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## Chemistry and Utilization of Western Hemlock Bark Extractives

Franklin W. Herrick

A review is presented of research in North America during the past 30 years leading to the production of several types of water-soluble extracts from western hemlock bark. The objective of this work was to utilize the polyflavanoid components of the bark. These components were solubilized by treating ground bark with hot aqueous solutions of sodium bisulfite, sodium sulfite, ammonia, or sodium hydroxide. End-use research was directed to devising selective extraction processes to produce products that were effective and competitive with imported tannins in such markets as vegetable tanned leather, dispersants for oil-well drilling muds, and additives for boiler and cooling waters. Development work was conducted on the use of alkaline extracts of bark as components of phenol-formaldehyde resin adhesives for exterior-type plywood, particle boards, and laminated timbers. Chemical grouting systems based on the reaction of alkaline extracts and formaldehyde and heavy metal salts were tested under field conditions. Metal complexes (Fe, Zn, Cu, Mn) of the sulfonated extracts were found to be useful as agents to correct micronutrient deficiencies in agriculture. The chemical composition of western hemlock bark and the chemical structure of polyflavanoid derived extract products are discussed.

This review will deal specifically with western hemlock (*Tsuga heterophylla* Raf. Sarg.) bark since the development of commercial products by ITT Rayonier was largely

based on hemlock bark. Our work on the utilization of western hemlock bark began in 1948 and was part of a revival of interest in tannins, waxes, and other useful products that might be obtained from the bark of the large conifer tree species native to the Pacific Northwest of the United States and Canada. Previous and contemporary research at the Oregon Forest Products Laboratory and

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Table I. Summative Analysis of Western Hemlock Bark

	% by weight, dry unextracted solids	
	fresh bark	mill-run bark
total extractives	29.3	19.9
phenolic acids	18.0	34.8
lignin	15.2	19.0
holocellulose	37.2	26.0
ash	0.3	0.3
total	100.0	100.0

Table II. Analysis of Extractives in Western Hemlock Bark

	% by weight, dry unextracted solids	
	fresh bark	mill-run bark
wax	2.8	3.2
flavonoids	3.6	2.7
tannin	12.7	3.2
phlobaphene	5.3	6.1
water-soluble carbohydrates	4.9	4.7
total	29.3	19.9

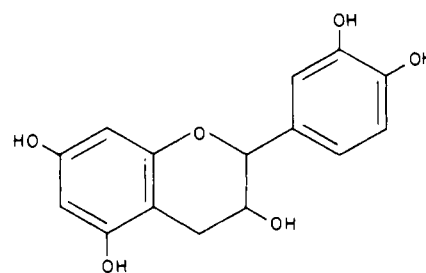
Oregon State University, Corvallis, OR, by E. F. Kurth and co-workers provided valuable direction (Hall, 1971). Work on hemlock bark carried out at the Western Forest Products Laboratory at Vancouver, British Columbia, by J. A. F. Gardner and co-workers was equally important (MacLean and Gardner, 1950).

By the early 1950's our research program had become quite broad and we envisioned several sizable markets, each of 10 000 tonnes/year, in products such as tannins, additives for oil well drilling fluids, and resin intermediates for exterior type plywood adhesives. At that time world production of the three major tannin extracts (quebracho and chestnut wood and wattle bark) was 300 000 tonnes/year (Howes, 1953).

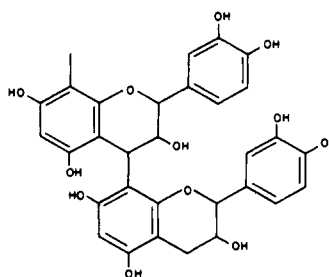
#### CHEMICAL NATURE OF WESTERN HEMLOCK BARK AND POLYPHENOLS

During the past 25 years many refinements have been made in the analyses and chemical structural concepts of different components of bark (Hergert, 1960). The analysis of fresh and mill-run (saltwater floated) barks, as shown in Tables I and II, is indicative of considerable variation (Hergert et al., 1965). Furthermore, composition was found to vary with the age of the tree, the fresh bark from young trees (20–25 years of age) being much richer in water-soluble tannins than that of older trees (60–80 years of age). Drying and oxidative aging of bark generally lowered the yield of the extractive component while increasing the yield of "phenolic acids". This last material has been defined as the fraction of extractive-free bark that is soluble in hot (97 °C) 1% aqueous sodium hydroxide during 2 h. It is now considered to be a polyflavonoid of higher molecular weight than the tannins and phlobaphenes and is perhaps the most important fraction of hemlock bark in the context of the present review. Even though the bark resource was variable with respect to the components listed in Tables I and II, each component, by virtue of its method of isolation was found to be quite consistent in chemical constitution.

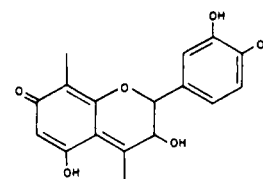
The polyflavonoids of hemlock bark are considered to be polymers of catechin (1) or catechin-like units which are converted by enzymatic oxidative coupling into water-soluble tannin 2. Further oxidation leads to the



Catechin

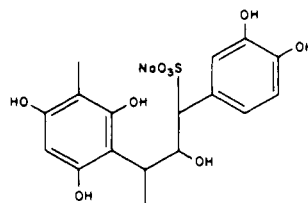


Tannin Terminating Unit

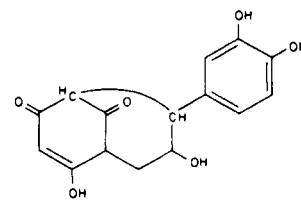


Phlobaphene Repeating Unit

formation of the more intensely colored phlobaphene 3 and the in situ "phenolic acid" polymers. A study of the thiolysis of these polyflavonoids with thioglycolic acid supported the view that the monomeric units of these polymers are joined by carbon-carbon linkages as in structures 2 and 3 (Sears and Casebier, 1968, 1970). Catechin was used as a model compound in studies to determine phenolic hydroxyl group reactivity (Sears and Engen, 1971) and the mechanism of the sulfonation of polyflavonoids with sulfite reagents (Sears, 1972). From the latter study it was concluded that the repeating unit in the sulfonated polymer is that of a sulfonated poly-chalcone (4). Finally, a concept of the structure of



Sulfonated Tannin Repeating Unit



Catechinic Acid

products derived from bark by alkaline extraction, including the so-called phenolic acids, was obtained from a study of the base rearrangement of catechin to form "catechinic acid" (5). The molecular structure of this compound was determined (Sears et al., 1974) and the titratable acidity was shown to be attributable to a conjugated enol functional group. It is considered that a similar rearrangement occurs in all polyflavonoids under strongly alkaline conditions and leads to the formation of intensely colored (black appearance) products. These products retain high phenolic hydroxyl content and formaldehyde reactivity, as will be discussed later on.

