

THE ROLE OF EXTRACTIVES IN THE HYDROPHOBIC BEHAVIOR OF LOBLOLLY PINE RHYTIDOME

Marshall S. White, Geza Ifju and Jay A. Johnson¹

Department of Forestry and Forest Products, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061

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ABSTRACT

Wettability, as indicated by contact angle with water, of phellogen and old phloem surfaces of loblolly pine (*Pinus taeda*) rhytidome was determined after extraction, heating, and aging. These two tissues are the predominant surfaces exposed after milling pine bark into small particles.

Contact angles measured for bark surfaces were over 50% higher than those published for wood. Old phloem gave an average angle of 118° while phellogen was significantly more wettable with an average contact angle of 106°. Extraction of bark by diethyl ether and methanol increased wettability. Furthermore, large contact angles were measured on glass plates covered with condensed bark extractives. Heat treatments at 105°C for 78 hr increased the contact angle, thus decreasing wettability. The influence of heating time on contact angle was described by an exponential function whose coefficients were used for quantitative assessment of the treatment effects. Surface aging was shown to involve the same general physico-chemical processes as heating. Effects of heating were shown to be related to ether and methanol soluble extractives in loblolly pine bark.

Additional keywords: *Pinus taeda*, phellogen, phloem, wettability, contact angles, extraction, heating, aging.

INTRODUCTION

The potential of tree bark as a source of raw material is currently under serious consideration. Bark residues of various tree species have been shown to be effective in removing oil contaminants from aquatic environments (Weldon 1971a, b). It has been reported that barks of several tree species contain various amounts of wax-like extractives (Crist 1972). Weldon (1971b) demonstrated that southern pine rhytidome is naturally hydrophobic and, as such, is well suited as an oil scavenger. Both Chow (1972) and Weldon (1971b) attributed this resistance to wetting to some of the extractives and proposed that the hydrophobic behavior can be enhanced by heating. It has also been suggested that bark may be a potential raw material for various composition boards (Maloney 1973). Bodig (1962) and others (Freeman 1959; Herczeg 1965; Chen 1970; Hse 1972) have shown

that wettability and strength of glue bonds formed by some adhesives on wood are related. Therefore, the strength of bark boards formed with liquid synthetic resins could also be affected by surface wettability which, in turn, could be influenced by the relative amount and location of the hydrophobic extractives. The role played by the hydrophobic nature of bark surfaces in such processes as the selective adsorption of oils and the gluing of bark particles into board products provided the justification for a thorough study of the wettability of bark surfaces.

The degree to which a particular liquid will wet (penetrate into, spread on, or adhere to) a solid depends on the "surface free energies" of the solid-vapor interface γ_{SV} , the liquid-vapor interface γ_{LV} , and the solid-liquid interface γ_{SL} . These interfacial energies are defined thermodynamically by

$$\gamma = \left(\frac{\partial F}{\partial A} \right)_{T, V, n_i} \quad (1)$$

where A = surface area
 V = volume

¹ Graduate Student, Professor, and Assistant Professor, respectively.

