NEW EVALUATION OF WATER REPELLENCY OF WOOD BY CONTACT ANGLE

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ABSTRACT

A new method for laboratory evaluation and screening of water repellency of preservative-treated wood surfaces is outlined. The method consists of the measurement of the contact angle of a small volume of water resting on the surface of the wood, under exactly defined, reproducible conditions.

The changes of contact angle plotted against the time of exposure (until the water disappears in the tested surface) provide a "water-repellent curve." An area between this curve and both coordinate axes (so-called "water-repellent area") is measured in minute-degrees and provides a basis for the water-repellency rating. An empirical rating is proposed in eight grades from zero repellency to absolute repellency.

The method is applied to the grading of white spruce and red pine treated with various water-borne preservatives and to white spruce treated with a methylene chloride solution of pentachlorophenol.

Additional keywords: *Picea glauca, Pinus resinosa*, preservatives, preservation, test methods, surface treatments, inorganic salts, pentachlorophenol.

INTRODUCTION

Development of new preservative compositions requires the testing and evaluation of properties of treated wood such as fungicidal efficiency, leaching resistance, and water repellency. We present a laboratory method for the evaluation of water repellency for easy screening of preservative formulations influencing this property of wood.

A large comparative study of methods for water repellency (WR) was carried out by Miniutti et al. (1961). This study evaluates results from seven laboratory methods and two weathering methods, applied to treated ponderosa pine sapwood. The weathering methods, also employed e.g. by Black and Mraz (1974) on many preservatives used for wood treatment, simulate very closely conditions of exterior exposure by combining the effects of high humidity, light, and heat to the surface of tested wood. These methods reflect water repellency indirectly but provide very important, complementary information on WR performance of wood in exposure to weather. The laboratory methods are based either on measurement of dimensional stability (derived from volumetric or linear swelling in the tangential direction) (Banks 1970; 1971) or on the measurement of weight gain after exposure of wood to water or water vapour. Directional swelling as a measure of dimensional stability and water repellency of treated wood is also used as a standard test (CSA Standard 0132.1—1965).

Another group of laboratory methods employs exposure of solids to liquids and evaluates wetting by measuring contact angle (Bartell and Ray 1952; Gans 1966; Grindstaff 1969), or capillary rise (Dyba and Miller 1969). However, these methods are overwhelmingly applied to those organic solids that for the most part do not absorb the liquid (such as plastics, paints or cellulose derivatives), and the exposure is limited to a short constant time interval.

With porous materials such as wood, which absorb liquids (water) even after chemical treatment of their surface, water repellency is reflected by the contact angle, but its changes must be measured as well and the exposure should continue until the water soaks into the surface.

Our method belongs to this group. It was applied to red pine and white spruce treated with water-borne preservative solutions comprising combinations of chromium-, copper-, and arsenic-containing salts. White spruce was also treated with pentachlorophenol in methylene chloride. Careful selection of samples for the experimental work considerably reduced the influence of variability in physical properties and anatomical composition of the wood.

The proposed method is described and a new classification of the water repellencies of preservatively treated wood is proposed on the basis of numerous measurements on wood treated with traditional and experimental preservatives in our laboratory.

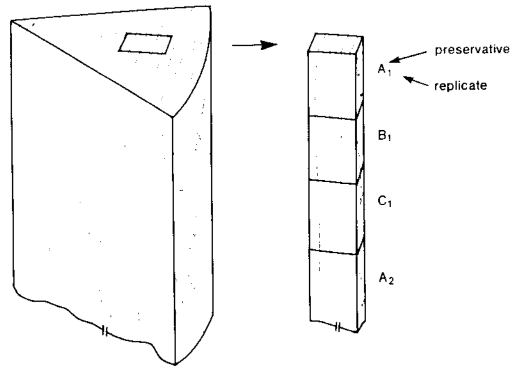

FIG. 1. Sampling scheme used for preparation of series of replicates for treatment with three preservative solutions.

