Rheological Approach to the Capillary Penetration of Coating Into Wood

Mari de Meijer, Barend van de Velde, and Holger Militz†—SHR Timber Research*

The penetration of water- and solventborne binders into the capillaries of wood was studied as a function of the viscosity, surface tension, and capillary pressure according to the Washburn equation.

During the penetration, water is selectively removed from the coating, which causes a strong increase in viscosity that limits the penetration. Waterborne dispersions and emulsions showed a rapid increase in viscosity with increasing solid matter content. Surface tension of the binder and the adsorption of surfactants to the wood have an additional influence on the maximum penetration.

INTRODUCTION AND THEORETICAL BACKGROUND

The flow of polymeric liquids into the capillary pore structure of wood takes place in many practical situations. The penetration of a coating into a wooden substrate is one important example,[1] but it also applies to the wetting and spreading of glues on wood[2] and the treatment of wood with polymer containing preservatives or water repellents.[3,4] The need to avoid the use of volatile organic compounds has caused a substantial change from solvent-based solution polymers to polymers that are dispersed or emulsified in water. The water- based polymeric liquids generally contain a large amount of smaller surface active molecules, which are used during the manufacture of the polymer to stabilize the product or to improve wetting by reducing liquid surface tension.

The aim of this work is to understand the penetration process of a polymer containing liquid into cell capillaries of wood. The factors that will influence the penetration rate, like viscosity, wetting, and liquid surface tension are studied as a function of increasing mass fraction polymer. From this information, the maximum penetration depth was calculated and compared with the data obtained experimentally. The capillary penetration process has been studied with four different commercially used polymeric binders intended for use in wood primers. Additional work involved studies on the influence of the addition of thickeners to the binders and the effect of surfactants on the capillary uptake of water.

Previous research on the penetration of coatings into wood focused on: the morphological or anatomical aspects of the wooden substrate,[1,5] the influence of the binder type,[6] or on the impact of the particle size or molecular weight within one category of polymer.[7,8,20] In numerous publications,[9-12] the principle of capillary penetration is based on the Washburn-equation,[13] which is derived from Poiseuille flow (equation [1]) with the capillary pressure (P_c), minus the counter pressure due to gravity (P_g) as the driving force for the flow.[14] Frequently, the influence of gravity has been neglected. If the penetration depth is small, this gives only a minor error, but at the equilibrium height of rise, considerable deviations will occur.

For a cylindrical capillary this gives,

$$\frac{V}{t} = \frac{\pi P r^4}{8\eta h} \tag{1}$$

$$P = P_c - P_g \quad P_c \frac{2\gamma_L \cos\theta}{r} \quad \text{and} \; P_g = \rho g h \tag{2}$$

V = volume (m^3)
P = pressure (Pa)
r = capillary radius (m)
h = height (or distance) of capillary rise (m)
A = area (m^2)
t = time (s)
g = acceleration of gravity constant (9.8 m s^{-2})
η = viscosity of the liquid (Pa s)
γ_L = liquid surface tension (mN m^{-1})
θ = contact angle between liquid and wood (°)
ρ = density of the liquid (kg m^{-3})

---

*P.O. Box 497, NL-6700 AL Wageningen, The Netherlands, e-mail: m.demeijer@shr.nl.
†Dr. Militz is also associated with Wageningen University, Wood Science Group, P.O. Box 342, NL-6700 AH Wageningen, The Netherlands.

With V= A h and A= π r^2 the following expression for the rate of capillary rise is obtained

$$\frac{dh}{dt} = \frac{2\gamma_L \cos\theta r - \rho g \pi h r^2}{8\eta h} \text{ if } \cos\theta > 0 \; (\theta < 90^\circ) \tag{3}$$

The relationship between liquid surface tension and contact angle is given by the Young's equation

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL} \text{ if } \cos\theta < 1 \; (\theta > 0^\circ) \tag{4}$$

The term $\gamma_L \cos\theta$ is determined by the difference between the surface tension of the solid (in equilibrium with air) (γ_S) and the interfacial tension (γ_{SL}) between the wood (solid) and the coating (liquid). If wetting by the liquid is complete ($\theta = 0$; $\cos\theta = 1$), equation (4) no longer applies and a decrease of the liquid surface tension will lower the capillary pressure. The rate of capillary rise is positively influenced by the capillary radius and negatively influenced by the viscosity and the height of rise. The maximum depth of capillary penetration is reached for the point where dh/dt approaches zero.

For a polymer containing liquid that penetrates the capillary cell structure of wood, none of the variables in equation (3) can be considered constant with respect to either time or height of rise. In softwoods, the capillary radius will vary between 3 and 30 µm[15] with the position of the cell in the wood (earlywood with wider cells and latewood with narrower cells) and with the length of the individual cell because the diameter decreases at the taper end of a tracheid.[16] Previous studies have shown that the penetration of a coating varies with capillary radius.[17,18] The micro-pores in the cell wall of the wood capillaries, with a size of 0.1-1 nm,[19] will only allow the lower molecular weight materials (Mw approximately below 3000 g mol^{-1})[20-23] to enter the cell wall. The larger polymeric molecules will remain inside the capillary. The previously mentioned process is visualized schematically in *Figure* 1. The selective removal of solvent or water during the penetration process will increase the polymer fraction in the liquid and, hence, the viscosity of the solution. The wetting and the liquid surface tension might also be influenced by the increasing polymer concentration.

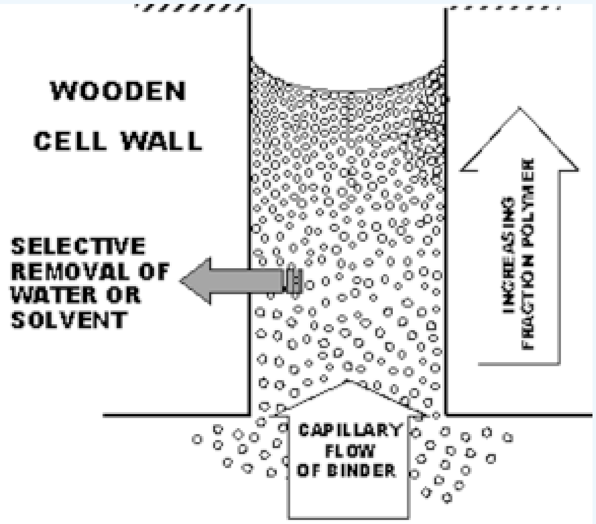

Figure 1–Schematic overview of the transport processes during penetration of a liquid containing polymeric material into a wood cell capillary.

The increase in polymer concentration during the capillary penetration into a wood pore cannot be measured directly, since this would require an in situ measurement of water or solvent transport from liquid to cell wall, which is not possible with the existing measurement techniques. The rate of transfer of water or solvent from a coating to the wooden substrate might, however, be estimated from a comparison of the evaporation rates on wood and an inert substrate like glass. This can be explained as follows, using existing theories for the drying of waterborne latex.[24-27]

During the initial drying of a waterborne dispersion coating, the rate of evaporation is constant and depends only on the environmental conditions. The polymer particles are assumed to be mobile in the water phase, evaporation takes place directly from the liquid water reservoir and the dry layer of polymer on the surface is not limiting the evaporation rate. During the initial stage, evaporation is independent of the coating thickness. The mass fraction polymer in the coating during the first drying stage is given by[27]

$$\phi_m(t) = \frac{m_p}{m_p + m_o - qAt} \quad \text{and} \quad \frac{dm}{dt} = -qA \tag{5}$$

ϕ_m (t) = mass fraction of polymer at time t (-)
m = mass of coating (kg)
m_o = mass of water or solvent at t=0 (kg)
m_p = mass of polymer (kg)
A = surface area (m^2)
q = evaporation rate of water or solvent (kg m^{-2} s^{-1})

After the first drying stage, the evaporation rate is no longer constant because the agglomeration and the coalescence of polymer particles reduce the evaporation of water. At this stage, the evaporation rate becomes dependent on film thickness. In a plot of cumulative mass loss against drying-time, as in *Figure* 3, the end of the first drying stage can be recognized by a deviation from the initial straight line. The time at which this occurs is here indicated by t_1 and the corresponding mass fraction polymer by $\phi_m(t_1)$. $\phi_m(t_1)$ can be considered as a coating property and is in principle independent from the time required to reach the end of the first drying stage.

During the first drying stage of a coating on wood, water or solvent will evaporate to the air and will be taken up into the wood. Later in the drying process, water or solvent originally taken up into the wood might evaporate again through the dried coating but this will take considerably longer. On a wooden substrate, the mass fraction polymer in the coating during the first drying stage is now given by

$$\phi_m(t) = \frac{m_p}{m_p + m_o - At(q^a + q^w)} \tag{6}$$

q^w = water or solvent evaporation rate to wood (kg m^{-2} s^{-1})
q^a = water or solvent evaporation rate to air (kg m^{-2} s^{-1})

The evaporation rate to the air can be measured directly from the mass-loss during drying. This can most accurately be measured on an inert substrate like glass, but might also be measured from the evaporation rate to the air from a coating applied on wood if all water or solvent taken up into the wood is released after the end of the first drying stage. During the initial drying stage, the evaporation rates of water or solvent to the air should be equal regardless of whether the coating is applied on wood or glass, because in both cases the evaporation occurs from a liquid reservoir inside the coating film.

