Influence of Coating System Composition on Moisture Dynamic Performance of Coated Wood

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Model coatings with known composition were assessed for liquid water permeability both as single coat systems and combined as primers and topcoats to form regularly used coating systems—in total 38 different systems. The water permeability of the coatings, expressed as water absorption value, was measured by a method similar to the method that now is proposed as a European standard for the assessment of liquid water permeability. During artificial weathering, the samples were measured for a water absorption value, thus showing the change in water permeability as a function of weathering.

The study has shown that an excess of surfactants in the alkyd emulsions has a negative effect on the coating's ability to exclude water from the test samples. A waterborne acrylic paint based on a dispersion of larger particle size (0.4 µm) showed a poor ability to exclude water compared to a similar paint based on smaller dispersion particles (0.1 µm). The alkyd emulsion paints, as single coats, showed high water absorption values compared to solventborne paints and acrylic paints.

INTRODUCTION

Coatings are used on exterior wood for two major purposes, decorative and protective. For decorative purposes, the coating should be durable and retain its gloss and color for an extended period of time, and either be unchanged by solar radiation or be degraded in a smooth and uniform way. For protective purposes, the coating should be durable and retain its physical (e.g., protective) properties for an extended period of time to keep maintenance intervals as long as possible. This will result in the best ratio between performance and cost. Furthermore, it is essential that the coatings have such properties that the coated constructions, over time, never accumulate more water and moisture than can be evaporated during dry periods.

In the 1960s, the concern for environmental pollution by solvents and occupational health aspects caused a great demand for more environmentally friendly coating systems. With the introduction of waterborne paints, mainly based on acrylic polymers dispersed in water, it was believed that this concern was met. Another advantage of acrylics compared to linseed oil and alkyds was better resistance against degradation by UV radiation. The acrylics, therefore, constituted a more durable paint surface.

These waterborne systems are much more complex than the solventborne systems. In a solventborne system, the binder is solubilized as a true solution of discrete molecules in a solvent or solvent blend. In a waterborne system, the binder is dispersed as small droplets in water phase by different additives.[1] Furthermore, the composition of the coating has an influence on the film formation. The mechanism of film formation of waterborne coatings is much more complicated than the film formation of solventborne coatings.[2-5]

In the 1970s, commercial coatings based on alkyds, emulsified in water or water/solvent mixtures, were

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Table 1—Coating Composition—Solventborne Paints (values in weight %)

	Priming Oil PO	Linseed Oil Paint LOP	Alkyd Paint AP	Alkyd Stain AS
Necomar F-2080	12.00	—	—	—
Alkyd (Bergvik S 78-70)	—	—	38.50	56.40
Linseed oil (raw)	—	23.00	—	—
Stand oil 20cP	—	11.50	—	—
Bayertitan R-KB-2	—	57.90	41.70	—
UV-Titan L 530	—	—	—	13.00
Zinc oxide pigment	—	5.00	—	—
Siccatol 938	—	1.90	2.00	2.90
Nuodex Co 12%	0.08	—	—	—
Luaktin	—	0.70	0.20	0.30
White spirit	47.92	—	17.60	27.40
Solvesso 100	40.00	—	—	—
Solid content (% by volume)	8.57	96.9	68.3	63.1
PVC (%)	0	28.9	20.4	5.2
Density (g/cm^3)	0.83	1.82	1.33	1.00

introduced. Hofland[6,7] has reviewed the development of alkyd emulsion as binder in coatings. In view of the environmental concern, much attention has been drawn towards the wide use of waterborne coatings. Although fundamental research in polymer science and other relevant areas finds its way into the coating business, a great proportion of coating formulation is still on an empirical basis.

Despite the good durability of waterborne coatings, damage to wooden claddings by microbiological degradation (e.g., rot or blue-stain colonization) has been detected in exterior wooden facades in Scandinavia[8,9] when these types of coatings are used. The reported bad performance of exterior coatings in Scandinavia initiated a comprehensive national survey to study the relation between coating composition and performance. The objective was to investigate if, or to what extent, differences in blue-stain colonization, adhesion to wood substrate, penetration of coatings into wood, and moisture dynamic characteristics could be correlated to coating composition. As part of this national survey, Bardage[10] has reported work regarding the susceptibility of painted wood to colonization by blue-stain fungi (*Aureobasidium pollulans*), Bardage and Bjurman[11] have reported work regarding the adhesion of waterborne paints to wood, and Nussbaum et al.[12] have reported studies about the penetration of coatings into wood. These three studies were performed with model coatings. The same model coatings have been used in the present study, where the objective was to assess the moisture dynamic properties as a function of physical and chemical composition. As a result, the three studies make it possible to compare moisture dynamic properties with susceptibility to microbial colonization, adhesion of coatings to wood, and penetration of coatings into wood.

It is a known fact that the performance of a coating is directly related to its chemical composition and physical state.[13-15] Numerous studies have been reported in literature regarding moisture transport through paint films,[16-26] together with review articles on water and moisture behavior in coated wood.[27-29] Although the moisture dynamic properties of coatings related to composition play an important role for the raw material suppliers as well as for the paint industry in developing new resins, little are actually reported in literature. However, most studies use commercial products with confidential formulations that limit generalizations.

The objective of this study was to assess the water absorption through coatings on wood related to the coatings' chemical and physical composition. Fourteen model coatings were used. The model coatings were: one priming oil, three solventborne paints, five alkyd emulsion paints, and five acrylic paints. These 14 model coatings were assessed both as single-coat systems and combined as primers and topcoats to form common coating systems. In total, 38 different systems were assessed. The water absorption properties of the coatings were measured by a "floating" method similar to

Table 2—Coating Composition—Alkyd Emulsion Paints (values in weight %)