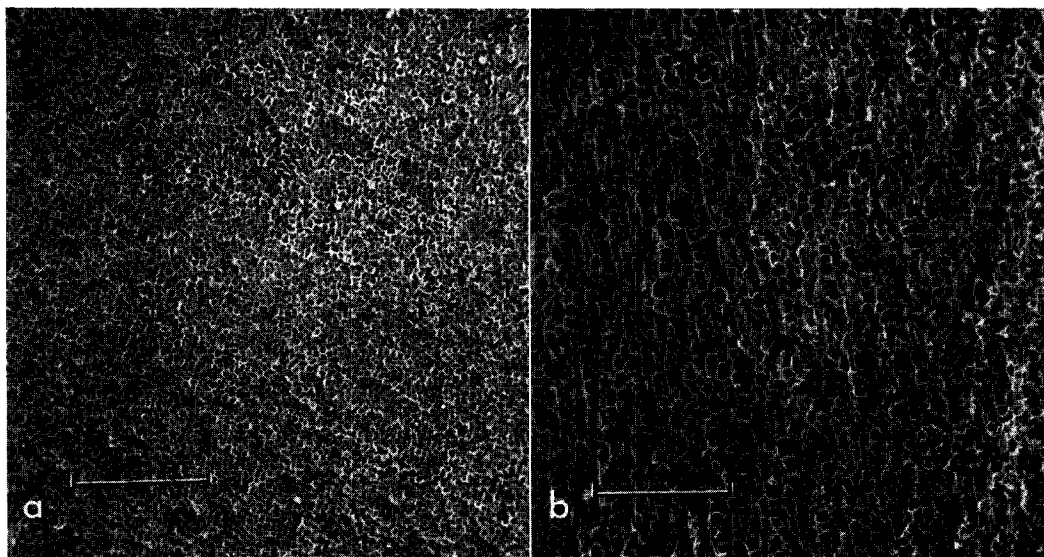


FIG. 1. Scanning electron micrographs of the bark surfaces used for contact angle measurements. a. Phellogen b. Old phloem

n_i = number of moles of component i

$F = U - TS$ = Helmholtz free energy

U = internal energy

T = absolute temperature

S = entropy.

When a liquid droplet is placed on a solid, the liquid comes to rest in the form of a lens. This equilibrium condition is generally expressed by Young's equation

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad (2)$$

where θ = contact angle formed by the lens edge.

There is some confusion concerning the theoretical interpretation of this equation. Originally, it was described by Thomas Young (1805) in terms of "forces":

The part (of the whole superficial cohesion of the fluid) which acts in the direction of the surface of the solid is proportional to the cosine of the inclination, and this force of the solid will be equal to the force of the common surface of the solid and the fluid.

However, a more plausible interpretation based on energy has been given by Johnson (1959), who has derived the relationship by assuming total free energy of the system at

constant temperature, volume, and mass is a minimum.

Measures of the three wetting processes, such as the coefficient of spreading K , the work of adhesion W , and the depth of penetration into a capillary L , have traditionally been expressed in terms of the liquid surface free energy γ_{LV} and the contact angle θ by the following relationships:

$$K = \gamma_{LV} (\cos \theta - 1) \quad (3)$$

$$W = \gamma_{LV} (\cos \theta + 1) \quad (4)$$

$$L = B \gamma_{LV} \cos \theta \quad (5)$$

where $B = rt/2\mu$

and r = radius of curvature of the capillary

t = time

μ = viscosity.

Thus for a given liquid, the contact angle θ is considered an indicator of the three wetting processes on a solid surface.

The objectives of this study were to characterize wettability of two surfaces of loblolly pine rhytidome in terms of contact angle and to determine the role of ether and methanol extractives in heat and aging sensitivity of bark wettability. The specific

surfaces selected were those most frequently exposed when loblolly pine bark is milled into small particles.

EXPERIMENTAL PROCEDURES

Material

Loblolly pine (*Pinus taeda* L.) rhytidome was obtained from several trees in a south-west Virginia grove and stored in plastic bags under refrigeration. The surfaces used for contact angle measurements were (1) a surface consisting of phellogen cells exclusively and (2), a surface composed of old phloem. These latter surfaces were prepared from regions of rhytidome between the thick-walled periderm layers by sanding off as much periderm tissue as possible with a medium commercial sandpaper in order to expose layers of included old phloem. This surface is called "old phloem" throughout this paper; however, it should be noted that expanded periderm cells were also present. This type of surface is often exposed when pine bark is processed into particles. The phellogen surfaces were primarily those exposed as a result of natural breaks during removal of the bark from the stem. Small flat samples with phellogen surfaces were excised from larger rhytidome sections with a scalpel.

Contact angle measurements

Contact angles were measured using the "drop buildup" method described by Collet (1972). The apparatus consisted of a horizontal student microscope with a goniometer eyepiece and a mechanical stage. For purposes of specimen moisture content control, a small glass conditioning capsule was attached to a source of saturated air. The capsule had two optical flats through which contact angles could be measured. Microscope magnification was 20 \times for all tests. The liquid droplets were introduced onto the solid surface using a calibrated syringe capable of producing droplets of 0.009 ml repeatedly.

The specimens were affixed to the mechanical stage of the microscope with the tangential surface in the horizontal position.