#### LABORATORY PREPARATION OF BARK EXTRACTS

Research on the extraction of western hemlock bark was initially oriented toward increasing the yield of the water-soluble tannin fraction obtained from bark typical of that available at our hemlock wood cellulose pulp mills.

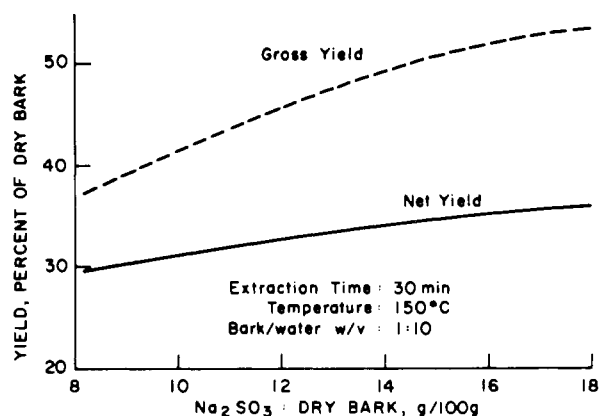


Figure 1. Effect of sodium sulfite concentration on the yield of extract from hemlock bark.

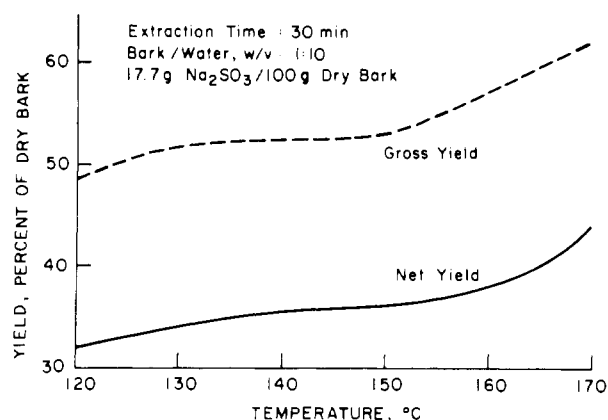


Figure 2. Effect of digestion temperature on the yield of extract from hemlock bark.

As already noted in Table I, the yield of hot water extract from mill-run bark was small and economically unattractive. Addition of small amounts of sodium bisulfite (1–2% based on dry bark weight) to the extraction water resulted in improved yield. Extraction of bark with excess hot dilute sodium hydroxide as in the "phenolic acids" procedure resulted in dissolution of about 50% of the bark material, but the products were not satisfactory as tanning agents for leather.

As experience was gained in using various chemical reagents in aqueous extraction schemes, it also was evident that each process step had to be controlled or duplicated in order to obtain products having reproducible yield and physical and chemical characteristics. It was also found desirable to prepare enough product for end-use tests, some of which required 0.5 kg of material. By 1953, a fairly complete bark extraction semi-works had evolved, which included stainless steel pressure vessels for operation up to 200°C, a vacuum evaporator, and a gas-heated spray drier with a nominal drying capacity of 0.5 kg/h.

**Routine Bark Extraction Procedure.** Clean, mill run bark was selected by hand in lots of 1–2 m<sup>3</sup>. The wet bark was ground using a hammermill to recover a coarsely shredded material passing through a screen having holes of 2 cm in diameter. This raw material was thoroughly blended and stored in moisture-proof drums. Ground wet hemlock bark from this source typically contained about 42% oven dry bark.

To prepare an aqueous sodium sulfite extract of the type used in the experiments illustrated in Figures 1 and 2, a 7.14-kg quantity of wet bark equivalent to 3 kg of dry bark, was placed in a 120-L stirred pressure vessel and treated with 531 g of sodium sulfite dissolved in 25.86 L of water.

Table III. Extraction of Hemlock Bark with Aqueous Sodium Hydroxide at 0.1 w/v, 0.08 w/w NaOH/Bark

temp, °C	time, min	gross yield, % of dry bark	phenolic hydroxyl, %
97	30	25.1	13.1
125	20	38.7	12.6
150	20	35.4	13.0
175	30	46.6	10.2

This provided a bark slurry of about 10% consistency, w/v of dry bark to water. Stirring was started, and the vessel was sealed and heated rapidly by a steam jacket to 150°C and held for 30 min at this temperature. After cooling to about 50°C, the digested bark and extract were drained from the pressure vessel into a fine screen filter. The bark residue was pressed and washed with 5 L of water. The filtered extract and wash water were weighed and analyzed for solid content. The dilute extract was then concentrated by vacuum evaporation at less than 100°C to a solids concentration of about 40%. This concentrate was spray-dried using an inlet air temperature of 300°C. The bark extract gross yield, including the weight of added chemical, was calculated from the weight and solids analysis of the dilute extract and was 52.5% of the dry bark weight. A net yield of 34.8% was calculated by subtracting chemical usage, or 17.7 g/100 g of dry bark, from gross yield, assuming negligible retention of chemical in the bark residue. The bark residue was also weighed and its solid content determined to provide a second check on extract yield. Spray-dried extracts were stored in closed glass or plastic containers to minimize moisture pickup. Larger batches of extracts were prepared by using wet bark corresponding to 10 kg of dry weight and an overall 100 kg charge in the 120-L pressure vessel.