	Alkyd Emulsion Paint AE 1	Alkyd Emulsion Paint AE 2	Alkyd Emulsion Paint AE 3	Alkyd Emulsion Paint AE 4	Alkyd Emulsion Paint AE 5
Alkyd emulsion 1 (anionic)	52.80	—	—	41.57	—
Alkyd emulsion 2 (nonionic)	—	52.00	—	—	—
Alkyd emulsion 3 (2x nonionic)	—	—	50.71	—	—
Alkyd emulsion 4 (Uradil XP 516 A Z)	—	—	—	—	50.78
Bayertitan R-KB-2	25.00	25.00	24.13	35.90	25.00
Acrysol RM8	1.10	3.00	5.08	2.70	1.44
Nopco NXZ	0.42	0.20	0.41	0.43	0.41
Orotan 731 SD	0.21	0.20	0.20	0.30	0.20
Siccatol 938	1.00	0.90	0.82	0.70	0.83
Exkin 2	0.64	0.60	0.61	0.60	0.61
Proxel GXL	0.10	0.10	0.10	0.10	0.09
Water	18.73	18.00	17.94	17.70	20.64
Solid content (% by volume)	40	39.8	38.2	40.6	44.5
PVC (%)	19.4	19.7	19.5	30.6	17.8
Density (g/cm^3)	1.099	1.275	1.243	1.433	1.275

Table 3—Coating Composition—Acrylic Paints (values in weight %)

	Acrylic Paint A 1	Acrylic Paint A 2	Acrylic Paint A 3	Acrylic Paint A 4	Acrylic Paint A 5
Acrylic dispersion, 0.1 μm	57.84	—	58.42	18.55	—
Acrylic dispersion, 0.4 μm	—	56.60	—	43.28	—
Acrylic dispersion, Multilobe 200	—	—	—	—	44.20
Bayertitan R-KB-2	23.00	22.51	23.25	24.60	21.70
Dowanol Tpnb	1.93	1.89	1.95	2.07	1.82
Propylene glycol	1.00	0.94	0.98	1.03	0.91
Acrysol RM8	0.94	2.84	—	1.43	0.69
Bermocoll E 411 FQ	—	—	0.50	—	—
Nopco NXZ	0.40	0.38	0.40	0.42	0.37
Orotan 731 SD	0.19	0.18	0.20	0.20	0.18
Exkin 2	0.58	0.57	0.59	0.62	0.55
Proxel GXL	0.09	0.09	0.11	0.10	0.08
Water	14.03	14.00	13.60	7.70	29.50
Solid content (% by volume)	35.0	34.0	35.4	38.0	34.0
PVC (%)	20.5	20.7	20.5	20.5	19.7
Density (g/cm^3)	1.293	1.289	1.307	1.323	1.275

the method that is now a European standard for the assessment of liquid water permeability.[30]

EXPERIMENTAL

Materials

Test Panels: Test samples of tangentially cut Norway spruce (*Picea abies*) were used. They had a dimension of 230 x 70 x 10 mm (longitudinal, tangential, and radial directions, respectively), were free from knots and cracks, were straight-grained, and had between four and seven annual rings per 10 mm. The densities of the test samples were between 400 and 500 kg/m^3, measured at 12% moisture content. The coatings were applied on the tangential bark side and the two longitudinal edges, leaving the reverse side untreated. All faces were fine sawn. The end grains of the test samples were sealed with an impermeable treatment consisting of one coat of solventborne alkyd primer followed by a flexible sealant. Prior to coating, the test samples were conditioned to a constant weight at 20°C and 65% RH, thus giving an initial moisture content in the test samples of approximately 12%.[31] One or two coatings were applied on each sample. In this way 38 different coating systems were tested.

The model coating formulations are given in *Tables* 1-3. The raw materials in the formulations were products regularly used in the coating industry. The model coatings were developed in close contact with, and approved by, coating manufacturers and raw material suppliers. Some ingredients, which normally occur in commercial paints, have been omitted in the model coating formulations, e.g., fungicides and some other additives that are regarded as not having influence on the moisture dynamic behavior.

Resins*:*

Drying Oils—Linseed oil and stand oil (polymerized linseed oil, viscosity 20 cP) were used in the linseed oil paint LOP. Chemically modified fish oil, Necomar® F-2080 from Ashland-Sud Chemie GmbH, was used as binder in the priming oil, PO.

Alkyd Resin—The alkyd resin, Bergvik Alkyd S 78/70, used as the binder in the alkyd paint AP, the alkyd stain AS, and the alkyd emulsions 1, 2, and 3 was manufactured by Arizona Chemical, Sandarne, Sweden. The resin had an oil length of 76% and a composition of 73% tall oil fatty acids, 19% isophtalic acid, and 8% pentaerythritol. For the solventborne coatings, the resin was processed to an acid value of 5.3 mg KOH/g alkyd, and a mean molecular weight of approximately 13,000, determined by gel permeation chromatography (GPC). For the waterborne alkyd emulsions, the alkyd resin was processed to an acid value of 11.7-12.5 mg KOH/g alkyd with a mean molecular weight of approximately 6,000, determined by GPC.

Alkyd Emulsions—For use in the waterborne coatings, the alkyd resin, Bergvik Alkyd S 78/70 N, was emulsified with different surfactants. It was emulsified with an anionic surfactant, sodium laurylmyristyl ethersulphate (Elfan NS 242 from Akzo Nobel Chemicals), to form alkyd emulsion 1. The alkyd resin was also emulsified with 5% nonionic surfactant (ethoxylated [EO=10] fatty alcohol [C$_{11}$], Berol 542 from Akzo Nobel Chemicals) to from alkyd emulsion 2, and emulsified with 10% of the same nonionic surfactant to form alkyd emulsion 3. The alkyd emulsions 1, 2, and 3 were manufactured by the Institute for Surface Chemistry, Stockholm, Sweden.

Additionally, a commercial alkyd emulsion, Uradil XP 516 A Z, from DSM Resins BV, NL, was used as alkyd emulsion 4. The emulsified alkyd was a long oil

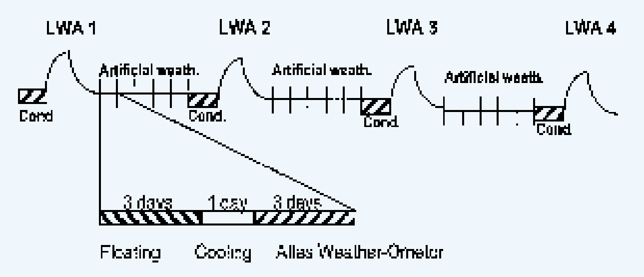

Figure 1—Artificial weathering schedule. Cond. = conditioning. LWA 1 – 4, see text.

