Efficacy of Organic Acids in Protection of Tropical American Woods Stored in the Form of Chips[1)]

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1. Introduction

The large resource of hardwoods indigenous to tropical forests has been used to date only on a very limited scale (J. NAVARRO, 1976). These forests are extremely heterogeneous; the New World tropical forests, for example, consist of hundreds of different hardwood species. Harvesting of these stands is presently highly species selective, resulting in only 3 to 10 percent of the wood volume being cut (M. CHUDNOFF, 1976).

Recently, however, there has been increased interest in species-tolerant processes, the application of which could permit more flexible harvest of tropical hardwoods. As an outcome of this interest, a study of the feasibility of pulping mixed species of secondary tropical hardwoods was carried out at the Forest Products Laboratory. It was subsequently found that mixed tropical hardwoods, regardless of source, were suitable for the production of kraft and neutral sulfite semichemical pulps (J. F. LAUNDRIE, 1978).

Increased use of tropical hardwoods for pulping, with concomitant increase in outdoor storage of these woods in chip form, likely would result in expanded losses of wood substance due to fungal attack. Stored

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[1] Presented at IUFRO Symposium on tropical wood protection July 17 - 21, 1978, at Xalepa (Veracruz), Mexico.
[2] In cooperation with the University of Wisconsin.

hardwood chips have generally been more readily decomposed by fungi than have softwood chips during outside storage (R.M. LINDGREN and W. E. ESLYN, 1961, J. K. SHIELDS, 1967).

In studies of chip storage piles consisting of mixed New Guinean hardwoods, H. GREAVES (1973) found wood losses to total 7 percent after 4 months' storage. Some form of chemical protection will evidently be required to decrease anticipated losses due to biodeterioration, if moderate to long-term storage of tropical hardwoods is to be undertaken.

With emphasis today being given to greater use of environmentally safe pesticides, chemicals being considered for protection of stored woodchips must be of low mammalian toxicity. Propionic acid, a chemical very low in such toxicity, has been found to be somewhat effective in control of stored woodchips (W. E. ESLYN, 1973 a). However, higher molecular weight monocarboxylic acids, while being somewhat greater in mammalian toxicity than propionic acid, have been reported by R. H. BAECHLER (1939) to be more effective fungicides.

Large amounts of these acids are produced as by-products of certain industrial oxidation processes. Their availability, coupled with their increased (over propionic acid) fungitoxicity, warranted investigation of their usefulness in protection of stored tropical hardwood chips. Hence, the by-products which were available, caproic acid and a mixture containing several acids, were investigated[3].

2. Materials and Methods

The method used was a modification of that used previously by the author (1973 b) to screen potentially effective woodchip protectants. A mixture of chips composed of 17 different Colombian hardwoods was obtained for study. The mixture was initially made up for use in pulping studies (J. F. LAUNDRIE, 1978) and was composed, therefore, to include a somewhat even distribution of tropical woods with different specific gravities. The tree species involved, their specific gravities, and ratio representation in the mixture are provided in table 1.

The chip mix was conditioned at about 27°C and 70 percent relative humidity for 1 week. Samples of these chips - each sample weighing between 15.00 and 15.05 grams - were subsequently removed. The samples were rewetted to a moisture content of about 57 percent, based on the ovendry weight of the wood, by soaking in distilled water for about 15 minutes.

The samples were then placed in glass cylinders (37 mm inside diameter, about 30 cm long), plugged at the top with a foam plug and at the bottom with a rubber stopper containing a hole for drainage (fig. 1).

[3] The author is indebted to Dr. E. PECHHOLD, of Du Pont de Nemours and Co., for acids used in these tests and to JAMES LAUNDRIE, Forest Products Laboratory, for supplying needed woodchips.

