

***Leachability of borate treated southern pine
influenced by
copper naphthenate treatment***

**Documentation of research internship
at
University of Tennessee
for
Marshall Plan Scholarship Programm**

Barbara Jordan
Forest Products Technology
& Timber Construction

Abstract

The internship dealt with the leachability of borates and the possible fixation of borates due to a further treatment with different copper naphthenate solutions. The copper and borate content of samples of southern pine was evaluated and compared with control samples.

The results have shown no significant better performance of leachability in the samples than the with the additional copper naphthenate treatment.

Key words:

Borate

Copper naphthenate

Leachability

Fixation of borate

Index

1. Introduction	4
2. Material	5
3. Methods	5
3.1. Pressure treatment	5
3.2. Leaching test	10
3.3. XRF- Analysis	10
3.4. Borate analysis	12
4. Results	13
4.1. Pressure treatment	13
4.1.1. Borate treatment (Control group 2)	13
4.1.2. Water-borne copper naphthenate	13
4.1.3. Oil-borne copper naphthenate	14
4.1.4. Control group 1	14
4.2. XRF-analysis	15
4.3. Borate analysis	16
5. Discussion	17
6. Literature References	18
7. Picture references	19
8. Chart and table references	20

1. Introduction

Due to a lot of advantages borate is often used as a preservative in wood. Borates are highly efficient in preventing infestations of insects or fungal decay while being inexpensive, harmless for mammals and environmental friendly. The efficiency wanes, when the borate treated wood is exposed to water because of the high leachability of borate. Due to the leachability the application of borate in wood is restricted. (McIntyre & Lake, 2011).

The fixation of borate in wood, while keeping the standards of preventing decay high, is still a challenge. To have a long-term protection it is inevitable to use protective additives as glycerol/glyoxal additives (Mohareb, et al., 2002). In general those additives are used as a coating to increase the water repellency.

Due to the increased use of borates with copper treatments as a preservative, the influence of these copper products on the leachability should be tested. Wood is more water repellent with the aid of oil-borne copper naphthenate. This additional quality can increase the period of application of wood in the outdoor area. Furthermore the penetration of the entire piece of wood is more advantageous than the coating. The coating protects the sample only on its surface. With this in mind we wanted to test, if there can be observed an influence of copper-containing biocides, as copper naphthenate, on the leachability of borate.

2. Material

The wood used for the samples was southern pine. They were chemically treated with Disodium Octoborate Tetrahydrate, copper naphthenate and diesel with mineral spirit. The copper naphthenate was based on a 5% concentrate for the water-born solution and on an 8% concentrate for the oil-born solution. Furthermore common mineral spirit from the hardware store and diesel from the gas station was used.

3. Methods

3.1. Pressure treatment

240 cubes with a side length of 10 mm were cut out of dried southern pine boards. Those were penetrated with a DOT solution. 5g of Disodium Octoborate Tetrahydrate were mixed with 1000 ml of water. For the penetration with vacuum and pressure, the cubes were put into a cylinder, covered with an acrylic glass panel and encumbered with weights to prevent the floating of the samples. The solution was added into the cylinder. It had to be checked, if there were any bubbles of air and all samples were covered with the liquid.



Figure 1: Samples in borate solution, before treatment

The prepared samples were put into a pressure cylinder which was closed and sealed airtight. Then a vacuum exhauster removed the air of the cylinder and the samples were kept in the vacuum for 30 minutes. After that the samples were kept for 30 more minutes at atmospheric pressure. This treatment was repeated, but this time pressure was used instead of vacuum. After the pressure treatment of 30 minutes and the samples rested for 30 minutes in the DOT-solution at atmospheric pressure, the samples were taken out of the solution and dried in a kiln for 24 hours at 103° C.



Figure 2: Pressure cylinder with vacuum pump

Now the samples were prepared for the treatment with copper naphthenate. The samples were divided into 4 groups to have an appropriate comparison:

- Water-borne copper naphthenate
The copper concentration of the water-born copper naphthenate was at 5 %. To get 1l of 0.4% solution, 50 ml of the concentrate were mixed with tap water.
- Oil-borne copper naphthenate
The solution for the oil-borne copper naphthenate was composed of a copper naphthenate concentrate (8 %), which was mixed with diesel and mineral sprit. Diesel and mineral spirit were poured together in a ratio of 4:6. The pursued concentration of the oil-borne copper solution was

0.4% of copper content, so the ratio of the copper naphthenate and the diesel/mineral spirit was 1:12.5.