The evaporation rate to the wood cannot be measured directly. However, on wood, the end of the first drying stage will be reached earlier because evaporation occurs in two directions. The time when the first drying stage on wood ends is denoted by t_1' with $t_1' < t_1$ if $q^w > 0$. The mass fraction polymer corresponding to the end of the first drying stage is, however, independent of time or substrate and, hence, $\phi_m(t_1) = \phi_m(t_1')$. This means that

$$\phi_m(t_l') = \phi_m(t_l) = \frac{m_p}{m_p + m_o - t_l'A(q^a + q^w)} \Leftrightarrow q^w = \frac{m_p + m_o - \dfrac{m_p}{\phi_m(t_l)}}{t_l'A} - q^a \qquad (7)$$

The evaporation rate to the wood can be derived from equation (7) by determining q^a from the evaporation rate to the air (on glass or wood). From the mass loss curves on glass, the end of the initial drying period (t_1) is determined and the corresponding $\phi_m(t_1)$ can be calculated. Finally, t_1' follows from the end of the constant evaporation rate during the drying of the coating on wood.

If it is assumed that the evaporation rate of water or solvent to the wood, as derived from a film on the surface, is equal to the evaporation rate by the coating inside the capillary to the cell wall, the increase in mass fraction polymer inside the capillary can be calculated as a function of time. This assumption can be justified by the fact that the drying film is in direct contact with the wooden cell wall, just like the coating inside the wood capillaries. Evaporation of water to the surrounding air during capillary uptake might be considered as zero as long as the wood is in direct contact with the liquid reservoir. The mass fraction polymer ($\phi_{cm}(t)$) inside the cylindrical wood capillary is then given by

$$\phi_{cm}(t) = \frac{m_p}{m_p + m_o - q_w A_c t} = \frac{V\rho f}{V\rho - q_w A_c t} = \frac{0.5\,r\,\rho\,f}{0.5\,r\,\rho - q_w t} \qquad (8)$$

$\phi_{cm}(t)$ = mass fraction polymer inside wood capillary (-)
V = volume of the liquid filled part of the capillary ($\pi r^2 h$) (m^3)
A_c = contact area between liquid inside capillary and cell wall ($2\pi rh$) (m^2)
f = mass fraction solid of the coating (-)
ρ = density of the polymeric liquid ($kg\ m^{-3}$)

The density of the polymeric liquid in principle depends on the mass fraction polymer but might be considered constant as long as the density of the polymer and water or solvent are approximately equal.

The relation between the relative viscosity of a dispersion, or a concentrated emulsion,[28] and the volume fraction of polymer particles can be described by the equations of Mooney[29] (equation 9a), Dougherty and Krieger[30] (equation 9b), or Frankel and Acrivos[31] (equation 9c).

$$\ln\frac{\eta}{\eta_b} = \frac{2.5\phi}{1-\phi/\phi_{max}} \qquad (9a)$$

$$\frac{\eta}{\eta_o} = (1-\phi/\phi_{max})^{-2.5\phi_{max}} \qquad (9b)$$

$$\frac{\eta}{\eta_o} = \frac{9}{8}\,\frac{(\phi/\phi_{max})^{1/3}}{1-(\phi/\phi_{max})^{1/3}} \qquad (9c)$$

η = viscosity of the polymeric liquid (Pa s)
η_0 = viscosity of the continuous phase (water or solvent) (Pa s)
ϕ = volume fraction of polymer (-)
ϕ_{max} = volume fraction polymer at which the viscosity goes to infinity (-)

The sharply increasing viscosity close to ϕ_{max} will rapidly decrease the capillary penetration rate and will eventually limit the penetration.

For many latex or dispersion paints, the viscosity also depends on the applied shear rate, in particular if thickeners or pigments are added.[32,33] The shear rate at the wall of a cylindrical capillary during the rise of the liquid is given by equation (10) as a function of the capillary radius and the rate and height of capillary rise.[34]

$$\tau_w = \frac{3+b}{r}\left(\frac{dh}{dt}\right) \text{with } b = \frac{d\log(dh/dt)}{d\log((h_\infty - h)/h)} \qquad (10)$$

τ_w = shear rate at the wall of the capillary (s^{-1})
h_∞ = equilibrium height of rise (m)

The factor b can be determined from a plot of the rate of capillary rise against the fractional height of rise. For Newtonian liquids, b was found to be one, whereas for pseudoplastic liquids b > 1. For example, for a four percent solution of polystyrene in toluene, b was found to be about 1.2.[34]

EXPERIMENTAL

Materials

The following commercial polymeric binders were used:

(1) ACEMUL: an emulsion of acrylic binder in water, particle size was not specified.

Table 1—Initial Mass Fraction Polymer ($\phi(t_0)$) and Average Amount of Coating Used in Evaporation Studies

Binder Type	Viscosity Level	$\phi(t_0)$	Mass Applied on Wood (g)	Mass Applied on Glass (g)
ACDIS	I	0.334	1.54	0.86
ACEMUL	I	0.326	1.84	1.55
ALKEMUL	I	0.326	1.58	1.16
SOLVALK	I	0.367	0.80	0.76
ACDIS	IV	0.342	0.81	1.02
ACEMUL	IV	0.334	1.00	0.93
ALKEMUL	IV	0.330	0.82	1.09
SOLVALK	IV	0.410	0.71	1.16

Table 2—Viscosities (Pa s) of the Binders at Different Levels of Thickening and Shear Rates

Binder Type	Viscosity Level	Shear Rate (s^{-1})				
		0.1	1	10	100	1000
ACEMUL	I	—[a]	—	0.007[b]	0.007	0.007
	II	—	—	0.013[b]	0.013	0.012
	III	203	32	5.3	1.0	—
	IV	2457	331	61	8.6	—
ACDIS	I	—	—	0.03[b]	0.03	0.02
	II	—	1.4	0.85	0.42	0.16
	III	17	7.6	2.6	0.75	0.21
	IV	275	38	6.9	1.5	0.35
ALKEMUL	I	—	—	0.005[b]	0.005[b]	0.005
	II	—	2.9	0.37	0.06	0.02
	III	—	—	1.4	0.20	0.05
	IV	222	39	8.5	2.0	0.45
SOLVALK	I	—	—	0.03[b]	0.03	0.03
	II	22	3.1	0.50	0.12	0.07
	III	177	25	3.3	0.58	0.22
	IV	1132	153	18	3.0	—

(a) — = no data available.
(b) extrapolated data.

(2) ACDIS: a waterborne acrylic dispersion with a monomodal particle size of about 50 nm.

(3) ALKEMUL: an alkyd resin emulsified in water with a weight averaged molecular weight of 50.000 g mol^{-1} and a particle size about 500 nm. The oil length was about 63%.

(4) SOLVALK: a solventborne alkyd dissolved in white spirit with a weight averaged molecular weight of 109.000 g mol^{-1} and an oil length of about 63%.

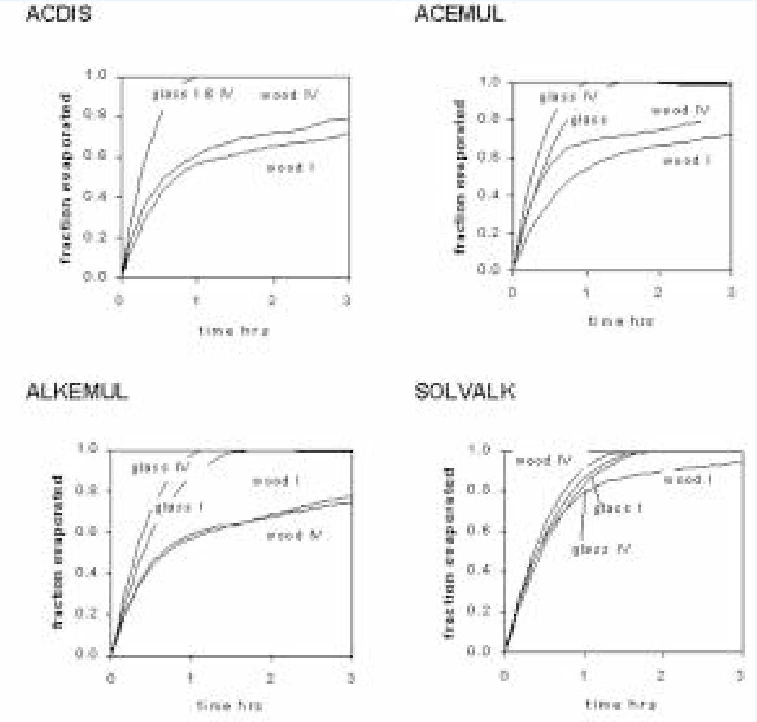

Figure 2–Fractional evaporation on glass and wood at viscosity level I and IV.