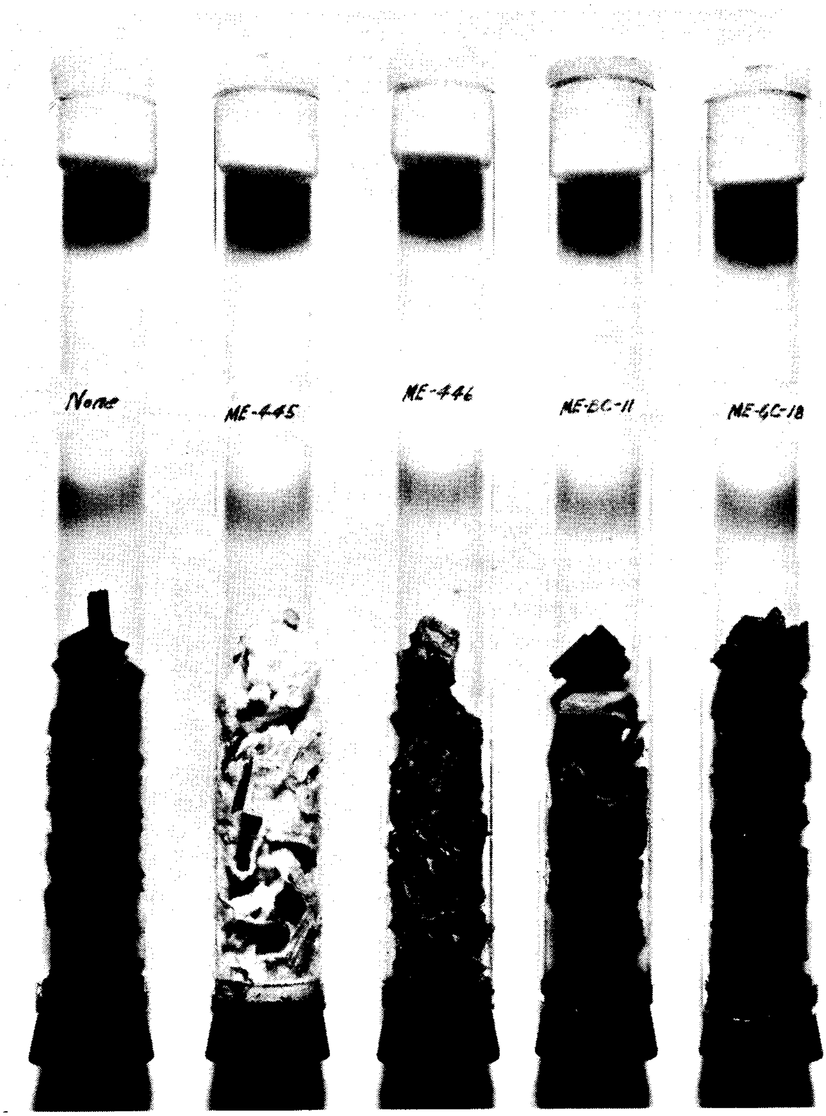

Fig. 1. Mixed Colombian hardwood chips in glass cylinders, at end of 12-week incubation period, illustrating test set-up and appearance of control and inoculated chips.

The cylinders containing chips were steamed for 30 minutes at 100°C. After cooling, the chips were treated with various aqueous concentrations of (1) an organic acid mix consisting of 57 percent valeric acid, 31 percent caproic acid, 7 percent cyclohexanol, and 5 percent mixed oxidation products; (2) 98 percent caproic acid plus 2 percent water; or (3) propionic acid. The propionic acid was included to compare its fungitoxicity with that of the higher molecular weight organic acids. Seven drops of Triton 100 emulsifier were added to each flask of chemicals to facilitate dispersion of the acids in the water carrier.

Tab1e **1.** Species composition of Colombian hardwoods chip mixture

Tree species		Specific gravity[a)]	Mixture composition
Common name	Botanical name		
Ceiba	*Ceiba pentandra*	.225	1/6
Yarumo	*Cecropia* sp.	.250	
Cirpo	*Pourouma* sp.	.369	1/6
Chingale	*Jacaranda copaia*	.372	
Dormilon	*Vochysia ferruginea*	.447	1/6
Sande	*Brosimum utile*	.494	
Sangretoro	*Virola sebifera*	.511	
Arenillo	*Castostemma alstonii*	.536	1/6
Canelo	*Nectandra* sp.	.546	
Perillo negro	*Couma macrocarpa*	.547	
Casaco	*Hieronyma* sp.	.603	1/6
Carbonero	*Enterolobium schomburgkii*	.634	
Chocho	*Ormosia paraensis*	.671	
Carreto	*Aspidosperma* sp.	.692	1/6
Lecheperra	*Helicostylis tometosa*	.785	
Tamarindo	*Dialium guianense*	.823	
Caimo	*Pouteria* sp.	.859	

a) **Dry weight, green volume basis.**

Treatment consisted of soaking the chips in each cylinder for 1 minute in 150 ml of treating solution. The solution was then poured off and the chips permitted to drain overnight. The chips were then inoculated with the thermotolerant fungus *Phanerochaete chrysosporium* Burds. (ME-446), or one of the mesophilic fungi *Coriolus versicolor* (ME-445), *Monodictys* sp. (ME-GC-18), or *Graphium* sp. (ME-BC-11). The latter two fungi are soft-rot organisms.

