UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MAR 29 2004

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OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

SUBJECT: Review of the Akzo Nobel Functional Chemicals LLC Wood Leaching Study for the Wood Preservative PXTS

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ID#: 75799-R

DP BARCODE: D299913

SUBMISSION: None

CASE: None

PC CODE: 006929

CHEMICAL NAME: Polyxylenol Sulfide

MRID#: 460626-25, 460626-26

(1)

Introduction:

Akzo Nobel Functional Chemicals LLC has submitted a release study for the active ingredient, polyxylenol tetrasulfide(PXTS) in a wood preservative. The name of the wood preservative product is PXTS Blend D. The data package were submitted as a part of the data packages for the new chemical, polyxylenol tetrasulfide. A number of other packages for this chemical are being reviewed under different "bean sheets" for the various scientific disciplines.

Background:

Polyxylenol tetrasulfide is a new chemical. No label is submitted with this data package containing this leaching study. Two MRID#'s were submitted for this wood preservative leaching study; MRID# 460626-25 which is a study that determined the retention of PXTS preservative in treated wood and MRID# 460626-26 which includes the leaching portion of the study and the analytical method for the determination of PXTS residues.

Conclusions:

If the registrant can satisfactorily respond to the information requested below under "Recommendations", RASSB could draw the following conclusions. Until these questions are satisfactorily answered, the following conclusions are only tentative. RASSB cannot at this time conclude that the leaching study is adequate to support registration.

1.The mean retention in lbs./cubic foot(pcf) of the PXTS Blend D formulation ranged from 20.0 to 20.8 and the average retention (pcf) of the active ingredient ranged from 11.1 to 11.6 per cube set. The target retention was 20 pounds per cubic foot (pcf) which provided 11.14 pcf of the active ingredient, the highest retention to be used in commercial applications.

2a. In freshwater leachates, all negative control samples except one had measured PXTS concentration less than the LOQ. The negative control from the final time point (313 hr) had a residual PXTS concentration that was confirmed by re-extraction of the original submitted sample. The measured concentrations for the treated samples generally deceased with time after reaching an average maximum at 24 hours. The 6-hour sample had an average measured PXTS concentration 0.467 mg/L, increasing to an average measured value 0.650 mg/L at 24 hours, and thereafter decreasing to an average measured value of 0.129 mg/L at 313 hours.

2b. In marine water leachates, all negative control samples had measured PXTS concentrations less than the LOQ. The measured concentrations for the treated samples generally decreased with time after reaching an average maximum at 24 hours. The 6-hour sample had an average measured PXTS concentration 0.888 mg/L, increasing to an average measured value 1.74 mg/L at 24 hours, and thereafter decreasing to an average measured value of 0.927 mg/L at 336 hours.

3. For freshwater, a total of 0.012 percent of the active ingredient in the treated wood leached during the 14-day period. For saltwater, a total of 0.044 percent of the active ingredient in

treated wood leached during the study period.

Recommendations:

The registrant must submit the following information **before** RASSB concludes that the leaching study is adequate to support registration.

A more detailed description of the analytical method and statistical analyses must be submitted. Method recoveries, sample stability, and storage stability data were not provided. A method validation study was not conducted. These information must be submitted to the Agency.

WOOD PRESERVATIVE LEACHING STUDY
DATA EVALUATION REPORT

PRODUCT FORMULATION: PXTS Blend D
ACTIVE INGREDIENT: Polyxylenol Tetrasulfide

BACKGROUND: This study was submitted to determine the leach rates of the active ingredient from polyxylenol tetrasulfide-treated wood. The study was conducted according to the American Wood Preservers' Association Standard E11-97.

MRID# 4760626-25

This MRID# provides information on the retention of polyxylenol tetrasulfide in wood.

