Bark Chemicals

from SHASTA RED FIR as STIFFENING AGENTS for CORRUGATING MEDIUM

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ACKNOWLEDGMENTS

Work reported here was done by several men, of whom 3 are most notable. Harold Ely began initial experiments, Dr. E. F. Kurth aided in early work, and Dr. Edward S. Becker contributed greatly in concluding the project.

SUMMARY

In these tests, phenolic constituents from bark of Shasta red fir were found ineffective as stiffening agents for corrugating medium. Other means of application, however, may be effective.

Gum from inner bark of Shasta red fir was not so effective as a beater additive as was locust bean gum, but it was effective as a coating agent. Most effective beater additives are mannogalactans; Shasta red fir gum is mainly an arabogalactan.

Conclusions were that:

- Phenolic constituents of bark from Shasta red fir were ineffective as beater additives.
- As an additive, gum from the bark was not so effective in increasing Concora values as was locust bean gum.
- The gum was effective in increasing Concora values when applied as a coating agent.

Bark Chemicals from Shasta Red Fir As Stiffening Agents for Corrugating Medium

An important property of corrugated material for such products as shipping containers is crushing strength, which is increased by adding small quantities of mannogalactan gums to pulp. Since locust bean gum now added to pulps as a stiffener sells for about 50 cents a pound, thought was that gum from bark might replace locust bean gum, at substantial saving.

Experiments were made at the Oregon Forest Research Center to determine effects of gum extracted from bark as beater additives for corrugating medium. Bark from Shasta red fir (Abies magnifica var. shastensis Lemm.) was chosen for study because it contains a fairly large amount of water-soluble gum. This bark, as are other coniferous barks, is rich in phenolic constituents that also were examined as possible stiffening agents.

ISOLATION OF MATERIALS

Bark of Shasta red fir was ground and extracted to obtain tannin, phlobaphene, phenolic acid, and carbohydrate gum. Chemical composition of the carbohydrate gum was determined.

Tannin and phlobaphene

Bark of Shasta red fir, hand-separated into inner and outer bark, was ground in a hog. Eight pounds of outer bark were extracted successively with benzene, ethyl ether, and 95 per cent ethanol. The ethanol extract was concentrated to a volume of two liters in a natural-circulation, vacuum evaporator.

Fifty ml of extract were stirred into 500 ml of water to separate insoluble phlobaphene. Soluble material then was treated with hide powder to determine amount of tannin. About 16.1 per cent of unextracted bark, based on dry weight, was tannin (Table 1). A measured amount of extract was dried and weighed, indicating yield of 24 per cent alcohol extractives. To determine yield of tannin with direct hot-water extraction of bark, analysis was made by the method of American Leather Chemists' Association. Results are given in Table 1.

Table 1. Composition of Extracts from Outer Bark of Shasta Red Fir.

Alcohol extract		Water extract	
Fraction	Portion of dry bark	Fraction	Portion of dry bark
	Per cent		Per cent
Phlobaphene	2.7	Insoluble solids	1.1
Tannin	16.1	Tannin	16.3
Non-tannin	5.2	Non-tannin	6.0
All	24.0	All solids	23.4

Enough tannin to be tested was prepared from the alcohol extract of outer bark. A 200-ml portion of concentrated extract was stirred into two liters of water. After insoluble phlobaphene was removed by centrifuging, the solution was vacuum-evaporated to a volume of 500 ml. Saturating the solution with sodium chloride caused a red-brown, flocculent precipitate to form. This precipitate was filtered, washed with saturated sodium chloride, and dissolved in warm water. The solution again was saturated with sodium chloride; the precipitate was filtered off, washed with saturated sodium chloride, and dried in a vacuum desiccator. A dry, red-brown powder was obtained. To remove impurities, this powder was extracted with benzene and ether. It then was extracted with methanol to separate tannin from insoluble sodium chloride. Evaporating the methanol under reduced pressure left a brittle red mass. This

fraction, ground to fine powder, met all tests of phlobatannin, and was tested as a beater additive.

