Wood Preservatives

- Creosote (1831)
- Cu naphthenate (1899)
- ACA, ACC, CCA, FCP, PENTA (‘30s & ’40s)
- ACZA, Borates (‘80s)
- ACQ, CA (‘90s)
- CuNap-W, PXTS, CX-A (‘00s)
- New (‘10s)
What about today?

- Residential vs. Industrial
- Processes
- Preservatives
Residential vs. Industrial

- Outdoor & Indoor exposures
  - Waterborne (95% = CCA)
  - Label Change in ’04
  - Public perception vs science
- SYP =
  - 70% of all treated
  - 86% of lumber & timbers
  - 44% of production is treated [7.63 Bbfm]
Residential vs. Industrial

• Mostly exterior exposure

• The big 3—creosote, penta, CCA/ACZA

• Restrictions threatened
Residential CCA Replacements

- Copper-organic systems
  - Ammoniacal copper quat (ACQ)
  - Copper Azole (CA)
  - Copper Xyligen (CX)
- Borates (non-ground contact)
Background

- CCA introduced in 1933
- Solid science behind CCA & its safety known for decades
- Faced opposition for decades
- Recent headlines: arsenic exposure
- Proposed state legislation banning CCA
- Class-action lawsuits
- Effect of negative publicity
Leading wood preservative mfg.’s amend CCA registrations with EPA leading to voluntary withdrawal of chromated copper arsenate (CCA)

- Feb. 12, 2002, leading wood preservative mfg.’s entered into agreement with EPA

- Withdrawal of CCA from residential applications only
• Where are we now?
Waterborne Wood Preservatives
[AWPA Book of Standards P5]

- CCA
- Ammoniacal Copper Quat [ACQ]
- Copper Azole [CBA-A and CA-B]
- Copper Xyligen [CX-A]
- Borates [SBX]
- ACZA
- Others
  - Cu bis(dimethyldithiocarbamate) [CDDC]
  - DDAC
  - Copper bis-(N-cyclohexylidiazceneniumdioxy) (Cu-HDO or Cu Xyligen)
Oil Systems

Creosote [P1/P13, P2, P3, P4]
Ban in ME and possible in other states?
• Rereg Elig Doc to be issued 1 August
  - No butt or thermal treatment
  - No remedial treatment

Carrier solvents [P9]
Pentachlorophenol

Restrictions on butt, thermal, remedial treatments

• Favored because it is organic
• ???
Copper naphthenate
• low mammalian toxicity
• not as copper rich
• low leaching \[ \approx 4 \text{ ppm} \]

Oxine copper \((\text{bis Copper-8-quinolinolate})\)
• FDA food contact approved
• Ni could be a problem
Chlorpyrifos [CPF]
• Insect protection only

Isothiazolinone
• Usually added as a moldicide

IPBC
• Millwork

Chlorothalonil
• Good efficacy but solubility problems
• Used with CPF
Inorganic Systems

- Borates
- Uncomplexed Copper Systems
  - ACQ
  - CA/CBA
- Complexed Metal-based Systems
  - CuHDO/CX
  - Cu8
  - CuN
  - ZnN
  - CDDC
  - TBTO
Organic Biocides/Preservatives

- **Azoles**
  - Cyproconazole
  - Propiconazole
  - Tebuconazole
- **Quaternary Ammonium Compounds**
  - DDAC
  - ABAC
  - BAC
  - ADBAC
- **IPBC**
- **Synthetic Pyrethroids**
  - Permethrin
  - Bifenthrin
  - Cypermethrin
  - Cyfluthrin
  - Deltamethrin

- **Organic Agrochemicals**
  - TCMTB
  - Chlorothalonil
  - Dichlofluanid
  - Isothiazolone
  - Fipronil
  - Imidachloprid
  - Methylene bis-thiocyanate

- **Oligomeric Alkylphenol Polysulfide** ([PXTS])
- **Polymeric Betaine**
  - [alternating quat, borate ether units]
- **Copper Betaine**
Ammoniacal Copper Quats (ACQ)

• Introduced ~1990 in the U.S.
• Used for 15 years in Europe, Japan, Australia, New Zealand, and Asia.
• Approved for full exposure to above ground, ground contact, and freshwater uses.
• Fixed preservative
ACQ

- Combines copper (II) and one of the quaternary compounds (quats)
- Usually in CuO:quat ratio of 2:1
- 3 types of ACQ available in North America:
  - ACQ-Type B (Ammoniacal based with Cu and DDAC as quat)
  - ACQ-Type D (Amine based with Cu and DDAC as quat)
  - ACQ-Type C (Alkaline based with Cu and BAC as quat)
Quat Properties

- Low mammalian toxicity
- Relatively inexpensive
- Broad activity against decay fungi and insects
- Excellent stability and leach resistance
- Surfactant-exposed wood wets easier
- Moderate efficacy
- Most often combined with other biocides
- Now mostly used as Carbonate ion instead of Chloride
Copper Azoles: History / Uses

- Copper azole treated wood products used worldwide since 1992.
- Copper azole is approved for full exposure to above ground, ground contact, and freshwater applications
- Fixed Preservative
Azoles