CITATION:

Author:	Darrel Nicholas, Ph.D
Title:	Determination of the Leachability of the Wood Preservative PXTS in Freshwater and Saltwater
Study Initiation Date:	December 18, 2002
Study Completion Date:	May 21, 2003
Laboratory:	Mississippi State University Forest Products Laboratory P.O. Box 9820 Mississippi State, MS 39762-9820
Sponsor:	Akzo Nobel Functional Chemicals LLC 5555 Spalding Drive, Suite 100 Norcross, Georgia 30092
Laboratory Report ID:	497C-159 (MRID 460626-26, the associated laboratory study)

OPPTS GUIDELINE: NONE

EXECUTIVE SUMMARY:

The leachability of PXTS was studied using AWPA Standard E11-97. A proposed use of the new wood preservative, PXTS, is the pressure treatment of lumber for use in marine applications (fresh water and saltwater). This study was designed to determine the amount of PXTS that leaches from the treated wood into the water where the wood is submerged, over a period of fourteen days. Since PXTS has very low water solubility, AWPA Standard E11-97 was modified as necessary so that the leachability of PXTS could be accurately determined. Cubes of wood, cut from a common board, were equilibrated to achieve a specified humidity, then impregnated with PXTS, and subsequently submerged in water for fourteen days. The water, stirred constantly, was sampled 6, 24, and 48 hours and then at 48 hours increments over the 14 day study period. The samples were then analyzed for the presence and amount of PXTS in water using HPLC/UV. The wood used in this leaching study was Southern Pine sapwood that was free of knots, visible resin, mold, stain, or wood-destroying fungi. The wood had between 2.5 and 4 rings per 10 mm (6 to 10 rings per inch) and contained between 40 and 50 percent summer wood.

The mean retention (pcf) of the PXTS Blend D formulation ranged from 20.0 to 20.8 and the mean retention (pcf) of the active ingredient ranged from 11.1 to 11.6 per cube set. The target retention was 20 pounds per cubic foot (pcf) which provided 11.1 pcf of the active ingredient, the highest retention to be used in commercial applications.

This study was not conducted according to an EPA guideline. It was conducted according to AWPA Standard E11-97, and does satisfy the criteria for that Standard. It was also not conducted in compliance with the Good Laboratory Practice Standards as published in 40CFR 160. The authors noted that the test substance used in the study was characterized in a GLP compliant study.

I. MATERIALS AND METHODS

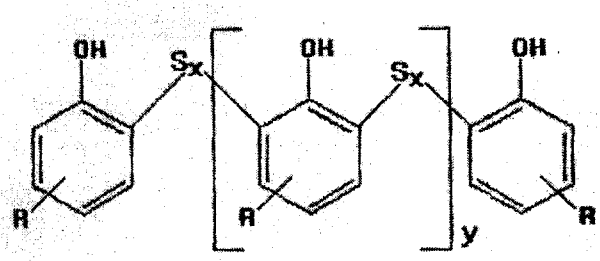
GUIDELINE FOLLOWED: Standard Method of Determining the Leachability of Wood Preservatives - AWPA E11-97.

COMPLIANCE: This study was not conducted in compliance with GLP standards (Title 40 CFR, Part 160). The test substance used in this study was characterized in the GLP-Compliant Study, MRID 460626-26.

A. MATERIALS:

1) Test Material PXTS Blend D

Chemical Structure:



CAS No: Pending

Description: The test substance, formulated as PXTS Blend D is a dark solid supplied by Akzo Nobel (Batch #16825-23). (MRID 46026-26)

Purity: 100% (MRID 46026-26)

Other Ingredients: [redacted] Inorganic Sulfur

Active Ingredient: **55.7%**

Storage conditions of test chemicals: The test substance, formulated PXTS Blend D, was supplied in a tightly sealed container, and stored at ambient conditions during the study.

Physical-chemical properties of PXTS:

Parameter	Values	Comments
Water solubility	12.5 µg/L	None
Vapour pressure	NR	None
UV absorption	NR	None
pK_a	NR	None
K_{ow}	NR	None
Stability of compound at room temperature	NR	None

* A certificate of analysis was provided in Appendix 2 of the Determination of PXTS Residue in Leachate Samples, MRID 460626-26. NR= not reported.

