PRESERVING TALL OIL AND TURPENTINE IN STORED PINE CHIPS USING SODIUM N-METHYLDITHIOCARBAMATE

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ABSTRACT

Fresh slash pine chips were treated by immersion in 0.44-percent and 0.22-percent solutions of sodium N-methyldithiocarbamate and stored under aerobic conditions in 4-ft^3 insulated boxes. The high-level treatment (3.5 lb/ton ovendry wood) completely stopped chip heating and the growth of visible microorganisms during 62 days of storage. Untreated chips lost 66 percent tal1 oil and 78 percent turpentine during this storage; high-level treated chips lost only 8 percent tall oil and 21 percent turpentine. The low-level treatment (2.1 lb/ton ovendry wood) was somewhat less effective; the chips lost 19 percent till oil and 41 percent turpentine in 61 days of storage. Both high- and low-level treatments were effective in preserving the strength of pulp produced from the chips.

Keywords: Chip storage, sodium N-methyldithiocarbamate, tall oil, turpentine, Pinus elliottij temparature, kraft pulp, by-products

In a previous study, fresh slash pine ohips were treated by immersion in a 0.11-percent solution of sodium N-methyldithiocarbamate (treatment level 0.8 lb/ton ovendry wood) and stored under aerobic conditions in 4-ft^3 insulated borer (1). This treatment resulted in partial preservation of tall oil during a storage period of 40 days. The treated, stored chips showed traces of microbial growth at 10 days, started heating at 14 days, and were covered with fungal mycelia at the end of the 40-day storage period. Microbial metabolism was undoubtedly responsible for a large part of the tall oil loss. The level of chemical treatment was apparently too low to stop the growth of certain microorganisms. Living parenchyma cells of the chips were killed by the sodium — N-methyldithiocarbamate treatment and thus could not be responsible for the loss. Direct chemical oxidation may have caused a small fraction of the loss. Although this test was only partially successful, it suggested that some higher level treatment might completely stop microbial growth and thus preserve most of the tall oil present in stored pine chips.

In the present study, two higher level treatments were evaluated by treating fresh slash pine (Pinus elliottii) chips with solutions of sodium N-methyldithiocarbamate and storing them in 4-ft^3 insulated boxes for periods of up to 60 days. The chips were imerssd for 15 s in 0.22-percent and 0.44-percent solutions, giving treatment levels of 2.1 and 3.5 lb of chemical per ovendry ton of wood. Treatment levels were determined by analyzing dried, ground chips for sodium content as in previous studies (1,3). Eight insulated boxes were used; three were filled with untreated chips, two with chips immersed in the 0.44-percent solution, and three with chips immersed in the 0.22-percent solution. All the boxes could not be filled in a single day; therefore, the low-level treatment boxes were filled 1 day after the other boxes.

Fresh batches of chips were prepared each day from slash pine logs randomly selected from a single shipment sent to the USDA Forest Service, Forest Products Laboratory in Madison, Wisconsin, from Southwest Forest Industries, Cottondale, Florida. Less than 2 weeks elapsed between felling the logs and chipping. The time between felling and chipping was kept to a minimum to reduce losses of tall oil and turpentine prior to ship storage in the boxes.

The boxes containing the untreated chips and the low-level treated chips were emptied after about 20, 40, and 60 days of storage; those containing the high-level treated chips were emptied after about 20 and 60 days of storage. All experimental techniques employed in this work were identical with those used in previous studies (1,2,3). As in those studies. each box was aerated with 1.4 ft^3 of water-saturated air per day.

RESULTS AND DISCUSSION

Temperature During Storage

Increases in temperature provided an indication of the magnitude of tho degradative processes occurring in the chips. A copper-constantan thermocouple was placed at the center of each box to observe chip temperatures during storage. The observed center temperatures and the temperatures of the air surrounding the boxes and being fed into the boxes (ambient temperature) are plotted in Figure 1.

As in the previous study (hereafter called Study 1), the temperature profiles of the untreated chips varied greatly. The temperature of chips stored for 62 days (U-60) rose to 110°F after 14 days, whereas the temperature of chips stored for 41 days (U-40) attained a maximum of only 87°F throughout the storage period. This large temperature difference occurred in spite of efforts to thoroughly homogenize the initial batch of chips and to randomly sample it when filling the boxes. The temperature differences may have resulted from differences in the quantity and type of initial microorganisms on the chips or differences in the quantity of living parenchyma cells in the chips.