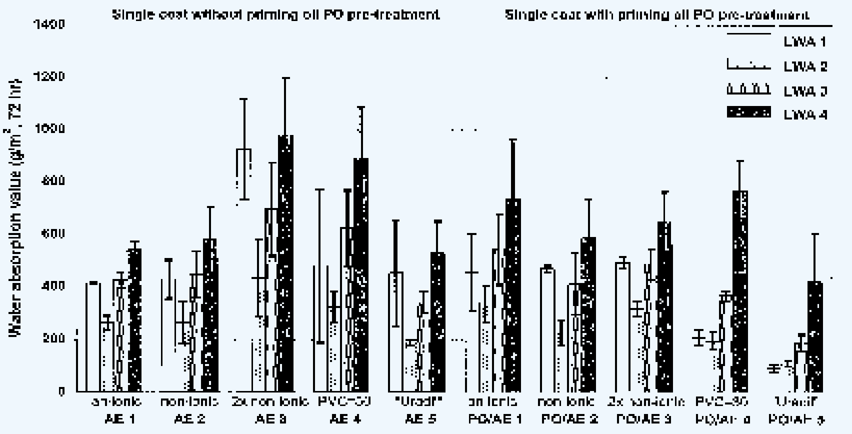

Figure 2—Water absorption values (WAV) for different alkyd emulsion paints. Mean values for three replicates and standard deviation are shown. White bars show WAV before artificial weathering. Gray bars show WAV after 5, 10, and 15 cycles of artificial weathering.

AE 1 = alkyd emulsion paint AE 1 (anionic surfactant)
AE 2 = alkyd emulsion paint AE 2 (nonionic surfactant)
AE 3 = alkyd emulsion paint AE 3 (nonionic surfactant in excess)
AE 4 = alkyd emulsion paint AE 4 (PVC = 30%)
AE 5 = alkyd emulsion paint AE 5 (commercial binder, Uradil)
PO/AE 1 = priming oil PO + alkyd emulsion paint AE 1 (anionic surfactant)
PO/AE 2 = priming oil PO + alkyd emulsion paint AE 2 (nonionic surfactant)
PO/AE 3 = priming oil PO + alkyd emulsion paint AE 3 (nonionic surfactant in excess)
PO/AE 4 = priming oil PO + alkyd emulsion paint AE 4 (PVC= 30%)
PO/AE 5 = priming oil PO + alkyd emulsion paint AE 5 (commercial binder, Uradil)

alkyd with an oil length of approximately 63% based on tall oil and with an average particle size of 0.25 to 0.5 μm and a solid content of 60%.

Acrylic Dispersions—The acrylic lattices used in the acrylic formulations, except for the commercial acrylic dispersion, were manufactured by Hoechst-Perstorp AB, Sweden. The lattice was a copolymer of butylacrylate, methylmethacrylate, and methacrylic acid (49/49/2). Sodium dodecylsulphate (SDS), 1.5%, was used as emulgator system. By modifying the emulsion polymerization, acrylic dispersions with two different particle sizes were manufactured with 0.1 and 0.4 μm average particle sizes, respectively. The 0.1 μm dispersion had a solid content of 40.3% and a density of 1.045 g/cm^3 whereas the 0.4 μm dispersion had a solid content of 40.3% and a density of 1.06 g/cm^3.

Additionally, a nonspherical acrylic lattice[32] was used in one model coating. It was an acrylic dispersion from Rohm & Haas, Rhoplex Multilobe™ 200, with a solid content of 53.5% and a density of 1.07 g/cm^3.

PIGMENTS: In all opaque formulations, except in the alkyd stain AS, a micronized rutile titanium dioxide pigment, Bayertitan R-KB-2, from Bayer AG, Germany, was used. The pigment was lattice-stabilized with aluminum oxide and coated with aluminum and silicon compounds and organically treated. The pigment had a mean primary particle size of 0.25 μm and a specific surface area of approximately 10 m^2/g, determined according to the B.E.T. method.[33]

In the alkyd stain AS, an ultra-fine rutile titanium dioxide pigment, UV-Titan L 530, from Kemira Oy, Finland, was used. UV-Titan L 530 has a crystal size of 30–35 nm and is surface modified with Al-, Si-, and Zr-oxides and trimethylolethane. Specific surface area, determined according to the B.E.T. method,[33] is 50-60 m^2/g. The pigment showed a UV cutoff at about 400 nm.

A zinc oxide pigment, Zinc Oxide White Seal Special®, from Grillo Zincoxide Ltd., UK was used in the linseed oil paint LOP. The pigment had a typical specific area, of approximately 4 m^2/g, determined according to the B.E.T. method.[33]

RHEOLOGY MODIFIERS: Acrysol® RM 8 was used as a rheology modifier in the waterborne formulations. Acrysol® RM 8, from Rohm & Haas, is an associative thickener based on a hydrophobically modified, etox-ylated urethane, (HEUR). In one of the acrylic formulations, A 3, a rheology modifier based on ethyl hydroxy ethyl cellulose, Bermocoll E 411 FQ, from Berol Kemi AB, Sweden (at present Akzo Nobel Additives Inc., USA), substituted the HEUR rheology modifier.

DRIERS: Siccatol® 938, from Akzo Chemicals BV, Holland, was used as drier in both the solventborne alkyd formulations and the waterborne alkyd emulsion formulations. Siccatol® 938 had a metal content of 0.9% Co, 5.4% Sr, and 3.6% Ca with 50–55% nonvolatile content. Nuodex CO 12% from Servo Delden BV, Holland was used as drier in the priming oil PO. The drier had a metal content of 12% cobalt.

OTHER ADDITIVES: Orotan® 731 SD (sodium salt of a polymeric carboxylic acid with anionic character), from Rohm & Haas, was used as dispersing agent in the waterborne coatings and Nopco® NXZ, from Diamond Shamrock, was used in the waterborne coatings as a defoamer. Luaktin® (methyl ethyl ketoxime), from BASF AG, Germany, and Exkin® 2 (methyl ethyl ketoxime), from Servo Delden BV, Holland, were used as antiskinning agents in the solventborne and waterborne coatings, respectively. Proxel® GXL (20% 1,2-Benzisothiazolin-3-one in aqueous dipropylene glycol solution), from ICI Specialty Chemicals, UK, was used as a preservative.