B. STUDY DESIGN:

1. Preliminary study:

A preliminary study was not conducted.

2. Experimental and analytical conditions:

The wood used in this leaching study was Southern Pine sapwood that was free of knots, visible resin, mold, stain, or wood-destroying fungi. The wood consisted of 2.5 to 4 rings per 10 mm (6 to 10 rings per inch) and contained between 40 and 50 percent summer wood. Cubes (19mm ± 0.2 mm) were cut from a common board and the volume (determined by a caliper) of each cube was 6.9 ± 0.2 ml. The cubes were in a constant humidity room controlled at 23 ± 3°C and 66 ± 2% relative humidity resulting in wood equilibrium moisture content of approximately 12%. The authors noted that the increase in moisture content from the AWPA Standard moisture content of 10% to the 12% used in this study had no impact on the leachability of PXTS.

The wood was impregnated with formulated PXTS (PXTS-D) to a target retention of 20 pounds per cubic foot (pcf), which provides 11.1 pcf of the active ingredient (the highest retention to be used in commercial applications). To achieve full penetration of preservative at this retention, pressure treatment was employed, using a sequence of steps that simulate a commercial treatment cycle. These steps are as follows:

1. Six cubes were selected and each weighed to the nearest 0.01 g (recorded at T1). The cubes were placed in a container and weight added to each cube to assure complete submersion and prevent floating during treatment.
2. PXTS formulation was heated to 120°C and then poured into the container where the cubes were fully submerged throughout the process. The amount of the formulation added to the container was measured and recorded.
3. The container with the wood cubes was placed into a treatment cylinder and heated to 120°C (applied with air, to 125 psig). The pressure was held for 30 minutes and released slowly until atmospheric pressure was achieved and the remaining formulation drained from the cylinder. The cylinder with the wood cubes remained at 120°C for an additional 30 minutes.
4. Following treatment, each cube was removed from the cylinder, surface formulation, and was then weighed to the nearest 0.01 g. After the cubes were impregnated with PXTS formulation D and weighed, they were place in a constant humidity room maintained at 23 ± 3 °C and 66 ± 2% relative humidity.

The retention of each cube was calculated using the following formula:

$$\text{Retention, pcf} = \frac{GC}{100V}$$

Where : G = T2 - T1, the weight of the formulation absorbed by the cube of wood
C = Grams of preservative in 100 grams of formulation
V = Volume of the cube in cubic centimetres

Three sets of six treated cubes (18 treated cubes total) and a set of untreated cubes were used to determine leaching of PXTS in freshwater. Three set cubes were impregnated with deionized water and another three sets of cubes were impregnated with saltwater using a vacuum/soak procedure. The container with the cubes were placed in pressure chamber, vacuum of 25 inches Hg was applied for 30 minutes. Then about 300 ml of deionized water was added to the freshwater cubes and 300 ml of saltwater to the for saltwater cubes. After introducing the leachate, the vacuum was held for an additional 30 minutes, slowly released until atmospheric pressure was attained and then soaked in the appropriate water for 2 hours to assure complete impregnation.

After water impregnation, six treated cubes were placed in each 500 ml flasks with the residual impregnating water, and the volume was brought to 300 ml with either deionized water or saltwater and stirred using a magnetic bar. The temperature was maintained at 23 ± 0.5°C in a constant temperature bath for the duration of the study. The leachate was removed and replaced with either freshwater of saltwater after 6, 24 and 48 hours, and at 48 hour increments through day 14. PXTS and any leaching wood components were extracted from the leachates and quantitatively analyzed using the HPLC/UV method. The leachates from the untreated wood were used to analyze for soluble wood components that might interfere with the baseline, or with the quantification of PXTS by having a column retention time identical to PXTS.