- Control group 1 (Treated with DOT and mineral spirit)
The control group 1 was treated with DOT and with the diesel/mineral spirit mixture, to see if these additional chemicals have an influence on the leachability of the DOT as well.
- Control group 2
The control group 2 was treated with DOT. There was no further treatment to have a reference value.

60 samples each were penetrated with a solution. The procedure was the same as during the pressure treatment with DOT: First the samples were penetrated with the solution in vacuum for 30 minutes, then they were kept for 30 minutes at atmospheric pressure. The next step was the treatment with pressure for another 30 minutes, after that the samples rested in the fluid for 30 more minutes.



Figure 3: Samples in water-borne copper naphthenate, after pressure treatment

Afterwards all samples were dried in a kiln for 48 hours at 50° C. This low temperature was necessary to avoid the self-ignition of the diesel residues. All samples were treated the same to have the same prerequisites.



Figure 4: Samples after treatment with borate (left row) and water-borne copper naphthenate (right row)

3.2. Leaching test

The required pretreatment for the leaching test was another cycle of vacuum-pressure treatment, as described before. The used fluid was water. 54 samples of each group were put into a sealable jar. For each 6 samples 300 ml of water had to be added, so in the beginning of the leaching test, the jars were filled with 1800 ml of water. The 4 jars were put onto a shaker table at a rotation frequency of 60 per minute at the temperature of 20° C.

According to the AWWA Book of Standards 6 samples had to be removed after 6, 24, 48, 96, 144, 192, 240, 288 and 366 hours. After the set of samples was removed, the water was removed. The jars had to be clean, residues had to be removed. As 6 samples had been removed, the jar was refilled with 300 ml less water than before. The samples were marked and dried in a kiln for 48 hours at 50° C.

3.3. XRF- Analysis

The content of copper naphthenate of the two sample groups was analyzed with the Lab-X 3500 XRF- Analyzer by Oxford Instruments. The samples were ground in a Wiley Mill individually. The sawdust was filled into small bins. The bottom of the bin had to be of mylar, a thin foil, to guarantee the precise XRF- analysis.