SOLVENTS: White spirit, with approximately 18% aromatic hydrocarbons and Solvesso® 100, an aromatic hydrocarbon blend with a boiling point of 155-181ºC, were used as solvents in the solventborne coatings. In the waterborne coatings, propylene glycol was used as cosolvent.

The model coatings were manufactured by The Swedish Institute for Wood Technology Research, Stockholm (priming oil), Engwall & Claesson AB, Stockholm (Swedish paint manufacturer) (coatings LOP, AP, and AS), and the Institute for Surface Chemistry, Stockholm (coatings AE 1–AE 5 and A 1–A 5).

Methods

Coating Application and Conditioning: The test samples were coated by brushing with the different coatings. The amount applied for each coating layer was calculated to give a dry film thickness of 80 μm for each coating layer. The test samples were weighed before and after application and the film thickness was calculated. The deviation from 80 μm was less than 10% for all samples. Three replicates were coated for each coating system. After application of the different coatings, each test sample was conditioned in an atmosphere of 20ºC and 65% RH according to ISO 554[34] until constant weight, thus the test samples reached a moisture content of approximately 12%.

Water Absorption Measurements: The liquid water permeability of the coatings and coating systems was measured according to a method similar to European standard: EN 927-5—"Assessment of the Liquid Water Permeability."[30] After the test samples were brush-coated and conditioned, each sample was exposed to deionized water for 72 hr at 20°C. The liquid water permeability was determined as the increase in weight of the test samples after 72 hr of floating on water with the coating being tested facing the water. For each set of three replicates, the arithmetic mean of the weight

Table 4—Least Significant Difference Test for LWA 4

Figure 2	**Alkyd emulsion paints**				**LSD = 328**					
		AE 2	**AE 3**	**AE 4**	**AE 5**	**PO/AE 1**	**PO/AE 2**	**PO/AE 3**	**PO/AE 4**	**PO/AE 5**
	AE 1	–35	**–437**	**–348**	18	–192	–41	–105	–222	125
	AE 2		**–401**	–313	53	–157	–6	–70	–187	160
	AE 3			89	**454**	244	**395**	**331**	215	**562**
	AE 4				**366**	156	307	243	126	**473**
	AE 5					–210	–59	–123	–240	107
	PO/AE 1						151	87	–30	317
	PO/AE 2							–64	–181	166
	PO/AE 3								–117	230
	PO/AE 4									**347**

Figure 3	**Acrylic paint**				**LSD = 104**		
		A 2	**A 3**	**A 4**	**A 5**	**PO/A 1**	**PO/A 2**
	A 1	**–189**	–19	–32	–9	6	**–127**
	A 2		**170**	**156**	**179**	**194**	62
	A 3			–14	9	24	**–108**
	A 4				23	38	–95
	A 5					15	**–118**
	PO/A 1						**–133**

Figure 5	**Linseed oil primer + different topcoats**					**LSD = 24**
		LOP/AP	**LOP/A 1**			
	LOP/LOP	**45**	**62**			
	LOP/AP		17			

Figure 6	**Alkyd emulsion paint + different topcoats**				**LSD = 17**					
		AE 1/A 1	**AE 2/AP**	**AE 2/A 1**	**AE 3/AP**	**AE 3/A 1**	**AE 4/AP**	**AE 4/A 1**	**AE 5/AP**	**AE 5/A 1**
	AE 1/AP	**23**	**–18**	6	**-23**	11	–3	12	0	15
	AE 1/A 1		**–41**	–17	**–46**	–12	**–26**	–11	**–23**	–8
	AE 2/AP			**24**	-5	**29**	14	**30**	**18**	**33**
	AE 2/A 1				**–29**	5	–9	6	–6	9
	AE 3/AP					**34**	**19**	**35**	**23**	**38**
	AE 3/A 1						–15	1	–11	4
	AE 4/AP							15	3	**18**
	AE 4/A 1								–12	3
	AE 5/AP									15

Figure 7	**Alkyd primers + different topcoats**				**LSD = 21**			
		AP/A 1	**AP/A 2**	**AP/A 3**	**AP/A 4**	**AP/A 5**	**AS/AP**	**AS/A 1**
	AP/AP	2	12	17	1	–11	**25**	8
	AP/A 1		10	16	–1	–13	**23**	6
	AP/A 2			6	–11	**–23**	13	–4
	AP/A 3				–16	**–28**	7	–10
	AP/A 4					–12	**23**	6
	AP/A 5						**36**	19
	AS/AP							–17

Note: Values in **bold** denote a statistically significant difference at 95% confidence level.

increase and the standard deviation were calculated. The arithmetic mean of the weight increase after 72 hr of floating is reported as the water absorption value and is expressed as g/m^2, 72 hr. This test procedure was carried out in a conditioning room at 20°C and 65% RH. This first measurement of the unweathered, coated test samples is called LWA 1 (first liquid water absorption measurement). After the floating period, the test samples were left to dry in the conditioning room.

After drying to approximately 12% moisture content, the test samples were subjected to artificial weathering. The artificial weathering test schedule is shown in *Figure* 1. The schedule involves four measurements of the water absorption value at four different occasions during the test. For further reference in the text, the times for the different measurements of water absorption value are designated LWA 1, LWA 2, LWA 3, and LWA 4, respectively. LWA 1 represents time = 0, i.e., before any artificial weathering. LWA 2, LWA 3, and LWA 4 represent the measurements of water absorption values after 5, 10, and 15 cycles (=weeks) of artificial weathering, respectively. Between these water absorption measurements, the samples were aged according to the artificial weathering schedule outlined in *Figure* 1.

