## PROS AND CONS OF CURRENT AND FUTURE WOOD PRESERVATIVES

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## 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

## <u>Residential</u> 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. <u>Industrial</u>

- 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 <u>residential</u> 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-cyclohexyldiazeniumdioxy) (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]





Oilborne Systems [P8] Pentachlorophenol

Restrictions on butt, thermal, remedial treatments

Favored because it is organic

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Copper naphthenate ·low mammalian toxicity ·not as copper rich

low leaching [≈ 4 ppm]

Oxine copper (*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
  - *C*u8
  - CuN
  - ZnN
  - CDDC
  - TBTO



Atomíc Number: 50 Atomíc Mass: 118.71 B Boron Atomic Number: 5 Atomic Mass: 10.81

## Organic Biocides/Preservatives

- Azoles •
  - Cyproconazole
  - Propiconazole
  - Tebuconazole
- Quaternary Ammonium Compounds
  - DDAC
  - ABAC
  - BAC
  - ADBAC
- IPBC •
- Atomic Mass: 35.45 Synthetic Pyrethroids
  - Permethrin
  - Bifenthrin
  - Cypermethrin
  - Cyfluthrin
  - Deltamethrin •



Chlorine

•

mic Number: 17

- **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



- 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 i 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 2<sup>nd</sup> Generation Systems

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- 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<sub>2</sub>-wood interface

#### Leaching of Cu

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

Mold, algae growth

N = 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 3<sup>rd</sup> 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<sup>nd</sup> or 3<sup>rd</sup> Generation Systems

- Organic systems (in Europe now)
  - expensive
  - oilborne
  - limited activity
  - appearance
  - leaching of non-fixed systems
  - New "micronized Sytems"

#### Polymeric xylenol tetrasulfide



Atomic Number: 16 Atomic Mass: 32.06

 Non-leachable borate systems???



 Aqueous copper naphthenate



Atomic Number: 29 Atomic Mass: 63.55

 Amoxidant, metal chelator, water repellent additives

#### <u>Cu Xyligen</u>

- Chlorothalonil (revisited)
- CuBorate systems
- <u>Solublized Cu8</u>
   <u>systems</u>
- <u>Acetylated wood</u>
- Polymer/furfurlated wood
- Polymeric Betaine
- Copper Betaine

- Vacsol Azure (teb:prop:imidachlorprid)
- <u>Isothiazolinones</u>
- <u>Nano-particle</u> <u>systems/micronzed</u>
- Non-amine dispersion systems
- Barrier systems

Less will be more

- Niche systems
- Micro-emulsions



#### Envelope treatments



 Multicomponent systems  Maybe shorter service life

## CHEMICALS

- Chemo priobia
  - biocide free; heat treatments
  - antagonistic microbes
  - Modification
  - Barrier wraps







Barrier Wraps

## **Processing Changes**

- Gas-phase treatments
- Supercritical CO<sub>2</sub>
- 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 hearth 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



## Engineered Wood Composites

- Wave of the future
- Increased durability essential
- Addition questions
- Compatibility
- ZnB (7+), Cu (1) used now



## <u>Current research is looking at:</u>

- 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