The treated chips showed very little or no heating during storage. High-level treated chips (3.5 lb/ton Ovendry wood) stayed essentially at ambient temperature for the 20-day (TH-20) and 62-day (TH-60)

[1] The Forest Products Laboratory is maintained in cooperation with the University of Wisconsin.

storage periods. Low-level treated chips (2.1 lb/ton ovendry wood) stored for 20 days (TL-20) stayed at ambient temperature; however, those stored for 40 (TL-40) and 61 days (TL-60) stayed at 2°F to 4°F above ambient temperature during most of the storage periods. Starting at about 50 days of storage, the low-level treated, 61-day chips exhibited a gradual increase in temperature. This was thought to indicate a growth of microorginisms in the box, and indeed when this box was opened at 61 days, the chips in the bottom one-third of the box were matted together with gray and white fungal mycelia. No visible microorganisms were present on the chips in the top two-thirds of the box.

Visible Microorganisms

At the end of storage, each box was examined for the presence of microorganisms on the chips that were visible to the naked eye. The results of these examinations are presented in Table 1. Data from Study 1 and two unpublished studies (Studies A and B) are also given. In Study 1, all stored boxes contained visible microorganisms. In the study reported here (hereafter called Study 2), the only treated chips that showed visible microorganisms at the end of storage were the low-level treated chips stored for 61 days. All other boxes containing treated chips were free of visible microorganisms at the end of storage. The untreated, stored chips were, of course, thoroughly covered with misroorganisms at the end of storage. The boxes were not sterilized prior to use.

The data from Studies A and B fit into the pattern of that from Studies 1 and 2. Study A low-level treatment data confirm the high-level treatment data of Study 2 in that an immersion in 0.40 percent sodium N-methyldithiocarbamate kept slash pine chips free of microorganisms for about 60 days. High-level treatment data of Study A and Study B show that immersion in an 0.80-percent solution will keep the chips microorganism-free for at least 90 days. As will be seen, great savings of by-products occur when the chips are kept near ambient temperature and free of visible microorganisms.

Tall Oil Preservation

Because of the previously observed lack of homogeneity in both content and composition of tall oil between intra- and extra-ship black liquor (1), comparative analyses of tall oil in the circulating black liquor were not used to evaluate the efficacy of the preservative treatments. Tall oil precursor content of the stored and unstored chips was determined by extracting chip samples with diethyl ether (4). A random sample of chips was taken from each box at the end of the storage period and frozen. It was then coarsely around, in the frozen state, in a Wiley[2] mill and extracted. Replicate determinations were made. The content of resin acids, fatty acids, and nonsaponifiables in the ether extracts was obtained by a combination of DEAE-Sephadex separation (5), saponification (4), and gas chromatography of the resin and fatty acids with a 15-m butanediolsuccinate glass capillary column at 190°C (6, 7). The total quantity and composition of the extractives of treated and untreated chips after various periods of storage are given in Table 2. Storage of untreated chips for 62 days resulted in the loss of 66 percent of the total tall oil precursors. The loss for the low-level treatment was 19 percent; that for the high-level treatment was 8 percent, even though the temperature did not rise and no microorganisms were visible on the chips.

The total tall oil precursor data, the resin acid data, and the total fatty acid component data is plotted in Figure 2. For the treated chips, the principal loss was that of fatty acids, although some loss of resin acids and nonsaponifiables (Table 2) also occurred. The difference between the initial data for the high- and low-level treatments is due to the previously mentioned use of two different initial batches of chips, one batch for the untreated and high-level treatment and another batch for the low-level treatment. These batches contained different quantities of tall oil precursors.