ARTIFICIAL WEATHERING: The artificial weathering was performed by letting the test samples float on water at 20°C for 72 hr with the coating being tested face down, followed by 24 hr in a refrigerator at +3ºC followed by 72 hr of UV and water spray exposure in an Atlas Weather-Ometer Ci65. The Weather-Ometer, with a 6500 W xenon arc lamp, was programmed for 102 min UV radiation followed by 18 min of UV radiation and water spray. This 168-hr artificial weathering cycle (=one week) was repeated five times before the next LWA. Before each LWA, the test samples were conditioned in 20°C and 65% RH until constant weight. The conditioning time was normally four weeks.

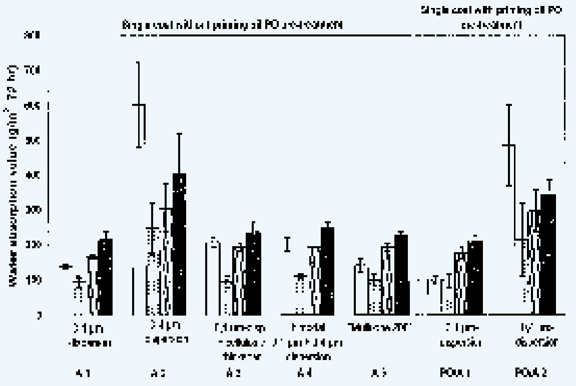

Figure 3—Water absorption values (WAV) for different acrylic paints. Mean values for three replicates and standard deviation are shown. White bars show WAV before artificial weathering. Gray bars show WAV after 5, 10, and 15 cycles of artificial weathering.

A 1 = acrylic paint A 1 (0.1 μm dispersion)
A 2 = acrylic paint A 2 (0.4 μm dispersion)
A 3 = acrylic paint A 3 (0.1 μm dispersion and cellulosic thickener)
A 4 = acrylic paint A 4 (bimodal distribution, 0.1 μm- and 0.4 μm dispersion)
A 5 = acrylic paint A 5 (commercial binder, Rohm & Haas, Multilobe 200)
PO/A 1 = priming oil PO + acrylic paint A 1 (0.1 μm dispersion)
PO/A 2 = priming oil PO + acrylic paint A 2 (0.4 μm dispersion)

STATISTICAL METHODS: Analysis of variance (ANOVA)[35] and least significant difference (LSD) method[35] was used to determine statistically significant differences in the water absorption values for the different systems. The F-ratios and p-values were calculated and compared with F-distributions for $\alpha = 0.05$ (i.e., confidence level = 95%). If the calculated F-ratio was greater than the critical F-ratio, a statistical significant difference exists between treatments and LSD tests were performed. ANOVA and LSD analysis are only shown for measurements at LWA 4. When statistical significant difference is reported, it is at a 95% confidence level.

RELATING THE ARTIFICIAL WEATHERING WITH NATURAL EXPOSURE: The 6500 W Xenon Arc lamp in the Atlas Weather-Ometer emits an irradiance of 40.0 W/m^2 in the region 300-400 nm and 375 W/m^2 in the region 400-800 nm.[36] This gives a total irradiance of 415 W/m^2 in the region 300-800 nm. The irradiation emitted from the Xenon arc lamp, during one cycle of artificial weathering in the test procedure (i.e., 72 hr), is therefore 30 kWh/m^2 (415 W/m^2 x 72 hr = 29.88 kWh/m^2). The test samples have been subjected to 15 cycles of artificial exposure. This exposure includes an irradiation of 450 kWh/m^2, which is equal to 4.5 months of natural irradiation in the summer or equal to the natural irradiation during the winter period from October to April in Scandinavia.

RESULTS AND DISCUSSIONS

Figures 2, 3, and 5-7 show the water absorption values for the different coatings and coating systems. The white bars show the initial water absorption value (i.e., before weathering) and the gray bars show the water absorption values after 5, 10, and 15 cycles of artificial weathering, respectively (*Figure* 2). Note the differences in scaling for the different figures. The results of the statistical analysis for the measurements for LWA 4 are shown in *Table* 4. The figures shown in *Table* 4 are the calculated differences between different treatments. The given LSD values (LSD=xx) in *Table* 4 show the minimum differences for statistical significant differences at a 95% confidence level.

Alkyd Emulsion Paints

Figure 2 shows the water absorption values for the different alkyd emulsion paints both with and without a pretreatment of the test samples with the priming oil PO. The single coat alkyd emulsion paints show water absorption values, before weathering, between 400 g/m^2, 72 hr and 500 g/m^2, 72 hr except for the alkyd emulsion paint AE 3 with excess of surfactant. That

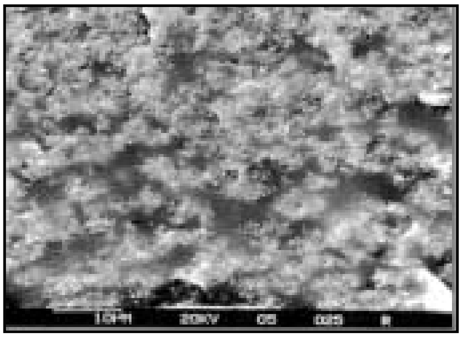

Figure 4a—Scanning electron microscope image of the surface of acrylic paint A 1 with 0.1 mm dispersion. (The picture is presented by courtesy of Dr. Stig Bardage, Swedish University of Agricultural Sciences, Uppsala, Sweden.)

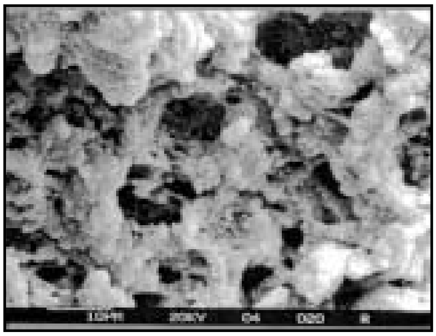

Figure 4b—Scanning electron microscope image of the surface of acrylic paint A 2 with 0.4 mm dispersion. (The picture is presented by courtesy of Dr. Stig Bardage, Swedish University of Agricultural Sciences, Uppsala, Sweden.)