The binders were first diluted to approximately the same solid matter content of 33% with respectively demineralized water or white spirit. Detailed mass fractions are given in *Table* 1.

From all four binders, three additional samples with three increased levels of viscosity were prepared by carefully adding a suitable thickener until a viscosity of approximately 2, 13, and 60 Pa s was reached (as measured with a Haake-FW® viscosity meter at 180 rotations per minute). The waterborne binders were thickened with associative thickeners in a concentration range between 30 and 90 g l^{-1}. The solventborne binder was thickened with a bentonite paste in a concentration range between 25 and 65 g l^{-1}. After addition of the thickeners, the viscosity of the samples was measured over a range of shear rate. *Table* 2 shows the viscosities of the unthickened and thickened binders at shear rates between 0.1 and 1000 s^{-1}. The four levels of viscosity are indicated with the codes I, II, III, and IV.

Apart from the addition of thickeners, the change of viscosity was also measured with increasing mass fraction polymer. The samples with increased solid matter content were prepared by evaporating the water or white spirit very slowly to avoid formation of a skin on the surface. Suitable conditions for this were 23°C and 55% relative humidity (RH) for the first 24 hr, followed by 24 to 72 hr at 75% RH, and finally at 95% RH depending on the desired level of concentration. The solid matter content of the coating was determined afterwards by drying for one hour at 125°C, according to ISO standard 3251. The density of the binders was measured with a pycnometer at the lowest mass fraction and densities were calculated for increased mass fractions of polymer. The density ranged between 1018 and 1034 kg m^{-3} for the water-based samples and between 865 and 892 kg m^{-3} for the solvent-based products depending on the concentration.

Four commercially available surfactants in demineralized water were used to prepare the aqueous solutions with reduced surface tension. Fluorinated alkyl polyoxyethylene ethanols were used as non-ionic surfactants, fluorinated alkyl quaternary ammonium iodides were used as cationic surfactant, potassium fluoralkyl carboxylates and sodium dodecylsulfate were used as anionic surfactants. The surfactants were used at at least two concentrations: around the critical micelle concentration and at a level 10 times above that concentration. All concentrations were expressed in percentage of mass of commercial surfactant per mass of total mixture.

Pre-dried pine sapwood (*Pinus sylvestris*) with an initial moisture content of 8.5-9% and a density of 500 kg m^{-3} was used to study capillary uptake because this wood species is known to have a high permeability. Dry mass of the wood was determined by drying at 103°C until a constant weight was reached.

Viscosity, Wetting and Surface Tension Measurements

The viscosities of the thickened samples were measured at shear rates between 0.01 to 1000 s^{-1} with a Bohlin® controlled stress rheometer with a coaxial cylinder at a temperature of 23°C. The viscosities of the concentrated polymeric liquids were measured with a Rheolyst® AR 1000N rheometer equipped with a cone and plate at a controlled shear rate between 0.1 and 100 s^{-1}. The sample compartment was sealed from the environment to avoid drying during the measurement. All measured data were averages of the viscosities obtained with increasing and decreasing shear rate. In general, the differences between these measurements were very small or below the detection limit.

Surface tensions of the liquids were measured with Wilhelmy-plate method according to DIN standard 53914. The contact angles were measured from coating droplets deposited on the wood with a digital video contact angle measuring device (Digidrop® from GBX, France). The measurements were taken on the tangential surface of the wood parallel to the grain. Contact angles were taken as soon as the angle changed at a constant rate, which means that equilibrium conditions were reached.

Evaporation Measurements

The evaporation of water or white spirit from the coatings applied on glass plates and wood boards (half-tangential surface) was measured by recording the weight loss as a function of time at an accuracy of 0.1 mg with maximum time intervals of two minutes, on an analytical balance with automated data acquisition. The evaporation studies were carried out in a climate chamber of 50% RH and 23°C with a slow internal air circulation. The samples were protected by the glass cover on the front and backside of the balance, but ports at the sides and top were opened to ensure air circulation. All measurements were continued for at least 10 hr, but in most cases only the evaporation data during the first hours were effectively used. The evaporation rates were obtained from two or three replicates. The total area for evaporation was 0.009 m^2 and an initial wet film-thickness of approximately 140 μm was applied with a film applicator. The averaged total amount of coating applied is given in *Table* 2.

Capillary Uptake

The capillary uptake of the binder into the wood was recorded from the increase in mass (0.1 mg accuracy) as a function of time. Wood blocks with dimensions of 15 × 12.5 × 20 mm (height × width × length) were hung under a microbalance and were carefully brought into contact with the liquid by raising the liquid container. After the desired contact time, the liquid was lowered until contact with the liquid was lost. The excess amount of binder present on the surface was removed and the weight determined. Thereafter, this procedure was repeated for the next time interval. The weight was recorded after approximately 15, 30, 60, 600, and 1,800 sec. Initially, attempts were made to record the weight continuously but this was impossible because of the disturbing influence of forces due to wetting of the edges of the wood blocks.

By sealing the sides of the blocks, it was ensured that the capillary uptake could only occur through the axial surface (end grain) of the wood, which was previously smoothed on a microtome to obtain well defined open ends of the wood capillaries. All measurements were made in air of 23°C and 50% RH with the penetrating liquid stored in a thermostatic bath with an accuracy of 23 ± 0.1°C. The presented data are an average of three to five individual determinations.

RESULTS AND DISCUSSION

Evaporation Rates-Mass Fraction Polymer

The evaporation rate was measured for all four binders at two levels of viscosity: without the addition of thickener (1) and with the highest concentration of thickener (4) as shown in *Table* 3. To make samples with different initial weights or solids contents comparable, the evaporation is expressed as a fraction of the total amount of water or solvent initially present. These fractional evaporation curves are shown in *Figure* 2. The error for three replicates

Table 3—Evaporation Data from Binders Applied on Glass and Wood

		Evaporation Rate					Evaporation Rate
Binder Type	Viscosity Level	q_{glass}^{air} (kg. $m^{-2}s^{-1}$)	q_{wood}^{air} (kg. $m^{-2}s^{-1}$)	t_1(s)	$\phi_m(t^1)$	t_1'(s)	q^{wa} (kg. $m^{-2}s^{-1}$)
ACDIS	I	4.10×10^{-5}	3.50×10^{-5}	400	0.40	220	8.71×10^{-5}
ACEMUL	I	3.35×10^{-5}	4.24×10^{-5}	900	0.42	680	3.31×10^{-5}
ALKEMUL	I	3.51×10^{-5}	5.04×10^{-5}	700	0.41	490	3.83×10^{-5}
SOLVALK	I	2.04×10^{-5}	3.54×10^{-5}	560	0.43	190	4.37×10^{-5}
ACDIS	IV	3.78×10^{-5}	3.16×10^{-5}	400	0.37	175	1.10×10^{-5}
ACEMUL	IV	3.95×10^{-5}	3.72×10^{-5}	550	0.38	290	0.21×10^{-5}
ALKEMUL	IV	3.47×10^{-5}	2.71×10^{-5}	220	0.36	200	1.27×10^{-5}
SOLVALK	IV	1.42×10^{-5}	2.09×10^{-5}	810	0.44	305	1.81×10^{-5}

(a) determined on the basis of q_{glass}^{air} according to equation (7).

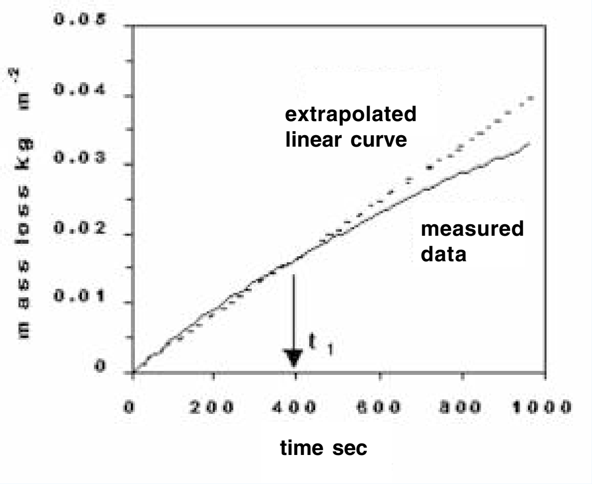

Figure 3–Mass-loss against drying time for ACDIS I on glass showing determination t_1.

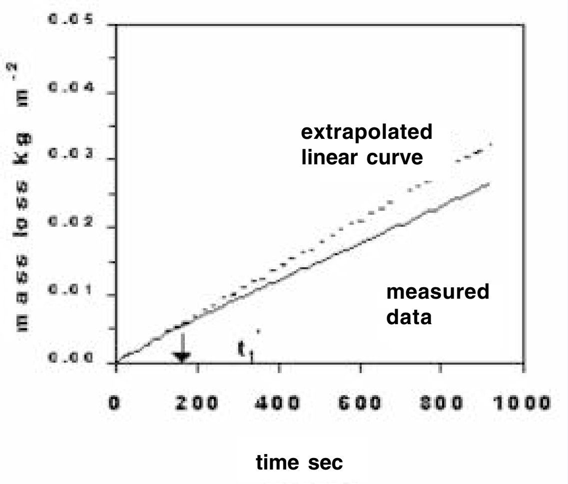

Figure 4–Mass-loss against drying time for ACDIS I on wood showing determination t_1'.