The effect of treatment and storage on the composition of the free and esterified fatty acids in the chips was similar to that of Study 1, except that the decrease in linoleic acid (18:2) content was more pronounced after 60 days. The effects on resin acid composition were also similar to those found in Study 1. Again, some chemical oxidation was evident in both the treated and untreated chips, even in the early stages of storage. This was shown by an increase in dehydroabietic acid content, arising from a concerted oxidation dehydration of levopimaric and, to a lesser extent, palustris acids. Oxidative losses were also shown by a decrease in neoabietic acid with concomitant relative increases in the more oxidatively stable pimaric, sandarcopimaric, and isopimaric acids. The treatment itself resulted in a small increase in dehydroabietic acid (also observed in Study 1 data) and the occurrence of a small amount of an unidentified acidic material (DEAE-Sephadex; r_{pm} = 1.10 on BDS (0.2 percent).

Turpentine Preservation

The turpentine contents of treated and untreated chip samples after various periods of storage are also shown in Table 2. Untreated chips stored for 62 days lost 78 percent of their initial turpentine content. The treated, stored chips lost a larger fraction of their turpentine content than of their tall oil content. Low-leve1 treated chips lost 41 percent of their turpentine in 61 days, and high-level treated chips lost 21 percent in 62 days. Patterns in compositional changes were essentially the same as in Study 1.

Figure 3 shows turpentine losses as a function of time. The data from Study 1 have been included on this plot. The initial difference is again due to using two separate batches of chips. Wood used in Study 1 contained much less turpentine than the batches used in Study 2. The reason for the apparent total preservation of turpentine in Study 1 is not known.

In Study 2, α-pinene and ß-pinene accounted for nearly 70 percent of the terpentine. After 20 days of storage for the untreated chips, α-pinene content

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showed a small decrease with increasing storage time. A significant decrease in ß–pinene was observed for all chip samples; this decrease was somewhat larger for the untreated chips. Another monoterpene with an exocyclic double bond, ß-phellanrene, showed a similar decrease. With the exception of α–terpineol, the initial turpentine contained no more than traces of oxygenated monoterpenes. Oxygenated monoterpenes did not increase during storage, indicating evaporation was the primary mechanism of loss.

Pulping and Pulp Strength

Storage of chips for prolonged periods can result in significant reductions in pulp yield and strength. To determine the effects of treatment and storage on pulp strength, samples of stored and unstored, treated and untreated chips were subjected to kraft pulping using tho following conditions:

Active alkali	18.0 percent
Sulfidity	25.0 percent
Liquor to wood	4:1
Time to 170°C	90 min
Time at 170°C	90 min

The pulps were thoroughly washed, and handsheets were made in accordance with TAPPI Method T–205. Strength and other physical tests were performed in accordance with TAPPI Method T-200.

The results from pulping and strength testing are given in Table 3. Even after 62 days of storage. untreated chips showed no significant decrease in pulp yield. For treated ships. no significant losses in pulp yield or pulp strength occurred before or during storage (a 1–percent yield difference is not significant). During storage, pulp made from the untreated chips showed small drops in tensile strength (5–10 percent) and bursting strength (6–9 percent). The most significant pulp strength redustion was in tearing strength. A 14 to 16–percent reduction was found after 62 days of storage. Both treatment, wars effective in preserving pulp strengths during storage. The slight reduction in tearing strength for the treated, stored chips at 300–ml Canadian Standard Freeness is probably not significant.

Comparison of Insulated Box and Pile Results

A comparison of tho center temperatures of the insulated boxes containing untreated chips (Fig. 1) with temperatures observed in outside piles of untreated Southern Pine chips indicates that the box conditions simulate conditions in the outer regions of piles. The inner regions of piles achieve considorably higher temperatures than the outer regions; therefore, it might be expected that higher by–product losses might occur in piles. Losses of tall oil and turpentine from the boxes in Study 1 and Study 2 are compared with pile losses in Figures 4 and 5. Pile data were reported in a previous publication (8). In Study 1, untreated chips in the boxes lost somewhat less tall oil and turpentine than pile chips. In Study 2, losses from untreated chips in the boxes were surprisingly almost identical with pile losses. The insulated boxes are apparently reasonably good simulators of outside piles, if one is primarily concerned with by–product losses.

