

# Copper Naphthenate Update

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**Presented to the**  
**American Wood Preservers' Association**  
**100<sup>th</sup> Annual Meeting**  
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# Agenda for Presentation

- Current Copper Naphthenate Usage
- Recommendations to Improve Copper Naphthenate Treated Wood Quality
- Recent Lab & Field Studies
- New Directions

# Copper Naphthenate

- Reaction product of naphthenic acid and copper compounds
- Used as a biocide since the late 1800's
- Oil-borne formulations added to AWWA Book of Standards in 1948
- Waterborne formulations are commercial products but not adopted by AWWA

# Naphthenic Acid & Copper Naphthenate in Wood Preservatives

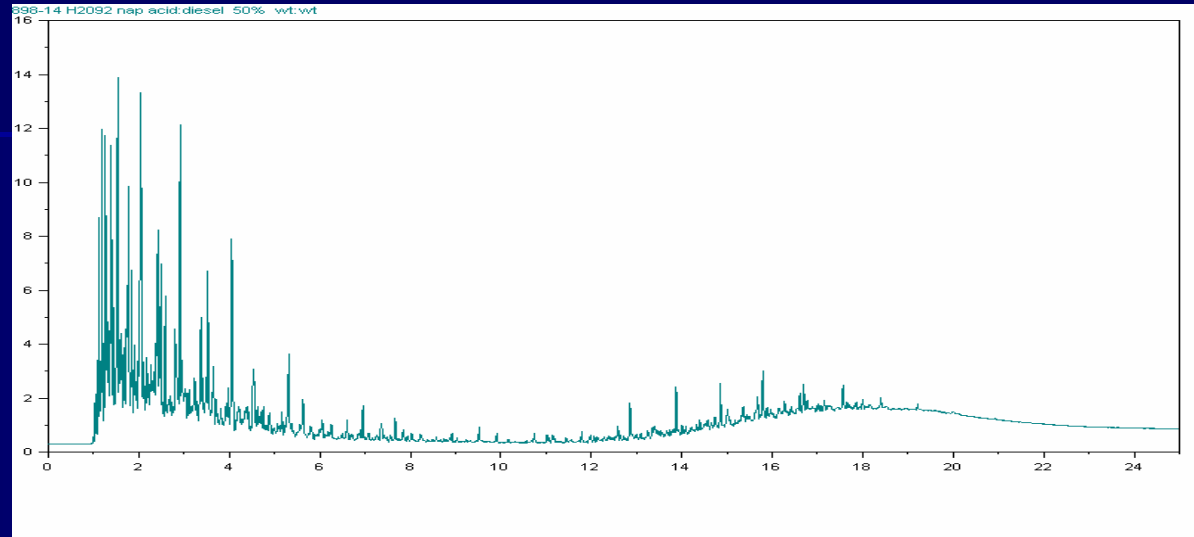
- AWWPA Standard P-8 Section 2
- Only petroleum-based alicyclic carboxylic acids with total acid numbers between 180-250 mg KOH/g
- Excludes synthetic and other non-naphthenic acids (AWWPA Standard P-8.2.1)
- Standard P8 Section 2 for copper naphthenate reaffirmed by AWWPA in 2003