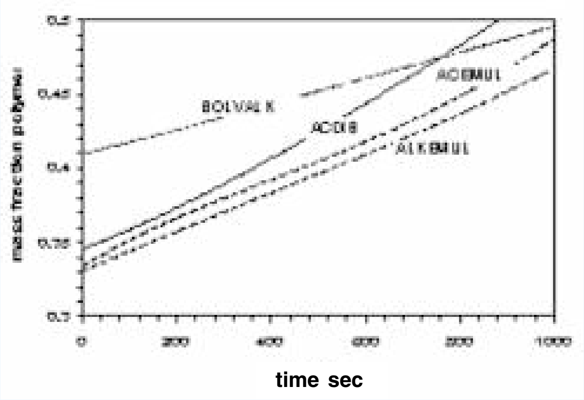

Figure 5–Mass fraction polymer as a function of drying time as determined on glass, viscosity level IV.

was around 5% on glass and 10% on wood. The differences between the wood and glass substrates were evident. On glass, the total amount of water or solvent present evaporated completely within one to two hours. If the waterborne binders were applied on wood, 40 to 60% of the water was initially stored in the wood and evaporated only slowly into the air. It took about 20 hr before all the water present in the coating evaporated into the air again. The white spirit in the solventborne binders (SOLVALK) was released from the wood far more rapidly. The influence of the thickeners on the fractional evaporation rates was dependent on the type of polymer. For the ACDIS binder no differences on the glass were observed and evaporation from wood proceeded slightly faster with a thickened binder. In combination with the ACEMUL and ALKEMUL binder, the fractional evaporation with thickener was somewhat faster on glass and, in the case of the ACEMUL, also on wood. These differences might, however, be due to the fact that a slightly higher amount of coating was applied at the lower viscosity level, which means that the fractional evaporation will be lower if the absolute evaporation rate is independent from film thickness during the initial drying stage. The fractional evaporation on wood of the SOLVALK with thickener was faster than without, which might be explained by the fact that less material had penetrated the wood, which will facilitate a faster evaporation.

The evaporation rates during the first drying stage were determined from the linear part of a plot of mass loss against time for coatings applied on glass (denoted by q_{glass}^{air}) and on wood (denoted by q_{wood}^{air}). These data are given in *Table* 3, while typical mass loss–time plots are given in *Figures* 3 and 4 for the evaporation from glass and wood, respectively. The initial evaporation rate was approximately constant, although in some cases, slight deviations from a straight line were observed which indicated slight changes in the evaporation rate during the initial stage. Nevertheless, the drying model described the experimental data fairly well for the alkyd emulsion (ALKEMUL) and solventborne alkyd binders (SOLVALK). From a theoretical point of view, the initial evaporation rates to the air should be equal from coatings applied on glass or wood. In practice, some differences were observed but no consistent trend could be seen. With a wooden substrate, the constant rate period was shorter and subsequently, the determination of the linear slope was less accurate. Therefore, the evaporation rates from glass were used to calculate the evaporation rate to the wood itself (q_w). The measured evaporation rates are comparable to data found in literature like 1.26-1.56 × 10^{-5} kg $m^{-2}s^{-1}$,[27] 1.1-3.4 × 10^{-5} kg m^{-2} s^{-1},[35] and 6.67 × 10^{-5} kg $m^{-2}s^{-1}$,[36] for various types of latex paints. Croll[26] reported values of 3.1, 3.5, 3.6, and 3.7 × 10^{-5} kg m^{-2} s^{-1} for the evaporation of water from a latex, a paint, a titanium-dioxide slurry, and pure water, respectively.

The constant evaporation rate period on glass (t_1) lasted between 220 (ALKEMUL IV) and 900 (ACEMUL I) sec, which was much shorter then the four hours reported by Eckersley and Rudin,[27] but in the same range as the results reported by Croll.[26] As expected, the constant rate on wood (t_1') was considerably shorter which corresponded with the finding that the constant rate period decreased with film thickness.[26] On wood, the drying occurred to two sides; this can also be interpreted as a decrease of the effective film thickness. The mass fraction polymer corresponding to the end of the initial drying period ($\phi m(t_1)$) was between 0.36 and 0.44 (see *Table* 3) which was only slightly higher than the initial mass fraction polymer ($\phi(t_0)$) as given in *Table* 2. The mass fraction polymer as a function of drying time is given in *Figure* 5.

The evaporation rates to wood (q^w) are given in *Table* 3 and were calculated according to equation (7). With the unthickened binders, the evaporation to the wood is higher than to the air for the ACDIS and SOLVALK binder. Although with the latter, the white spirit was released from the wood much faster than the water as can be seen from the fractional evaporation plots (*Figure* 2). For the ACEMUL and ALKEMUL binder, the evaporation to air and wood is about equal. Addition of a thickener reduced the evaporation to the wood considerably, which was mainly due to the shorter constant evaporation rate period and the lower corresponding mass fraction polymer. It might indicate also that the increase in viscosity, which will reduce the substrate penetration, had a marked effect on the amount of water or solvent transferred to the wood. The evaporation rate to the air, as measured most accurately on glass, was not much affected by the addition of thickener.

The mass fraction polymer inside a wood capillary as a function of time was calculated according to equation (8) and is given in *Figure* 6 for the different binders for a capillary with a radius of 5 and 25 µm. The curves were extrapolated to higher mass fractions, mainly to show the differences clearly. In reality, some deviations might occur at high mass fraction because the evaporation rate will no longer be constant at high mass fractions. The influence of the evaporation rate to the wood and the capillary radius on the increase in mass fraction polymer can clearly be seen. For waterborne binders, this is in good agreement with previous observations,[1,18,37] where the deepest penetration was found in the widest capillaries. However, for solventborne binders, the opposite was observed.[37] This might be an indication that for this binder, equation (3) was not valid all the time and that penetration was directly dependent on capillary pressure (equation [2]), which predicts a deeper penetration with decreasing capillary radius.

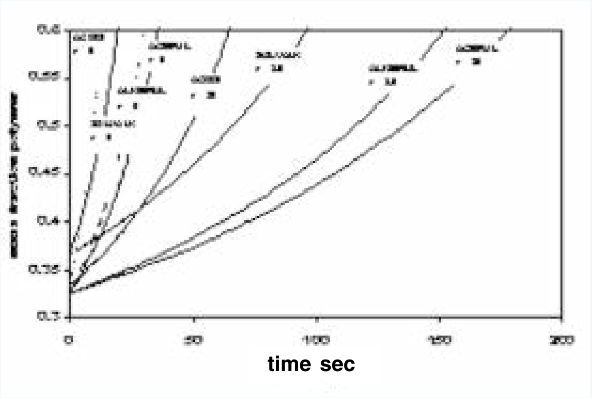

Figure 6–Increase in mass fraction polymer inside a wood capillary with a radius of 5 or 25 µm as a function of time, data are plotted for binders with the lowest initial viscosity (I).

Relation Between Viscosity and Polymer Concentration

By careful evaporation of water or solvent, concentrated polymeric liquids up to 57% solids were prepared from the polymeric binders without additional thickener. The viscosity was expressed relative to the viscosity of the continuous phase, which was 0.001 Pa s for the waterborne binders and 0.0012 Pa s for the solventborne binders. The change in relative viscosity with increasing mass fraction solids is given in *Figures* 7a to 7d for the binders, ACEMUL, ACDIS, ALKEMUL and SOLVALK, respectively. The viscosities are given at four shear rates of 0.1, 1, 10, and 100 s^{-1} respectively. The standard error of viscosity measurements was less then one percent. The acrylic dispersion ACDIS showed a sharp increase of the viscosity at higher mass fraction polymer, in particular at low shear rates. The viscosity of the acrylic emulsion (ACEMUL) also increased strongly with solid matter content, but the dependence on shear rate was less pronounced. The viscosity of the alkyd emulsion (ALKEMUL) increased relatively slowly up to a mass fraction polymer of 0.55. Above this mass fraction, samples were not stable. During the viscosity measurement, an instantaneous change for a liquid to a paste-like structure occurred. Most likely, the shear forces applied on the liquid caused a phase inversion of an oil in