II. RESULTS AND DISCUSSION

Retention rates were calculated for each cube and average rates were derived for each cube set. The average retention results are shown in Table 1. Retention per cube and per set were also calculated in milligrams. Total retention (mg) and total active ingredient (mg) per cube set is shown in Table 2.

Table 1. Average Retention Rates

Set Number	Avg. Retention of Blend, pcf	Avg. Retention of A.I., pcf
1	20.5	11.4
2	20.5	11.4
3	20.8	11.6
4	Untreated Control	Untreated Control
5	20.0	11.1
6	20.2	11.3
7	20.2	11.3
8	Untreated Control	Untreated Control

Table 2. Sample Set Retentions

Set Number	Total Retention (mg)	Total Active Ingredient (mg)
1	13750	7658.75
2	13940	7764.58
3	14090	7848.13
4	Untreated control	Untreated control
5	13380	7452.66
6	13620	7586.34
7	13580	7564.06
8	Untreated control	Untreated control

Residue values in the accompanying report, MRID# 460626-26, were reported and interpreted as the percentage of PXTS leached from treated wood. For freshwater, a total of 0.012 percent of the active ingredient in the treated wood leached during the 14-day period. For saltwater, a total of 0.044 percent of the active ingredient in treated wood leached during the study period.

MRID#460626-26:

This MRID# provides information on the leach rate of polyxylenol tetrasulfide from treated wood and the analytical method used in the analyses.

CITATION:

Authors:	Frank Lezotte, Raymond L. Van Hoven and Willard B. Nixon
Title:	Determination of PXTS Residues in Leachate Samples
Study Completion Date:	May 14, 2003
Laboratory:	Wildlife International, Ltd. 8598 Commerce Drive Easton, Maryland 21601
Sponsor:	Akzo Nobel Functional Chemicals LLC 5 Livingstone Avenue Dobbs Ferry, New York 10522
Laboratory Report ID:	497C-159

EXECUTIVE SUMMARY:

This study was conducted to determine PXTS residue levels in leachate freshwater and

saltwater samples. Leachate samples were extracted and analyzed for PXTS by reverse phase, gradient elution using HPLC with UV detection. The measured concentration time intervals (hours) were 6, 24, 48, 96, 144, 192, 240, 288, and 313. In freshwater leachates, all submitted control samples except one had measured PXTS concentrations less than the LOQ (0.0625 mg PXTS/L). One control value from the final time point (313 hr) had a residual PXTS concentration value of 0.119 mg PXTS/L that was confirmed by re-extraction of the original submitted sample. The measured concentration for the treated samples generally decreased with time after reaching an average maximum at 24 hours. The 6-hour sample had an average measured PXTS concentration 0.467 mg/L, increasing to an average measured value of 0.650 mg/L at 24 hours, and thereafter decreasing to an average measured value of 0.129 mg/L at 313 hours.

In marine water leachates, all submitted negative control samples had measured PXTS concentrations less than the LOQ(<0.0625) mg PXTS/L. The measured concentrations for the treated samples generally decreased with time after reaching a mean maximum at 24 hours. The 6-hour sample had a mean measure PXTS concentration 0.888 mg/L, increasing to a mean measured value 1.74 mg/L at 24 hours, and thereafter decreasing to a mean measured value of 0.927 mg/L at 336 hours.

Measured concentrations of PXTS in these leachate waters were significantly above water solubility (<12.5 µg/L). These findings were attributed to presence of a soluble organic component(s), apparently derived from the wood, which acted as a carrier solvent that retained PXTS in the leachate samples at the measured elevated levels.

Study Acceptability: This study was not conducted according to EPA guideline requirements. It was conducted according to a Sponsor approved protocol. The study followed the reporting format set forth in the Protocol, however the Protocol did not provide a detailed study Methodology. All phases of this study were conducted in compliance with GLP standards (Title 40 CFR, Part 160).