THE PROPOSED METHOD

The method is based on the measurement of the contact angle between the surface of a water drop and the surface of the treated wood. Changes of the contact angle are measured until the drop disappears into the wood surface. The contact angle plotted against time ("water repellency curve") provides a graphical basis for an evaluation of water repellency, expressed on the graph by the area between the coordinate axes and the water-repellency curve ("water-repellent area"). The larger the water-repellent area, the higher the water repellency of the sample.

Sapwood samples are preferred. They should be free of knots, reaction wood, and large accumulations of resin. When heartwood is selected, it should be used in all experimental series uniformly.

Eight grades of water repellency were arbitrarily established according to the size of the water-repellent area. Wood samples 3 mm (⅛ inch) in tangential, 6 mm (¼ inch) in radial, and 25 mm (1 inch) in longitudinal directions were cut from air-dry wood (8–10% moisture content (MC)), then oven-dried for 4 h at 105 C, and cooled for 30 min to room temperature in a desiccator over phosphorus pentoxide; oven-dry weight was then recorded.

A circular, 12-inch diameter combination saw was used at 3,400 RPM at a feed speed of approximately 5 ft/min to provide a smooth and reproducible surface. Any

TABLE 1. *Water-repellency grading*

Grade		Water Repellent Area		Water Repellency Rating
Group	Level	cm^2	minute-degrees ($x10^2$)	
I	a	>300	>120	absolute
	b	250-300	100-120	excellent
II	a	250-300	80-100	very good
	b	150-200	60-80	good (reliable)
III	a	100-150	40-60	moderately good
	b	50-100	20-40	low
IV	a	5-50	2-20	very low
	b	0-5	0-2	none

TABLE 2. *Chemical composition of preservative solutions (g of salts in 100 ml of solution)*

Preservative	Concentration g/100 ml Solution				Oxide Concentration % w/v	Solution Density g/cm^3	Solution pH
	CrO_3	CuO	As_2O_5	Solvent			
Cr-Cu	0.802	0.312	--	H_2O	1.114	1.0079	1.51
CCA-C[a]	0.802	0.312	0.574	H_2O	1.688	1.0115	1.52
Cu-As-1	--	0.312	0.574	H_2O	0.886	1.0065	2.04
Cu-As-11	--	0.312[c]	0.574	NH_4OH[d]	0.886	0.9794	11.2
ACA[b]	--	0.574[c]	0.574	NH_4OH[d]	1.148	0.9864	11.4

[a] Chromated copper arsenate, type C
[b] Ammoniacal copper arsenate
[c] CuO applied as $CuCO_3 \cdot Cu(OH)_2$; otherwise applied as $CuSO_4$
[d] $NH_4OH(7\%NH_3)$

chemical contamination and mechanical contact with the radial face before contact angle measurement were avoided. A required minimum of five samples was used, and these were cut parallel to the grain. Each measured sample contained 3 to 5 annual rings in the radial direction. Samples were end-matched to reduce variation of results. Every fifth sample, when five different preservatives were tested, was treated with the same preservative (Fig. 1). Samples were continuously immersed in the preservative and saturated by cycling under intermittent vacuum of 28–29 inches Hg and atmospheric pressure. High retentions of preservative, as required for heavy-duty protection, were applied to the samples.

Samples were then air-dried for 18 to 24 h on a wire rack (the surface area to be tested was uppermost) and oven-dried for 6 h at 105 C. Each sample was weighed wet and oven-dry after treatment.

Wood samples prepared as outlined above and treated under the same conditions can achieve a coefficient of variation for preservative retention not exceeding 10%. We considered this variation to be a required condition of homogeneity, which should be met when a given retention is desired. This requirement was met in our experimental work.

For measurement of contact angle the treated, oven-dry sample was placed, radial face up, in a closed, narrow glass compartment (to minimize loss of water by evaporation) on the stage of a horizontal mi-

TABLE 3. *Preservative oxide retentions in white spruce and red pine*

Preservative	WHITE SPRUCE Ave Retention pcf	WHITE SPRUCE Ave Retention kg/m^3	WHITE SPRUCE Coef. Var. (%)	RED PINE Ave Retention pcf	RED PINE Ave Retention kg/m^3	RED PINE Coef. Var. (%)
Cr-Cu	0.40	6.41	3.2	0.42	6.73	5.0
CCA-A	0.45	7.21	4.5	0.44	7.05	4.8
Cu-As-1	0.40	6.41	4.4	0.41	6.57	6.2
Cu-As-11	0.39	6.25	5.8	0.40	6.41	3.9
ACA	0.49	7.85	6.1	0.51	8.17	3.3

Coefficient of variation for averages of various preservative oxide retentions in white spruce is 10.04%, in red pine 10.08%.

croscope. The compartment was 32 × 8 × 8 mm.