Phenolic acid

About 6.5 pounds of outer bark were extracted successively with benzene, ether, ethanol, and hot water. Extractive-free residue then was extracted with 14 liters of water containing 565 grams of sodium hydroxide. The mixture was held at 80-90 C for 12 hours, then allowed to cool. A supernatant solution was siphoned off and acidified with concentrated hydrochloric acid. A red suspension resulted, and solids were removed by centrifuging, washed with water, and again centrifuged. The red-brown solids then were dried in a vacuum oven and extracted with ether, then ethanol. The ethanol solution was stirred into a large volume of water, and precipitate was filtered off and dried in a vacuum desiccator. This phenolic acid fraction was tested as a beater additive.

Carbohydrate gum

Inner bark of Shasta red fir was the source of carbohydrate gum. A two-gram sample of bark was extracted for three hours with 600 ml of boiling water; the extract was filtered, and the bark was extracted two more times in the same manner. Part of the combined water extract was dried to indicate a yield of 35.5 per cent water-soluble extractives, based on oven-dry weight of unextracted bark. Remaining extract was concentrated to a volume of 200 ml and stirred into 600 ml of acetone. A crude carbohydrate fraction was precipitated that amounted to 16.0 per cent of the oven-dry weight of unextracted bark.

To isolate a large amount of carbohydrate material, 600 grams of alcohol-extracted inner bark were extracted, at room temperature, with three batches of water totaling 24 liters. The combined extract was vacuum-evaporated to a volume of 740 ml. Ten ml of the extract were dried to indicate a yield of 2.6 per cent cold-water extractives. To iso-

late gum soluble in cold water, one liter of acetone was stirred into the concentrated extract. Precipitated crude gum was washed with acetone-water (3:1) to remove all soluble tannin and was re-dissolved in warm water. This solution of crude gum, soluble in cold water, was tested to establish its composition and to discover its value as a beater additive and paper coating.

Inner-bark residue from cold-water extraction was extracted further with hot water in six batches. The combined hot-water extract was vacuum-evaporated to a volume of four liters, and sediment was allowed to settle. Supernatant solution was siphoned off, and carbohydrate was precipitated by stirring in 12 liters of ethanol. After washing with more ethanol, the precipitate was dissolved in 2500 ml of warm water to yield a two per cent solution of carbohydrate gum extracted with hot water. This fraction was tested as a beater additive and paper coating.

Samples of gum soluble in cold water and gum extracted with hot water were hydrolyzed for 10 hours with two per cent sulfuric acid. Hydrolyzates were chromatographed using several solvent systems and

Table 2. Composition of Gum Hydrolyzate from Inner Bark of Shasta Red Fir.

Component	Portion
	Per cent[1]
Arabinose	38
Galactose	29
Glucuronic acid	--[2]
Unknown desoxy hexose A	4
Unknown desoxy hexose B	6
Aldobiuronic acid	--[2]

[1] Based on dry, unhydrolyzed gum.

[2] Undetermined.

spray reagents. Simple sugars were identified and approximate amount of each was determined by the method of Hirst, Hough and Jones[1]. Results listed in Table 2 demonstrated that the gum from bark of Shasta red fir is an arabogalactan.

[1] Hirst, E.L., L. Hough, and J.K.N. Jones. "Quantitative Analysis of Mixtures of Sugars by the Method of Partition Chromatography. II. Separation and Determination of Methylated Aldoses." Journal of the Chemical Society, pp. 928-933. 1949.

PREPARATION OF PULP

To prepare a supply of pulp for tests, two similar cooks of Douglas fir chips were made under conditions listed in Table 3.

After removal from the digester, cooked chips were passed through a Bauer attrition mill and washed with water. Excess water then was removed in a forming box. The pulp, at about 12 per cent consistency, was stored for testing.

Table 3. Conditions for Preparation of Pulp for Testing Extracts from Bark of Shasta Red Fir.

Charge	Liquor alkalinity portion NaOH	Liquor weight	Weight of chips	Bauer plate setting	Chemical consumption	Yield of pulp	Time to 90 psi	Time at 90 psi
	Per cent	Pounds	Pounds	Inches	Per cent	Per cent	Hours	Hours
1	2.9	180	27.5	0.015	12.8	58.8	1	2.25
2	2.9	180	24.9	.015	--[1]	62.0	1	2.0

[1] Undetermined.