**Study of Extraction Variables.** Three aqueous chemical extraction processes were of primary interest for commercial development. These involved extraction of hemlock bark in the presence of (1) sulfite reagents, (2) sodium hydroxide, and (3) ammonium hydroxide. The goal of much of our work in bark extraction was to devise selective processes that would provide products in high yield and having optimum properties in a given end-use. It thus became necessary to conduct end-use research concurrently with that on bark extraction, as will be discussed later.

The sulfonation of hemlock polyflavonoids was found to proceed very readily under neutral or slightly acidic (pH 5–6) conditions (Hergert et al., 1965; Van Blaricom and Gray, 1958; Gray and Van Blaricom, 1961). The effects of sodium sulfite concentrations and extraction temperature on yield of bark extract are illustrated in Figures 1 and 2. The net yield of extract obtained in 30 min at 150°C levels off at a sodium sulfite usage of about 14 g/100 g of dry bark, possibly indicating the end of efficient sulfonation of polyflavonoids. If the temperature is raised to 170°C, additional chemical reagent is consumed, including the sulfonation and solubilization of the bark lignin fraction. From end-use tests as dispersants it was determined that bark extracts obtained in gross yields above 50% were less effective. Even mild alkalinity during extraction promoted hydrolysis of waxes and fats to produce soaps that caused foaming in end-use applications. The optimum selective extraction procedure for preparing sulfonated bark polyflavonoids included the use of mildly acidic conditions and limits in sulfite reagent usage, extraction temperature, and time.

The effect of increased temperature on the yield of a sodium hydroxide extract of hemlock bark is illustrated

Table IV. Extraction of Fresh Hemlock Bark with Aqueous Ammonia at 0.1 w/v for 30 min at 150 °C

NH <sub>3</sub> /bark, w/w	yield % of dry bark	extract analysis, %	
		combined nitrogen	phenolic hydroxyl
0.02	20.5	0.9	8.7
0.10	26.4	1.9	7.3
0.20	32.5	2.6	6.4
0.40	38.6	2.9	5.3

in Table III (Gray and Crosby, 1957). While the analysis of the four products indicated high phenolic hydroxyl content, this value was decreased as extraction temperature and yield were increased. However, only the mildest conditions (97 °C) yielded a satisfactory product based on formaldehyde reactivity and plywood adhesive tests (Herrick and Bock, 1958a,b, 1962a,b).

Extraction of bark for 30 min at 150 °C with increasing concentrations of ammonium hydroxide (Herrick and Bock, 1958a,b; Steinberg and Gray, 1958) resulted in increased product yields as shown in Table IV. Phenolic hydroxyl analyses were lower as compared with those of the sodium hydroxide extracts. The first three products were found to be very reactive as resin intermediates when converted to sodium polyphenolates by treatment with sodium hydroxide. Selective extraction with ammonium hydroxide was found to be quite flexible or tolerant of temperature variations in the range of 120 to 150 °C and ammonia to bark w/w ratios as high as 0.4 at the lower and 0.15 at the higher temperature. In all of our experience, the sodium polyphenolate products derived by extraction of bark with ammonium hydroxide always had the edge of higher reactivity and utility in resin intermediate applications.

**Organic Solvent Extraction.** Although none of the solvent extraction processes developed for hemlock bark were carried out on a commercial scale, some of our experiences and results may be of current interest. For this work, fresh hemlock bark from newly harvested logs was air-dried and finely ground to pass through a screen with 2–5 mm openings. A methanol-soluble fraction was prepared in 2.7-kg batches by continuous percolation of solvent through 18 kg of dry bark contained in a cloth-lined canister, drained back to a reboiling, distillation vessel. Methanol (200 L) was recycled for 6 h at 64 °C. Extract solids were obtained in 15% yield. This product gave a satisfactory test in solvent tannage of leather (Kremen, 1962). The same apparatus was used to extract 18 kg of dry bark with 200 L of a 50:50 v/v mixture of acetone and water containing 360 g of sodium bisulfite (2% of dry bark weight), except that the solvent was heated to 56 °C and recycled for 2 h to the bark charge by means of a small pump. The recovered dry extract (5.4 kg) was obtained in 30% yield and had a tannin purity of 70%.

A bark extraction system that was studied quite extensively involved the alcoholysis of bark with butanol and hydrochloric acid (Anderson et al., 1958; Herrick et al., 1962). Because of the corrosive nature of the acid reagent all work was conducted in glass or glass-lined equipment. Optimum extract yields of nearly 50% (Figure 3) were obtained by stirring dry bark for 4 h in boiling butanol that contained 10 g of HCl/100 g of dry bark. However, this material was partly soluble in water. Further treatment and fractionation as in Figure 4 resulted in a yield of 24.3% of alcohol-soluble resin intermediate of use in phenol-formaldehyde laminating resins.

#### END-USE RESEARCH

For each of the following research areas, industrial or

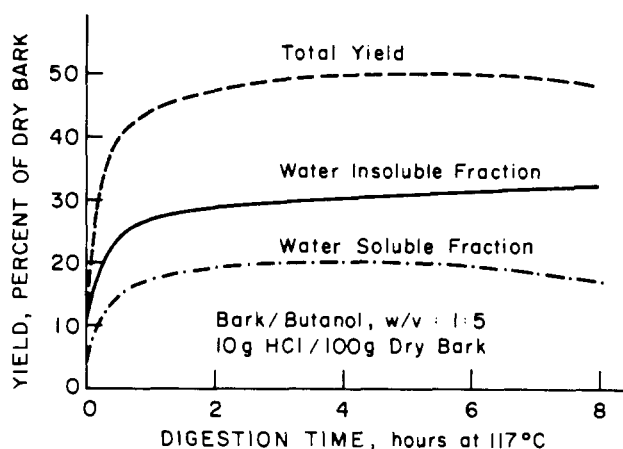


Figure 3. Extraction of hemlock bark with butanol-HCl.