Figure 5: Grinding of the samples in the Wiley Mill

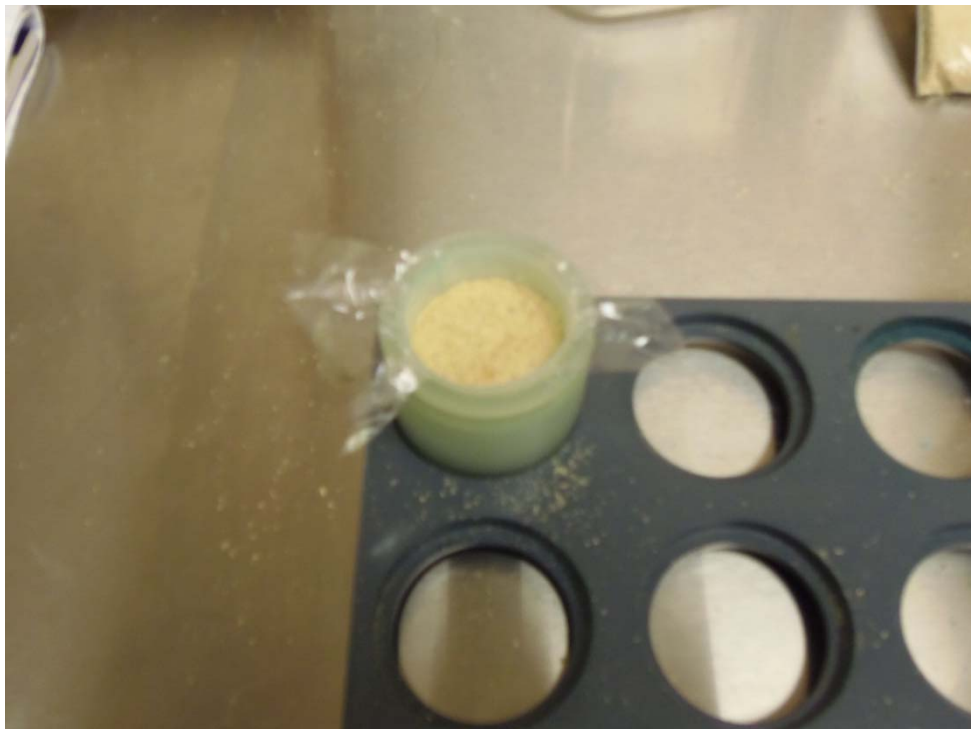


Figure 6: Bins filled with sawdust for XRF-analysis

The bins were inserted into the XRF-Analyzer. The analysis was executed automatically.



Figure 7: Oxford Instruments Lab-X 3500 XRF- Analyzer

3.4. Borate analysis

The borate analysis was executed in a lab of Nisus Corp., because the University of Tennessee didn't provide equipment precise enough. The samples were analyzed on 11/28/2012.

4. Results

4.1. Pressure treatment

To see, how efficient the pressure treatment was, 6 samples were taken out of each group.

4.1.1. Borate treatment (Control group 2)

The borate treatment was successful. The untreated samples had an average weight of 3.465 g, after the pressure treatment the average weight of all samples was 7.627 g. That's an average gain of weight of 220%.

4.1.2. Water-borne copper naphthenate

The samples treated with the water-borne copper naphthenate had an average weight of 6.380g after the treatment. That is an average increase of weight of 180% (Table 1).

Table 1: Weight of samples, water-borne copper naphthenate

Water-borne copper naphthenate					
Sample No.	Weight [g]	Weight after borate treatment [g]	Increase of weight [%]	Weight after CuNap5 treatment [g]	Increase of weight [%]
B1	3,523	7,879	223,645%	6,583	186,858%
B2	3,707	7,868	212,247%	5,686	153,385%
B3	3,439	7,784	226,345%	6,685	194,388%
B4	3,457	7,945	229,824%	6,339	183,367%
B5	3,371	7,547	223,880%	6,559	194,571%
B6	3,741	7,834	209,409%	6,429	171,852%
Average	3,540	7,810	220,892%	6,380	180,248%

4.1.3. Oil-borne copper naphthenate

The samples of the oil-borne copper naphthenate group had an average weight of 3.373 g before the treatment and 6.701 g after the treatment. That's an increase of weight of 199% (Table 2).

Table 2: Weight of samples, oil-borne copper naphthenate

Oil-borne copper naphthenate					
Sample No.	Weight [g]	Weight after borate treatment [g]	Increase of weight [%]	Weight after CuNap8 treatment [g]	Increase of weight [%]
A1	3,119	6,692	214,556%	6,637	212,793%
A2	3,209	7,285	227,018%	6,571	204,768%
A3	3,421	7,656	223,794%	6,465	188,980%
A4	3,589	7,757	216,133%	6,878	191,641%
A5	3,448	7,647	221,781%	6,928	200,928%
A6	3,452	7,755	224,652%	6,724	194,786%
Average	3,373	7,465	221,322%	6,701	198,651%

4.1.4. Control group 1

The control samples started with an average weight of 3.484 g and had an average weight of 6.672 g after the treatment. That is an average weight gain of 192% (Table 3).

Table 3: Weight of samples, control group 1

Diesel control samples					
Sample No.	Weight [g]	Weight after borate treatment [g]	Increase of weight [%]	Weight after CuNap5 treatment [g]	Increase of weight [%]
C1	3,476	7,572	217,837%	6,401	184,148%
C2	3,308	7,491	226,451%	6,661	201,360%
C3	3,495	7,69	220,029%	6,949	198,827%
C4	3,512	7,642	217,597%	6,608	188,155%
C5	3,288	7,417	225,578%	6,614	201,156%
C6	3,822	7,838	205,076%	6,799	177,891%
Average	3,484	7,608	218,761%	6,672	191,532%

Therefore the pressure treatments with all solutions can be considered a success.

4.2. XRF-analysis

Due to technical failure, the last 12 samples of each group of the leaching test were lost due to a fire in the kiln. Nevertheless the remaining samples were tested.

The analysis of the copper naphthenate content after the leaching test showed no significant decrease of the copper naphthenate concentration (Figure 8).