# Copper Naphthenate Analysis

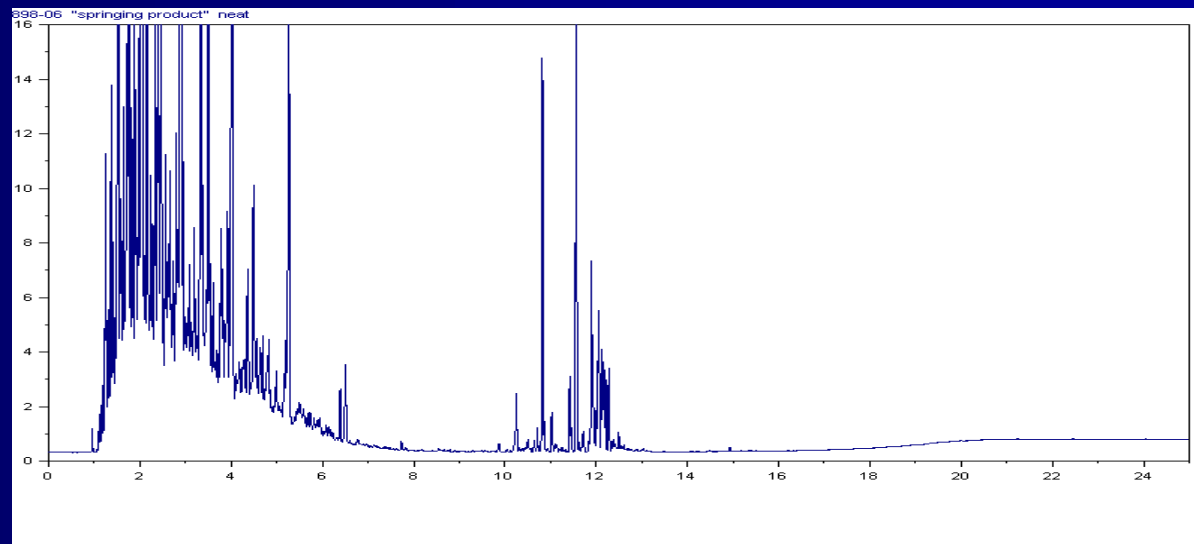
- Brient et al., "Copper Naphthenate: An Analysis of the Materials Found in the Worldwide Marketplace Using A New Analytical Technique", IRG WP/00-30224, Kona, HI June, 2000.
- Identified an analytical method to verify the conformance of copper naphthenate to AWWA Method P8.2 standard for naphthenic acid component

# Copper Naphthenate Analyses

Naphthenic  
Acid-based



Synthetic  
Acid-based



solvent

synthetics naphthenic acids

# Copper Naphthenate Analyses

- A survey of commercially available samples found that US-based products are essentially pure naphthenic acid, although some contain minor (<5%) amounts of synthetic carboxylic acids
- Two samples produced in Europe and Australia contain either naphthenic acid/synthetic acid blends or 100% synthetic acids
- Using non-naphthenics can lead to reduced preservative performance, emulsion problems during treating, and increased leaching potential

# Copper Naphthenate

## Typical Properties

Copper naphthenate produced from 180-250 TAN  
naphthenic acid contains 9-12% Cu

	Concentrate	Ready to Use
% Cu	8	1 & 2
% Copper Naphthenate	65-80	10-20
% Solvent	20-35	80-90
Pour Point, °F	0	-25
Visc @ 75°F, cP	2200	40



# Copper Naphthenate Usage

- Pressure Treatment
  - Utility Poles, Piles, Cross Arms, Bridge Timbers, Posts, Glue-lam, Ties
- Non-Pressure Treatment
  - Over-the-Counter Markets
  - Remedial Treatments: Brush-on, paste, wraps

# AWPA UC 4A, 4B, & 4C Standards for Copper Naphthenate Treated Poles (U1 Commodity Specification D)

- 0.06, 0.08, and 0.13 pcf (as copper) for Southern Pine poles
- 0.075, 0.095, and 0.150 pcf (as copper) for Douglas Fir poles, outer zone
- 0.12 pcf (as copper) for Western Red Cedar

# Other UCS Standards

## Southern Pine

- U1 Specification A: Sawn Products
  - UC3A/B: 0.04 pcf Cu
  - UC4A: 0.06 pcf Cu
  - UC4B/C: 0.075 pcf Cu
  
- U1 Specification B: Posts
  - UC4A: 0.055 pcf Cu
  - UC4B: 0.069 pcf Cu
  
- U1 Specification E: Piles
  - UC4C: 0.10 pcf Cu

# AWPA M4 Standard for Remedial Treatment with Copper Naphthenate

1-2% minimum copper, in solvent or waterborne systems

- Appropriate for poles originally treated with other preservatives, including waterborne preservatives
- Certified Applicators License not required for field treatment