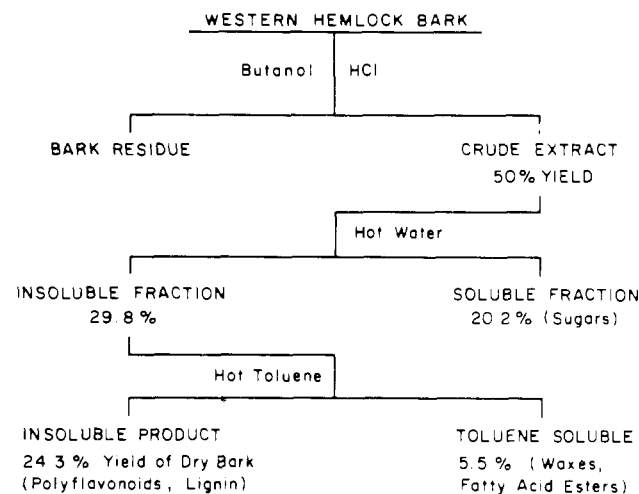


Figure 4. Fractionation of bark by alcoholysis and solvent treatment.

Table V. Analysis of Commercial Spray-Dried Extracts Derived from Hemlock Bark

	% by weight, except as noted	
	sodium polyphenol sulfonates	sodium poly- phenolates
moisture	5.0	7.0
sodium	9.0 (6.5)	10.5
phenolic OH	7.8	8.0
methoxyl	1.4	1.0
sulfur	6.1	
pH, 1% solution	8.2 (6.8)	10.6
color	red-brown	black

application technology is quite specialized and utilizes a distinct vocabulary of terms in describing the desirable characteristics of a given material. It was found necessary to equip a complete laboratory for each end-use area. There were few shortcuts in the final critical tests required to obtain comparative and competitive performance data. Testing by outside laboratories, where available, was valuable in confirming performance data, but was not relied upon in exploratory work. Because of the empirical nature of most end-use testing, it was necessary to develop a high degree of expertise and performance judgement in several apparently unrelated technologies.

As background for most of the discussion that follows, a typical chemical analysis of the two types of extracts that were of primary interest is given in Table V. The sodium polyphenol sulfonates were generally tested in the form of a slightly alkaline compound (pH 8.2), although neutral



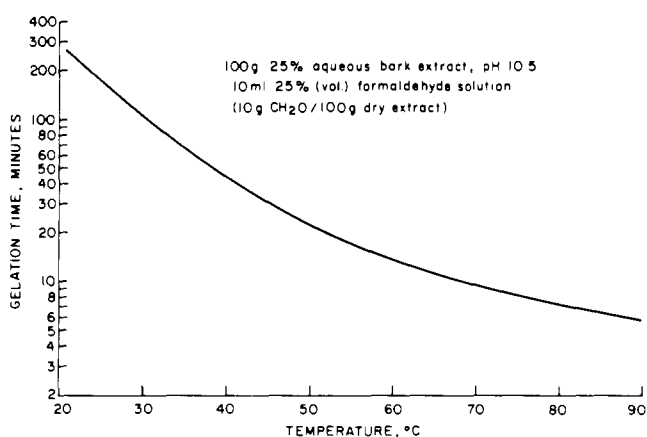


Figure 7. Gelation properties of a sodium polyphenolate extract of hemlock bark and formaldehyde.

hydrocolloid yielded excellent high-temperature fluid loss control when used at a rate of about 8 g/L of fluid.

**Phenolic Resin Intermediates.** This work spanned 12 years beginning in 1950. A wood products research program was active during this period and was concerned principally with exterior type or weather resistant plywood, particle and fiber boards, and laminated timbers. To a lesser extent, the bark extract polyphenols were also viewed as intermediates for phenolic laminating and molding resins. The main thrust of the adhesives program was in the development of bark extracts that were compatible with phenolic resins and reactive toward formaldehyde to yield boil-proof adhesive bonds in Douglas fir or western hemlock and cedar woods. The Douglas-fir plywood test was the most convenient means for comparing the effectiveness of different thermosetting adhesive formulas (Herrick and Bock, 1958a,b, 1962a,b, 1965). Laminated timber tests were developed for comparing cold-setting adhesives (Herrick and Conca, 1960; Herrick and Bock, 1966; Conca et al., 1966).

The sodium polyphenolate bark extracts were used as such in most adhesive studies. Isolation of the bark phenolic acid fraction was also of interest. Precipitation with dilute hydrochloric acid yielded as high as 87% of ash-free product. This material was dark brown, amorphous, and had no melting point, but was nearly completely soluble in methanol. A convenient and rapid procedure for preparing the methanol soluble polyphenol fraction involved mixing the alkaline bark extract with excess  $H^+$  cation exchange resin and methanol at a 1:2:10 weight ratio. This slurry was stirred at 25 °C for 15 min and filtered to recover the methanol solution. The yield of polyphenol was about 70% of the dry sodium polyphenolate weight. Use of this fraction, redissolved in sodium hydroxide, did not significantly improve adhesive test results or formaldehyde reactivity properties.

The gelation properties of aqueous solutions of the sodium polyphenolates and formaldehyde (Figure 7) and the amount of formaldehyde that reacts with the polyphenol at different temperatures (Figure 8) were studied extensively. The first test was valuable for screening a large number of extract products and was used in production quality control. The slope of the curve in both figures was found to be very characteristic of a given product of a specified quality. The sodium polyphenolate-formaldehyde reaction was not found to be useful in the formation of boil proof adhesive bonds as required in the U.S. plywood standards.