TESTS AND RESULTS

Materials tested as stiffening agents, either as additives or as coatings, were as follows:

Locust bean gum (Iscolized)

Extracts from bark of Shasta red fir

Gum, cold-water-extracted

Gum, hot-water-extracted

Tannin powder, alcohol-extracted

Phenolic acid

Hot-water extract of outer bark

Hot-water extract of inner bark

Bark phlobaphene was not tested as an additive, since it was completely insoluble in water.

Five series of pulps were made and tested.

Test series A

Pulp for test series A was beaten to freeness of 180 in a Valley laboratory beater. Materials to be tested were added to 1000 ml of pulp at consistency of 1.57 per cent, and the pulp then was stirred for ten minutes. Ninety-ml samples of pulp slurry were dipped out to make standard handsheets, and 190-ml samples were dipped out for heavy-weight sheets. The handsheets were dried in a conditioning room, and values of Concora (crushing strength) were determined. Concora values were determined with fluter and crusher at the Lebanon mill of the Crown Zellerbach Corporation. The basis weight was pounds to 500,000 square inches, or 35.897 times the dry weight of a standard-size handsheet. Results of series A tests are listed in Table 4. These results show that:

- Bark gum of Shasta red fir as an additive was only about one-third as effective as was locust bean (Most effective additives are mannogalactans;

Shasta red fir gum is mainly an arabogalactan).

- Tannin, even at high concentrations, did not increase crushing strength.
- Phenolic acid did not increase crushing strength.

Test series B

Low strengthening effect of bark gum, experienced in test series A, could have been caused by poor retention on pulp fibers. An attempt was made to detect increase in weight of handsheets made from weighed amounts of pulp, plus small amounts of gum. Although data were not accurate, the gum appeared to be at least partially retained. A preferable method for determining gum retention is to analyze handsheets for individual sugars; however, this method is quite laborious and was beyond the scope of the present study.

Test series C

Since bark gum was not effective as an additive, it was tested as a coating agent. Heavy-weight handsheets, made from pulp beaten to three different degrees of freeness, were dipped in several concentrations of gums and allowed to dry. Concora values were determined, and results are shown in Table 5.

Concora values definitely were increased by coating handsheets with bark gum, and increases were greater than those obtained by coating with locust bean gum.

Test series D

Test series C indicated that the gum did increase Concora values but did not indicate the amount of gum retained by each handsheet. In test series D, 19 heavy-weight handsheets were prepared from pulp beaten to a freeness of 427. The sheets were oven-dried, and again weighed. Amount of gum retained was shown by increase in weight of

Table 4. Strength of Handsheets Treated with Additives of Locust Bean Gum and Extracts From Bark of Shasta Red Fir.

Additive	Amount added	Concora[1]	
		Value	Increase
	Per cent[2]		
None		78	
Locust bean gum	1	85	7
Locust bean gum	2	90	12
Locust bean gum	3	99	21
Hot-water-extracted gum	2	79	1
Hot-water-extracted gum	3	87	9
Tannin	2	79	1
Tannin	5	83	5
Tannin + $Al_2(SO_4)_3$	2, 1	80	2
None		76	
Phenolic acid	2	79	3
Phenolic acid[3]	2	75	- 1
Phenolic acid	4	81	5
Phenolic acid[3]	4	80	4
Hot-water extract of outer bark	2	80	4
Hot-water extract of outer bark[3]	2	79	3
Hot-water extract of outer bark	4	83	7
Hot-water extract of outer bark[3]	4	78	2
Hot-water extract of outer bark + $Al_2(SO_4)_3$	4, 1	83	7

[1] Crushing strength; crushing pressure (psi) times 100, divided by basis weight (lb/500,000 sq in.).

[2] Based on dry weight of untreated handsheet.

[3] Handsheet heated for 1 1/2 hours at 105 C.

Table 5. Strength of Handsheets Made from 3 Consistencies of Pulp and Coated with Locust Bean Gum and Extracts from Bark of Shasta Red Fir.