# Regulatory Status of Copper Naphthenate

- EPA: Not a restricted use pesticide
  - General Use Classification
- Non-hazardous waste or air pollutant
- No reportable quantity required for spills
- Copper Naphthenate Wood Preservation Wastes are Neither "Listed" nor "Characteristic" Hazardous Wastes under RCRA
- Multiple copper naphthenate registrants in US and Canada

# Recent Laboratory and Field Studies with Copper Naphthenate

# USDA Forest Products Lab

## Data FPL-RN-01

- M.H. Freeman, D. Crawford, P. Lebow, and J.A. Brient. Comparison of Wood Preservatives in Post Tests - 2004 Update: 53 years of Testing in Mississippi. AWWPA 2004, in press
- SYP Fence Posts, pressure treated, installed in MS in 1949

# Copper Naphthenate

## Results from FPL-01 Posts

Tests In Mississippi (Hazard Zone 5)

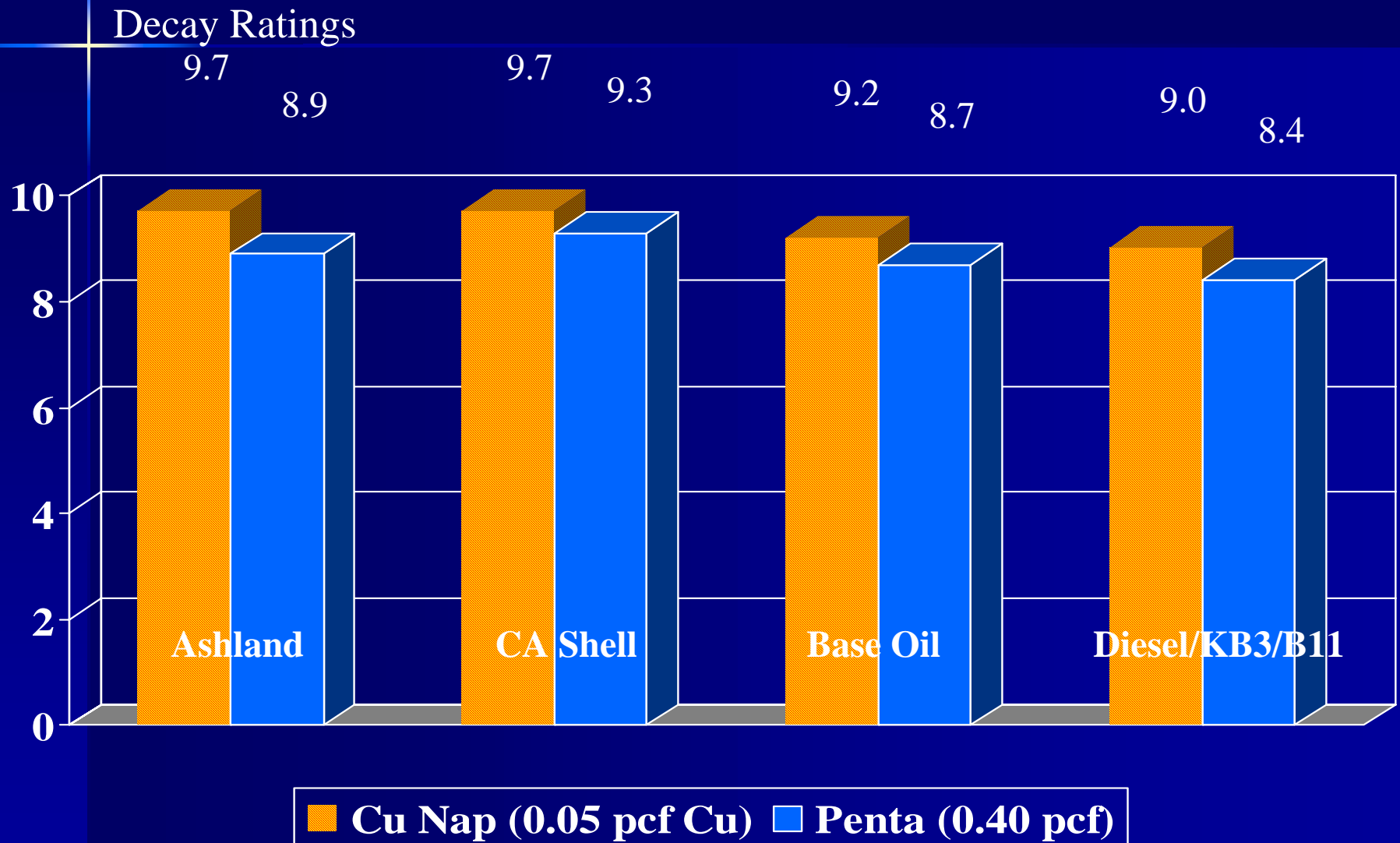
<u>Retention, pcf Cu</u>	<u>Average Life, years</u>
0.0 (untreated control)	Less than 3
0.03 (55% of AWWA UC4A retention standard for posts)	> 65 years