In the utilization of sodium polyphenolates in blends with phenol-formaldehyde resins, such as would yield

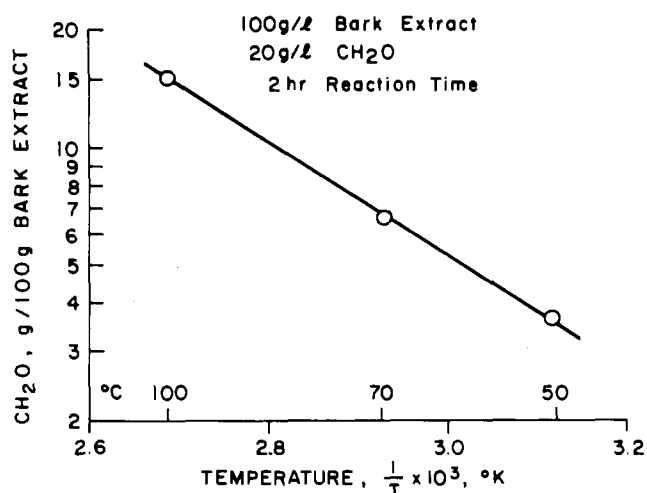
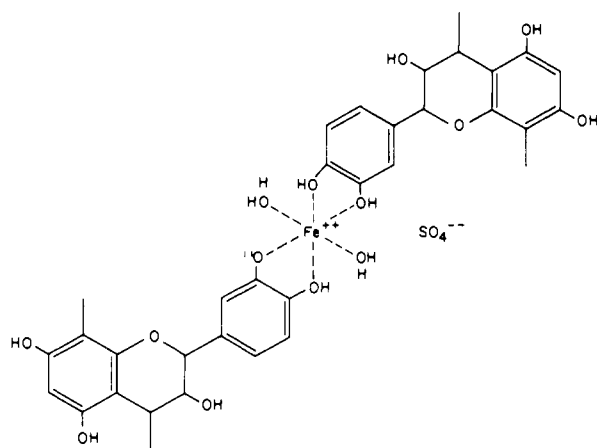


Figure 8. Formaldehyde reactivity of a sodium polyphenolate extract of hemlock bark.

satisfactory exterior plywood, it was found that high methylol, low-molecular-weight phenol-formaldehyde condensates could be used with much higher proportions of bark extract. The development of the product termed "polymethylolphenol" (6) almost became a prerequisite to the commercial acceptance of the bark extract plywood adhesives. A continuous process was developed for pilot plant production of the polymethylolphenol solution (Herrick and Bock, 1958a). This product was also successfully spray-dried. Adhesive formulations containing as high as 60% bark extract and 40% polymethylolphenol, based on total resin solids, yielded acceptable exterior type plywood. Curing time requirements for these adhesives were about 10% longer than those of the fastest curing phenolic resins.

In the laminated timber adhesive studies, blend formulations of bark extracts were prepared directly with available commercial resorcinol- and phenol-modified resorcinol-formaldehyde resins. Acceptable softwood lamination was demonstrated repeatedly in commercial facilities, using Douglas fir and western hemlock lumber. The bark extract could be used in place of as much as 50% of the resorcinol resin or 30-40% of the phenol-resorcinol resin weight. Minor adhesive formulation changes were made to improve assembly time characteristics.

**Agricultural Micronutrients.** Synthetic organic chelating agents such as those based on ethylene-diamine tetraacetic acid have been used for several decades as carriers for elements, notably iron, zinc, manganese, and copper, that are required in very small or micronutrient quantities for proper plant or tree growth. In mineral deficient agricultural regions, many crops suffer from chlorosis or other deficiency conditions that severely reduce yields and may under some circumstances lead to crop failure. The search for lower-cost carriers for micronutrient elements led to experimental production of several metal complexes of the sulfonate bark extracts. A ferrous complex of the bark polyphenol is illustrated in 7 where the ferrous ion acts as an intermolecular linkage. These complexes were found to produce a response, particularly when applied as a foliar spray to a variety of crops (Durkee, 1965). Field tests were conducted over a period of years on many orchard fruit and nut crops. Special spray formulas were developed for citrus trees (Gray et al., 1972). Though generally effective in the correction of micronutrient deficiencies, proper early application was necessary to prevent fruit stain. The metal complexes of the polyphenol sulfonates also had a low degree of phytotoxicity



Ferrous Complex of Bark Polyphenols

in comparison to direct mineral salt application. A partial chemical analysis of four commercial metal complex products is given in Table VI.

**Chemical Grouting Systems.** The procedure or technique known as "chemical grouting" has evolved in the heavy construction industry during the past 30 years. Chemical grouting involves injection of various inorganic and organic chemicals, monomers and polymers, usually in water solutions, into soils, sands, gravel, and porous rock. The components of the solution interact, during or after injection, to form an immobile polymer or cross-linked polymer, usually as a water gel of water-insoluble material.

The purpose of chemical grouting is to stabilize, solidify, and generally increase the strength and load bearing capacity of the material being grouted in order to facilitate heavy construction and tunnel and shaft driving. Reinforcement and sealing against water flow is also provided for earth-fill dams, foundations, subways, sewers, and other underground passages or buildings. The applications of chemical grouting are so varied as to require division of the field into a number of distinct areas having their own specialized engineering technology and process equipment. For example, permeation grouting into very fine sand or porous rock can be accomplished only with monomeric or low-molecular-weight dilute grouts designed for long gel times, whereas stopping water flow through gravel may require a polymer solution that gels within seconds after injection.

