USE OF SINESTO B AS ANTISAPSTAIN CHEMICAL

by

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Chlorophenoxides have been the most preferred antisapstain chemicals up to date. Nowadays there is an impending risk that their registration may be cancelled in many countries. Also the sawn timber treated with these products will be refused as time goes on. More and more customers will want a more harmless but, however, cost-effective antistain chemical. Some countries (Sweden, Indonesia, and Spain) have already banned NaPCP.

Kymmene Corporation, a former producer of chlorophenoxides, has faced these facts and the decision to develop an alternative chemical was made some years ago. The result of this development work was Sinesto B.

SINESTO B

Sinesto B is an alkaline water solution that contains several salts, a quaternary ammonium chloride, the Na-salt of a branched short-chain fatty acid, borax and NaOH. The total solids content of the product is about 47.5 %. The content of the quaternary ammonium salt is 14 %.

Sinesto B is normally used from the beginning of March or April until December depending on the weather conditions. During the winter months only some big sawmills equipped with the spray system use chemical treatment. The concentration of the dipping solution is normally 5 %, in spraying solutions 8 % is being used.
8 - 12 g SINESTO B/m² is needed for good protection. As far as we know, the users have been happy with the product. No complaints have been made. That is to say, no special problems concerning the efficacy as well as problems in the [illegible] or in the occupational area have turned up.

SALES OF SINESTO B IN FINLAND AND IN SOME EUROPEAN COUNTRIES

Finland	The production of Sinesto B was started year 1984. Since that time sales have almost doubled year by year in Finland. Now we have more than 70 % market share.
Other countries	Sales to other countries have been rather limited. We have preferred to have more experience in the home market at first. We have exported Sinesto B to Spain during the last two years. Smaller amount have been exported to Holland and Sweden.

THE SIZE AND MATERIAL OF CONTAINERS IN WHICH SINESTO B IS MARKETED .

Finland	Stainless steel containers	á 1000 kg
	Plastic (polyethylene) cans	á 25 kg
	Road tankers, volume	13.5 m^3
Other countries	One-way containers on pallets	á 1000 kg

The material is polyethylene which has been reinforced by sheet metal.

REGISTRATION OF SINESTO B IN EUROPEAN COUNTRIES

Country	Date	Registration Number
Finland	11.04.84	6628/567/83
Sweden	10.11.86	3697
Spain	25.06.87 19.01.88*)	17838/89 37.4098/Cat-1148
Holland (temporary permit)	21.11.86	9553 N

*) The registration for use in timber in contact with food.

In Finland Sinesto B has been registered as an antisapstain chemical for sawn wood without any restrictions of use. It can also be used in interior constructions without any other protective covering because it does not evaporate from the wood surface or give off noxious gases. For the same reason, Sinesto B is safe to use for the protection of pallets and crates against sapstain and mould fungi.

In Finland there is actually no special legislation concerning protective treatment of packaging materials in contact with food. However, chemicals classified in the 1st toxicity or poison class or as toxic chemicals according to EEC directives are not allowed for use in food packages. Chlorophehoxides belong to that group. The chemicals giving off bad odour or taste or colour to the food are also banned.

Sinesto B is classified in the 2nd toxicity class or as harmful if swallowed due to its oral toxicity value of 1500 mg/kg. Sinesto B is not harmful in contact with skin because its acute dermal toxicity (LD 50; rat) is over 2000 mg/kg. However, Sinesto B is irritating to the skin allthough it had as such no sensitizing effect in the Magnusson-Kligman test on guinea-pigs. It is not harmful by inhalation either, because it does not contain volatile components. The components of Sinesto are not mutagenic.

The toxicological hazards when using Sinesto B seem to be quite small. Therefore the users of Sinesto B as well as the users of pallets or crates treated by Sinesto B can feel safe from the toxicological point of view provided that the normal safety precautions are taken.