Freeness of pulp	Type of gum	Gum concentration	Concora[1]	
			Value	Increase
		Per cent		
180	None		85	
180	Cold-water-extracted	1.28	98	13
180	Cold-water-extracted	1.28	94	9
180	Cold-water-extracted	1.28	100	15
480	None		67	
480	Locust bean	0.5	76	9
480	Locust bean	1.0	78	11
480	Hot-water-extracted	0.6	74	7
480	Hot-water-extracted	2.0	79	12
480	Cold-water-extracted	1.28	84	17
480	Hot-water-extract of inner bark	1.5	79	12
185	None		70	
185	Locust bean	0.5	82	12
185	Locust bean	1.0	79	9
185	Hot-water-extracted	0.6	79	9
185	Hot-water-extracted	2.0	92	22
185	Cold-water-extracted	1.28	74	4
185	Hot-water extract of inner bark	1.5	72	2

[1] Crushing strength; crushing pressure (psi) times 100, divided by basis weight (lb/500,000 sq in.).

handsheets. Concora values then were determined for each sheet. Results are shown in Table 6.

Eight handsheets were oven-dried to determine increase in weight, while remaining sheets were air-dried only. Effectiveness of locust bean gum as a coating agent was increased greatly by oven-drying handsheets. Oven-drying did not seem necessary for handsheets with bark gum. Results indicated that Concora value could be increased about 10 points by coating paper with about 2 per cent gum or total inner-bark extractives.

Test series E

Specimens of a corrugating medium produced from residue chips of Douglas fir by Crown Zellerbach Corporation were dipped in gum, and Concora values were determined. When some paper strips were oven-dried to determine amount of gum retained, they became brittle. When passed through the fluting machine, these strips broke into small pieces.

Results of test series E indicated that bark gum, as a coating agent, was effective in raising Concora values of this commercial corrugating medium.

Table 6. Crushing Strength When Oven-dried and When Air-dried and Portion of Gum Retained by Handsheets Coated with Locust Bean Gum and Extracts from Bark of Shasta Red Fir.

Gum	Concentration of gum	Gum retained	Concora[1]	
			Value	Increase
	Per cent	Per cent[2]		
Oven-dried sheets				
None			66	
Locust bean	1/8	1.01	72	6
Locust bean	1/2	2.0	82	16
Locust bean	1	4.1	81	15
Hot-water-extracted	1/4	1.12	69	3
Hot-water-extracted	2/3	2.3	78	12
Hot-water-extracted	1	3.1	79	13
Hot-water-extracted	2	5.3	84	18
Air-dried sheets				
None			66	
Locust bean	1/8	1.2	72	6
Locust bean	1/2	2.1	72	6
Locust bean	1	4.5	70	4
Hot-water-extracted	1/4	1.3	65	- 1
Hot-water-extracted	2/3	2.5	75	9
Hot-water-extracted	1	3.3	79	13
Hot-water-extracted	2	5.6	84	18
Cold-water-extracted	1.28	3.1	77	11
Hot-water extract of inner bark	1.5	3.0	79	13
Hot-water extract of inner bark	1.5	2.8	79	13

[1] Crushing strength; crushing pressure (psi) times 100, divided by basis weight (lb/500,000 sq in.).

[2] Based on dry weight of untreated handsheets.

OREGON FOREST RESEARCH CENTER

Two State programs of research are combined in the Oregon Forest Research Center to improve and expand values from timberlands of the State.

A team of forest scientists is investigating problems in forestry research of growing and protecting the crop, while wood scientists engaged in forest products research endeavor to make the most of the timber produced.

The current report stems from studies of forest products.

Purpose . . .

Fully utilize the resource by:

- developing more by-products from mill and logging residues to use the material burned or left in the woods.
- expanding markets for forest products through advanced treatments, improved drying, and new designs.
- directing the prospective user's attention to available wood and bark supplies, and to species as yet not fully utilized.
- creating new jobs and additional dollar returns by suggesting an increased variety of salable products. New products and growing values can offset rising costs.

Further the interests of forestry and forest products industries within the State.

Current Program . . .

Identify and develop uses for chemicals in wood and bark to provide markets for residues.

Improve pulping of residue materials.

Develop manufacturing techniques to improve products of wood industries.

Extend service life of wood products by improved preserving methods.

Develop and improve methods of seasoning wood to raise quality of wood products.

Create new uses and products for wood.

Evaluate mechanical properties of wood and wood-based materials and structures to increase and improve use of wood.

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