding increased usage.

These will be augmented by a wide variety of new “organic” systems that may or may not be delivered in oil:

- new azoles
- amine oxides
- synthetic pyrethroids
- organic agrochemicals
- oligomeric alkylphenol polysulfide (PXTS)
- polymeric betaine
- antioxidant with a metal chelator and water repellant

Table 2. ~ *Possible and **probable** preservative systems for utility uses.*

Copper xyligen	**Organic combos (fungicide/insecticide)**
Chlorothalonil (revisited)	Isothiazolinones
Copper borate	**Copper-DCOIT**
Acetylated wood	Nano-particle systems
Polymer/furfurylated wood	**Micronized dispersion systems**
Polymeric betaine	**Barrier systems**
Copper azoles-C, D, E....	**PXTS**

But many of these new developments will not be suitable for utility uses. **Table 2** presents the full range of possible preservatives for future utility uses. The ones that in our opinion will most likely surface as viable candidates for utility use are highlighted. Each of these candidates will be visited in more detail.

Chlorothalonil

Some time ago, chlorothalonil was proposed as a replacement for pentachlorophenol. Chlorothalonil is very effective against a broad range of organisms, the full gamut of wood preservative testing has been done, and the molecule has low mammalian toxicity. However, chlorothalonil is difficult to dissolve and only selected oils can be used. Recently, several “micronized” systems have been developed where solids are ground to sub-micron particles and then dispersed in aqueous solutions. Such an approach could be used to overcome the chlorothalonil dissolution problems.

Copper Azole, Type C

Similarly, a new copper azole, Type C, is also beginning the standardization process. This system uses a synergistic combination of azoles, and, in this case, 8-year stake data showed equivalent performance to CCA. One would surmise that this system will also be subject of a few years lag.

Copper-DCOIT

A new combination of copper and isothiazolinone (DCOIT) was recently introduced to the wood preserving community. Full details have not been disclosed but some 5-year field stake data showed performance essentially the same as CCA. Obviously there will be the “lag” of 2 to 3 additional years as the formulation is further developed.

Micronized Dispersion Systems

Micronized systems were mentioned above and have found use with the existing CCA alternates as a means to eliminate the amine or ammonia solvent. The copper solids are ground to less than 1 micron in these formulations but there is currently a debate whether this is small enough to preclude soft rot attack in the S2 layer of the cell wall. The question essentially evolves to whether evidence from laboratory investigations outweighs performance data gathered from field testing.

Organic Combos (Fungicide/Insecticide)

Combinations of organic fungicides and insecticides have already been used in wood preservation. For example, the AWPA lists a chlorothalonil-chlorpyrifos combination, and there are azole-imidichloprid systems in use. We expect that other organic fungicides and insecticides from the agrochemical industry will find their way into the wood preservative arena.

Barrier Wraps

Barrier wraps are not new to the utility industry since they have been used to prevent leaching of remedial chemicals for over 70 years. The use of non-preservative containing barrier wraps, however, is a relatively recent development. In the 1960s, Forintek investigated polyethylene bags while in the late 1980s work began on wrap systems in South Africa.

Interestingly, there are over 70 publications available on the use of barrier wraps and 10 patents exist. The key points in these documents are that barrier wraps greatly extend the service life of the wrapped wood member, and the wraps prevent migration of preservatives into the soil. This latter aspect is very apparent in a study involving some 300 booted poles compared to 50 unbooted control poles (**Fig. 2**). After just 4 years of exposure, results showed that the unbooted poles had lost just more than 40 percent of the original retention at the groundline while the booted poles had increased in retention an equivalent amount.

Although barrier wraps are under test on square stock at Oregon State University and on round stock at Mississippi State University with "reduced" retentions, it is unlikely that preservatives will be eliminated completely. There are too many wood destroyers, such as Formosan termites, for the complete elimination.

PXTS

PXTS or polymeric xylenol tetrasulfide has been listed by the American Wood-Preservers' Association as an oilborne treatment. It has low toxicity to mammals and the available data shows good efficacy. Thus, this could be used as a replacement for creosote or other oil-type preservatives.

Conclusions

Although no clear favorite has yet emerged from the many candidates, we feel that one or more of the systems discussed will find its way into the utility market.

Finally, for the future within the wood pole industry, we foresee increasing threats from alternate products such as steel and concrete. These products are here to

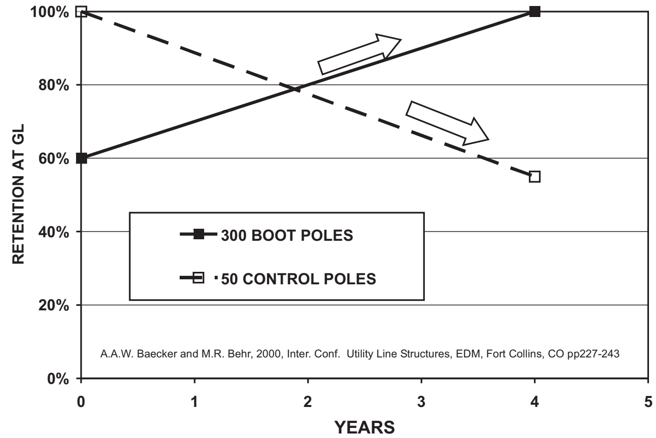

Figure 2. ~ *Retentions at groundline (GL) for creosote poles with or without boots.*

stay and their continued evolution to address use issues will generate more usage.