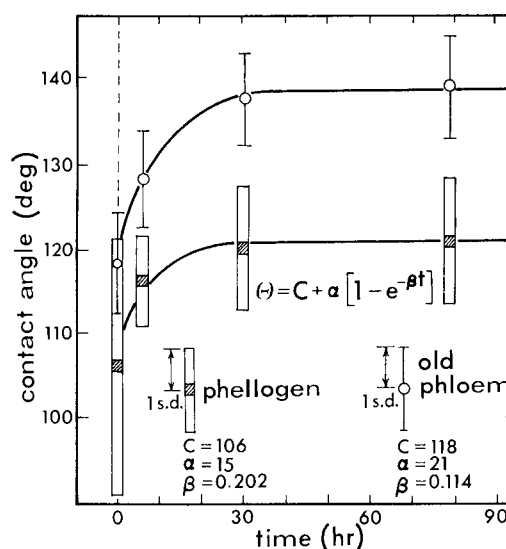


FIG. 2. Relationship between heating time (t) and contact angle (θ) of water measured on loblolly pine phellogen and old phloem surfaces.

Droplets of 0.009 ml were added to the surface in succession. Two readings on each side of the progressively growing drop were taken at the five drop volumes between 0.018 and 0.054 ml. The contact angle was defined as the average of these ten readings.

Thermal treatments

Twenty specimens from each tissue, phellogen and old phloem, were prepared as previously described. After conditioning the bark in the laboratory, contact angles of water were measured on both surfaces. The same 40 specimens were then heated for periods of 6, 30, and 78 hr in a convection oven at 105 C. After each heating period, the specimens were allowed to equilibrate to about 8% equilibrium moisture content, and the contact angles were measured again. This procedure was also followed for a set of previously extracted rhytidome surfaces using heat treatments up to 180 hr. Another set of specimens of each tissue was heated for 126 hr and extracted as described above. These samples were reheated again for 6, 30, and 78 hr before testing.

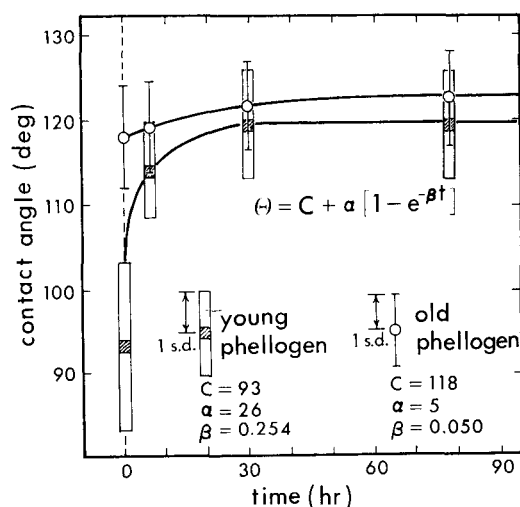


FIG. 3. Relationship between heating time (t) and contact angle (θ) of water on young and old phellogen surfaces of loblolly pine.

Extractions

Chen (1970) has shown that extraction of wood increases wettability. It was thought that extraction would influence wettability of pine rhytidome. To determine this influence, contact angle measurements were made on extracted and unextracted materials.

Forty specimens, twenty each of phellogen and old phloem, were air-dried in the laboratory. Contact angles were measured and the specimens were air-dried again. All specimens were extracted with diethyl ether in a Soxhlet apparatus for seven days and placed in a small desiccator under vacuum, over paraffin, for an additional seven-day period to remove the ether solvent from the surfaces of the bark samples. After desiccation, the bark was equilibrated in the laboratory and the contact angles were measured again with water. Finally, the same specimens were extracted for seven days with methanol, conditioned, and tested using the procedure outlined above.

Test of extracts on glass surfaces

By dipping glass microscope slides into a solvent-extract mixture of bark and subsequently evaporating the solvent, films of ether and methanol extracts could be formed

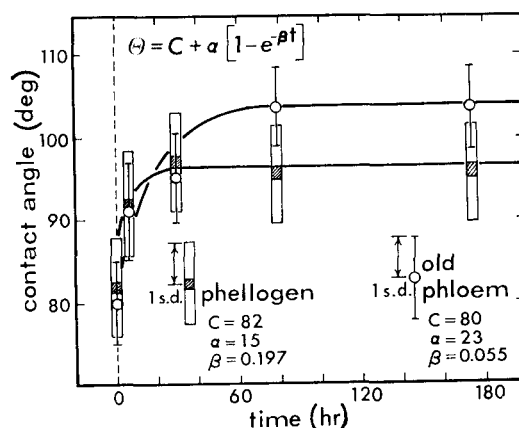


FIG. 4. Relationship between heating time (t) and contact angle (θ) of water on loblolly pine phellogen and old phloem surfaces extracted with diethyl ether and methanol.