Tall oil loss data from Study 1 are consistent with that of Study 2 (Figs. 4 and 5); increasing the treatment level resulted in a decrease of tall oil loss. Althongh no visible microorganisms were present in the boxes at the highest treatment level, some losses of tall oil still occurred. Direct chemical oxidations must be responsible for these losses. Turpentine loss data from Study 1 are not consistent with those from Study 2. If turpentine is lost mainly through evaporation, it seems reasonable to assume that some loss should have occurred from the treated chips in Study 1. Therefore, treated chip data from Study 1 are probably in error.

CONCLUSIONS

Dip treatment of fresh slash pine chips in a 0.22–percent solution of sodium N–methyldithiocarbamate (2.1 lb/ton ovendry wood) maintained the stored chips free of visible microorganisms for 40 days, prevented chip heating for 50 days, and preserved substantial quantities of tall oil and turpentine. After 61 days of storage, untreated chips lost 66 percent of their initial tall oil and 78 percent of their turpentine. The treated chips lost 19 percent tall oil and 41 percent turpentine.

Dip treatment in a 0.44–percent solution (3.5 lb/ton ovendry wood) maintained the chips free of visible microorganisms and completely stopped heating for 62 days. The treated chips lost only 8 percent tall oil and 21 percent turpentine after the 62–day storage period. Complete prevention of chip heating and complete inhibition of the growth of visible microorganisms did not completely prevent by–product losses. Some tall oil and turpentine constituents are lost through direct chemical oxidations occurring at ambient temperature, and some turpentine is lost by evaporation. Although complete by–product preservation by chemical treatment is not possible, this work shows that large savings can be achieved.

Sodinm N-methyldithiocarbamate is the most promising biocide found to date for preservation of by–products in stored softwood chips. The present data suggest that its use could be cost effective. This product has been registered with the U.S. Environmental Protection Agency for use on stored chips.

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Table 1: Treatment level to achieve microorganism-free storage of slash pine chips

	Sodium N-methyl-dithiocarbamate			
Study	Percent in solution	Ovendry wood (lb/ton)	Storage time (days)	visible microorganisms present at end of storage
1	0.11	0.8	10	Few
	0.11	0.8	20	Many
	0.11	0.8	40	Many
2	0.22	2.1	20	None
	0.22	2.1	40	None
	0.22	2.1	61	Many
2	0.44	3.5	20	None
	0.44	3.5	62	None
A	0.40	ND[a]	30	None
	0.40	ND	60	None
	0.40	ND	90	Many
A	0.80	ND	30	None
	0.80	ND	60	None
	0.80	ND	90	None
B	0.80	ND	30	None
	0.80	ND	60	None
	0.80	ND	90	None

[a]ND indicates not determined.

Table 2: Extractives content of untreated and treated chips

Storage time (days)	Ovendry extractive-free weight per green weight	Tall oil precursors (mg/g wood[a])						Total precursor loss (percent)	Turpentine per 100 g[b] (ml)	Turpentine loss (percent)
		Resin acids	Fatty acids			Nonsaponifiables	Total precursors			
			Free	Esters	Total					
					Untreated					
0	0.476	15.6	0.9	9.2	10.1	2.5	28.2	0	0.41	0
20	0.463	11.4	4.9	2.0	6.9	2.3	20.6	27	0.20	51
41	0.464	12.9	3.4	1.8	5.2	2.6	20.7	27	0.13	68
62	0.475	6.8	0.6	0.8	1.4	1.4	9.6	66	0.09	78
					Low-level treated (2.1 lb/ton ovendry wood)					
0	0.435	16.6	1.4	10.0	11.4	2.8	30.8	0	0.46	0
20	0.435	15.9	4.3	6.5	10.8	2.4	29.1	6	0.45	2
40	0.435	15.0	3.5	4.9	8.4	2.4	25.8	16	0.33	28
61	0.429	15.3	3.5	3.8	7.3	2.2	24.8	19	0.27	41
					High-level treated (3.5 lb/ton ovendry wood)					
0	0.456	14.2	0.9	8.8	9.7	2.6	26.5	0	0.38	0
20	0.435	13.7	3.0	6.4	9.4	2.3	25.4	4	0.33	13
62	0.440	14.2	3.1	5.1	8.2	2.1	24.5	8	0.30	21

[a]Ovendry and extractive-free wood.

[b]Ovendry wood.