I. MATERIALS AND METHODS

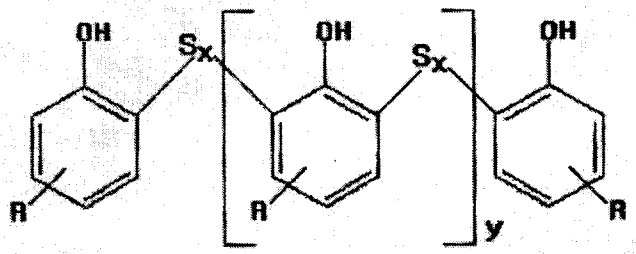
GUIDELINE FOLLOWED: The study was conducted according to Protocol entitled "Determination PXTS Residues in Leachate Samples". The Protocol was approved and signed Ralph Freudenthal (Sponsor's Representative), Frank Lezotte (Study Director) and Willard Nixon (Laboratory Manager).

COMPLIANCE: All phases of this study were conducted in compliance with GLP standards (Title 40 CFR, Part 160).

A. MATERIALS:

1) Test Material PXTS

Chemical Structure:



Description: PXTS is a dark solid supplied by Akzo Nobel (Batch #1685-23)

Purity: 100% (Expiration date March 28, 2005)

Storage conditions of test chemicals: The test substance was received from Akzo Nobel on April 1, 2002. It was assigned Wildlife International Ltd. identification number 5942 upon receipt and was stored under ambient conditions.

B. STUDY DESIGN:

1. Preliminary study:

A preliminary study was not conducted.

2. Materials and Method:

The reference substance was received from Akzo Nobel on April 1, 2002. It was assigned Wildlife International, Ltd. identification number 5942 upon receipt and was stored under ambient conditions. The test substance, a dark solid, was identified as PXTS; code number 1685-25-2; batch number 1685-23. The test substance had a reported purity of 100% (Appendix 2 of the Study Report) and an expiration date of March 28, 2005. A stock solution of PXTS was prepared by accurately weighing 0.100 g of the test substance on an analytical balance. The test substance was transferred to 100-mL class A volumetric flask, and brought to volume using acetone. The primary stock solution contained 1.00 mg/mL of PXTS. Aliquots of the 1.00 mg/mL stock solution were transferred to 100-mL Class A volumetric flask, evaporated to dryness under a gentle stream of nitrogen and used to prepare calibration standards in 80% methanol: 20% NANOpure® water. All leachate samples received were stored under ambient conditions until extracted and analyzed. Each sample was labelled with a unique identifier, the date of collection and length of exposure to PXTS treated wood samples.

The analytical method consisted of extracting the submitted samples and analyzing by reverse phase, gradient elution using HPLC with UV detection and ultracentrifuged. An aliquot of the supernatant from each sample was extracted with ethyl acetate, evaporated to dryness, reconstituted with ethyl acetate and transferred to a separate centrifuge tube. The ethyl acetate,

extracts were then evaporated to dryness, reconstituted with 1.00 milliliter of methanol and loaded onto C_{18} preparatory columns. The initial 1-mL volume and an additional 2 mL aliquot of methanol loaded onto each column were eluted and discarded. A 5-mL aliquot of methanol was then loaded onto each column, eluted and further processed for PXTS determination. For negative control and low-level residues, the extract was evaporated under nitrogen to 2.00 milliliters. For all samples, an appropriate volume was removed and replaced with an equal volume of reagent water to produce a final solvent concentration ratio of 80% methanol: 20% water. These samples were used for HPLC/UV analysis.

Five calibration standards of PXTS in 80% Methanol: 20% NANOpure® water, ranging in concentration for 1.00 to 10.0 mg/L, were analyzed with each sample set. The calibration set was injected at the beginning and end of each analytical sequence (except one) with one calibration standard injected after every five study samples. Linear regression equations were generated using the maximum peak height response for each standard within a preset retention time window versus the respective concentrations of the calibration standards. The concentration of PXTS in the samples was determined by substituting the peak height response into the applicable linear regression equation. The limit of quantitation (LOQ) for the leachate sample analyses (0.0625 mg PXTS/L) was calculated as the product of the low-level calibration standard (1.00 mg PXTS/L) and the dilution factor of the negative control leachate samples (0.0625).