# EPRI-funded Long-term Field Stake Test

- D. Nicholas and M. Freeman, "Comparative performance of pentachlorophenol and copper naphthenate in a long term field stake test", IRG WP/00-30243, Kona, HI June 2000.
- Performance of copper naphthenate and pentachlorophenol treated pine stakes against decay and termite attack were compared using four different petroleum oils meeting AWPA Standard P9-A

# Field Stake Decay Ratings At Dorman after 11-Years Exposure



# Leaching and Migration from Utility Poles

- J. A. Brient, "Soil Leaching from Copper Naphthenate-Treated Utility Poles ", International Conference on Utility Line Structures, March 2002
- Cu levels in soil 4" from poles averaged 220 and 1124 mg/kg at two sites after 8-14 years, less than half the WA state cleanup level
- TPH levels in soil averaged an order of magnitude below the cleanup level of 2000 mg/kg listed for diesel range organics

# Copper Naphthenate Aqueous Leaching Study and Model

- K. Brooks, "Literature Review, Computer Model and Assessment of the Potential Environmental Risks Associated with Copper Naphthenate Treated Wood Products Used in Aquatic Environments ", 2003. At [www.wwpinstitute.org](http://www.wwpinstitute.org)
- 30-day evaluation of copper in leachate water exposed to copper naphthenate-treated piles.
- Risk assessment used to determine environmental risks associated with the use of piling immersed in freshwater

# Copper Naphthenate Aqueous Leaching Study and Model

- Copper losses from wood treated to 0.08 to 0.14 pcf copper are predicted to be 18.9  $\mu\text{g Cu/cm}^2\text{-day}$  on the first day of immersion.
- Initial loss rates decline exponentially and approach the long-term loss rate of 1.2  $\mu\text{g Cu/cm}^2\text{-day}$  in about three or four weeks.
- CuNap leachate is  $\sim 1/3$  as toxic to *Daphnia* as ionic copper in a 21-day bioassay.

# Follow Up Long-Term Aqueous Leaching Study and Model

- Treated wood from 30-day test placed in pond for 15 months, then the 30-day dynamic Cu leaching test repeated to determine long-term Cu loss rate.
- A long-term loss rate of  $0.56 \mu\text{g Cu/cm}^2\text{-day}$  is estimated from the follow-up study vs.  $1.2 \mu\text{g Cu/cm}^2\text{-day}$  previously estimated.

# Recent Improvements in Copper Naphthenate and Copper Naphthenate- treated Wood Products

# Improvements in Copper Naphthenate

- Since mid-1990's, ALL SYP is Kiln-Dried to avoid incipient decay
  - Kiln dried to low moisture content before treatment
  - Time/Temperature ensures sterilization
  - Low moisture content gives improved treatment



# Improvements in Copper Naphthenate

- Enhanced Inspection
  - 100% inspection of SYP poles regardless of size
  - Enhanced inspection and warranty available

# Improvements in Copper Naphthenate

- Manufacturing methods now give product with reduced impurities
  - 100% filtered products
  - Produced in ISO 9002 facility
  - Highest quality and consistency

# Improvements in Copper Naphthenate

- Improved control of solution moisture content by controlling/minimizing emulsion formation
  - Excess H<sub>2</sub>O removed by separation
  - Treaters now using easily separable formulations