EFFICACY OF SINESTO B

The efficacy of Sinesto B has been tested in Finland, Sweden, West Germany, Spain, Portugal, Chile, Canada, USA, Australia (Queensland), New Zealand and Indonesia. The tests have been

- miniboard tests in the laboratory
- field tests at the sawmills

The results have generally been very good or acceptable depending on the concentration of the dipping solution, the length of the storage period and the wheather conditions.

In our laboratory, the tests were made according to the NWPC standard 1.4.1.3/79. The test pieces, so-called miniboards were 10 x 50 x 300 mm wood pieces made of the green sapwood of pine.

The other half of the miniboards was dipped in Sinesto B of 5 - 6.25 - 7.5 % concentration and left to dry. They were then inoculated with spores of the test fungi. After 3 weeks incubation period in 23°C and 100 % humidity they were visually rated for sapstain and mould growth.

The test fungi are listed in the transparence as follows:

Sapstain fungi	Moulds
Aureobasidium pullulans	Aspergillus amstelodam
Ceratocystis pilifera	Penicillum Sp.
Sclerophoma entoxylina	Cladosporium sphaero-spermum

The fungi had been received as pure cultures from the Technical Research Centre of Finland's Wood Products Laboratory.

For comparison, some tests were also made using miniboards cut at Halla sawmill from wood felled in winter and stored for 6 - 8 months a) on the ground b) in water.

Results and their evaluation

The results of the miniboard tests are presented in Table 1 A - 1 B.

Table 1 A

RESULTS OF THE MINIBOARD TESTS MADE IN THE RESEARCH LABORATORY OF KYMMENE CORPORATION

Test No (30 Aug.- 20 Sept. 1983	Protective Substance	Dipping Solution			Sapstain Score		Mould Score		
		Concent. %	pH	Added borax %	Halla timber	Fresh(green) miniboards	Halla timber	Fresh(green) miniboards	Mean of all mould scores
					mean $\bar{x}_5$	mean $\bar{x}_5$	mean $\bar{x}_5$	mean $\bar{x}_5$	
1	Ky 5	1.5 (Mixture of Chlorophenoxides)	12.00	-	0.4	1.8	0.2	1.3	0.75
2	Product X	1.0 (W/W)	5.10	-	0	0.8	2.4	2.0	2.20
3	"	2.0 "	4.90	-	0	0	0.7	1.6	1.15
4	Sinesto B Lot.32	7.50 "	12.15	-	0	0	0.1	0.8	0.45
5	"	6.25 "	12.10	-	0	0	0.2	2.1	1.15
6	"	5.00 "	12.00	-	0	0	0.8	1.3	1.05
7	"	7.50 "	10.05	1	0	0	0.2	0.3	0.25
8	"	6.25 "	9.95	1	0	0	0.3	2.4	1.35
9	"	5.00 "	9.90	1	0	0	0.7	2.5	1.60
10	Sinesto B Lot.11	6.25 "	11.45	-	0	0	0.7	1.0	0.85
11	"	6.25 "	9.45	1	0	0	0.1	1.3	0.70

Grading P ints: 0: no fungus growth
1: traces of fungus growth (a few fungus spots)
2: some fungus growth (less than 10 % of board's surface)
3: considerable fungus growth (10 - 50 % of board's surface)
4: heavy fungus growth (50 - 100 % of board's surface)

Table 1 B

T[illegible] RESULTS OF THE MINIBOARD TESTS: THE AVERAGE SCORE OF FUNGAL DETERIORATION **)

P[illegible]tective ch[illegible]mical	Additional chemicals %	Concentration in dipping %	pH	Water-stored wood			Green wood		
				Stain	Moulds		Stain	Moulds	
				average **)	average	average **)	average **)	average	average **)
Si[illegible]esto*)		6.25	7.5	0	0.2	0	0	0	0
Si[illegible]esto*)	0.72 NaOH	"	12.3	0	0.4	0	0	0	0
Qu[illegible]t. amm. salt Q	-	"	7.5	0	0.8	0.4	0.6	0.6	0.4
2-[illegible]HA/Na	-	"	7.5	1.8	0.4	0.8	4	0	1.4
NaCl	-	"	7.5	4	4	4	4	4	4