on a glass substrate for contact angle measurements. In this experiment, air-dried bark was separated into old phloem and dense periderm tissues. Dense periderm was chosen instead of phellogen since the relative amount of phellogen in pine rhytidome is small. Separation of the two tissues was done manually with a scalpel, and therefore complete isolation was difficult. The mixing of small amounts of dense periderms with old phloem and phloem with periderm could not be entirely prevented. Once separated, the samples were milled to pass through a 40-mesh screen. Two-gram samples were extracted with diethyl ether in a Soxhlet apparatus for 24 hr. The amount of extract removed from each tissue was determined gravimetrically after evaporation of the solvent. The same two-gram samples were then extracted with methanol for another 24-hr period and the amount of extract was again determined. The procedure followed was similar to that proposed by Browning (1967).

Contact angle measurements with water were made on freshly cleaned glass and also on extractive film covered glass surfaces. The films on the glass surfaces were heated at 105 C for periods of 6, 24, and 48 hr. Between each heating period contact angles were again measured. The results were

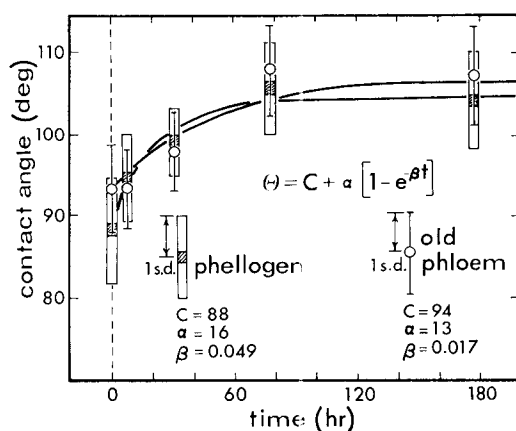


FIG. 5. Relationship between heating time (t) and contact angle (θ) of water on old phloem and phellogen surfaces after previous heating for 126 hr and subsequent extraction with diethyl ether and methanol.

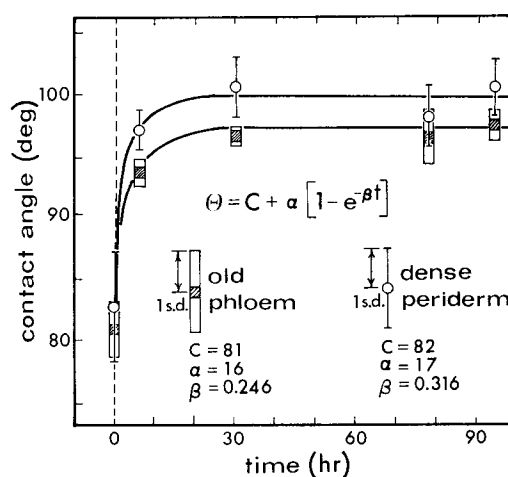


FIG. 6. Relationship between heating time (t) and contact angle (θ) of water on glass surfaces covered with films of old phloem and dense periderm ether extracts of loblolly pine rhytidome.

then compared to the response of unextracted bark surfaces.

Surface aging

Specimens with secondary phloem surfaces only were prepared by sanding excised air-dried samples. As many specimens as could be processed within an hour were exposed to a laboratory environment of 23 C and 45% RH for a period of 1, 6, 12, 48, 216, 452 and 848 hr. Contact angles were measured after each time interval. It was hoped that the effects of these tests would be representative of the aging processes occurring in loblolly pine bark surfaces.

RESULTS AND DISCUSSION

The results of the experiments are shown in Figs. 2 through 7. Obviously, the contact angle is related to time of heating at 105 C or to time of aging in laboratory conditions. The boxes or circles in the diagrams represent mean values of ten observations of contact angle. The curves are best-fit, nonlinear regression equations of the form:

$$\theta = C + \alpha (1 - e^{-\beta t}) \quad (6)$$

where θ = contact angle (degrees)

t = time

C, α, β = parameters.