The microscope was equipped with a goniometer eyepiece (10 ×) to read changes of angle up to 360° with one-half degree accuracy, and an objective (10 ×). The sample was illuminated from the side, using an illuminator approximately 40 cm away, equipped with a heat-absorbing filter. Room temperature was controlled to ± 1 C. A special microscope equipped with a temperature-controlled compartment is also convenient because it eliminates the need for the temperature control in the testing room. The air in the glass compartment was saturated with water vapour by putting a small drop of water in it prior to introducing the sample.

When the edge of the upper (radial) surface of the sample was in focus, distilled water (0.01 ml) at room temperature was put on the sample by a microsyringe in such a manner that a drop was formed at the tip of the syringe needle and transferred to the sample by touching the drop to the wood surface.* A stop watch was started and the contact angle measured by the goniometer within the first 30 sec. This interval was short enough to record the initial changes of contact angle.

Readings continued at regular 30-sec intervals during the first 3 min, then readings at 3 (or 4 or 5 min) intervals followed until the water drop disappeared in the wood surface. Identical time intervals of reading contact angles for various samples permitted a direct calculation of average values and plotting the average "water-repellency curve." Most data could be plotted on an 8½- by 11-inch sheet, using 2 min equal to 5 mm and one degree of contact angle equal to 1 mm, to provide an equivalent of 1 cm^2 to 40 min-degrees. The water-repellent area was measured by an automatic integrator (such as the Hewlett-Packard Calculator Model 9100B and Digitizer Model 9107A), or by a polar planimeter with a minimum accuracy of ± 0.1 cm^2. The resulting "water-repellent area" in minute-degrees was used as a direct measure of water repellency.

We have rated water repellency (WR) by 8 grades (4 groups I–IV, with two levels a, b in each group, Table 1), assigning the highest WR—Ia, or absolute—for wood having pores blocked at the surface and for nonporous solids. The four groups were convenient for the general classification of preservatives. The additional two levels in each group were useful for more detailed ratings when, for example, changes of water repellency were examined. The method was tested on wood treated with various preservatives. Examples are described in Results.

EXPERIMENTAL

White spruce and red pine were treated with five preservative formulations based on combinations of salts containing chromium, copper, and arsenic. The combinations of salts were formulated (Table 2) to examine the effects of chromium, copper sulphate, and copper carbonate on water repellency. The only solution containing all three elements was CCA (type C).

Five samples of white spruce and red pine for each preservative were treated under intermittent vacuum to an average oxide retention of preservatives ranging between 0.39 PCF (6.25 kg/m^3) and 0.51 PCF (8.17 kg/m^3), Table 3. For comparison with the water-borne preservatives, the spruce was also treated with 5% (w/w) pentachlorophenol in methylene chloride. In this case the solvent was removed from the treated samples by air-drying for 17 h and oven-drying for 2 h at 105 C. Retention of solid preservative averaged 6.5% (w/w). Contact angle changes for all samples were plotted against time.

As an example of the procedure, contact angles of five spruce samples treated with

* The water drop, which has a diameter approx. 2.7 mm, should be always positioned on the latewood and earlywood of two neighboring annual rings. When samples of slow growth (narrow annual rings) are measured more annual rings are covered by the drop. This drop is also large enough to saturate the closed glass compartment (containing sample) with water vapour. When the compartment with sample contains e.g. air with 55% RH approximately 5.5% of the water by weight can be lost from the drop as vapour.