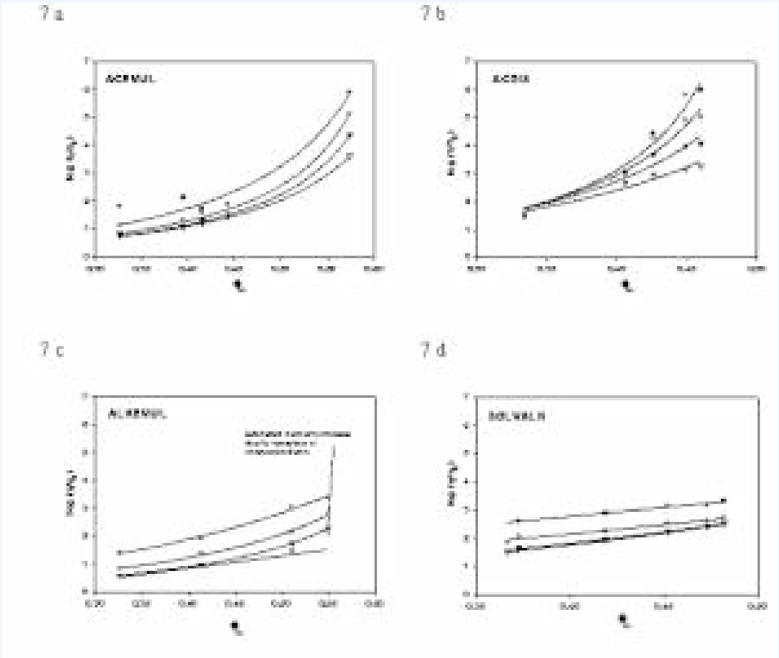

Figure 7–Relative viscosity of the binder as a function of solid matter content on mass basis. Shear rates: ● 0.1 s^{-1}; ○ 1 s^{-1}; ▼ 10 s^{-1}; ▽ 100 s^{-1}.

Table 4—Fit Parameter for the Relationship between Relative Viscosity and Mass Fraction Polymer

		Shear Rate s^{-1}			
Binder Type		**0.1**	**1**	**10**	**100**
Acemul	c:	0.529 (0.093)	0.761 (0.074)	0.845 (0.033)	0.830 (0.017)
	d:	0.751 (0.165)	1.130 (0.130)	1.242 (0.0057)	1.169 (0.030)
ACDIS	c:	0.495 (0.092)	0.463 (0.065)	0.418 (0.068)	0.384 (0.061)
	d	0.916 (0.206)	0.817 (0.147)	0.679 (0.155)	0.543 (0.141)
ALKEMUL	c:	0.352 (0.032)	0.661 (0.051)	0.977 (0.030)	0.830 (0.035)
	d:	0.351 (0.062)	0.840 (0.097)	1.340 (0.057)	0.934 (0.067)
SOLVALK	c:	0.134 (0.013)	0.224 (0.021)	0.361 (0.015)	0.353 (0.032)
	d:	0.025 (0.029)	0.094 (0.048)	0.394 (0.016)	0.417 (0.036)

Numbers in parentheses are the standard errors of the fit parameters.

water emulsion to a water in oil emulsion. According to Beetsma,[38] the drying and film formation of an alkyd emulsion involves such a change from a concentrated oil in water phase, through a metastable state into a water in oil emulsion. The latter phase will have a high viscosity due to the high molecular weight of the alkyd resin. The solventborne alkyd resin (SOLVALK) showed the slowest increase in viscosity with mass fraction polymer, and the increase at lower shear rates was independent from the mass fraction polymer.

The viscosity-mass fraction polymer relations were fitted by the following, semi-empirical relation with fit parameters c and d[39]

$$\log\left(\frac{\eta}{\eta_o}\right) = \frac{\phi_m}{c - d\phi_m} \tag{11}$$

This is a modified version of equation (9a) but based on mass fraction polymer and without the need to know the volume fraction polymer at infinite viscosity. Equation (11) was preferred over equations (9a to 9c) because it fitted the measured data much more accurately with r-squares over 0.9. Fitted values of 9c and 9d are given in *Table* 4 including standard errors. The reason that the theoretical models from equation (9) could not describe the measured data adequately might be twofold. First, the polymer fraction on a volume basis had to be known whereas only the polymer fraction on a mass basis could be measured directly. A simple conversion into volumetric fractions based on liquid density was not realistic because it required knowledge about the volume to weight ratio, which will change upon drying due to polymer swelling and electrical double layer effects.[36] Second, the theoretical models required knowledge of the limiting polymer fraction ϕ_{max}, which should be determined from a plot of polymer fraction against reciprocal viscosity. This resulted in values with a large error, due to the absence of observations at high and low polymer fractions.

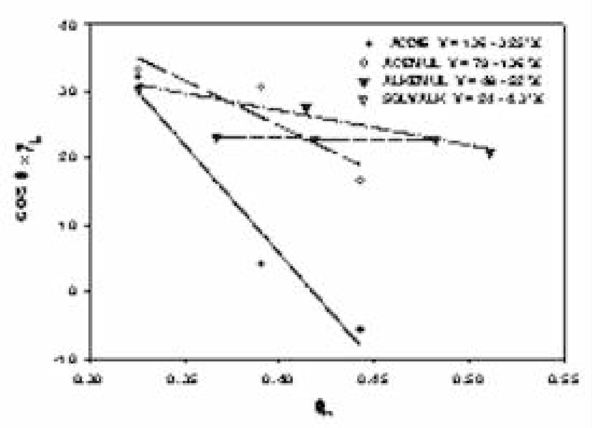

Figure 8–Cosine of the contact angle on wood times the liquid surface tension as a function of mass fraction polymer.

Relation Between Polymer Concentration and Wetting

The capillary pressure, which is the driving force for the capillary penetration is directly proportional to the product of liquid surface tension and cosine of the contact angle between liquid and wood. Therefore, the surface tensions and the contact angles were measured as a function of polymer concentration. In principle, the contact angle should be determined from the meniscus of the wetting liquid inside the wood capillary, however, this was not experimentally possible. Therefore, the contact angle was measured from a droplet on the tangential surface of the wood. Equilibrium contact angles were used because these were least influenced by substrate penetration.

For the ALKEMUL and SOLVALK binders, the surface tension remained constant with increasing solid matter content. The ACEMUL binder showed only a minor decrease in surface tension from 40 mN/m at a mass fraction of 0.33 to a value of 38 mN/m at a mass fraction of 0.44. The ACDIS binder had the strongest decrease in surface tension: from 33 mN/m at a mass fraction of 0.33 to a value of 24 mN/m at a mass fraction of 0.44. An increasing concentration of surfactant could explain the decreasing surface tension.

The wetting of the polymeric liquids decreased with increasing solid matter content. For the SOLVALK binder, the contact angle increased from 16° at a mass fraction of 0.37 to an angle of 23° at a mass fraction of 0.48. For the ALKEMUL binder, it changed from 7° at a mass fraction of 0.33 to 47° at a mass fraction of 0.51. For the ACEMUL binder the change was from 34° at a mass fraction of 0.33 to 64° at a mass fraction of 0.44. The contact angle of the ACDIS binder changed from 15° at a mass fraction of 0.33 to 103° at a mass fraction of 0.44. The latter represented a non-wetting case, which meant that the capillary pressure was negative. Under these circumstances, the penetration of the coating in the wood will be limited by the absence of capillary pressure rather than the increase in viscosity. The lower contact angle with decreased liquid surface tension would normally not be expected and means that the interfacial tension (γ_{SL}) between binder and wood increased as follows from equation (4) (note that γ_S will remain constant). The higher contact angle might be due to the increased viscosity, which could limit both the spreading and the mobility of surfactants. The relation between $\cos\theta \times \gamma_L$ and ϕ_m could be reasonably described by a linear trend that is given in *Figure* 8 including individual data and regression equations. The error of the shown data points was between 5 and 10%.

Capillary Uptake of Binder Into Wood

The capillary uptake into the axial direction of the wood was determined for all binders at four different levels of thickener after a fixed time span of 30 min. The results are given in *Table* 5 in different ways: (1) as the total uptake of material (polymer and water or solvent) on both mass and volume basis; (2) as measured oven-dry weights of penetrated polymeric binder; and (3) on a theoretical oven-dry mass basis calculated from the uptake of total binder times its mass fraction solids. For the oven-dry cases, corrections for the impact of wood moisture content were made because the wood lost water during drying. The solid matter content was calculated from the mass of oven-dry binder in the wood divided by the amount of total uptake and compared with the solid matter content as determined according to ISO 3251.

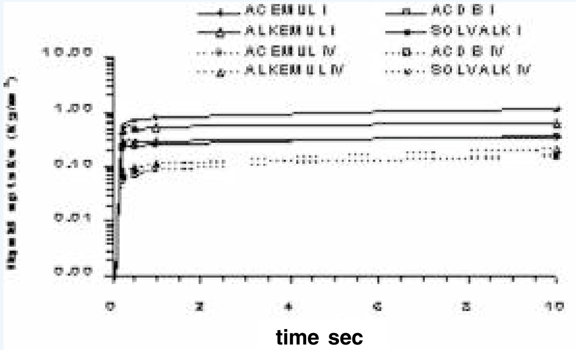

Figure 9–Uptake of liquid binder at viscosity levels I and IV as a function of time.