# BEFORE TEST—AGED WATER



# 30 MINUTES—AGED WATER



*Previous Copper  
Naphthenate*

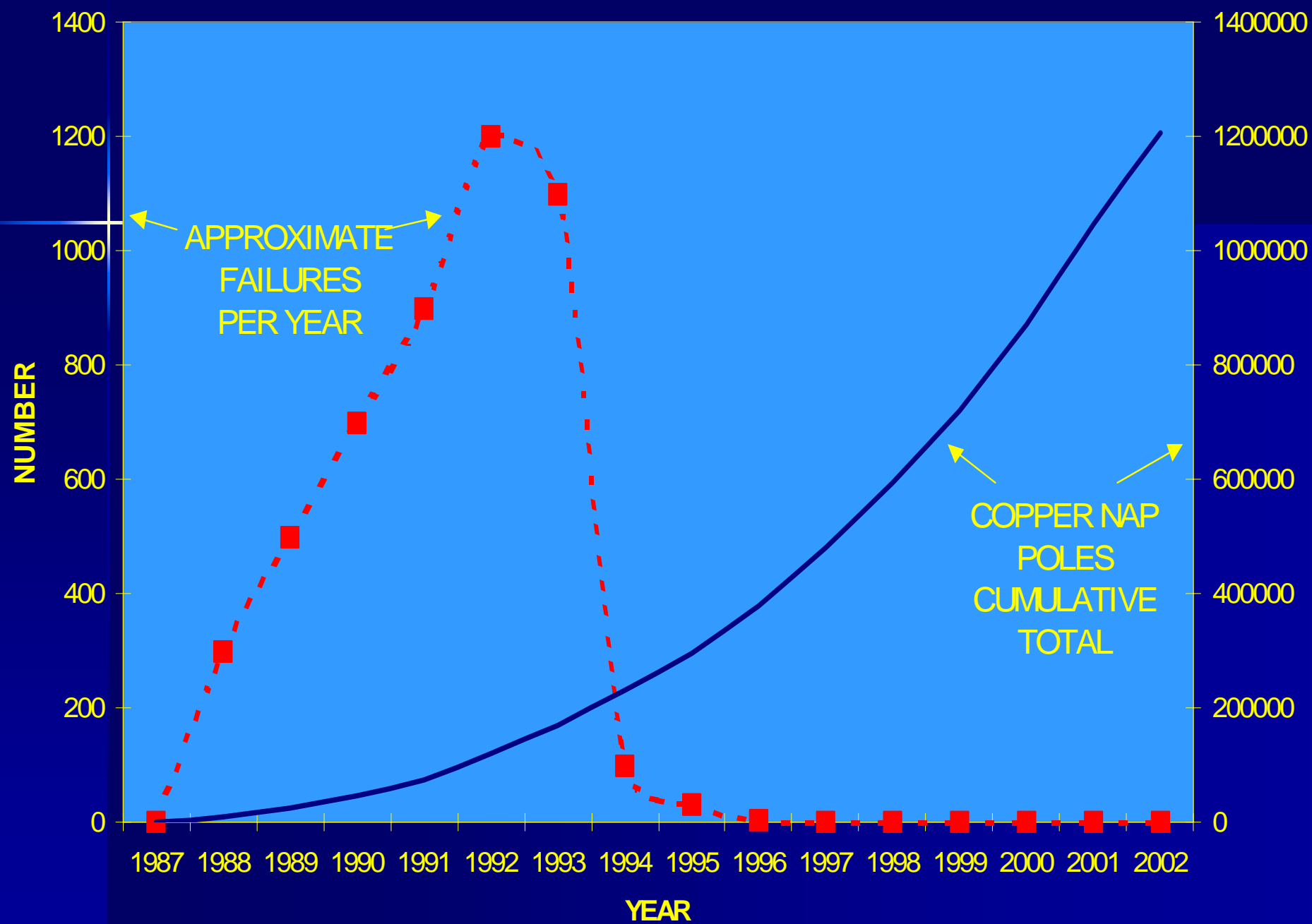
*Current Copper  
Naphthenate*

# Improvements in Copper Naphthenate

- AWWA P8 Standard revised to specifically exclude the use of non-naphthenic (synthetic) acids
  - Synthetics may be less efficacious and contribute to emulsions
  - Analytical method developed and included in AWWA to differentiate acids
  - Manufacturers certify 100% naphthenic acid