There will be systems developed and targeted for a specific end use. For example, there may be a crossarm preservative. It is probable that the new systems will allow generally lower retentions and hence lower losses to the environment. The use of preservative-treated composite wood products will be introduced and may lead to a composite pole product.

About the Authors

Craig R. McIntyre has over 30 years of extensive experience with wood preservatives and fire retardants. Following his graduate education, he joined the Koppers Co. where he managed Research and Development functions that spanned all of the company's activities related to wood treatment. This work gave Craig a broad base of knowledge on the "Big Three" preservatives (creosote, copper chromated arsenate [CCA], pentachlorophenol), fire retardants, wood treatment practices, customer specifications and, most importantly, customer concerns.

In 1992, Craig started McIntyre Associates as a private consultant. Since then, he has worked on litigation involving treated wood including several cases involving copper naphthenate-treated poles. He has testified in cases involving CCA and pentachlorophenol poles and he has worked on fire-retardant issues. Craig also provides a number of clients with development expertise on preservative formulations in their search for new products.

A member of AWPA since 1978, Craig recently served on the Executive Committee and he has also had a number of officer positions with the lumber, pole, and fire retardant committees. He has been awarded the Association's highest award, the Award of Merit. Craig is an active member of all of the organizations that involve treated wood – AFPA, ASTM, CWPA, FPS, IRG, and SWST – and he has been a member of the American

Chemical Society for 35 years. Craig has over 30 publications involving treated wood including several on copper naphthenate. He was a co-inventor of the CCA-OIL system for utility poles and he has four other patents involving preservative chemistry.

Mike H. Freeman is a Consulting Independent Wood Scientist in Wood Preservation from Memphis, Tennessee. Previously, he was Technical Manager of ISK Biosciences, Industrial Biocides Division in Memphis where his responsibilities included product chemistry, patents, research and product development, new products and existing product technical support, and regulatory affairs. Prior to ISK, he was Vice-President, Sales and Marketing of Chapman Chemical Company of Memphis, Tennessee and Wood Products Manager of Forshaw Chemicals, Inc./Wood Protection Products, Inc. in Charlotte, North Carolina.

He is a member of the Society of Wood Science and Technology, American Chemical Society–Cellulose Division, American Wood-Preservers' Association, American Society of Testing and Materials, the Forest Products Society, International Research Group on Wood Protection, Federation of Societies for Coating Technology, and Xi Sigma Pi – National Honor Society. He is the past Chair of the AWPA Treatment Subcommittee T-2 on Treatment of Lumber and Timber. He is a Past Chair of the AWPA Subcommittee P-3 on Organic and Organo-Metallic Wood Preservatives, including creosote and creosote systems, and the Past Chair of the Forest Products Society Treated Wood Technical Interest Group.

Mike is the author or coauthor of over 145 technical publications on wood preservation. He has been involved in the wood preservation business for almost three decades. He is the author of three separate chapters in two current books on wood preservation and the co-editor of the new book on wood preservation and molds by the American Chemical Society. He has traveled extensively to all 50 U.S. states and over 40 countries to date. He received his BS degrees in Wood Science and Chemistry from North Carolina State University.

Mike Barnes received a BSF degree (1965) in Forestry and a MS degree (1968) in Forest Products Technology from Louisiana State University. His PhD in Wood Products Engineering is from the State University of New York College of Environmental Science & Forestry (1973). He has been a member of the faculty in the Department of Forest Products/Forest Products Lab, Mississippi State University since March 1971 where he is currently a Professor of Wood Science & Technology. He has served as a Visiting Professor in the Department of Biology at the Imperial College of Science, Technology & Medicine in London for a year and was a Visiting Professor/Scientist at Oregon State University during two summers. His research interests include the effect of treatments on the properties and durability of wood and wood-based composites, treatment mechanics, preservation and deterioration of wood members, components and structures, and the evaluation of new preservatives and fire retardants. During his career he has published over 200 articles and given countless presentations to scientific, technical, and lay groups worldwide. His teaching assignments have included courses in wood physics, wood anatomy, wood processing, and deterioration and preservation. His professional affiliations include the Forest Products Society (currently President-elect), Society of Wood Science & Technology (past President), American Wood-Preservers' Association, Railway Tie Association, International Academy of Wood Science (Fellow), Institute of Wood Science (Fellow), International Research Group on Wood Protection, ASTM Committee D07, ANSI Committee 05, Society of American Foresters, and the Renewable Natural Resources Foundation. He prefers to be thought of as an 'old wood pickler'.