Inoculum was prepared by growing the basidiomycetes in flasks containing 50 ml of 0.5 percent glucose plus 0.5 grams of oats, while the soft-rot fungi were cultured similarly except that Abrams solution was substituted for the glucose. Inoculation of the chips was effected by shaking each flask vigorously to break up clumps of mycelial growth, and then aseptically pouring the contents of one flask into each cylinder of chips. The cylinders were then shaken to (distribute the mycelium and infected oats throughout and to ensure wetting of all chips with nutrient solution.

The cylinders were incubated for 6 weeks, at the end of which time their contents were rewetted with 50 ml of sterile distilled water and the cylinders returned to the incubator for an additional 6 weeks. Incubation temperatures were 40°C far chips inoculated with *P. chrysosporium* and 27°C for those inoculated with the other three fungi.

At the end of 12 weeks the chips were removed, reconditioned, reweighed, and the percent weight losses calculated. To correct for gain in weight due to the treating chemical or to a loss in weight due to leaching, noninoculated but chemically treated chip samples were incubated at both 27°C and 40°C with the inoculated samples, and their weight changes determined. The weight changes encountered were used to adjust the final weights of inoculated chip samples.

Table 2. Weight losses in mixed Colombian hardwood chips treated with organic acids and stared for 12 weeks

Chemical	Concen-tration %	Weight Losses[a])			
		P. chryso-sporium	*C. versi-color*	*Monodic-tys* sp.	*Graphi-um* sp.
Water (control)	–	**9.4**	**16.0**	**7.3**	**6.9**
Organic acid mix	**0.75**	**8.7**	**28.9**	**0.1**	**3.8**
	1.00	**12.9**	**22.6**	**0**	**3.6**
	1.50	**6.4**	**8.6**	**0**	**0**
	2.00	**0**	**0**	**0**	**0**
Caproic acid	**0.75**	**8.4**	**14.8**	**3.4**	**1.5**
	1.00	**0**	**17.5**	**0**	**0.7**
	1.50	**0**	**0.3**	**0**	**0**
Propionic acid	**1.75**	**0**	**0**	**0**	**1.9**
	2.25	**0**	**0**	**0**	**0.4**

a) Weight losses are averages of three replications.
b) Organic acid mix consists of 57 percent valeric. 31 percent caproic, 7 percent cyclohexanol. and 5 percent mixed oxidation products.

3. Results and Conclusions

Appearance of nontreated, inoculated controls after 12 weeks' incubation is shown in fig. 1. Weight losses experienced in these chips and in those treated with organic acids are included in table 2. Weight losses in controls ranged from a high of 16 percent in chips inoculated with Coriolus versicolor to a low of 6.9 percent in those attacked by Graphium sp.

When the organic acid mix was used at lower concentrations, i.e., 0.75 and 1.0 percents, C. versicolor was apparently stimulated, resulting in weight losses rising to averages of 28.9 and 22.6 percent respectively. When the concentration of the acid mix was increased to 2.0 percent, effective control of all fungi was attained.

Caproic acid used alone was the most effective acid treatment tested. It controlled wood deterioration by all four test fungi when applied at a concentraction of 1.5 percent.

Propionic acid, which was found to be effective on red pine at a concentration of about 1.75 percent (W. E. ESLYN, 1973 a), was able to prevent most deterioration on mixed Colombian hardwoods also when applied at that concentration. Only *Graphium* sp. caused weight losses at the 1.75 percent treatment level and these losses were of minor magnitude.