The first ideas on using the sodium polyphenolate bark extracts as components of a chemical grouting system were based on the gelation reaction with formaldehyde. When appropriately heated in the temperature range of 20–90 °C, a 25% solution of the bark extract containing 0.1 w/w of formaldehyde based on dry extract, had gel times in the range of 6–300 min (Figure 7). It was also noted that the sodium polyphenolates were very reactive toward chromium, iron, and other metal salts or compounds. Sodium dichromate was chosen as the most effective and readily available setting agent, because formation of the trivalent chromium complex of the bark polyphenol did not upset the pH of the bark extract-formaldehyde system and a relatively homogeneous transition could be obtained from the grout solution to the gels. The strength properties of gels and grouted sands were found to increase linearly with polyphenol concentration and as a logarithmic function of temperature and time, after mixing with the formaldehyde and sodium dichromate components (Herrick and Brandstrom, 1968). A grouting system was also developed, utilizing ferrous sulfate as a setting agent component. However, this system required special mixing

Table VI. Analysis of Commercial Spray-Dried Metal-Complexed Extracts of Hemlock Bark

	% by weight, except as noted			
	Fe	Zn	Mn	Cu
moisture	6.4	5.0	4.5	4.7
sodium	4.2	4.4	4.2	5.2
total metal	9.6	11.1	9.6	7.6
complexed metal	9.0	10.7	9.4	6.0
sulfur	10.1	9.6	10.6	8.6
pH, 1% solution	4.3	6.0	6.2	3.8

Table VII. Composition of Setting Agent Solutions for 20% Sodium Polyphenolate Chemical Grouts

dichromate, %	Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O, g/L
5.0	57
7.5	83
10.0	114
15.0	171
20.0	227

pumping ratio, v/v, bark extract sol/setting agent sol	4	6	8	10
37% formaldehyde sol, mL/L (0.05 w/w CH <sub>2</sub> O dry extract)	120	180	240	300

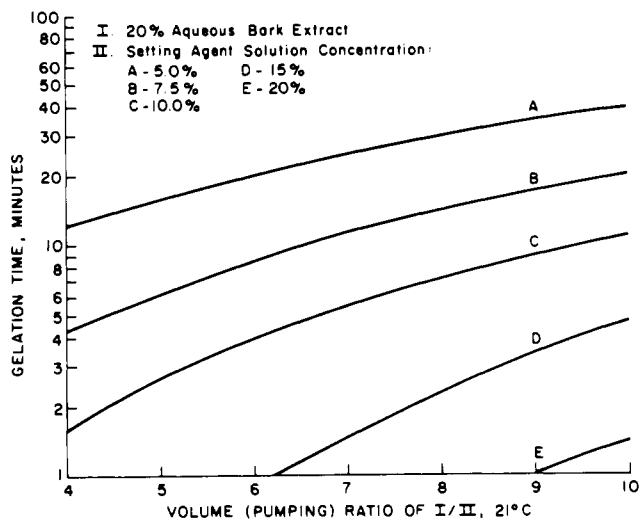
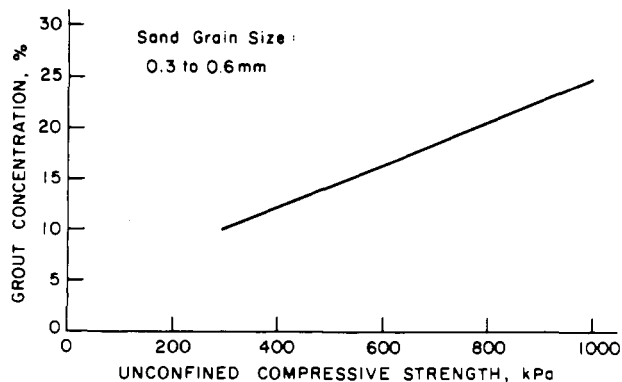


Figure 9. Gelation properties of a chemical grout prepared from a sodium polyphenolate extract of hemlock bark formaldehyde, and sodium dichromate.

conditions and was eventually replaced with a stabilized ferrous hydroxide complexing agent (Herrick et al., 1970).

Field testing of sodium polyphenolate grouting systems was carried out over a period of 10 years during which much time was spent in designing and building better application and injection equipment. A considerable volume of commercial application and performance data was made available to the construction industry and to soil mechanics engineers. Figure 9 is an example of a graph of gelation time at 21 °C for a 20% bark extract grout treated with various amounts of setting agent solution. This graph was used in conjunction with the setting agent composition chart, as shown in Table VII, to plan for a given grouting job. If a gel time of 10 min was needed, the setting agent B could be used at volume ratio of 7:1 of the bark extract and setting agent solutions. From Table VII, this setting agent solution would contain 83 g/L of sodium dichromate dihydrate and 210 mL/L of commercial 37% formaldehyde solution. These graphs and tables were prepared for grout concentrations in the range of 10–25%





**Figure 10.** Unconfined compressive strength of sand and chemical grouts prepared from a sodium polyphenolate extract of hemlock bark, formaldehyde, and sodium dichromate.

based on bark extract weight and temperatures in the range of 0–40 °C.

Our soil mechanics research eventually included triaxial testing of grouted soil (sand) cylinders prepared under very exacting and efficient laboratory permeation grouting conditions, as developed in Europe. Figure 10 is a graph of the unconfined compressive strength after 7 days of a medium sized sand grouted with a sodium polyphenolate- $\text{CH}_2\text{O}$ -Cr gel of increasing solids concentration. The bark extract grouts were outstanding in performance under water shut-off conditions and in sealing against water leakage in underground construction. Satisfactory performance was demonstrated under a wide variety of field conditions and general service grouting applications. They were not designed for use in very fine soils or sands nor for major contribution to high structural strength.

**Additives for Boiler and Cooling Waters.** This application area eventually became a very significant and important market for the sodium polyphenol sulfonates. A modest research program included testing of bark derivatives by different companies in the water treatment industry. The sulfonated bark extracts were excellent dispersants for scale-forming minerals. Metal complexing and corrosion inhibition were comparable to that provided by more expensive tannins. A clarified sodium polyphenol sulfonate product was highly favored in the formulation of additives for cooling waters as used in the air conditioning systems of large buildings.