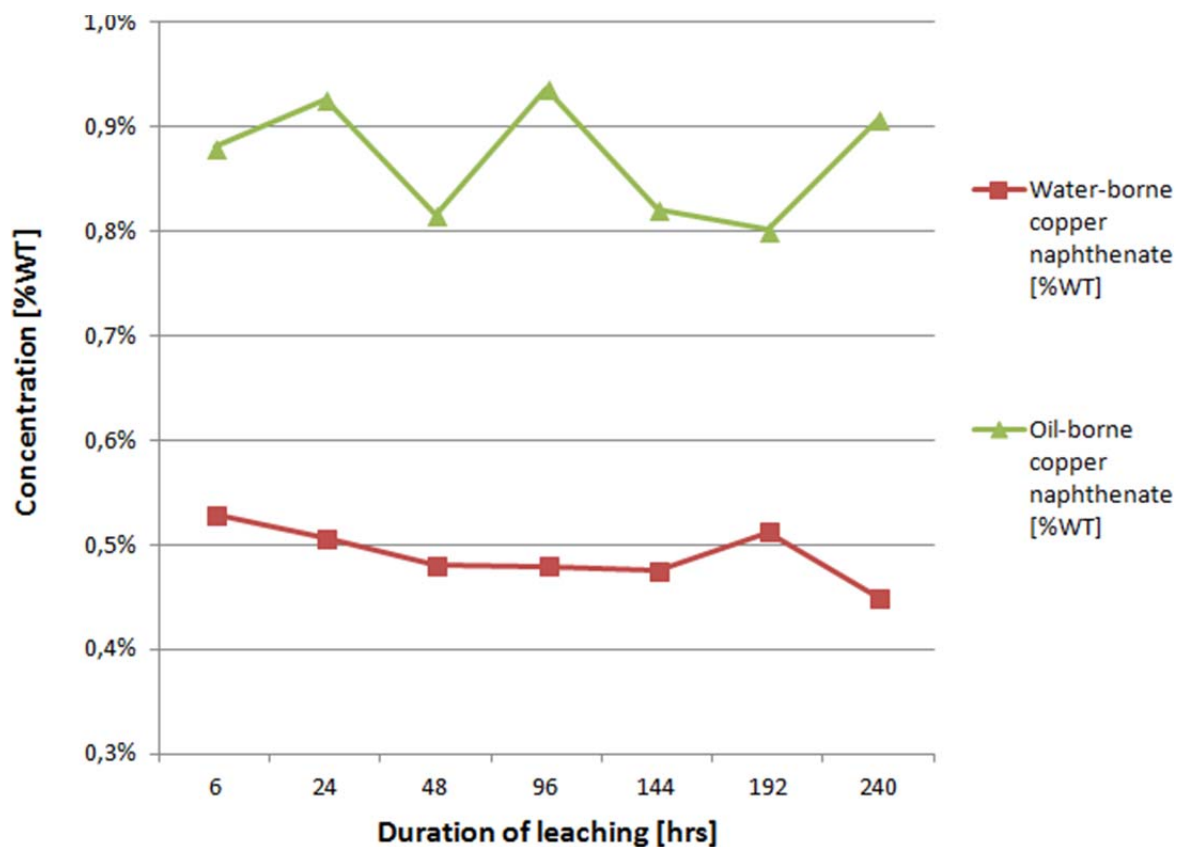


Figure 8: Copper content after leaching test

4.3. Borate analysis

The analysis showed a quite similar picture for all tested groups. The Retention of DOT declined in the course of the leaching test (Figure 9). Only the treatment with the water-borne copper naphthenate showed slight improvement.