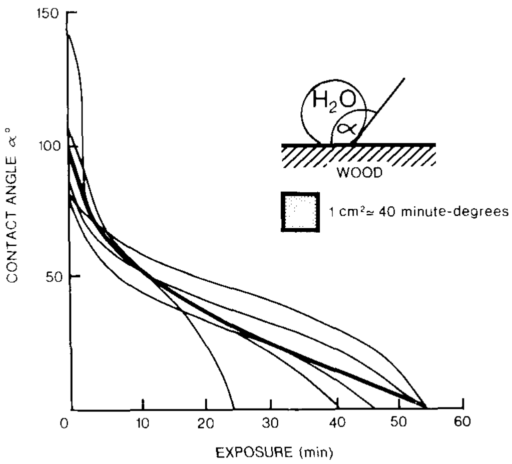

FIG. 2. Changes of contact angle of water drop during exposure on surface of five spruce samples treated with the copper-arsenic preservative. The "water-repellent area" (expressed in minute-degrees) lies between the "water-repellent curve" and coordinate axes. Average value—bold line.

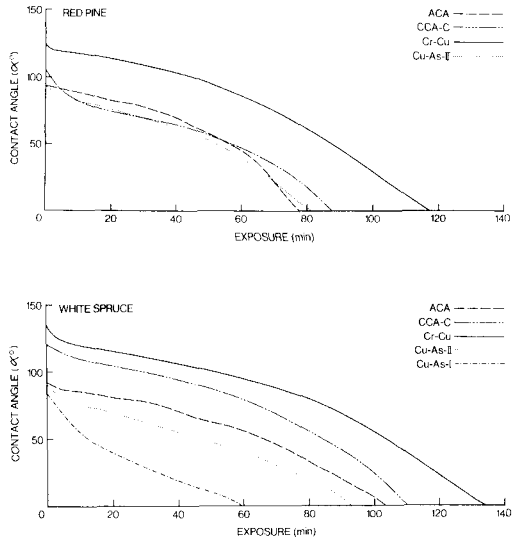

FIG. 3. Changes of contact angle of water drop during exposure on spruce and pine treated with various preservative formulations (each curve reflects averaged values).

the same preservative are plotted in Fig. 2. The water-repellent areas in each group of samples treated with the same preservative were statistically evaluated (Table 4), average "water-repellency curves" were plotted (Fig. 3 a, b, and water repellencies were graded (Table 5).

These experiments were compared with water uptake by larger samples of spruce and pine treated with the same preservative formulations. Ten wood samples 1-inch cube (16.39 cm^3) for three preservative formulations (Cr-Cu, CCA-C and Cu-As-1) were cut from the same pieces of spruce and pine sapwood as the samples for contact angle measurements, but the samples were not matched in the longitudinal direction. After the samples were treated under

TABLE 4. *Water-repellent area of treated spruce and pine*

Preservative	White Spruce: Water Repellent Area Min (minute-degrees x10^2)	Ave	Max	Coef. Var. %	t	Red Pine: Water Repellent Area Min (minute-degrees x10^2)	Ave	Max	Coef. Var. %	t
Cr-Cu	86.21	104.15	115.63	18.0		69.22	89.99	105.04	17.9	
CCA-C	59.26	84.07	104.55	10.7		35.13	49.06	64.32	14.9	
Cu-As-1	12.03	19.17	25.10	25.1	9.9**	---	---	---	---	
Cu-As-11	42.08	44.84	56.72	7.2	5.4**	38.48	44.22	51.01	7.7	2.2^{ns}
ACA	43.12	57.80	58.14	7.3		45.40	48.56	50.91	5.8	

** Difference significant at the 99 percent level of probability

ns No significant difference

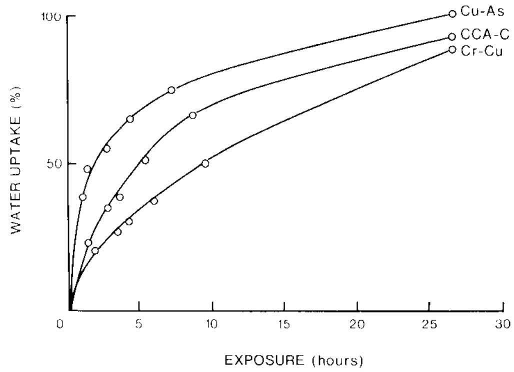

FIG. 4. Water uptake by oven-dry white spruce samples treated with three preservative solutions.