*) Sinesto: According to Finnish patent application, containing trimethylalkylammonium chloride, Q 36 % and 64 % of the Na-salt of 2-ethylhexanoic acid (2-EHA/Na)

**) Inoculated according to NWPC 1.4.1.3./79

From the results it can be seen that in respect of sapstain fungi, the acceptable degree of protection as laid down by the standard (less than 1 grading point), was achieved with all SINESTO solutions, regardless of which timber was used. The 1.5 % "Ky" and the 1 % Product X solutions did not give results considered to be acceptable. In the moulding tests with Halla timber, all the solutions gave good protection with the exception of Product X at 1 %. When using fresh timber, only the 7.5 % SINESTO B gave an acceptable result in accordance with the standard, and that was boosted by the addition of 1 % borax in the treating solution. The second best result was with basic SINESTO at 6.25 % and "Ky 5" at 1.5 %. Product X at 2 % proved to be the next most efficient.

From the results it can be observed that the type of timber chosen for use in the tests has a strong effect on the results as well as the quality of fungal infections. Water-stored wood seems to be more infected by moulds inherent in the wood than green wood. It is possible that using green wood and fungal inoculation as in the NWPC-test, the relative efficiency of different products compared with one another is accentuated. However, results corresponding more realistically to practical circumstances are only achieved when stored timber is used.

Field tests have been made in Finland and in Sweden, Canada, USA, Chile, Queensland and Portugal.

In tables 2 - 3 test results obtained at two swedish sawmills are presented. The tests were conducted in co-operation with the University of Uppsala. In these tests 1) spruce boards in open

Table 2

FIELD TRIAL OF SINESTO B FOR ITS ABILITY TO PREVENT SAPSTAIN AND MOLD OF UNSEASONED TIMBER I

Test No	Treatment concentration %	Package	Wood Species	Time (weeks)	The mean-% and number of boards in different quality classes				Total amount of boards
					U/S A(clean)	B(weakly infected)	V	VI	
1	5	Open stacked	Spruce	5	92.0	8.0	-	-	
				23	97.3 (178)	2.7 (5)	-	-	(183)
2	5	Open stacked	Spruce	23	89.1 (197)	9.5 (21)	1.4 (3)		(221)
3	Untreated	Open stacked	Spruce	5	45.0	14.0	41.0	-	
				23	12.0 (25)	10.6 (22)	73.1 (152)	4.3 (9)	(208)

Höör sawmill in Sweden 30.10.84 - 22.04.85

Table 3

FIELD TRIAL OF SINESTO B FOR ITS ABILITY TO PREVENT SAPSTAIN AND MOLD OF UNSEASONED TIMBER II

Test No	Treatment concentration %	Package	Wood Species	Time (weeks)	The mean-% and number of boards in different quality classes				Total amount of boards
					U/S A(clean)	B(weakly infected)	V	VI	
1	5	Stickers in alternate layers	Scots*) pine	15	37.9 (53)	13.6 (19)	39.3 1) (55)	9.3 1) (13)	(140)
2	5	Stickers in alternate layers	Scots**) pine*)	15	84.7 (549)	12.0 (87)	3.2 2) (21)	- 2)	(657)
3	Untreated	Stickers in alternate layers	Scots pine	15	6.5 (29)	27.5 (123)	65.6 (293)	0.2 (1)	(446)

*) Contained internal sapstain

**) Stored in water for an extended period of time.

1) Fungal growth occured at two opposite surfaces

2) Generally mould growth

Trollwood sawmill in Sweden 30.12.84 - 21.04.85

packages (with stickers between the boards) or 2) water-stored pine sapwood in partly closed packages (there were stickers only in every second layer) were used. The results were quite good especially in cases when stickers were used and when the wood was not infected with internal stain.