coating shows a water absorption value as high as 926 g/m², 72 hr. For all alkyd emulsion paints used as a single coat, AE 1–AE 5, the water absorption values show a decrease after five cycles of artificial weathering, i.e., at LWA 2. This is also found when these coatings are combined with the priming oil, PO/AE 1–PO/AE 4. This decrease in water absorption value is probably a consequence of leaching water-soluble, hydrophilic material from the coating thus making the coating more water impermeable. Perera[37] found that leaching water-soluble substances from a coating led to a decrease in the diffusion coefficient (d_p). The same decrease in the diffusion coefficient after weathering has been reported by Holsworth et al.[38] The decrease in water absorption values between LWA 1 and LWA 2 may also be due to the heating of the coated surface by radiation from the UV lamp, resulting in a less permeable paint film.[36] After a decrease in water absorption values between LWA 1 and LWA 2, the values increased as exposure progressed. The water absorption values versus exposure time thus form a "bathtub-shaped" curve. These "bathtub-shaped" curves show quite interesting similarities with the "bathtub-shaped" hazard rate curve shown by Martin et al.[39] They suggest that those high hazard rates in early stages of exposure result from a mixture of failure modes and might be due to, for example, blistering, alkyd leaching, surfactant leaching, and edge swell.

The alkyd emulsion paints used both as single coats and combined with the priming oil PO show high water absorption values after 15 cycles of artificial weathering. However, the effect of the priming oil seems to be negligible. Pair-wise comparisons between alkyd emulsion paint with and without priming oil pretreatment showed no statistically significant differences after 15 cycles of weathering except between AE 3 and PO/AE 3 (see *Table* 4). The expected hydrophobic effect of the priming oil PO is likely to be more pronounced if the coating film showed cracking or checking. The alkyd emulsion paint with a high amount of surfactant, AE 3, showed a high water absorption value both before and after artificial weathering. This may be a consequence of the hydrophilic character of the surfactant.

ANOVA showed that there are statistically significant differences between treatments ($F_{9,20}$= 2.47, p=0.0443). LSD test (see *Table* 4) showed that there is a statistically significant difference between the water absorption values for systems AE 1, AE 2, and AE 5 on one hand and systems AE 3 and AE 4 on the other). Between systems AE 1, AE 2, and AE 5 there are no significant differences. The difference in water absorption

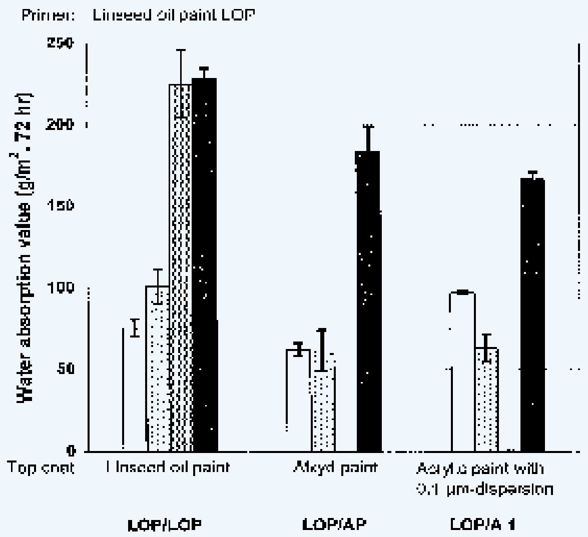

Figure 5—Water absorption values (WAV) for the linseed oil paint as primer with different topcoats. Mean values for three replicates and standard deviation are shown. White bars show WAV before artificial weathering. Gray bars show WAV after 5, 10, and 15 cycles of artificial weathering.

LOP/LOP = primer LOP (linseed oil paint) + topcoat LOP (linseed oil paint)
LOP/AP = primer LOP (linseed oil paint) + topcoat AP (solventborne alkyd paint)
LOP/A 1 = primer LOP (linseed oil paint) + topcoat A 1 (0.1 mm dispersion)

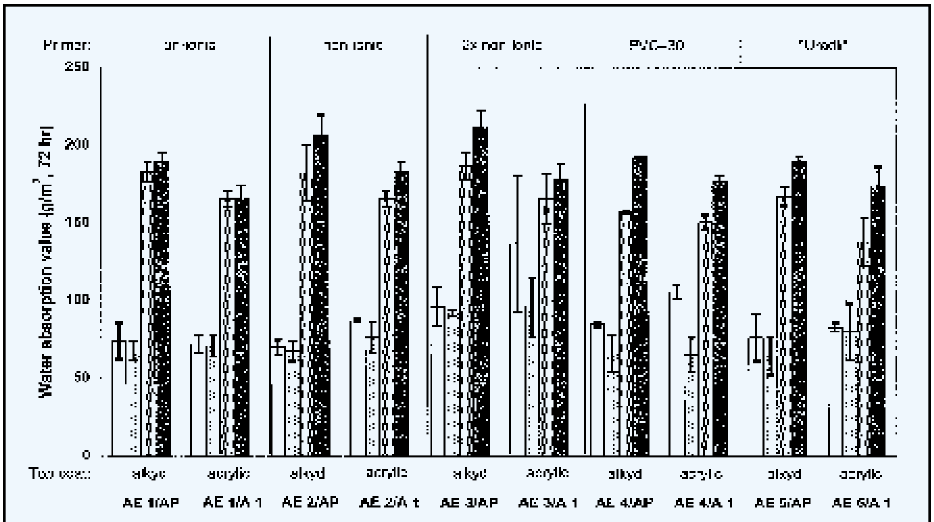

Figure 6—Water absorption values (WAV) for different alkyd emulsion paints as primers with different topcoats. Mean values for three replicates and standard deviation are shown. White bars show WAV before artificial weathering. Gray bars show WAV after 5, 10, and 15 cycles of artificial weathering.

AE 1/AP = primer AE 1 (anionic surfactant) + topcoat AP (solvent-borne alkyd paint)
AE 1/A 1 = primer AE 1 (anionic surfactant) + topcoat A 1 (water-borne acrylic paint)
AE 2/AP = primer AE 2 (nonionic surfactant) + topcoat AP
AE 2/A 1 = primer AE 2 (nonionic surfactant) + topcoat A 1
AE 3/AP = primer AE 3 (nonionic surfactant in excess) + topcoat AP
AE 3/A 1 = primer AE 3 (nonionic surfactant in excess) + topcoat A 1
AE 4/AP = primer AE 4 (PVC = 30%) + topcoat AP
AE 4/A 1 = primer AE 4 (PVC = 30%) + topcoat A 1
AE 5/AP = primer AE 5 (commercial binder, Uradil) + topcoat AP
AE 5/A 1 = primer AE 5 (commercial binder, Uradil) + topcoat A 1

values between the different alkyd emulsion paints with priming oil pretreatment does not prove to be significant after 15 weeks of artificial weathering except between PO/AE 4 and PO/AE 5.