The binders showed clear differences in capillary uptake of both total and dry material. The SOLVALK had the highest total uptake, followed by the ALKEMUL, ACEMUL, and the ACDIS binders. The samples with increased thickener concentration and viscosity showed a decrease in total uptake. In the case of the waterborne binders, the amount of dry polymer that penetrated into the wood was much lower than the amount that would be expected from the total uptake of material times its solid matter content. This proved that water was selectively removed from the waterborne binders during the capillary penetration, in particular with the ACDIS and ACEMUL samples and to a lesser extent also with the ALKEMUL binder. The difference in solid content between the liquid inside the wood and that of the bulk increased at higher levels of thickener. Most likely, the high viscosity prevented the capillary uptake of polymer whereas the water could still penetrate the wood.

The SOLVALK binder showed no indications of selective removal of solvent into the wooden cell wall during capillary penetration. The solid matter content of material in the wood and the bulk was identical within the limits of experimental error. On a volumetric basis, the uptake of white spirit was identical to that of the SOLVALK binder

Table 5—Capillary Uptake of Binder into the Axial Directions of Pine Sapwood after a Fixed Tme Span of 30 Minutes

Binder Type	Viscosity Level	Total Uptake Mass (g)	Total Uptake Volume (ml)	Oven-Dry Mass (g) Measured[a]	Oven-Dry Mass (g) Calculated[b]	%-Solids in Wood[c]	%-Solids[d]
ACEMUL	I	0.126 (0.012)	0.122	0.036 (0.006)	0.042	29	33
	II	0.129 (0.011)	0.125	0.040 (0.006)	0.043	31	33
	III	0.067 (0.002)	0.066	0.009 (0.001)	0.022	13	33
	IV	0.070 (0.003)	0.068	0.009 (0.001)	0.023	12	33
ACDIS	I	0.091 (0.017)	0.089	0.021 (0.008)	0.030	23	33
	II	0.078 (0.004)	0.077	0.013 (0.003)	0.026	17	33
	III	0.058 (0.002)	0.057	0.006 (0.001)	0.019	10	33
	IV	0.062 (0.011)	0.061	0.006 (0.001)	0.021	10	34
ALKEMUL	I	0.203 (0.027)	0.200	0.072 (0.011)	0.067	33	33
	II	0.119 (0.011)	0.117	0.041 (0.005)	0.039	34	33
	III	0.104 (0.010)	0.102	0.036 (0.004)	0.034	35	33
	IV	0.081 (0.011	0.079	0.010 (0.001)	0.027	12	33
SOLVALK	I	0.360 (0.032)	0.416	0.144 (0.013)	0.130	40	36
	II	0.127 (0.023)	0.146	0.046 (0.008)	0.047	36	37
	III	0.107 (0.014)	0.121	0.040 (0.006)	0.042	37	39
	IV	0.050 (0.007)	0.056	0.020 (0.003)	0.020	40	41
Water		0.840 (0.007)	0.840	—	—	—	—
White spirit		0.330 (0.016)	0.420	—	—	—	—

(a) oven-dry weight after penetration binder - oven-dry weight wood.
(b) total mass uptake x % solids.
(c) measured oven-dry mass divided by total mass uptake.
(d) solid matter content determined by drying on inert substrate according to ISO 3251.
Numbers in parentheses are the standard errors of the measured data.

without thickener, whereas the uptake of water was four to ten times higher in comparison to the uptake of waterborne binders.

The rate of capillary uptake is given in *Figure* 9 for all four binders at the lowest and highest level of viscosity. Error of measurements was between 3 and 22% for the lowest and 2 to 14% for the highest viscosity. Most of the material penetrated into the wood within the first minute. In the later stage the increase was possibly limited to the uptake of water or organic solvent.

Modelling of the Capillary Penetration of Binders into Wood

The depth of penetration of the binder into the wood was calculated by a combination of the models for the mass fraction polymer inside a wood capillary (equation [8]), the relation between mass fraction polymer and the viscosity at a shear rate of 0.1 s^{-1} (equation [11]), $\cos\theta \times \gamma_L$ as function of polymer fraction and the Washburn equation for capillary rise (equation [3]). The height of rise (equation [12]) and rate of capillary rise (equation [17]) were calculated as a function of time by a stepwise numerical calculation. The steps in time (Δt) used ranged from 1×10^{-4} sec during the initial stage of capillary uptake to 10 sec at the final stage.

$$\left(\frac{\Delta h}{\Delta t}\right)_t = \frac{2r(\cos\theta\gamma_L(\phi_m)) - \rho\, g\, h_t(r)^2}{8\eta(\phi_m)h_t} \qquad (12)$$

$$h_t = h_{t-1} + \left(\frac{\Delta h}{\Delta t}\right)_{t-1} \times \Delta t \qquad (13)$$

The measured height of capillary rise was calculated from the measured weight increase as follows:

$$h_{meas} = \frac{m_{meas}}{\rho\, A_{eff}} \qquad (14)$$

With m_{meas} as the total uptake on mass basis, ρ the density of the liquid, and A_{eff} the effective area for capillary uptake. A_{eff} was calculated from[40]

$$A_{eff} = A\,(1 - G(0.667 + 0.01u)) \qquad (15)$$

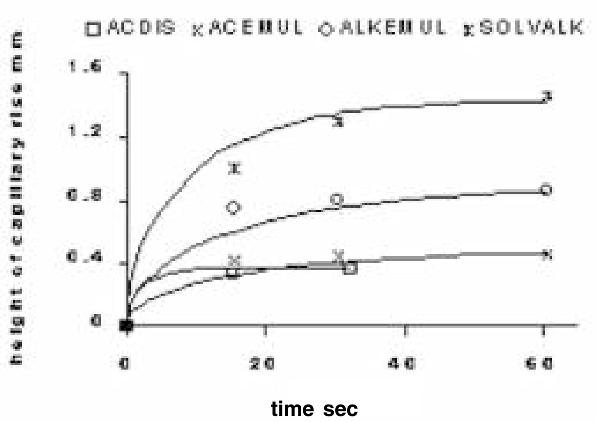

Figure 10–Experimental data and adjusted model calculations for height of capillary rise.

In this case, for wood with a specific density* (G) of 0.50 and a wood moisture content (u) of 9%, the ratio between A_{eff} and A was 0.62. Because the binder showed only a small change in density with increasing mass fraction polymer, the initial density values were used. An average value of 15 µm was used as the radius of the wood capillaries, which were assumed to be perfectly cylindrical.

The model calculations predicted a limitation of the height of capillary rise by the increase of viscosity for the ACEMUL, ALKEMUL and SOLVALK binders, whereas the ACDIS binder was limited by zero capillary pressure and a sharp increase in viscosity at the same time. However, the maximum penetration depth was overestimated, most severely for the waterborne binders. The calculated depths for the ACDIS, ACEMUL, ALKEMUL and SOLVALK binders were respectively: 4.4 mm, 24 mm, 17 mm, and 1.8 mm. The deviation between the measured and the calculated data might be explained by the fact that the limiting increase of the viscosity in the model calculation was reached much later than in reality. In order to adjust the model to the experimental data, the effective viscosity factor (E) was introduced to define the effective capillary viscosity (η'):

$$\eta' = E\,\eta \qquad (16)$$

The experimental penetration data and the adjusted model predictions are given in *Figure* 10. The effective viscosity factors for the various binders were 1.6 (SOLVALK), 150 (ACDIS), 400 (ALKEMUL), and 2700 (ACEMUL).

Most likely, the effective viscosity factor represents two phenomena. The first phenomena is the increase of the viscosity at shear rates below 0.1 s^{-1} in combination with a high mass fraction of polymer. It was estimated that with a high viscosity, and, therefore, a low rate of capillary rise, the shear rate applied on the penetrating binder would be below 0.1 s^{-1}. This effect will be most important for the ACEMUL and ACDIS binders, where the increase in viscosity at low shear rates was highest (see *Figures* 7a and b). Second, the actual viscosity might be higher due to a faster transfer of water or solvent from liquid to cell wall. The data used in the model calculations originated from evaporation rate experiments that represented the transport in the bulk of the material. On a microscopic level, the loss of water or solvent from the penetrating liquid to the surrounding cell wall might happen faster. Furthermore, at the front of the penetrating binder, water or solvent will also evaporate to the air inside the capillary, this will cause an additional increase in solid matter content at the front of the penetrating liquid.

Influence of Surfactants

Waterborne binders and coatings contain significant amounts of surfactants, which will lower the surface tension and might improve wetting. The uptake of distilled water into the wood containing different types of surfactants was tested at concentrations around and 10 times above the critical micelle concentration (CMC). The gravimetric uptake of the anionic potassium fluoroalkyl carboxylate surfactant solutions is shown in *Figure* 11. At all surfactant concentrations, the wood was wetted completely

---

*Specific density is defined by the wood density (kg m^{-3}) divided by the density of water.