Sample analysis was conducted using the Hewlett-Packard Model 1090 HPLC system with variable wavelength UV detection under the following conditions:

Instrument:	Hewlett-Packard Model 1090 High Performance Liquid Chromatograph (HPLC) with a Hewlett-Packard HP 1100 Variable Wavelength Detector (VWD)
Analytical Column:	Vydac 214TP Column (50 mm x 4.6 mm, 5-µm particle size)
Guard Column:	Supelco Supelguard LC-304 Column (20mm)
Stop Time:	20.00 minutes
Flow Rate:	1.000 mL/minute
Oven Temperature:	40.0°C
Mobile Phase:	Solvent A: 40:60 Acetonitrile: NANOpure® Water Solvent B: 95:5 Acetonitrile: NANOpure® Water
Injection Volume:	150 µL
PXTS Peak Retention Time:	~11.0 minutes
Primary Analytical Wavelength:	250 nm

II. RESULTS AND DISCUSSION

Table 1 presents the average measured concentrations for all samples.

Table 1. Mean Measured Concentrations by Time Interval

Time Interval (hours)	Measured PXTS (mg/L) avg. ± SD	
	Freshwater	Saltwater
6	0467 ± 0.075	0.888 ± 0.0979
24	0.650 ± 0.144	1.74 ± 0.523
48	0.513 ± 0.161	1.35 ± 0.309
96	0.381 ± 0.073	1.54 ± 0.218
144	0.369 ± 0.148	1.53 ± 0.036
192	0.304 ± 0.035	1.04 ± 0.270
240	0.113 ± 0.0314	1.08 ± 0.134
288	0.0894 ± 0.0104	1.00 ± 0.215
313	0.129 ± 0.024	0.927 ± 0.224

In freshwater leachates, all negative control samples except one had measured PXTS concentration less than the LOQ. The negative control from the final time point (313 hr) had a residual PXTS concentration that was confirmed by re-extraction of the original submitted sample. The measured concentrations for the treated samples generally deceased with time after reaching a average maximum at 24 hours. The 6-hour sample had an average measured PXTS concentration of 0.467 mg/L, increasing to an average measured value of 0.650 mg/L at 24 hours, and thereafter decreasing to an average measured value of 0.129 mg/L at 313 hours.

In marine water leachates, all negative control samples had measured PXTS concentrations less than the LOQ. The measured concentrations for the treated samples generally decreased with time after reaching an average maximum at 24 hours. The 6-hour sample had an average measured PXTS concentration of 0.888 mg/L, increasing to an average measured value 1.74 mg/L at 24 hours, and thereafter decreasing to an average measured value of 0.929 mg/L at 336 hours.

The leachate samples in freshwater and marine water matrices contained a significant amount of a soluble organic component(s); apparently derived from the wood used in this study. This component is evident in the first five minutes of each sample chromatogram. PXTS appears to be significantly more soluble in this organic components(s). The organic component(s) apparently acted as a vehicle or carrier, and as such, retained PXTS in the water samples at levels that far exceed its water solubility limit (<12.5 µg/L(1)). Whether acting as a carrier solvent or a binding agent, the organic components(s) was apparently irreversibly associated with PXTS and could not be removed without a corresponding loss of PXTS. Therefore, the PXTS concentrations in the leachate samples are the levels determined in the presence of the organic components(s)".

A final conclusion on the validity of the data submitted and discussed data is reserved until the

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analytical data requested below under "Comments" is submitted **and** the submitted data satisfactorily respond to the data request.

III. COMMENTS:

The study was conducted according to a Sponsor approved Protocol that was attached to the Study Report.

A more detailed description of the analytical method and statistical analyses must be submitted. Method recoveries, sample stability, and storage stability were not provided. A method validation study was not conducted. These information must be submitted to the Agency. These information are needed **before** RASSB can conclude that the leaching study is adequate to support registration.