Increasing the pigment volume concentration (PVC) from 20 to 30% increased the water absorption value in systems AE 4 and PO/AE 4. The effect of pigmentation on permeability is generally a decrease in water permeability with increasing PVC up to the critical pigment volume concentration (CPVC). Well dispersed, nonhydrophilic, impermeable pigments reduce the diffusion of water through the coating by increasing the volume fraction of impermeable substances in the coating.[40] However, if incomplete dispersion, flocculation, irregular distribution, poor bonding between pigment and resin, or non-ideal pigmentation, (e.g., hydrophilic pigments) exist, these non-ideal conditions can even lead to an overall increase in moisture transport through the coating with increasing PVC.[28] The difference between expected and observed results may be due to some of the previously mentioned conditions.

Acrylic Paints

Figure 3 shows the water absorption values for the different acrylic paints both with and without a pretreatment of the test samples with priming oil PO. Generally, a decrease in the water absorption value between LWA 1 and LWA 2, which was observed for the alkyd emulsion paints, was also observed for all the single-coat acrylic paints. The water absorption values for single-coat acrylic paints before weathering showed values between 100 g/m^2, 72 hr and 200 g/m^2, 72 hr and with quite small standard deviations except for the acrylic paint A 2 based on the 0.4 μm dispersion, with a mean value of 604 g/m^2, 72 hr. The results shown in *Figure* 3 clearly indicate that the particle size of the acrylic dispersions has a great influence on water permeability. The waterborne acrylic paint A 2 based on the 0.4 μm dispersion, used single as system A 2 or combined with a priming oil, in system PO/A 2, showed a poor ability to exclude water before weathering compared to the acrylic paint A 1 based on the 0.1 μm dispersion. Although the presence of the hydrophobic priming oil should be expected to lower the water absorption value, the effect of the priming oil is negligible. *Figure* 4 shows scanning electron microscope images of the surface made by a cast from the acrylic paint A 1 with particle size 0.1 μm (*Figure* 4a) and from the acrylic paint A 2 with particle size 0.4 μm (*Figure* 4b). The surface of the acrylic paint with particle size 0.4 μm showed a much more porous structure than the acrylic paint with particle size 0.1 μm.

The acrylic paint A 4 based on a bimodal dispersion with the particle sizes 0.1 μm and 0.4 μm, showed the same water absorption as the acrylic paint A 1 based on pure 0.1 μm dispersion. This was probably due to the fact that the smaller particles fill out the voids between the 0.4 μm particles and make a film with almost the same properties as a dispersion with particle size distribution similar to the smallest particles. Substituting the HEUR rheology modifier in the acrylic paint A 1 based on the 0.1 μm dispersion with the cellulosic rheology modifier, forming acrylic paint A 3, had no significant effect on water permeability.

ANOVA showed that there is a statistically significant difference between treatments ($F_{6,14}$=4.76, p=0.0076). LSD test (*Table* 4) showed that there is a statistical significant difference between the water absorption value for the acrylic paint A 2 with the 0.4 μm dispersion versus the other acrylic paints. Between the acrylic systems, A 1, A 3, A 4, and A 5 there are no statistically significant differences after 15 cycles of weathering. The difference in water absorption values between the acrylic paints A 1 and A 2 with priming oil PO pretreatment showed a statistical significance after 15 weeks of artificial weathering.

Linseed Oil Paint as Primer in Combination with Different Topcoats

Figure 5 shows the water absorption values for three different combinations with linseed oil paint as primer with the linseed oil paint, the alkyd paint, and the acrylic paint with the 0.1 μm dispersion, respectively, as topcoats. No measurements of water absorption values were made after 10 cycles of artificial weathering for LOP/AP and LOP/A 1. The water absorption values for all three systems were below 100 g/m^2, 72 hr before the artificial weathering. The water absorption values increased with weathering for the all-solventborne systems, LOP/LOP and LOP/AP, whereas for the system with the waterborne topcoat, LOP/A 1, a decrease in water absorption value between LWA 1 and LWA 2 was found, which is characteristic for waterborne coatings. Even after 15 cycles of artificial weathering, the water absorption values are well below 250 g/m^2, 72 hr. It is also interesting to note the very small standard deviations for the measurements indicating a robustness in performance of the systems.

ANOVA showed a strong significant difference between treatments ($F_{2,6}$=22.32,p=0.0017). LSD test is shown in *Table* 4. The systems with the acrylic topcoat A 1 or the alkyd topcoat AP showed less water permeability after 15 cycles of artificial weathering than the all-linseed oil paint system. There is a statistically significant difference at the 99% confidence level when comparing the all-linseed oil system, LOP/LOP, with the other two systems, LOP/AP and LOP/A 1. When linseed oil paint primer was used, the acrylic topcoat A 1 offered the best protection while the linseed oil topcoat was less efficient. However, for all these systems, water absorption values remained on quite a low level even after 15 cycles of artificial weathering.

Alkyd Emulsion Paints as Primers and Different Topcoats

Figure 6 shows the water absorption values for the different alkyd emulsion paints as primer together with the alkyd paint AP or the acrylic paint A 1 with 0.1 μm dispersion as topcoats. As can be seen in *Figure* 6, for the majority of systems, the water absorption value before weathering and the water absorption value after five cycles of artificial weathering (LWA 2) were close. Exceptions were the acrylic topcoat A 1 in combination with the primer alkyd emulsion paint AE 3 with excess of surfactant or the alkyd emulsion paint AE 4 with 30% PVC. The water absorption value before weathering was in the order of 60 to 100 g/m^2, 72 hr, with the exception of the system AE 3/A 1 where the value was 135 g/m^2, 72 hr.