Table 3: Yields and physical properties of kraft pulps produced from treated and untreated. stored and unstored slash pine chips

Storage time (days)	Yield (per-cent)	Kappa number	Brightness (percent)	Canadian standard freeness (ml)	Beating time (min)	Burst index	Tear index	Tensile index	Sheet density (kg/m^3)
				Untreated					
Unstored	46	38	18	500-300	41-56	7.8-8.1	13.4-13.4	111-113	629-650
41	46	33	20	500-300	36-51	7.7-8.2	13.0-13.1	106-102	630-638
62	46	35	19	500-300	38-51	7.3-7.4	11.2-11.5	104-105	630-650
				Low-level treated (2.1 lb/ton ovendry wood)					
Unstored	46	37	18	500-300	39-56	7.9-8.1	13.8-13.8	106-112	630-657
62	45	36	18	500-300	39-55	8.2-8.6	13.8-12.7	107-110	627-643
				High-level treated (3.5 lb/ton ovendry wood)					
40	46	38	18	500-300	35-51	8.2-8.3	13.1-12.6	110-113	652-665
61	45	37	17	500-300	40-51	8.6-8.6	13.8-12.8	109-110	643-655

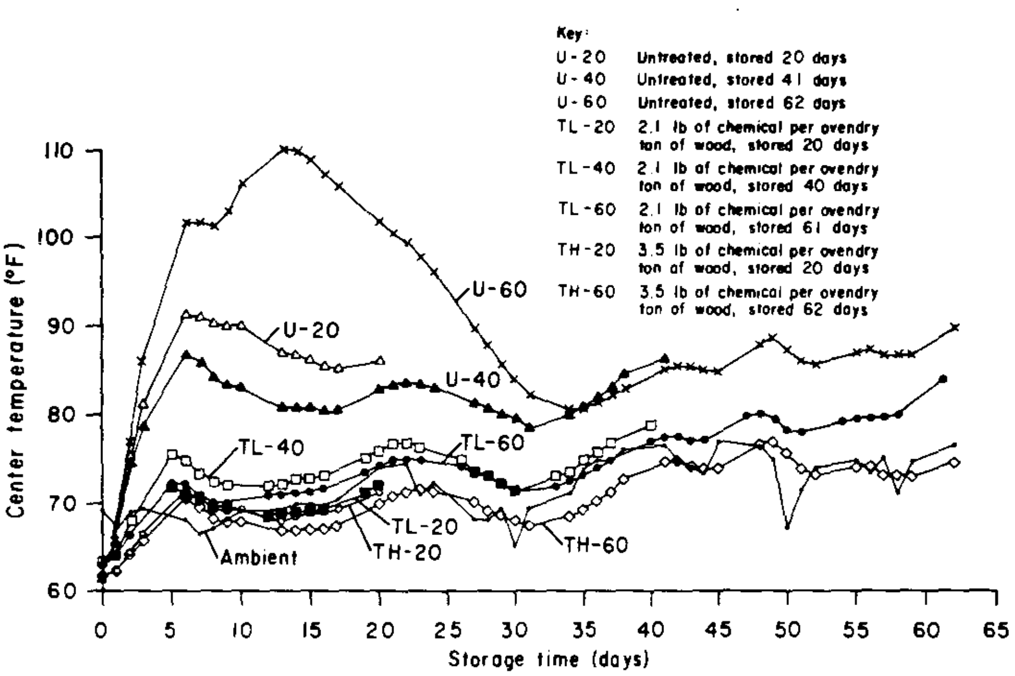

Figure 1. Center temperatures in insulated boxes containing treated and untreated slash pine chips. (ML89 5692)