# Premature Failure Issues

- Problems Overstated
  - Failure Rate was Low (<0.5% of total population)
  - No problems in any species other than SYP
- All of the identified potential root causes have been addressed and resolved
- Time lag shows the problems are behind us





# Market Developments

## Merichem Chemicals & Refinery Services LLC

manufacturer of copper naphthenate, has formed an agreement with

## Osmose Wood Preserving Division

to provide sales/marketing services for CuNap-8™ copper naphthenate.

# Market Developments

In 2002, Pacific Wood Preserving re-opened the former Taylor Lumber plant in Sheridan, OR to provide copper naphthenate for full-length treated poles.

Oregon DEQ allowed treatments using only non-arsenical pesticides.

# Market Developments

In 2003, J.H. Baxter Wood Preserving Company began providing butt treated copper naphthenate wood poles.

# Market Developments

In 2003, Wheeler Lumber's Whitewood, SD treating plant was destroyed by fire.

They have rebuilt the plant and are now treating using only copper naphthenate.

"As the treated wood industry is changing and chemical issues are changing, this was a good time for us to move into the future to be more environmentally friendly."

- Jeff Parrett, V.P. of Operations

# Market Developments

## Wheeler Lumber products



# Market Developments

Wood Preservers, Inc. (Warsaw, VA) will commence treating with copper naphthenate in mid-2004



# What's in the future for Copper Naphthenate?



# Usage in Ties

- Task Force established in T3 to add copper naphthenate for crossties and switch ties in Standard U1, Commodity Specification C at 2004 Fall Technical Meeting
- Multiple studies have been conducted on hardwoods in the lab and in field tests to demonstrate efficacy
- Copper naphthenate-treated ties in service for 13 years confirm efficacy



# Usage in Ties

- H.M. Barnes et al. (2003). Performance of Copper Naphthenate-treated Hardwoods. IRG/WP/01-30269
- Copper naphthenate-treated hardwood stakes tested in FL and MS and rated for decay and insect attack by AWWPA E7
- Based on a rating of 70, 4.5 pcf creosote is roughly equivalent to 0.08 pcf (Cu as metal) in oak.

# Usage in Ties

- J. Brient and D. Webb. 2002. The Performance of Copper Naphthenate Ties in Service. *Proc. AWWA*, Vol. 98, 112-115.
- Copper naphthenate-treated ties with 0.03-0.05 pcf Cu, in actual service for 13 years, were equivalent to ties treated with 7.8 pcf creosote