ANOVA showed a strong significant difference between treatments ($F_{9,20}$=5.99, P=0.0004). LSD test is shown in *Table* 4. Comparing the water absorption values for different alkyd emulsion paints as primers with the alkyd paint AP or the acrylic paint A 1 as topcoats showed that using the acrylic paint A 1 as topcoat resulted in a lower water absorption value than using the alkyd paint AP as topcoat. Statistical evaluation, LSD test, of the systems in *Figure* 6 by pair-wise comparison of the water absorption values for the alkyd topcoat AP and the acrylic topcoat A 1 on different alkyd emulsion primers showed that the systems with the acrylic topcoat, after 15 cycles of artificial weathering, showed lower water absorption values than the systems

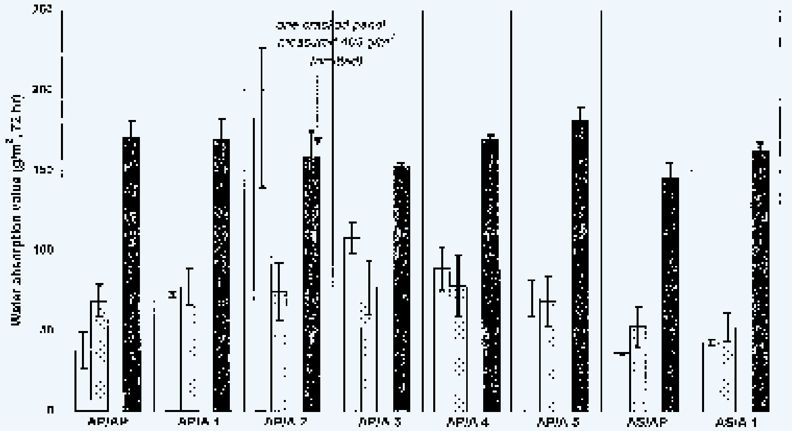

Figure 7—Water absorption values (WAV) for the alkyd paint as primer with different topcoats and for the alkyd stain as primer with different topcoats. Mean values for three replicates and standard deviation are shown. White bars show WAV before artificial weathering. Gray bars show WAV after 5 and 15 cycles of artificial weathering.

AP/AP = primer AP (solventborne alkyd paint) + topcoat AP (solventborne alkyd paint)

AP/A 1 = primer AP (solventborne alkyd paint) + topcoat A 1 (0.1 μm dispersion)

AP/A 2= primer AP (solventborne alkyd paint) + topcoat A 2 (0.4 μm dispersion)

AP/A 3= primer AP (solventborne alkyd paint) + topcoat A 3 (0.1 μm dispersion and cellulosic thickener)

AP/A 4 = primer AP (solventborne alkyd paint) + topcoat A 4 (0.1 μm and 0.4 μm dispersion)

AP/A 5 = primer AP (solventborne alkyd paint) + topcoat A 5 (commercial binder, Multilobe 200)

AS/AP = primer AS (solventborne alkyd stain) + topcoat AP (solventborne alkyd paint)

AS/A 1 = primer AS (solventborne alkyd stain) + topcoat A 1 (0.1 μm dispersion) with the alkyd topcoat. For primers AE 1, AE 2, and AE 3 the differences are statistically significant. The explanation for this may be that micro-cracking or checking were more frequent in the alkyd paint than in the acrylic paint after a long time of weathering.

Solventborne Alkyd Paint as Primer in Combination with Different Topcoats

Figure 7 shows the water absorption values for the different combinations of alkyd paint AP as primer with the alkyd paint AP and the different acrylic paints A 1-A 5 as topcoats and the alkyd stain AS as primer with the alkyd paint AP or the acrylic paint A 1 with 0.1 μm dispersion as topcoats. No measurements of water absorption values were made after 10 cycles of artificial weathering. All systems showed similar water absorption values after 15 cycles of artificial weathering with water absorption values of 150 to 170 g/m^2, 72 hr. One test sample with acrylic paint A 2 with particle size 0.4 µm showed large cracking at LWA 4 resulting in a very high value, 403 g/m^2, 72 hr. Results from this test sample have been omitted in the calculations.

ANOVA showed statistically significant differences between treatments ($F_{7,15}$=2.97, p=0.0363). LSD test is shown in *Table* 4. The systems with alkyd stain as primer and alkyd paint as topcoat (AS/AP) showed lower water absorption values than most of the other treatments in *Figure* 7. The differences are statistically significant.

CONCLUSIONS

The single coat alkyd emulsion systems showed higher water absorption values than all the other tested systems. The water absorption values for the alkyd emulsion paints, regardless of composition, decreased during the first step of artificial weathering to a minimum, after which the water absorption values increased with weathering. The same variations in the water absorption values during weathering were also observed for the acrylic paints. The decrease in water absorption values during the first stages of weathering that was observed for the waterborne coatings was not observed for the solventborne coatings.

It was clearly shown that an excess of surfactants in the coating had a negative effect on the coating's ability to prevent water ingress, which most likely is due to the hydrophilic character of the surfactant. Increasing the PVC from 20 to 30% increased the water absorption value. This result differed from expected results. The effect of pigmentation on permeability is generally a decrease in water permeability with increasing pigment volume concentration. The difference between expected and obtained results may be due to non-ideal pigmentation. The type of surfactant, anionic or nonionic, as emulsifier for the alkyd resin, seemed to have no significant influence on water permeability.

The particle size of the acrylic dispersion had a great influence on water permeability. Waterborne acrylic paint based on a dispersion of large particles (0.4 μm) showed a poor ability to prevent water ingress compared to the similar paint based on a dispersion of small particles (0.1 μm). The acrylic paint based on a bimodal distribution of dispersion particles (0.1 and 0.4 μm), showed the same water absorption characteristics as a similar acrylic paint based on a mono-modal distribution (0.1 μm). There is reason to believe that the smaller particles in the bimodal dispersion filled out the voids between the 0.4 μm particles and thus made a paint film with almost the same sorption characteristics as a paint film formed from a 0.1 μm mono-modal dispersion. The change from a polyurethane (HEUR)-based rheology modifier to a cellulose-based rheology modifier had no significant influence on water permeability.

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