#### COMMERCIAL PRODUCTION OF HEMLOCK BARK EXTRACTS

Our first bark extract production facility was put into operation in 1954 at our Grays Harbor Division, Hoquiam, WA. This plant had a capacity that varied from 5 to 10 tonnes/day depending on the yield and type of extract being produced. Key items of equipment included a horizontal screw-agitated continuous pressure digester, screw press, vacuum evaporator, and spray drier. Manufacture of several products by continuous extraction of bark with aqueous sulfite reagents and sodium and ammonium hydroxide was pioneered in this unit and was successful both in terms of quality control and production rate goals. This plant was also used in pilot studies on the manufacture of new products from bark or bark extracts, for example, in the reaction of the sulfonated polyflavonoid extract with polymethylolphenol to produce an additive for oil well drilling fluids that was effective as a fluid loss control agent. Spray-drying of sodium polyphenolate bark extracts in mixtures with polymethylolphenol to prepare a stable dry product for plywood adhesives was also successfully pioneered.

In 1956 a larger, versatile commercial plant was in op-

eration, adjacent to the Marpole Division (Hemlock lumber) of Rayonier Canada (B.C.) Ltd., Vancouver, British Columbia. Meanwhile the plant at Hoquiam, WA, was converted and expanded for the manufacture of products derived from sodium lignin sulfonate raw material available at the Grays Harbor Division cellulose pulp mill. Late in 1967, the Hoquiam plant was again expanded by the addition of a new bark extraction plant having the capability for producing improved and new types of extracts. The commercial bark extraction plants at Vancouver, B.C., and Hoquiam were designed for a daily production capacity in the range of 20–30 tonnes/day of dried extract or about 10 000 tonnes/year of the higher yield sulfonated extracts.

Key equipment and unit processes for the commercial plants were of the same general design as employed in the original commercial plant, except for larger sizing. Clarification of the dilute extract was first improved by use of multiple settling tanks and later by installation of continuous vacuum filtration units, where the extract was filtered through a layer of bark residue. Equipment was also added for blending concentrated extract solutions with salts such as ferrous sulfate to form complexed metal-sulfonated polyflavonoid products. Spray-dried bark extract powders were also converted to pelleted or densified granules to increase bulk density from about 400 g/L to over 800 g/L, thus saving on packaging materials and warehouse and shipping space. Packaging for most products was in 22.73 kg (50 lb) moistureproof multiwall paper bags.

The commercial extraction processes were similar to those developed in the laboratory, with some exceptions. Bark (dry) concentration with respect to water was increased to about 0.2 w/v to obtain a more concentrated extract, at some penalty in extract yield. Average extraction (retention) time in the continuous digester was 30 min. This could be varied by perhaps 10 min shorter or longer. Extraction with sulfonating agents was carried out at temperatures in the range of 160 to 170 °C. These extracts were quite stable and could be concentrated to 45% solids and spray dried using a 330 °C inlet gas temperature, provided drier outlet temperature was kept below 126 °C. The alkaline products resulting from sodium hydroxide extraction, or extraction with ammonium hydroxide and conversion to the sodium polyphenolate with ammonia recycle, were considerably more heat and oxidation sensitive. Excessive extraction or evaporation temperature and time resulted in product modification and quality loss.

All commercial products were subject to manufacturing and product quality specifications. Much of this information is still proprietary. Average analytical data, such as given in Tables V and VI, and the results of physical, chemical, and end-use tests, were described in commercial product literature that was provided to potential customers. Many end-use tests were also devised in cooperation with customers. In most cases it was possible to combine several chemical or relatively fast physical tests in order to insure good product quality during production. No major insoluble quality control problems were encountered during 22 years of commercial production.

The Vancouver B.C. bark extraction plant was in operation from 1956 to 1976. Peak production exceeded 7600 tonnes/year in the first decade of operation and declined during the second decade to about 5000 tonnes because of severe competition for markets from the less expensive products derived from lignin sulfonate. Sodium polyphenolates were produced only at a rate of about 500 tonnes/year. The product derived by ammonium hy-



dioxide extraction was not produced after 1963 because of higher production cost and low market demand. The decision to stop production at Vancouver was based on a combination of rising production costs and diminishing markets.

The Hoquiam extraction plant was in operation for 6 years from 1967 to 1972. Daily and monthly production capacity was demonstrated. Since this plant was integrated with the manufacture of lignin products, utilizing a common evaporator and spray drier, the bark extract products were only produced as needed to supply various markets. Production of the sodium polyphenolate extract was stopped in 1972, because the market of 300 tonnes/year was not large enough to meet production and storage costs.

#### MARKETING OF BARK EXTRACT PRODUCTS

After 25 years of experience in this endeavor there is more to tell than would fill several volumes. The word "heroic" is appropriate for the efforts of a number of "technical sales" representatives, as our marketing personnel were called. These men carried the good news of the bark "polyflavonoids" or polyphenols to every market area or potential industrial application, often accompanied by research personnel to reinforce the message. One of the characteristics of the bark extraction program seemed to be that of perennial optimism and out of the ashes of one part of the program we were able to kindle a fire in another. It is a tribute to the patience of ITT Rayonier management that the entire program was not terminated after 5 or 10 years, as was the fate of bark programs in some companies.

Some of the reasons for success or lack of success in our marketing of bark extract products may be of interest. Western hemlock tannin of high quality was offered to the leather industry in the 1950's. Because this tannin yielded a darker colored leather than other vegetable tannins, it was unacceptable. If we could have produced a low cost, "blue sky" product that would yield leather with a combination of all the best properties and produced by a very fast and clean tanning process, we might have penetrated this market. Fortunately, the oil well drilling industry was very active at that time and bark extract color was of little consequence as long as end-use performance in controlling drilling fluid viscosity was good. Marketing of additives for oil well drilling fluids was the outstanding success of the entire bark extract venture. Although applicable largely to top-hole drilling and low electrolyte fluids, improved additives containing small amounts of complexed iron or zinc remained competitive on a cost-effectiveness basis and would probably have a good market in the present highly active oil and gas exploration industry.