A twelve-month field trial of SINESTO B was conducted by Forintek in Canada. 12 percent SINESTO B protected both hem-fir- and S-P-F-lumber. For comparison sodium tetrachlorophenoxide (NaTCP) was used. 2 percent was needed for good protection. At four month tests 6 percent SINESTO B was effective on both hem-fir and S-P-F-lumber (see the table 1 in Appendix).

RETENTION OF SINESTO B IN SAWN WOOD

1

Leaching

We have studied the leaching of Sinesto B in our own laboratory as follows:

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Testing methods and results

The wood material used was obtained from Halla sawmill. The timber had been felled in winter and seasoned in the open for 6 - 8 months.

Miniboards of 10 x 50 x 100 mm were dipped into a solution containing 6.25 % of Sinesto B active ingredients for 2 min and kept in open air for ≥ 1 hr, whereafter they were leached in water for 1 hr and 24 hrs. All tests were carried out on 30 miniboards. The quantity of water in leaching was 2 l. After the treatment the borax, 2-ethyl hexanoic acid and trimethylalkylammonium chloride contents of the solution were determined.

The results are presented in table 4.

Table 4 LEACHING OF SINESTO B

RETENTION OF QUATERNARY AMMONIUM SALT, BORAX AND 2-ETHYL HEXANOATE IN SAWN WOOD

Leaching period	Quaternary salt			
(h)	Impregnated into wood		Retained	
	mg	g/m²	mg	%
1	811	2.08	811	100
24	834	2.14	834	100
Leaching period	**Na-2-ethylhexanoate**			
(h)	Impregnated into wood		Retained	
	mg	g/m²	mg	%
1	1393	3.57	894	64.2
24	1518	3.89	547	36.0
Leaching period	**Borax**			
(h)	Impregnated into wood		Retained	
	mg	g/m²	mg	%
1	336	0,86	116	65,5
24	367	0,94	195	53,1

The fixation of the quaternary component was very good. The fixation was 100 % also when the dipping time was only 20 sec and the leaching period 5 hours. In this case 1.8 g/m² of the quaternary salt was absorbed.

When 5 % dipping solution was used then the fixed amount was ~ 1.2 g/m², that is to say, ~ 8.6 g Sinesto B/m². The penetration depth was only < 1 mm.

As for Na-2-ethylhexanoate component more studies were conducted as follows:

10 miniboards of 100 x 50 x 10 mm were dipped for 20 sec in 6.25 % (a.i.) solution of the antisapstain chemical and then dried at room temperature for

a) 1/2 h b) 24 hrs.

Thereafter the boards were leached in 400 ml of water for a) 15 min b) 30 min and c) 60 min. The 2-ethyl hexanoic acid content dissolved into the water was determined as follows: 200 ml of the sample was acidified with H_2SO_4 to the ph ≤ 2 and extracted using 4 x 75 ml of ether. The ether solution was evaporated to 50 ml and the 5 ml sample taken from it was methylated for gas chromatographic analysis. The results of the analysis are presented in Table 5 below.

Table 5

RESULTS OF THE LEACHING TESTS

Drying period (h)	Leaching period (min)	Absorption of protective substance (g)	Dissolved into water, % of absorbed 2-EHA
1/2 h	15	18.8	-
	30	18.2	-
	60	22.7	77.9
24 hrs	15	20.2	-
	60	27.0	14.8

Thus some Na salt of the 2-EHA is dissolved into water if leaching takes place immediately after dipping. In the long run the 2-EHA seems to become relatively well fixed into the wood.

Evaporation tests

Na-ethylhexanoate

Miniboards of 100 x 50 x 10 mm dipped into 6.25 % solution of the antisapstain chemical were kept for 10 h at 60°C in a closed round distillation flask, through which air was blown.