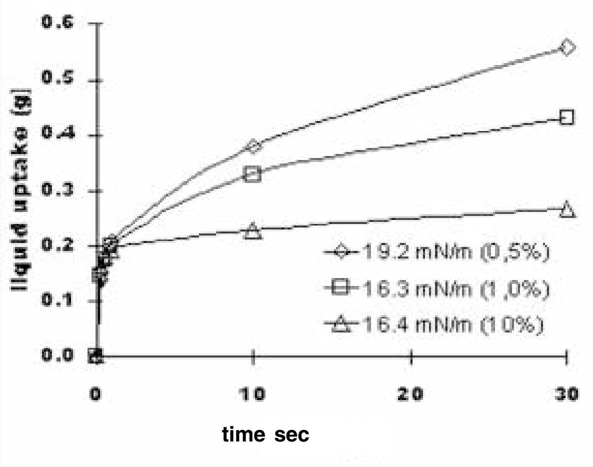

Figure 11–Influence of potassium fluoroalkyl carboxylate surfactant concentration on capillary uptake of water.

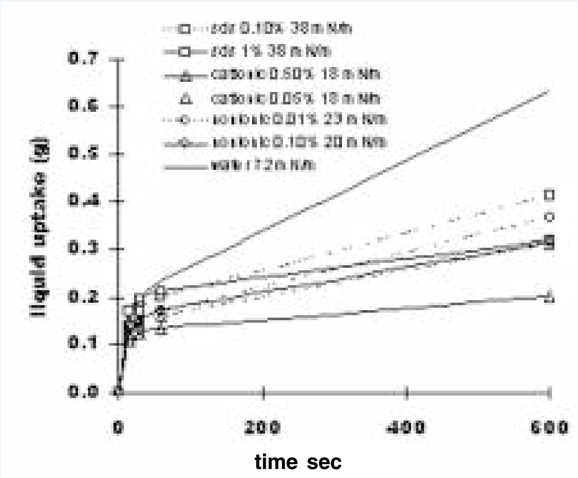

Figure 12–Influence of surfactant type on capillary uptake of water. Concentrations are around and 10x above the CMC.

(contact angle was zero) and as predicted by the Washburn equation (equation [3]) under these circumstances, the uptake was reduced with decreasing surface tension. Addition of surfactant did not cause a noticeable increase of the viscosity.

Increasing the surfactant concentration from 1% (around the CMC) to 10% caused an additional decrease in uptake, although the surface tension of the liquid was not reduced any further. This might indicate that surfactant molecules were adsorbed at the wooden cell wall during the capillary penetration. Adsorption of surfactant to the cell wall will decrease the concentration inside the capillary and, hence, will increase the actual surface tension of the penetrating liquid at concentrations below or around the CMC. Far above the CMC, sufficient surfactant molecules will be present to compensate the loss due to adsorption at the cell wall, and the surface tension of the liquid remains unaffected. Adsorption of surfactants at wood fibres was also reported in other studies on the wetting of wood.[41]

The influence of surfactant types on the capillary uptake of water is given in *Figure* 12. All types of surfactants caused a reduction of the capillary uptake and a complete wetting of the wood. Regardless of the fact whether the surfactant was non-ionic, anionic, or cationic, a lower uptake was found at a concentration 10 times above the CMC. This indicated that different types of surfactants tested could be absorbed to the wood. Anionic surfactant solutions showed the highest uptake, followed by the nonionic surfactant. The solution containing the cationic surfactant had the lowest uptake.

CONCLUSIONS

This study has shown that during the drying and capillary penetration of coatings on wood, water or organic solvent was selectively transferred from the polymer containing liquid to the wood. This resulted in a more rapid increase in polymer concentration during drying on wood, in comparison to an inert substrate like glass. Inside a wood capillary, the polymer concentration increased because water entered the cell wall whereas polymer particles were too large to migrate into the cell wall. The evaporation rate to the wood was estimated from the constant evaporation rate period, the evaporation rate to the air, and the mass fraction polymer at the end of the constant rate period. Depending on the binder type, the evaporation rate to the wood was equal or even higher than the evaporation rate to the air. This was observed for both waterborne and solventborne binders, but the solvent taken up into the wood was released again much faster. With the waterborne binders, the selective removal of water increased after the addition of a thickener. This effect was absent with a solventborne binder.

The viscosity of the binders rapidly increased with mass fraction of polymer, in particular for the waterborne binders. For the ACDIS and ACEMUL binders, the increase in viscosity was much higher at low shear rates. For the ALKEMUL binder, the viscosity was increased extremely as soon as a water in oil emulsion was formed. Because of the increasing polymer concentration, the viscosity of the binder appeared to be the limiting factor in the capillary penetration of coatings into wood. Increasing the initial viscosity by addition of a thickener reduced the capillary uptake for all types of binder investigated.

The driving force for capillary penetration, which is the product of liquid surface tension and the cosine of the contact angle of the liquid on the wood, also decreased with increasing mass fraction polymer. This was due to decreased liquid surface tension and a poorer wetting that resulted in higher contact angles. This effect was strongest for the ACDIS and least important for the SOLVALK binder. Separate studies on the capillary uptake of water containing various types and concentrations of surfactants showed reduced capillary penetration with lower surface tension if the wetting of the wood was complete. A subsequent reduction of penetration at a surfactant concentration well above the CMC indicated that adsorption of surfactants on the wooden cell wall took place. Surfactant adsorption will increase the actual liquid surface tension inside the capillary until there is sufficient surfactant to compensate the losses by adsorption.

The measured penetration of the binders into wood showed clear differences between binder types. The lowest penetration was observed for the acrylic dispersion (ACDIS) and emulsion (ACEMUL), the waterborne alkyd (ALKEMUL) showed deeper penetration and the solventborne alkyd (SOLVALK) penetrated deepest, which was in good agreement with previous findings. The maximum depth of capillary penetration was calculated from the Washburn equation for capillary penetration, taking into account the increasing viscosity and decreasing capillary pressure. In comparison to the experimental data, the maximum penetration was severely overestimated which indicated that in reality the viscosity increased much faster than could be predicted from evaporation rate measurements and the mass fraction-viscosity relationships. To adapt the model to the experimental data, the effective viscosity factor was introduced. The effective viscosity was about 1.6 (SOLVALK) to 2700 (ACEMUL) times higher than the viscosity with the highest mass fraction polymer, measured at a shear rate of 0.1 s^{-1}. This might be explained by a lower shear rate in practice or by a more rapid increase in mass fraction polymer, due to a faster drying on a micro-scale at the front of the penetrating binder. More detailed studies on the viscosity of concentrated dispersions or emulsions at high mass fractions and direct measurements of the solids content during capillary penetration will be needed to fully understand the capillary penetration of coatings into wood.

Finally, it can be concluded that to obtain a good penetration and pore filling of a coating on wood, the viscosity at very low shear rates and high mass fractions polymer is the most decisive factor. The addition of a thickener will reduce the penetrating capacity. Reducing the surface tension of the coating, if the wetting of the wood is already complete, will only decrease the penetration.

SUMMARY

The capillary penetration of coatings into wood and the drying behavior of unpigmented coatings on wood with four different polymeric binder types, including waterborne dispersions, emulsions and solventborne solutions were studied and discussed. The influence of thickeners and surfactants was also taken into account. The rate of capillary penetration of a coating into wood can be described by the Washburn equation. Accordingly, the rate of capillary penetration is proportional to the capillary radius, the liquid surface tension, and the cosine of the contact angle and is inversely proportional to the viscosity and the height of rise of the liquid in the capillary.

During drying and penetration of a coating that is applied on wood, a large amount of either the water or the solvent is selectively taken up by the cell wall. Hence, the solid matter content of the coating will increase during penetration into the wooden capillary. To estimate the amount of water taken up by the wood, the evaporation of a coating on wood and glass was compared. From the period during which the evaporation rate was constant and the mass fraction polymer at the end of the constant drying period, the evaporation rate to the wood was estimated. The magnitude of the evaporation rate to the wood depended on the type of binder and was at least as large as the evaporation rate to the air. This means that the mass fraction polymer, and subsequently the viscosity, will increase more rapidly on wood in comparison to an inert substrate.

The viscosity of the binders was measured at increasing mass fractions from 0.33 to 0.55 at shear rates between 0.1 and 100 s^{-1}. In particular, the waterborne binders showed a rapid increase in viscosity at higher mass fractions, especially at lower shear rates. The rapid increase in viscosity appeared to be the limiting factor in the penetration in most cases. However, the liquid surface tension and wetting also changed with increasing mass fraction polymer and might limit the penetration as well. Studies with increasing levels of thickener at the same mass fraction of binder showed a decrease in capillary uptake into the wood. At higher levels of thickener, the selective uptake of water increased and the amount of binder that penetrated the wood was reduced.

The capillary penetration of various binders was determined experimentally and considerable differences between binder types were observed. Comparison of the experimental data with the model calculations showed that the viscosity was actually more rapidly increasing than it was predicted from model calculation based on independent evaporation rate, surface tension, and viscosity measurements.