This particular function was chosen not only on the basis of the form suggested by the data but also because the treatments themselves may reflect reaction-rate type of processes. The mathematical model indicates that as time of heating or aging increases, the contact angle asymptotically approaches a constant value $C + \alpha$. The value of C is the contact angle at $t = 0$, which is the contact angle measured on untreated surfaces. The parameter α represents the magnitude of the increase in the contact angle due to the treatment and the parameter β is a measure of the rate of change in the contact angle that can be seen by differentiating equation 6:

$$\frac{d\theta}{dt} = -\beta \{\theta - (C + \alpha)\}. \quad (7)$$

Thus, a large value of β indicates a rapid increase to the final value and a high level of sensitivity to the treatment. The three parameters are given in each figure and can be used for characterizing and comparing the surfaces studied as well as their response to treatments.

Surface texture

Although an attempt was made to manufacture uniform bark surfaces, variations did

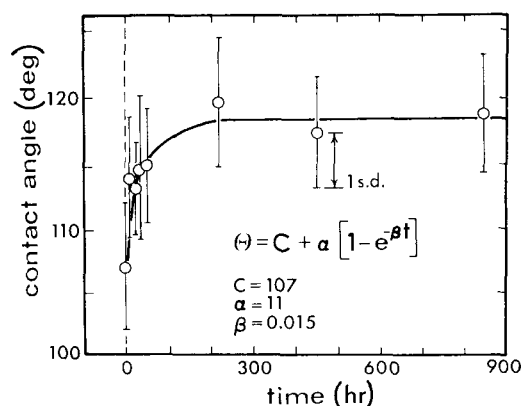


FIG. 7. Effect of aging on contact angle (θ) of water on old phloem surfaces of loblolly pine rhytidome.

occur in the texture of the surfaces generated. In other systems it has been found that surface roughness influences the contact angle. Since Young's equation is only valid for ideally smooth surfaces, Wenzel (1936) proposed the following generalization to account for surface texture:

$$\cos \theta_a = R \cos \theta_t = R \left\{ \frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}} \right\} \quad (8)$$

where θ_t = true contact angle for an ideally smooth surface

θ_a = apparent contact angle actually measured on a rough surface

R = ratio of the true surface area to the area projected on a plane perpendicular to the normal of the overall surface ($R > 1$).

It is noted that if θ_t is less than 90° , the apparent contact θ_a decreases with increasing roughness R . Conversely, if θ_t is greater than 90° , θ_a increases with R .

For some systems, a surface profile analysis can be used to estimate the surface roughness R . However, according to Marian (1963), other factors, such as the height and slope of surface asperities or porous openings in the solid, may also contribute to the deviation between the apparent and the true contact angle. Cassie and Baxter (1944), for example, have proposed the

following modification of Wenzel's equation for microscopically porous surfaces:

$$\cos \theta_a = R (f_1 \cos \theta_t - f_2) \quad (9)$$

where f_1 = fractional area of the liquid-solid interface

f_2 = fractional area of the liquid-air interface.

For bark surfaces, f_2 would correspond to the amount of lumen area in the total cross section. Since Cassie and Baxter (1944), as well as Dettre and Johnson (1964), have demonstrated that θ_a increases with f_2 , it might be expected that the apparent contact angle would increase with the size of lumen openings, provided the cell wall thickness remained constant.

Electron micrographs of typical phellogen and old phloem surfaces used in this study are shown in Fig. 1. Although a more quantitative examination of the degree to which surface roughness affects contact angle phenomena is currently being conducted, scanning electron micrographs were used during this study to qualitatively assess the contribution of surface roughness. Notice, for example, the difference in the lumen sizes of the cells of the two surfaces shown in Fig. 1.

Characteristic contact angles of water on phellogen and old phloem

Table 1 is a comparison of contact angle on the two characteristic surfaces of loblolly pine rhytidome. Included in the table are mean contact angles measured after ether and alcohol extractions of phellogen and old phloem surfaces. The relatively high values of contact angle should be noted. All but the double-extracted surfaces gave obtuse contact angles. Douglas-fir earlywood and latewood surfaces have been reported to give 74.0° and 77.2° angles with water, respectively (Herczeg 1965). A comparison of these values with the 118° and 106° angles for old phloem and phellogen, respectively, reveals that bark surfaces are markedly less wettable than wood.