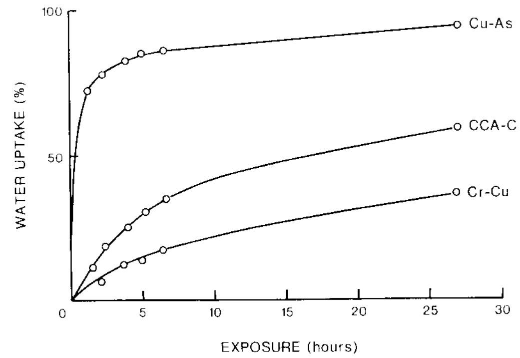

FIG. 5. Water uptake by oven-dry red pine samples treated with three preservative solutions.

intermittent vacuum of 28 inches Hg, the weight of saturated samples was taken, then the samples were air-dried for 48 h and oven-dried for 10 h at 105 C. Average retentions of salts were between 6.7 and 7.2% (w/w). Water uptake by treated samples was calculated as a percent increase of oven-dry weight of sample, and the average values were plotted against time of the exposure in water (Figs. 4, 5). Reciprocal values of water uptake were calculated (Table 6) at the moment when the water drop soaked into the wood in the parallel contact angle measurements (approximately after 2 h).

RESULTS

From five different preservatives (see Table 2 for their composition) used for treatment of white spruce and red pine, we find that the Cr-Cu preservative imparts to these species the highest water repellency (WR), Table 5. The spruce has excellent WR (Ib), the pine only very good WR (IIa). WR is slightly less with wood treated with CCA-C (spruce, very good WR -IIa; pine, moderately good WR -IIIa) and is very much less with Cu-As-1 preservative (spruce very low WR -IVa; pine, none -IVb). Chromium correlates well with repellency in this series of three

TABLE 5. *Water-repellency rating of treated spruce and pine*

Species	Preservative	Water repellent area minute-degrees x10^2	Water repellent rating	WR Grade
White Spruce	Cr-Cu	104.15	excellent	Ib
	CCA-C	84.07	very good	IIa
	Cu-As-1	19.17	very low	IVa
	Cu-As-11	44.84	moderately good	IIIa
	ACA	57.80	moderately good	IIIa
	pentachlorophenol (in methylene chloride)	38.72	low	IIIb
Red Pine	Cr-Cu	89.99	very good	IIa
	CCA-C	49.06	moderately good	IIIa
	Cu-As-1	Ø	none	IVb
	Cu-As-11	44.22	moderately good	IIIa
	ACA	48.56	moderately good	IIIa

TABLE 6. *Comparison of water-repellent area and reciprocal value of water pick-up*

Preservative	White Spruce		Red Pine	
	Reciprocal value of water pick-up	Water repellent area (proportional value)	Reciprocal value of water pick-up	Water repellent area (proportional value)
Cr-Cu	5.00	5.00	3.70	4.32
CCA-A	4.17	4.04	2.02	2.36
Cu-As-1	2.70	0.92	---	---

acid preservatives (see Table 4, Cr-Cu, CCA-C, Cu-As-1). Formulations containing this element showed higher WR.

In the group of alkaline preservatives (see Table 2) tested, the Cu-As-11 formulation is different from Cu-As-1 in that the copper component is not in the form of copper sulphate but in the form of basic copper carbonate, although each has the same content of oxides in the formulation, Cu-As-11 provides for both spruce and pine moderately good WR (IIIa), which is higher than that of Cu-As-1. Further increase of the content of basic copper carbonate as in the ACA formulation compared to Cu-As-11 formulation increases the WR (at the 99% probability level in spruce; in pine, no significant difference) even though the WR rating remains the same for the two preservatives (IIIa). These results confirm that copper as basic copper carbonate provides higher WR than copper as copper sulphate.

Spruce treated with pentachlorophenol in methylene chloride solution provides only low (IIIb) water repellency.

Trends of water repellency derived from the "water-repellent area" agree well with trends obtained from the reciprocals of water uptake measured on spruce and pine, with the three acid water-borne preservatives (Table 6 and Figs. 4 and 5).