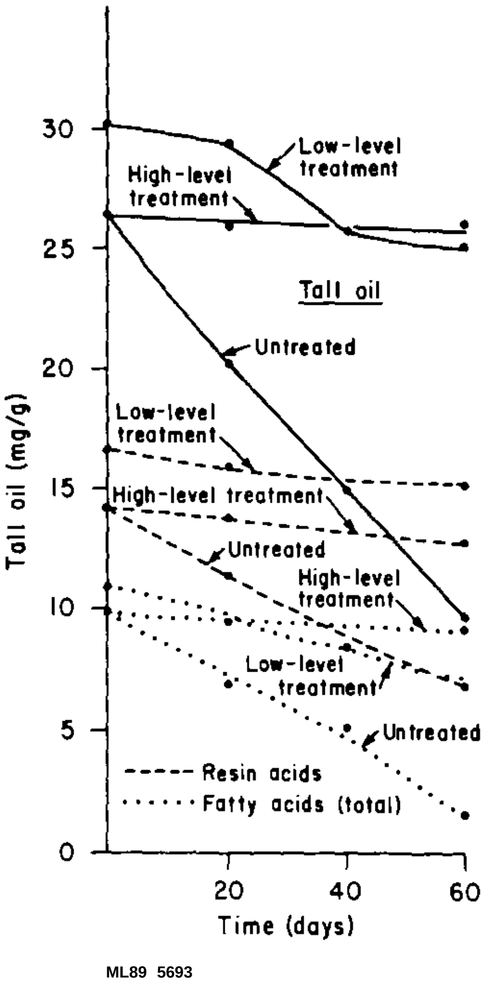

Figure 2. Losses of tall oil (ovendry extractive–free wood) during storage of slash pine chips is insulated boxes. (ML89 5693)

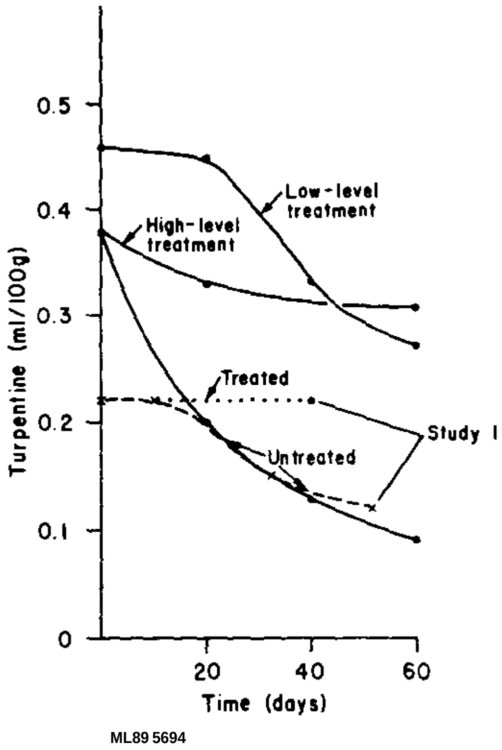

Figure 3. Losses of turpentine (ovendry extractive–free wood) during storage of slash pine chips in insulated boxes. (ML89 5694)

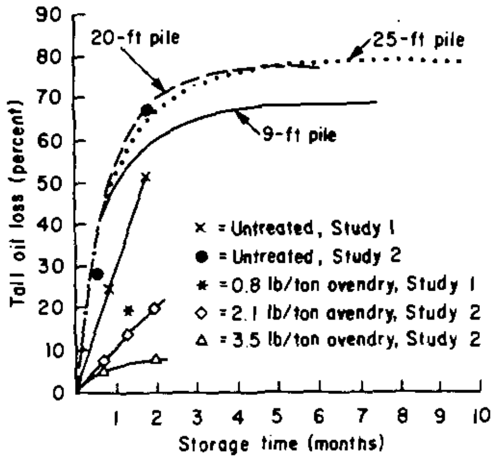

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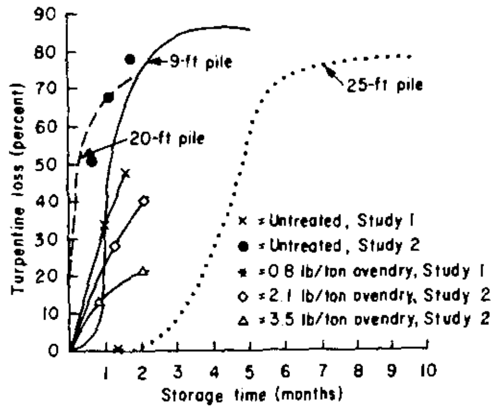
Figure 4. Comparison of tall oil losses in insulated boxes with those in outside chip piles. (ML89 5695)



ML89 5696

Figure 5. Comparison of turpentine losses in insulated boxes with those in outside chip piles. (ML89 5696)

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