Another important result of this study is

TABLE 1. Mean contact angles (θ) of water on phellogen and old phloem after seven days of Soxhlet extractions by ether and methanol

Treatment	Tissue				t-value Between Tissues
	Old Phloem		Phellogen		
	θ (Degrees)	Coefficient of Variation (%)	θ (Degrees)	Coefficient of Variation (%)	
Untreated	118	6.24	106	8.43	4.12**
Ether Extracted	109	5.48	95	5.17	3.14**
Ether and Methanol	80	6.26	82	10.41	0.23

** Significant at the 1% level of probability.

the difference between the contact angle measured on old phloem and on phellogen tissues. This difference remained significant even after a seven-day-long Soxhlet extraction by ether. However, when the ether-extracted samples were further extracted by methanol, wettability of the two tissues became the same. Scanning electron microscope observations, at various magnifications, indicated no discernible physical changes of the bark surfaces due to extraction with ether and then methanol. It seems unlikely that the extractions caused texture changes, thus equalizing the effect of surface roughness. The methanol, if not adequately removed from the surfaces before the contact angle measurements were made, could have masked the surface with a con-

taminating layer, thus equalizing the measured contact angles. However, we feel that the difference in wettabilities of old phloem and phellogen lies primarily in the chemical nature of these two surfaces. Of secondary importance in this connection may be the anatomical structure of these tissues.

Effect of thermal treatments on wettability

The effect of heating bark at 105°C on the contact angle formed on old phloem and phellogen is shown in Fig. 2. The initial contact angles C for the two surfaces are those given in Table 1 for the unextracted tissues. The final angles, $C + \alpha$, after prolonged heating are 121° for phellogen and 139° for old phloem. These are remarkably high values when compared with contact

TABLE 2. Analysis of variance of contact angle of water on two loblolly pine bark surfaces extracted by two different solvents

Source	DF	Sum of Squares	Mean Squares	F	Probability for $F_{table} > F$
Tissue (T)	1	2,477	2,477	19.4**	0.0001
Extraction (E)	2	15,931	7,965	62.5**	0.0001
T x E	2	630	315	2.5	0.0869
Residual	155	14,656	127		

** Significant at the 1% level of probability.

TABLE 3. *A comparison of contact angles before and after heating*

Substrates	C (before heating)		C + α (after heating)		α (difference)	
	Old Phloem	Dense Periderm	Old Phloem	Dense Periderm	Old Phloem	Dense Periderm
Unextracted Material	118	106†	138	121†	20	15†
Extract Film Covered Glass	81	82	97	100	16	18

†These contact angles were measured specifically on the phellogen layer of the dense periderm.

angles obtainable for wood surfaces (Gray 1962; Herczeg 1965).

It should be noted in Fig. 2 that both tissues responded to heat treatment in the same general manner. Increasing time at 105 C resulted in increasing hydrophobic behavior. The difference between the two may be seen in the magnitude of the final angles and in the increase in β .

The boxes and circles in Fig. 2 represent average values of ten independent contact angle determinations. The vertical bars associated with the boxes represent standard deviations around the mean values. It is noted that the variability of data is appreciably greater for phellogen than for old phloem. An especially large variation in contact angle was measured on the initial, untreated phellogen surfaces. This difference in standard deviations prompted a closer examination and, consequently, a stratification of the phellogen tissues.

During surface preparations, it was noted that some phellogen specimens were darker in color than others. This color variation was found to be related to the relative position of the phellogen surface in the rhytidome. In general, older phellogen tissues, further away from the cambium, tended to give the darker surfaces. Interestingly, these darker specimens gave consistently higher contact angles with water than did the younger, light-colored ones. On the basis of this observation, a separate experiment was conducted in which phellogen tissues from the same

bark pieces were separated into two groups: the older ones near the outside of the rhytidome and the younger ones from the side near the living phloem tissue. Contact angles were determined for each group both in the original, untreated state as well as after heat treatments at 105 C.