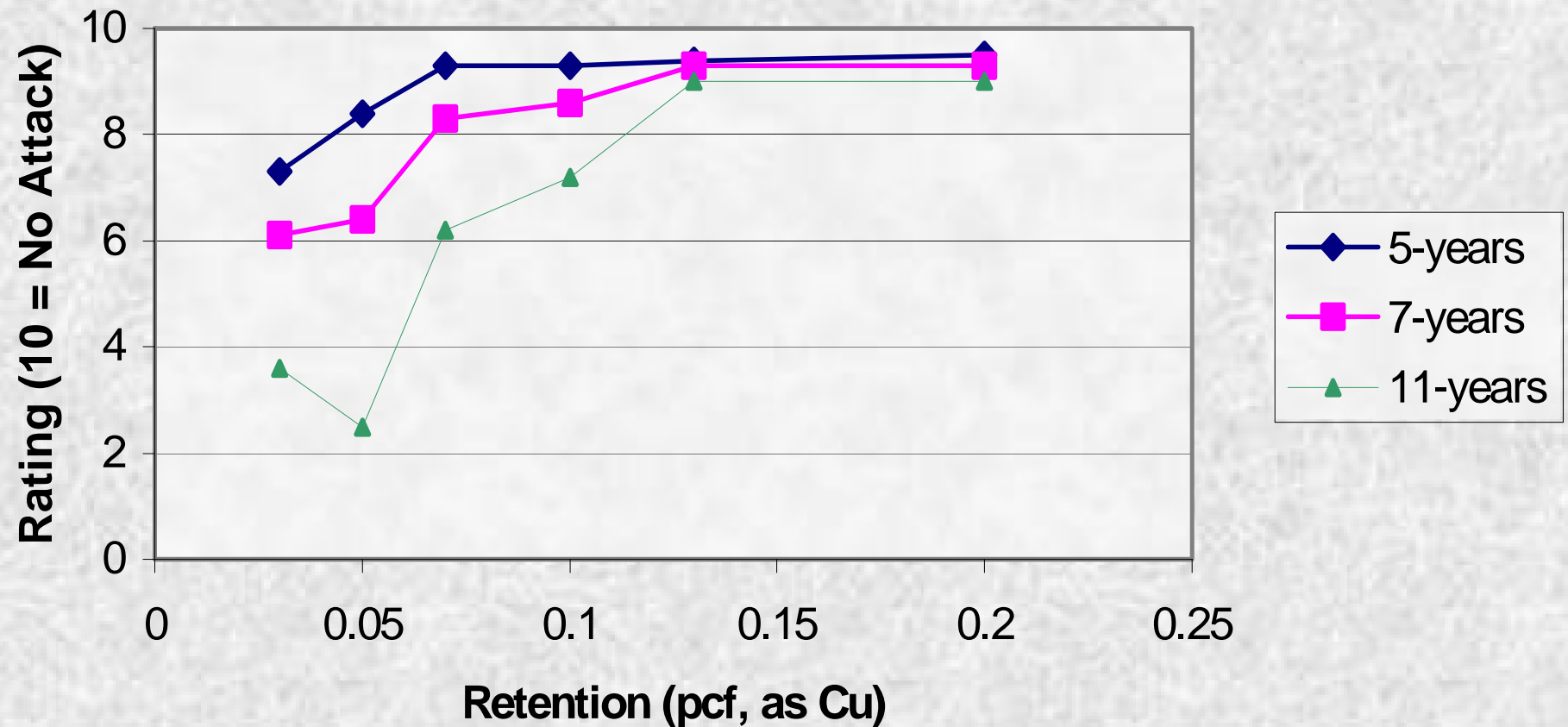
# Waterborne Copper Naphthenate

- Alternative to CCA in pressure-treated wood for consumer / residential uses
- Available for non-pressure treatment applications (brush-on, spray, dip, remedial) uses as an EPA-registered product since 1980
- Waterborne formulations are not currently listed in AWWPA Book of Standards

# Field Stake Studies on Waterborne Copper Naphthenate

- J. L. Shaw (1994) "Results of Test Activity on a Waterborne Copper Naphthenate Wood Preservation System". *Proc. AWWPA*, Vol. 90, 167-174.
- 3/4" SYP stakes treated with CCA, pentachlorophenol, and oil borne or waterborne Copper Naphthenate and installed in Bainbridge, GA (Hazard Zone 5)
- 0.15 pcf WB CuN = 0.13 pcf OB CuN = 0.60 pcf CCA
- 0.08 pcf WB CuN = 0.45 pcf pentachlorophenol

## Dosage-Response, Waterborne Copper Naphthenate-treated SYP Stakes in AWPA Zone 5



# Field Stake Studies on Waterborne Copper Naphthenate

- M. Freeman et al. (2003) "Water-Borne Copper Naphthenate: A Chromium and Arsenic Free Preservative for Wood and Composites". *Proc. AWWPA*, Vol. 99
- Softwood and hardwood stakes treated and installed in MI, MS, and FL

# Field Stake Studies on Waterborne Copper Naphthenate

- Comparable ratings obtained after 5-7 years in various AWWPA Hazard Zones include:

Waterborne Copper Naphthenate at

0.08 pcf Cu

Oil borne Copper Naphthenate at

0.06 pcf Cu

CCA-C at 0.35 pcf

# More Information

on copper naphthenate  
is available at

[www.merichem.com](http://www.merichem.com)