The evaporated gases were led into an 1-n NaOH solution, from which the dissolved 2-EHA was determined by extraction with ether in acid solution (pH 2). The extract was examined by gas chromatography.

The result obtained was = 0, i.e. no 2-EHA had evaporated from the wood. Through the action of wood acids, pH fell during evaporation to such an extent that the pH of the water condensed into the evaporation flask was 4.

The quaternary salt

Evaporation tests were not carried out as the compound concerned is not volatile.

Conclusions

The results indicate that

1) the fixation of the quaternary salt into sawn wood is nearly 100 %;

2) both Na-2-ethyl hexanoate and borax are to some extent leached during the water treatment, the quantity depending on the length of the leaching period. Based on this, it may be concluded that sawn wood treated with Sinesto B should be stored under cover to prevent rain water from dissolving the protective substances from it.

If the treated wood is left to dry under roof for some hours, the hexanoate component will not be easily leached out any more.

ENVIRONMENTAL ASPECTS

Even though this product is more harmless to the environment than many other protective chemicals it must not be let into the sewer, ground water or water courses. The same rules hold for the treatment solution.

1
Biodegradation and migration

11
Soil

The quaternary ammonium salt will be retained by soil and the soil microorganisms will bio-oxidize it in due time. 2-Ethyl hexanoate- and borate-ions can migrate in the soil. 2-Ethylhexanoic acid is however, also biodegradable. Therefore, the occasional spills of SINESTO B on the ground cannot presumably have any serious consequencies. The polluted land can be collected and composted separately.

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Water

SINESTO B and its components are biodegradable in small concentrations in the presence of acclimatized biomass. They are not enriched in the food chain. The acclimatization takes time anyhow. Therefore, sporadic discharges of wastewaters containing SINESTO B or its components must be avoided.

2
Ekotoxicology

The fish toxicity of SINESTO B and its components:

LC 50 (96)	mg/l	
SINESTO B	6,5	(Salmo gairdneri)
2-Ethylhexanoic acid	99,5	(Salmo gairdneri)
Alkyltrimethylammonium chloride (C_{12}-)	6,0	(Salmo salar)

The most toxic component of SINESTO B is the quaternary ammonium salt. 2-Ethyl hexanoic acid seems to be relatively well tolerated. Small concentrations of this chemical (some mg/l) can be found in the condensate waters of the kiln dryers but this hardly causes any harm for fishing.

APPENDIX

Table 1

Averaged Ratings* (Scale = 0 to 10) after 4 Months and 12 Months Storage for Moulds, Sapstain, Decay, and All Three of These Fungal Types.

Wood Species Group	Treatment	Concentration	Mould 4 (months)	Mould 12 (months)	Stain 4 (months)	Stain 12 (months)	Decay 4 (months)	Decay 12 (months)	All Three Fungal Types 4 (months)	All Three Fungal Types 12 (months)
Hem-fir	Control	-	1	1	4	6	0	3	5	7
	NaTCP	2.0%	1	1	0	0	0	0	1	1
	"	1.0%	1	1	0	1	0	0	1	2
	"	0.5%	1	0	0	2	0	0	1	2
	Sinesto	4.8%	0	0	0	2	0	0	1	2
	"	2.4%	1	0	0	2	0	0	1	3
	"	1.2%	1	2	1	4	0	0	2	4
S-P-F	Control	-	4	3	6	6	3	7	9	9
	NaTCP	2.0%	0	1	1	2	0	1	1	2
	"	1.0%	1	1	1	2	0	1	1	3
	"	0.5%	1	1	1	3	0	1	2	4
	Sinesto	4.8%	0	1	0	2	0	1	1	3
	"	2.4%	0	0	0	1	0	0	1	1
	"	1.2%	3	2	1	3	1	5	4	7

*Calculations are made from figures in Appendix I; the sums of the scores for fungal growth are divided by 400 (the theoretical maximum of 80 pieces) and multiplied by 10.