Results of contact angle measurements are given in Fig. 3. There is a striking difference between the wettabilities of old and recently produced phellogen surfaces. First, there is a very large difference between the C values, 93° for young and 118° for old phellogen. In fact, old phellogen had an initial contact angle of the same magnitude as the old phloem. Upon heating, however, the relative increase of the angle was small, $\alpha = 5^\circ$, for the old phellogen with a very slow rate of increase, $\beta = 0.050$. Corresponding values for young phellogen were $\alpha = 26^\circ$ and $\beta = 0.254$. The C + α value for old phellogen remained somewhat higher than for the younger tissue after prolonged heat treatments.

Influence of extractives on contact angle

Table 1 shows the effects of extractions on wettability of old phloem and phellogen tissues. The contact angle measured on both surfaces decreased markedly with each extraction. The reduction in contact angle is shown to be greater for the old phloem than for the phellogen resulting in an equalization between the two tissues. Analysis of variance of the results is given in Table 2. It is apparent that the difference is

highly significant not only between the two tissues but also among surfaces extracted with the two solvents. The interaction is significant at only a low level of probability (8.69%) indicating that the two tissues responded somewhat differently, in terms of contact angle, to extraction.

The extracted surfaces were then exposed to heat at 105 C and the contact angles were measured. Figure 4 shows the effects of heating to 180 hr on the wettability of old phloem and phellogen. First, the values of C , as earlier shown in Table 1, are appreciably lower than those for the unextracted specimens. The values of 80° and 82° for C are comparable to those reported for wood (Gray 1962; Herczeg 1965). This result shows indirectly that the basic difference between wettabilities of bark and wood probably lies in the differences in extractive contents. Second, the final values of contact angle, $C + \alpha$, achieved by heating at 105 C are very much lower than those of the unextracted surfaces: 97 for phellogen and 103 for old phloem. Third, the values of β are also lower than those for the unextracted barks.

These results point quite conclusively to the extractives as those components in bark most sensitive to heat treatments. These ether- and methanol-soluble materials undergo either a chemical reaction, such as oxidation of unsaturated fatty acids and esters as proposed by Hemmingway (1969) that makes them increasingly hydrophobic, or the concentration of these extractives increases at the surface due to thermally induced migration.

It is interesting to note that the curves representing phellogen and old phloem in Fig. 4 do not differ from each other as much as those for unextracted tissues in Fig. 2. This indicates again that the differences in wettability between the two tissues are due at least in part to the differences in extractive contents. Removal of ether- and methanol-soluble extractives from the surfaces of the two tissues reduces the differences in contact angles.

The increase in contact angle on the extracted surfaces upon heating as shown by

the values of α in Fig. 4 may be interpreted as a result of migration of small amounts of unremoved extractives to the surfaces. Such migration of extraneous materials has been reported to be responsible for producing refractory surfaces, often called "case hardened" surfaces, in veneer during high temperature drying (Hancock 1963). Vapor-phase transport has also been shown to occur with stearic acid in paper (Swanson and Cordingley 1959). Although seven-day extractions were extensive, the relatively thick bark specimens and their very low permeability may very well inhibit removal of some of the extractives. It is also plausible that other materials, even major components, of bark may undergo some type of oxidation reaction at high temperatures producing less wettable surfaces.

In order to test the solubility of ether and methanol extractives after heating, specimens were heated at 105 C for 126 hr and then extracted the same way as the non-treated ones. These preheated and subsequently extracted phellogen and old phloem tissues were again heated and the change in contact angle was measured. Figure 5 shows the relationships of contact angle to time of heating for the two preheated and extracted surfaces. In Fig. 5, the initial angles C for both tissues are higher than those for the unheated and extracted specimens; 88° for phellogen and 94° for old phloem. In addition, the final angles, $C + \alpha$, are virtually the same for the two surfaces but higher than those in Fig. 4. These results indicate that preheating of bark resulted in a general increase in contact angle that could not be eliminated by simple extraction. Perhaps the ether- and methanol-soluble extractives underwent a polymerization reaction upon heating that rendered them insoluble in the solvents. Further heating after extraction could have resulted in pyrolysis, continued polymerization and/or oxidation of these substances.