Studies with solutions of surfactant in water showed decreasing penetration with increasing surfactant concentration if the wetting of the wood was complete. This was even observed above the CMC, which might be explained by the fact that surfactants were adsorbed on the wood surface. Surfactant adsorption will deplete the surfactant solution inside the capillary, which will increase the actual surface tension of the liquid during penetration.

ACKNOWLEDGMENTS

This research was financed by the Dutch Innovative Research Program on Coatings (IOP-verf). Furthermore, technical and financial support was given by Akzo Nobel Coatings, Sigma Coatings, DSM Resins, Zeneca Resins, and Johnson Polymer. The authors would like to thank Wiro Cobben for the experimental work and Dr. J. Lavèn from the Technical University Eindhoven for his critical comments and the assistance with the viscosity measurements.

References

(1) Meijer, M. de, Thurich, K., and Militz, H., "Comparative Study on Penetration Characteristics of Modern Wood Coatings," *Wood Sci. Technol.*, 32, 347-365 (1998).

(2) Scheikl, M. and Dunky, M., "Measurement of Dynamic and Static Contact Angles on Wood for the Determination of Its Surface Tension and the Penetration of Liquids into the Wood Surface," *Holzforschung*, 52, 89-94 (1998).

(3) Militz, H. and Peek, R-D., "Möglichkeiten der Verbesserung einiger Eigenschaften von Pappelnholz durch Tränken mit wasserlöslichen Harzen," *Material und Organismen*, 28, 55-73 (1993/94).

(4) Banks, W.B., "Water Uptake by Scots Pine Sapwood, and Its Restriction by the Use of Water Repellents," *Wood Sci. Technol.*, 7, 271-284 (1971).

(5) Loon, J. van, "The Interactions Between Paint and Surface," *J. Oil & Colour Chemists' Assoc.*, 49 (10), 844-867 (1966).

(6) Rødsrud, G. and Sutcliff, E.J., "Alkyd Emulsions-Properties and Application. Results From Comparative Investigations of Penetration and Aging of Alkyds, Alkyd Emulsions, and Acrylic Dispersions," *Surf. Coat. Int.*, 77 (1), 7-16 (1994).

(7) Nussbaum, R.M., Sutcliffe, E.J., and Hellgren, A.C., "Microautoradiographic Studies of the Penetration of Alkyd, Alkyd Emulsion, and Linseed Oil Coatings into Wood," Journal of Coatings Technology, *70*, No. 878, 49 (1998).

(8) Nussbaum, R.M., "Penetration of Waterborne Alkyd Emulsions and Solventborne Alkyds into Wood," *Holz als Roh- und Werkstoff*, 52, 389-393 (1994).

(9) Dulien, F.A.L., El-Sayed, M.S., and Batra, V.K., "Rate of Capillary Rise in Porous Media with Nonuniform Pores," *J. Colloid Interface Sci.*, 60 (3), 498-506 (1977).

(10) Marmur, A., "Capillary Rise and Hysteresis in Periodic Porous Media," *J. Colloid Interface Sci.*, 129 (1), 278-285 (1989).

(11) Denesuk, M., Smith, G.L., Zelinski, B.J.J., Kreidl, N.J., and Uhlmann, D.R., "Capillary Penetration of Liquid Droplets into Porous Materials," *J. Colloid Interface Sci.*, 158, 114-120 (1993).

(12) Borhan, A. and Rungta, K.K., "An Experimental Study of the Radial Penetration of Liquids in Thin Porous Substrates," *J. Colloid Interface Sci.*, 158, 403-411 (1993).

(13) Washburn, E.W., "The Dynamics of Capillary Flow," *Physical Review*, 17, 273-283 (1921).

(14) Tollenaar, D., "Capillarity and Wetting in Paper Structures: Properties of Porous Systems," In: *Surfaces and Coatings Related to Paper and Wood*, 1st ed., Marchessault, R.H. and Skaar, C. (Eds.), Syracuse University Press, Syracuse, NY, pp. 196-197 (1967).

(15) Fengel, D. and Grosser, D., "Holz, Morphologie und Eigenschaften," In: *Ullmanns Encylopädie der Technischen Chemie*, 4th Ed., Vol. 12, Verlag Chemie, Weinheim, pp. 669-679, 1976.

(16) Stamm, A.J., "Passage of Liquids, Vapors, etc. through Softwoods," *U.S. Dept. Agr. Technical Bulletin*, No. 929 (1946).

(17) Rijckaert, V., Acker, J. van, Stevens, M., Meijer, M. de, and Militz, H., "Quantitative Analysis of the Penetration of Waterborne Primers into Wood by Means of Fluorescence Microscopy," in *Advances in Exterior Wood Coatings and CEN-Standardization*, Proc. of PRA-Conference Brussels, paper 19, 1998.

(18) Meijer, M. de, Militz, H., and Thurich, K., "Surface Interactions Between Low VOC Coatings and Wooden Substrates," *Proc. 23rd FATIPEC Congress Brussels*, Volume C, 191-214 , 1996.

(19) Kerr, A.J. and Goring, D.A.I., "The Role of Hemicellulose in the Delignification of Wood," *Can. J. Chem.*, 53 (6), 952-959 (1975).

(20) Tarkow, H., Feist, W.C., and Southerland, C.F., "Interaction of Wood with Polymeric Materials, Penetration Versus Molecular Size," *For. Prod. J.*, 16 (10), 61-65,(1966).

(21) Coté, W.A. and Robison, R.G., "A Comparative Study of Wood," Journal of Paint Technology, *40*, No. 525, 427 (1968).

(22) Schneider, M.H., "Scanning Electron Microscope Study of a Coating Component Deposited from Solution into Wood," *J. Oil & Colour Chemists' Assoc.*, 62, 441-444, (1979).

(23) Schneider, M.H. and Sharp, A.R., "A Model for the Uptake of Linseed Oil by Wood," Journal of Coatings Technology, *54*, No. 693, 91-96 (1982).

(24) Vanderhoff, J.W., Bradford, E.B., and Carrington, W.K., "The Transport of Water Through Latex Films," *J. Polym. Sci.*, 41, 155-174 (1973).

(25) Croll, S.G., "Drying of Latex Paint," Journal of Coatings Technology, *58*, No. 734, 41 (1986).

(26) Croll, S.G., "Heat and Mass Transfer in Latex Paints During Drying," Journal of Coatings Technology, *59*, No. 751, 81 (1987).

(27) Eckersley, S.T. and Rudin, A., "Drying Behaviour of Acrylic Latexes," *Prog. Org. Coat.*, 23, 384-402 (1994).

(28) Sherman, P., "Rheological Properties of Emulsions," in *Encyclopedia of Emulsion Technology,* Vol. I, Becher, P. (Ed.), Marcel Dekker, New York, pp. 403-437, 1983.

(29) Mooney, M., *J. Colloid Sci.*, 6, 162 (1951).

(30) Dougherty, T.J. and Krieger, I., *Adv. Colloid Interface Sci.*, 3, 111 (1972).

(31) Frankel, N.A. and Acrivos, A., *Chem. Eng. Sci.*, 22, 847 (1967).

(32) Janssen, J.W., Blom, C., and Mellema, J., "The Flow Curves of Latex Dispersions with Added Thickener," (In Dutch), *Verfkroniek* 61 (6), 254-258 (1988).

(33) Janssen, J.W., Blom, C., and Mellema, J., "The Flow Curves of Latex Dispersions with Added Pigment and Thickener," (In Dutch), *Verfkroniek*, 62 (7/8) (1989) 283-293.

(34) Kissling, R.L. and Gross, P.H., "Capillary Behaviour of Viscous Liquids," *J. Phys. Chem.*, 74 (2), 318-326 (1970).

(35) Dillon, P.W., "Application of Critical Relative Humidity, an Evaporation Analog of Azeotropy, to the Drying of Waterborne Coatings," Journal of Coatings Technology, *49*, No. 634, 38 (1977).

(36) Löfflath, F., Gebhard, M., "Rheological Changes During the Drying of a Waterborne Latex Coating," Journal of Coatings Technology, *69*, No. 867, 55 (1997).

(37) Meijer, M. de, Thurich, K., and Militz, H., "Quantitative Measurements of Capillary Coating Penetration in Relation to Wood and Coating Properties," *Wood Sci. Technol.*, in press.

(38) Beetsma, J., "Alkyd Paints: From the Ease of Organic Solvents to the Difficulties of Water," *22nd FATIPEC Conference Budapest* Vol. 2, 157-167, 1994.

(39) Patton, T.C., *Paint Flow and Pigment Dispersion: A Rheological Approach to Coating and Ink Technology*, 2nd ed. John Wiley and Sons, New York, p. 99, 1979.

(40) Siau, J.F., *Transport Processes in Wood*. Springer, Berlin, p. 29, 1984.

(41) Deng, Y. and Abazeri, M., "Contact Angle Measurement of Wood Fibers in Surfactant and Polymer Solutions," *Wood Fiber Sci.*, 30 (2) 155-164 (1998).