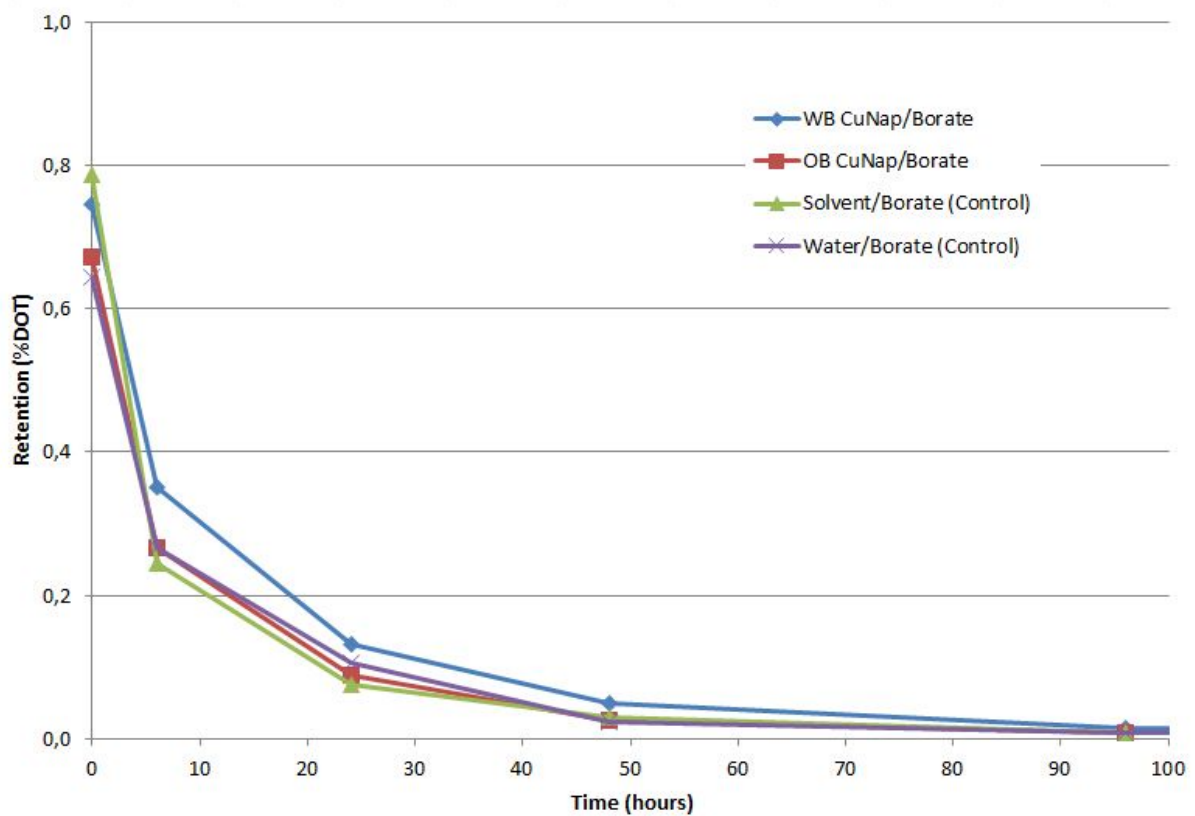


Figure 9: Analysis of the borate leaching test

5. Discussion

Even though the pressure treatment was successful, no evidence of improvement of the leachability due to copper naphthenate treatment could be found.

There is a hint of improvement due to the treatment with the water-borne copper naphthenate, but more testing is required to get a valid theory based on facts.

6. Literature References

McIntyre, C. R., & Lake, M. A. (2011). Fixed Borates Anyone? (p. 5). MS, USA: The International Research Group on Wood Protection.

Mohareb, A., Van Acker, J., & Stevens, M. (2002). Effect of protective additives on leachability and efficacy of borate treated wood. In T. I. Preservation (Hrsg.). (S. 5). Alexandria, Egypt: The International Research Group on Wood Preservation.

7. Picture references

Figure 1: Samples in borate solution, before treatment	6
Figure 2: Pressure cylinder with vacuum pump	7
Figure 3: Samples in water-borne copper naphthenate, after pressure treatment	8
Figure 4: Samples after treatment with borate (left row) and water-borne copper naphthenate (right row)	9
Figure 5: Grinding of the samples in the Wiley Mill	11
Figure 6: Bins filled with sawdust for XRF-analysis	11
Figure 7: Oxford Instruments Lab-X 3500 XRF- Analyzer	12
Figure 8: Copper content after leaching test	15
Figure 9: Analysis of the borate leaching test	16

8. Chart and table references

Table 1: Weight of samples, water-borne copper naphthenate 13

Table 2: Weight of samples, oil-borne copper naphthenate..... 14

Table 3: Weight of samples, control group 1 14