- Triazoles (cyproconazole*, propiconazole, tebuconazole)
- **Copper azole with boron (CBA)**
  - Cu:boric acid:tebuconazole ratio of 49:49:2
- **Copper azole without boron (CA)**
  - Cu:tebuconazole ratio of 96.1:3.9
Azole Properties

• Highly active against wood decay fungi

• Soluble in hydrocarbon solvents

• Good stability and leach resistance

• Expensive, although cost effective

• Little activity against sapstains, molds, and insects/termites

• Usually combined with other fungicides or termiticides
Borates: History

• Recorded use as early as 1913

• Borate treated wood products established in New Zealand in 1950

• Widely used in New Zealand, Europe, and Southeast Asia before U.S.

• Introduced to U.S. 25 years ago.
Types of Borates

- Sodium octaborate, sodium tetraborate, boric acid, sodium pentaborate [SBX]
- Calcium borate
- Zinc borate
- Trimethyl borate
Borates

• Usually formulated as a mixture of borax and boric acid

• Extremely low mammalian toxicity

• Broad range of activity against decay fungi and insects

• Limited to uses with minimal or no leaching exposure
Concerns with 2nd Generation Systems

- Cost increase 2-4x
- Disposal
- Not as forgiving
  - Formulating tricky
- Ammoniacal/amine
- Corrosion to treating plants and fasteners
- Grow mold
Corrosion
- Increased rate by dissolving Zn, further attack Fe at the $O_2$-wood interface

Leaching of Cu
- > CCA because Cu rich
- Aquatic toxicity causing hard look

Mold, algae growth
- $N = \text{more growth}$
Current Processes

• Same basic processes
• Modified full-cell
• Best Management Practices
Where are we going?

Concerns & Challenges

• How long will the current ‘new’ systems be with us?

• What will 3rd generation systems look like?

• Will processing change?

• Competitive materials?
How Long?

• Probably 10 years

• Pressure on heavy metals

• Some European countries are eliminating Cu [Denmark, Norway, Holland]

• Lawyers are salivating

• ‘Real vs. Imagined’
Improved 2\textsuperscript{nd} or 3\textsuperscript{rd} Generation Systems

- Organic systems (in Europe now)
  - expensive
  - oilborne
  - limited activity
  - appearance
  - leaching of non-fixed systems
  - New “micronized Systems”
- Polymeric xylenol tetrasulfide
- Non-leachable borate systems???
- Aqueous copper naphthenate
- Antioxidant, metal chelator, water repellent additives

**Sulfur**
- Atomic Number: 16
- Atomic Mass: 32.06

**Boron**
- Atomic Number: 5
- Atomic Mass: 10.81

**Copper**
- Atomic Number: 29
- Atomic Mass: 63.55
- **Cu Xyligen**
- Chlorothalonil (revisited)
- CuBorate systems
- **Solublized Cu8 systems**
- Acetylated wood
- Polymer/furfurlated wood
- Polymeric Betaine
- Copper Betaine

- Vacsol Azure (teb:prop:imida-chlorprid)
- **Isothiazolinonones**
- **Nano-particle systems/micronized**
- Non-amine dispersion systems
- Barrier systems
• Less will be more
• Niche systems
• Micro-emulsions

• Envelope treatments
• Multi-component systems
• Maybe shorter service life

• Life cycle analysis

CHEMICALS

• Chemo phobia
  - biocide free; heat treatments
  - antagonistic microbes
  - Modification
  - Barrier wraps
Barrier Wraps
Processing Changes

• Gas-phase treatments

• Supercritical \( \text{CO}_2 \)

• Improvements in refractory wood treatment
• Mechanical stressing has been shown to improve treatability

• Vapor boron has been successful with a wide range of composites including plywood, OSB, LVL, MDF
Challenges

- Mold issues
- Formosan termite
- Engineered composites
- Public education
Mold Issues

• Emotional—no scientific proof that *Stachybotrys* caused health problems (CDC)

• “The mold issue has only become a problem because the public now perceives it as a health threat and... attorneys are bringing the issue before juries to seek large judgments.”

• Cure the moisture problem!
Formosan Termite

- In affected areas, high demand for treated wood
- $2+ billion problem
- Borate-treated lumber would seem to offer a solution
*C. formosanus* known infestations and projected northern migration

35° N Latitude
Engineered Wood Composites

- Wave of the future
- Increased durability essential
- Addition questions
- Compatibility
- ZnB (7+), Cu (1) used now
Current research is looking at:

- Composite durability, modeling
- Addition methods
- New preservatives
- New products such as Steam Pressed Scrim Lumber with enhanced properties
Public Education

- Perceive health risk
- Unfamiliar with CIS
- Long-term exposure
- Technology transfer
What About the Future?

- Stabilizing wood is a continuing goal
- Threats from substitutes are real
- Systems targeted to a specific end use
- Lower retentions = less environmental impact
- Composites
- Better education
“Conserve the forests by preserving the wood”
Mike H. Freeman
Independent Wood Scientist

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