DISCUSSION

Water repellency of wood is a complex property reflected in the initial contact angle of a water drop, its changes during exposure to the surface, and in the time to its disappearance. All these factors influence the shape of the water-repellent curve and thus they are reflected in the "water-repellent area," both measures of water repellency. Slow reading of the initial contact angle can influence the accuracy of the measurement if the angle changes rapidly.

When the first reading is taken within 30 sec and is followed by readings at ½-min intervals up to 3 min of exposure, the beginning of the water-repellent curve is well defined. Further regular readings can be taken at 3-min intervals until the drop disappears. This frequency of reading results in accuracies of ± 0.05 cm^2 which means that for the smallest "water-repellent area" (Grade IVa) such as from 5 to 50 cm^2 for copper arsenate would involve a relative error of 1.0% to 0.1%.

The definition of water repellency in minute-degrees and the measurement of its value for each sample treated provide convenience of statistical evaluation and a basis for general classification of water repellency as influenced by preservative treatments. The known variability of structure and physical and chemical properties of wood were minimized in our method by a selection of testing samples. The physical conditions of measurement such as the adjustment of the water drop volume, temperature control during measurement, minimization of water drop evaporation, and the preparation of the sample surface were well defined to ensure reproducibility.

Water repellency depends on the chemical composition and properties of the preservative applied to the wood. However, a low solubility of the preservative salt in water does not necessarily mean that wood treated with that salt must be highly water repellent. For example, a tertiary copper arsenate with its negligible water solubility (0.063 g/100 ml at 20 C) imparts a very low water repellency to wood (Table 5).

Water repellency also reflects several wood-related factors, such as the nature of the bond between the preservative salt and components of the wood, crystalline or amorphous nature of the preservative deposit, and the mechanical accumulation of preservative in certain parts of the wood structure (bordered pits, rays etc.). More permeable red pine shows lower water repellency than less permeable white spruce when treated with the same preservative at the same retention (compare the data in Table 4). The microstructure of wood will be partially reflected in the water repellency of wood as well. For the same reason some changes of wood microstructure, for example those due to chemical interaction of preservative solution with wood, will be reflected finally in the water repellency of wood. This method offers a means for studying those anatomical, physical, and chemical factors that influence water repellency. The water-repellency measurements, the method for its evaluation, and the proposed WR rating were illustrated mainly on a group of waterborne preservatives, some of them (CCA-C and ACA) with well-established performance in ground contact exposures (e.g. Smith 1969; Gjovik and Davidson 1973). Even when the WR participates in the field performance of treated wood only as one factor (besides e.g. toxicity, fixation, and distribution of preservative in the wood), its rating by the proposed method can be a useful tool for fast laboratory screening of preservatively treated wood.

CONCLUSIONS

A new method for evaluation of water repellency (WR) from contact angle measurements and a WR rating system was tested on white spruce and red pine treated with six various preservatives. The method is fast, simple, and reproducible for screening preservatives and for studying other factors (such as wood structure, treating schedule) influencing water repellency of wood.

The results of WR measurements were:

1. The WR of white spruce and red pine is highest when treated with a Cr-Cu formulation from a group of acid copper-chromium-arsenic preservatives; CCA-C is less effective, and the Cu-As-1 formulation, less still.
2. In the group of alkaline preservatives containing copper and arsenic in a weak ammonium hydroxide solution (Cu-As-11) which has its copper component as basic copper carbonate (replacing copper sulphate in the Cu-As-1 formulation), WR is significantly higher at the 99% probability level than that of Cu-As-1 treated wood for both species.
3. The WR is further increased with the increase of basic copper carbonate content in the formulation ACA, in which the weight of CuO almost equals the As_2O_5 with a difference significant at the 99% probability level for spruce, but not for pine. These results prove the positive role of basic copper carbonate in comparison with copper sulphate in preservative formulation on WR of wood.
4. The WR of spruce is higher than that of pine, when treated with the same preservative from the group of three formulations (Cr-Cu, CCA-C, Cu-As-1) and to the same preservative retentions.
5. Pentachlorophenol deposited into spruce with methylene chloride solvent imparts only low (IIIb) WR.

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