The sodium polyphenolate products posed the most difficult marketing problems. In the exterior plywood adhesive market, the price of phenol was about 40¢/kg in 1950. By the time our product was commercially available at 26¢/kg in 1955, the price of phenol had dropped to about 25¢/kg and from 1960 to 1972 ranged in price from 15 to 20¢/kg. It was not possible to sell a bark extract, even at 20¢/kg under these circumstances. Again, fortunately, another type of phenolic resin based on resorcinol (\$1.50/kg in 1960, \$3.09/kg, 1979) was quite expensive. The formulation of cold-setting waterproof adhesives for laminated timbers by combining formaldehyde reactive bark extracts and resorcinol resins still makes economic sense. Adhesive strength characteristics are certainly more than adequate for softwood lamination. The marketing problem in the 1960's was caused partly by competition from the lower-cost, phenol-modified resorcinol resins and

partly by the need for long-term testing of the bark extract modified resins for which no commercial performance record or standards existed.

Finally, the development of chemical grouting systems based on the sodium polyphenolate extracts had all of the indications of sound economics in relation to competitive products. The optimistic view in the early 1960's, that chemical grouting would rapidly become a major heavy construction procedure in the United States, proved to be incorrect. Although chemical grouting is used more routinely in Europe than elsewhere, it is evident that the application industry will be slow in developing. Tannin-formaldehyde systems have now been developed for this market and, along with the chrome-lignin and silicate systems, share the modest market for the lower cost grouts.

#### ACKNOWLEDGMENT

The long-range bark utilization program summarized in this review was participated in and contributed to by more than forty chemists and engineers employed by ITT Rayonier, including those named in the literature cited.

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## REVIEW

### Heterocyclic Compounds Found in Cooked Meats

Takayuki Shibamoto

Heterocyclic compounds occurring in cooked meat products (boiled beef, canned beef, cooked chicken, canned beef stew, cooked pork liver, roast beef, cooked ovine fat, shallow-fried beef, ground beef, roasted lamb fat) are reviewed. The compounds reviewed include thiophenes, furans, pyrazines, thiazoles, thiazolines, pyrroles, cyclic polysulfides, oxazoles, oxazolines, and pyridines. The odors of these chemicals in relation to cooked meat flavors are discussed.

Many cooked meat constituents have been isolated and identified over the last 20 years. Some fatty acids were found in raw meat and reported by early researchers (Hornstein and Crowe, 1960; Hornstein et al., 1961; Hornstein and Crowe, 1963). Around the same time some low boiling point compounds (hydrogen sulfide, acetone, acetaldehyde, methyl mercaptan, etc.) were identified in cooked beef (Pearson et al., 1959; Kramlich and Pearson, 1960; Pippen and Nonaka, 1960).

Following the development of gas chromatographic techniques and other instrumental methods (MS, NMR, GC/MS), more information concerning cooked meat constituents began to appear. Fifty-five compounds had been reported as volatile compounds in heat-treated meat by the end of 1966 (Herz and Chang, 1970). In the late 1960's, the introduction of the capillary column to gas chromatographic analysis made it possible to make a more comprehensive analysis of cooked meat volatiles. Nonaka et al. (1967) identified 62 of the approximately 227 compounds evident on the chromatogram of the isopentane extract of cooked chicken meat. The compounds identified included 2-methylthiophene and seven alkylfurans.

The trace heterocyclic compounds in meat volatiles began to be identified from that time. Recently, heterocyclic compounds, including, pyrazines, thiophenes, thiazoles, and furans, have received much attention as producers of characteristic cooked meat aromas.

**Thiophenes.** The first thiophene compound reported in cooked meat volatiles was 2-methylthiophene (Nonaka et al., 1967). Thiophenes are responsible for the mild sulfurous odor of cooked meat. Table I summarizes the thiophenes identified in cooked meats.

The formation of thiophenes in cooked meat has been described by several researchers. The sulfur in a thiophene ring may come either from amino acids (cysteine, cystine, methionine) or from a vitamin B<sub>1</sub> (thiamin). Dwivedi and Arnold (1973) obtained some thiophene derivatives (2-methylthiophene, 4,5-dihydro-2-methylthiophene) from a

thiamin solution maintained at 120 °C for 1 h. This is good evidence that thiamin could serve as a thiophene precursor. Hydrogen sulfide, which is formed during the Strecker degradation of cysteine with a diketone (Kobayashi and Fujimaki 1965), has been considered as a precursor of various compounds associated with meat aroma (Pippen and Mecchi, 1969; Brinkman et al., 1972; Shibamoto and Russel, 1976). Shibamoto (1977) obtained 2-thiophene-carboxaldehyde from the reaction of furfural (sugar caramelization product) and hydrogen sulfide. This indicates there was an exchange of S and O in the furan ring during heat treatment. Many thiophene derivatives were formed in the reaction of D-glucose and hydrogen sulfide (Sakaguchi and Shibamoto, 1978). These experimental results indicate that the thiophene derivatives form from a sugar or carbohydrate and hydrogen sulfide or amino acid in meat during heat treatment (cooking).

**Furans.** It is well known that various furans are produced from sugar caramelization or degradation (Hodge, 1967). Some furan derivatives have been thought, therefore, to be present in cooked meat. Table II shows the furans found in cooked meat products. The presence of a furan in raw chicken meat was reported in 1967 (Grey and Shrimpton, 1967). A series of alkylfurans was found in cooked chicken soon thereafter (Nonaka et al., 1967). Herz (1968) reported that a small GC peak which had a meaty flavor was identified as 5-thiomethylfurfural. It was the first furan compound recognized as a meaty-flavor-giving constituent. Various furan compounds which do not contain sulfur possess a wide variety of aromas, none of them meaty (Herz and Chang, 1970). Tonsbeek et al. (1968) isolated two furan compounds from beef broth. They were 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone, which has a caramel-like odor (Hodge, 1967), and 4-hydroxy-5-methyl-3(2*H*)-furanone. Persson and von Sydow (1973) identified nine alkylfurans in a headspace sample obtained from canned beef using gas chromatographic-mass spectrometric techniques. The furans identified included unsubstituted furan and 2-methylfuran, which has a sickly, nasty smell and gives an off flavor to canned beef. Musinan and Walradt (1974) identified 179 volatile compounds, including 23 furan derivatives in pressure-cooked

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