Direct effects of ether extracts on contact angle

Old phloem contained 6.33% ether extracts calculated on the basis of the unex-

tracted oven-dry weight of the samples and the dense periderm contained 8.35%. This latter extract was tinted yellow in color, whereas that from the old phloem was virtually colorless. After ether extraction, the dense periderm tissues contained 10.16% methanol-soluble materials and the old phloem only 7.51%. Extraction of these residues with water demonstrated that the alcohol extract contained most of the water-soluble substances. The ether extract from either tissue was waxlike in texture and was easily deposited as a thin film on glass microscope slides. This was not possible with the methanol extract because upon evaporation of the solvent, the extract became a powder and did not adhere to the glass.

When the glass was coated with the ether extract from old phloem, the average contact angle measured was 81° ; and when it was coated with the dense periderm extract, 82° . Clean, uncoated glass exhibited an average contact angle of 24° with water. Obviously, the film determines the contact angle and the ether extracts are very hydrophobic.

After the coated glass was heated for periods of 6, 30, 78 and 94 hr, the contact angle measured on the cooled surfaces increased rapidly with heating time and tended to be constant after 30 hr. The observed data are shown in Fig. 6 along with the best-fit curves. These curves are remarkably similar to those obtained for the rhytidome surfaces themselves, except that they lie at a somewhat lower level. This decrease could be attributed to the smooth texture of the glass-coated surface and therefore is consistent with Wenzel's definition of surface roughness. In Table 3 the average contact angles measured on unextracted phellogen, old phloem and extracted coated glass, before and after heating are compared. Despite the difference in texture between the bark surfaces and the coated glass surfaces, the values of α are similar for both bark components. Therefore, the response of both bark surfaces to heating appears to be due to the thermal response of the ether-soluble extracts. Crist

(1972) has shown that the concentration of extractives varies through the thickness of the dense periderm, thus a comparison of the α values for the unextracted material and the extractive film is not strictly valid. However, this appears to be of minor significance in relation to the overall similarity of the α values.

Effect of aging on old phloem surfaces

It has been noted that surface aging of wood adversely affects wettability and glue bond strength (Gray 1962; Hancock 1963; Herczeg 1965; Stumbo 1963). The effects are possibly due to chemical interactions of the substrate and air or to the deposition of air-suspended particles contaminating the solid surface.

Figure 7 shows the result of the aging experiment. The contact angle measured on the old phloem surfaces of loblolly pine rhytidome increased rapidly with time of aging for the first 100 hr. The increase appears to be most significant up to 6 hr of exposure to air and virtually nonexistent after 200 hr. Herczeg (1965) demonstrated that the contact angle measured on Douglas-fir latewood and earlywood increased from 40.8° to 74.8° and from 43.0° to 77.2° , respectively, after 45-hr exposure. In a corresponding period of time the contact angle measured on old phloem increased by only 8° as shown in Fig. 7.

Because the change in wettability occurs so rapidly, it is felt that the actual average contact angle C at time equal to zero is considerably less than the 107° measured (Fig. 7). The time between preparation and initial measurement at $t = 0$ was about one hour. Within this period of time the surface probably changed markedly.

The general form of the function describing variation in contact angle with respect to time of aging is very similar to those calculated for the effect of heating. This should indicate a close relationship between the processes of aging and heating. In fact, heating could be looked upon as accelerated aging as indicated by the darkening of the ether extracts after heating, the implication being that some portion of the

ether-soluble material changes in color and its wettability is decreased. This may be the reason for the darker color and lower wettability of old phellogen as opposed to young phellogen surfaces observed in this study.

CONCLUSIONS

From the results of this investigation, the following conclusions may be drawn:

1) Extractives are responsible for the low wettability of loblolly pine bark; their changes upon heating are responsible for the increase of contact angle of water on the bark surfaces most frequently exposed in mechanical processing.

2) Phellogen surfaces are significantly more wettable than tissues containing old phloem.

3) Heating increases the contact angle of water on both rhytidome surfaces tested, apparently because of a thermal reaction of ether soluble extractives.

4) Surface aging increases contact angle of water on bark. The effect of aging is similar to that of heat treatments.

5) The relatively high contact angles measured on the bark surfaces are good indicators of the hydrophobic nature of rhytidome. Low wettability of bark by water is the reason for the suitability of this raw material for adsorption of oil from aqueous environments.

6) Surfaces of loblolly pine bark particles are appreciably less wettable than wood particle surfaces. This may adversely affect the strength of the bark-adhesive bond.

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