A major deterrent to use of propionic acid in woodchip storage piles has been its high cost per unit of wood when applied at a rate of 1.75 percent (W. E. ESLYN, 1973 a). Caproic acid was effective in the present tests at a lower concentration than propionic. In addition, because caproic is produced on a large scale as a by-product, there are indications that it could be supplied at a cheaper price than propionic acid. Hence, caproic acid may prove to be economically acceptable for use in protection of woodchip storage piles. A drawback to its possible usage, however, is its disagreeable odor. Hopefully, this problem can be resolved.

Toxicity, as LD_{50} (rats), of the acids and cylohexanol has been kindly provided by Dr. E. PECHHOLD, Senior Research Chemist at Du Pont. These data include:

Propionic acid	4290 mg/kg
Caproic acid	2050 mg/kg (mixed isomers)
Valeric acid	1120 mg/kg (mixed isomers)
Cyclohexanol	2060 mg/kg

While propionic acid is seen to be considerably safer to mammals than higher molecular weight organic acids, these acids are still much safer than such commonly used wood preservatives as pentachlorophenol. The latter, for example, has an LD_{50} to rats of 210 mg/kg (H. MARTIN, 1953).

4. Summary

Wood chip samples, composed of 17 different Colombian hardwoods, were treated with varying concentrations of caproic acid, propionic acid, or a mix of organic acids and then placed into decay tests to determine their possible usefulness in control of biodeterioration in stored chips. Caproic acid proved to be most effective, preventing wood substance losses when applied at a concentration of 1.5 percent. Propionic acid controlled most test fungi at a concentration of 1.75 percent, permitting minor decay by *Graphium* sp. to occur. The organic acid mix prevented decay entirely at a concentration of 2.0 percent.

Zusammenfassung

Wirksamkeit von organischen Säuren zum Schutz von tropischen amerikanischen Hölzern bei Lagerung in Spanform

Holzspanproben von 17 verschiedenen Laubhölzern aus Kolumbien wurden mit unterschiedlichen Konzentrationen von Capronsäure, Propionsäure oder einer Mischung organischer Säuren getränkt und dann in einer Pilzprüfung auf ihre mögliche Verwendbarkeit zur Verhütung von Zerstörung durch Organismen an gelagertem Spangut untersucht. Capronsäure war die wirksamste Substanz, um Spangutverluste zu verhindern, wenn sie in einer Konzentration von 1,5% angewendet wurde. Propionsäure in einer Konzentration von 1,75% bekämpfte die meisten Prüfpilze, ließ aber geringfügigen Befall durch *Graphium* sp. zu. Bei einer Konzentration von 2% verhinderte die Mischung der organischen Säuren Pilzbefall völlig.

Résumé

Efficacié d'acides organiques pour préserver des bois tropicaux américains en dépôt en forme de copeaux

Des échantillons de copeaux de bois, composés de 17 feuillus colombiens différents, ont été traités par des concentrations variables d'acide caproïque, d'acide propionique ou d'un mélange d'acides organiques et ont été ensuite soumis à des essais de pourriture pour suivre le contrôle de la détérioration biologique dans des conditions de stockage. L'acide caproïque s'est révélé être le plus efficace, empêchant les pertes de bois lorsqu'appliqué à une concentration de 1,5 pour cent. L'acide propionique a maîtrisé la plupart des drampignons d'essai à une concentration de 1,75 pour cent mais a permis une légère pourriture par le *Graphium* sp. Le mélange d'acides organiques a complètement empêché la pourriture a une concentration de 2,0 pour cent.

Resumen

La eficacia de ácidos orgánicos para la protección de maderas tropicales americanas almacenadas en forma de viruta

Muestras de virutas de 17 distintas maderas de fronda colombianas fueron impregnadas con diferentes concentraciones de ácido caproico, ácido propiónico, o bien, una macla de ácidos orgánicos y sometidas al ataque de hongos, con el fin de determinar la posible utilidad de tales ácidos en la prevención de la biodegradación de virutas almacenadas. El ácido caproico, con una concentración del 1,5%, demostró la mayor eficacia en evitar pérdidas de la madera. El ácido propiónico, a una concentración del 1,75%, resultó ser eficaz contra la mayoría de los hongos sometidos a prueba, excepto en el caso del *Graphium* sp., que consiguío causar un leve grado de degradación. La mezcla de ácidos orgánicos, con una concentración del 2%, evitó cualquier infestación por hongos.

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