

The development of a novel polymer composition for use in waterborne primers with excellent anti-knot bleeding properties

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Abstract

When the waterborne primers of today are applied on wood in most cases discoloration of the topcoat occurs. This is caused by organic wood components that are extracted when these primers are applied. These components then migrate to the coating surface and cause discoloration. This is particularly pronounced on the knots where the concentration of resins and tannins are high. In this contribution we describe the development of a waterborne wood primer that exhibits excellent anti-knot bleeding properties. In the approach we have taken, we have eliminated several of the drawbacks of the current state-of-the-art polymers and primers. In particular, we will discuss the role of the polymerization process and the polymer composition on the knot bleeding properties and we will show that these two synergistically act together. By combining the right polymerization process with the optimal polymer composition, aqueous wood primers have been developed that exhibit a significant step-change in anti-knot bleeding performance.

Introduction

Wood is a complex natural material composed of cellulose, lignin, hemicelluloses and varying amounts of extraneous materials.¹ These extraneous materials are both inorganic and organic. The inorganic materials consist of trace minerals accounting for only 0.1 to 1.0 percent of the dry weight of the wood substance. The organic components of the extraneous materials are referred to as extractives because they can be removed by extraction with solvents. Extractives include chromophoric compounds like tannins, essential oils, fats, resins, waxes, gums and starch. Depending upon the type of wood the total extractive content of wood substance may range from less than 1 to 30 percent in extreme cases.

Extractives are often classified according to the type of solvent used to extract them, like water, alcohol or ether. From the standpoint of paint discoloration, by far the most important type of extractives are those that are water soluble. Discoloration of paint may occur when extractives dissolved by water reach the painted surface and there they discolor into grey to reddish-brown stains. The discoloration occurs because the extractives are already colored or are discolored by the action of (UV-)light giving the topcoat a brownish-greyish appearance. This is called extractive bleeding and water is typically responsible for this.

To prevent extractive bleeding typically primers or sealers are used, in particular two-component solvent borne systems like epoxy systems or those that require isocyanates for curing. However, these are not preferred because of the safety, health and environmental concerns related to the solvent and the isocyanate crosslinkers. Since most water-soluble components are anionic in nature, cationic polymer systems should prevent this species from migrating through a coating by locking them. This is well known and various cationically stabilized waterborne latex systems are claimed to exhibit stain-blocking or anti-knot bleeding properties and are used to prevent extractive bleeding.²

A particular demanding application is the so-called knot bleeding, which occurs when a knot contains excessive amounts of extractives. In these cases, the extractives consist mainly of rosin, fats and turpentine, and these extraneous materials can make up as much as 50% of the

knot by weight.² Especially for this demanding application many of the primers currently available in the market place are unsuitable. This means that the knots sections cannot be used, causing the joinery manufactures a lot of work and losses to remove the knots. This adds to the cost in terms of time and expenses.

Many wood extractives are acid functional and it is well known that cationic systems can prevent bleeding of wood.³ In this paper we describe the development of novel cationic waterborne primers with excellent anti-knot bleeding properties. In addition to being waterborne these systems also are physically drying and do not need toxic crosslinkers like isocyanates or aziridines or additives like zinc oxides, which are also under scrutiny. This technology in this paper eliminates these two major drawbacks of the primers used to date. In this contribution we compare two cationic systems with very similar polymer compositions but that have been prepared by two distinctly different polymerization processes. We will show that it is this difference that is responsible for the fact these two systems behave completely different from the moment they are prepared until their final use as anti-knot bleeding primers. The first part discusses the preparation and knot bleeding properties of the cationic oligomer and cationic oligomer-polymer systems. One system is prepared by emulsion polymerization whereas the other system is prepared by a solvent assisted dispersion process and these two systems show a world of difference in terms of knot bleeding. The second part describes a detailed study of these two systems that explains why the difference in preparation method results in such a dramatic difference in knot bleeding performance.

Experimental

EO1 is a methyl methacrylate/dimethylamino ethyl methacrylate (MMA/DMAEMA 85/15 wt/wt) polymer prepared by conventional emulsion polymerization technique employing a chain transfer agent to control the molecular weight and using ammonium persulphate as free radical initiator and an anionic surfactant.

SO1 (MMA/DMAEMA 85/15) was prepared by a standard solution polymerization process using 2,2'-Azobisisobutyronitrile (AIBN) as free radical initiator and chain transfer agent for molecular weight control.

At the end of the polymerization both polymers were treated with a solution of formic acid at a 1:1 molar ratio with the DMAEMA.

EO1 and SO1 were used in a subsequent emulsion polymerization step using standard free radical initiators. In this step a polymer phase was prepared in the presence of EO1 or SO1, giving EOP1 or SOP1, respectively. The specifications of EO1 and SO1 are shown in Table 1, the specifications of EOP1 and SOP1 are shown in Table 2.

Primer formulation

The polymer dispersions EOP1 or SOP1 were formulated with TiO₂, filler, pigment dispersant, wetting agent, defoamer, coalescent and thickener into a primer formulation.

Test method knot-bleeding

Freshly cut pine wood panels with dimension 15x6.5 cm² each containing one fresh knot are used. The primer was applied (150g/m² wet) and dried for 4 hours at room temperature. Then a white pigmented topcoat based on NeoCryl XK-90 was applied (100 g/m² wet). This was allowed to dry for 1 week at ambient temperature. Next the test panels were placed in a QUV cabinet with the coated side facing downwards. The panels were subjected to 24 hours cycles each consisting of 12 hours UV (B) and 12 hours condensation at 50 °C. After a certain number of cycles the panels were rated on discoloration determined by the bleeding of the knot. Rating was done on an average of five panels and ranged from 0 (strongly discolored) to 3 (slightly discolored) to 5 (no visual change).

Cationic oligomers – preparation and properties

Two cationic oligomers were prepared with identical monomer compositions, MMA/DAMEMA 85/15 wt/wt. One was prepared by emulsion polymerization (EO1) using a standard recipe. The solution oligomer SO1 was prepared by free radical solution polymerization. Both oligomers were made cationic by treating them with formic acid and for both oligomers the molar ratio DMAEMA:formic acid was 1:1. The particle size of EO1 prior to the addition of formic acid was about 200nm, upon adding formic acid the oligomer dissolved almost completely. The solid content of the solution prior to the addition of formic acid was 60 wt%. After completion of the polymerization water/formic acid was added resulting in a cationic oligomer dispersion with a 25 wt% solid content. SO1 contains 19.6 wt% solvent, whereas EO1 contains no solvent. The specifications of the two oligomers are shown in Table 1. Also the anti-knot bleeding properties of the oligomers are shown.

Table 1. Specifications of EO1 and SO1.

Cationic oligomer prepared by	Emulsion polymerization (EO1)	Solution polymerization (SO1)
Solid content (%)	24.0	25.7
Solvent (%)	0.0	19.6
pH	4.2	4.8
Viscosity at rt (mPas)	10	1900
Surface tension (mN/m)	40.8	33.4
Mw (kDa)	27.0	35.3
Anti-knot bleeding		
# cycles to rating 3	2	30
# cycles to rating 0	5	40

As is evident from Table 1, the cationic oligomer prepared by solution polymerization is by far superior in anti-knot bleeding to the cationic oligomer prepared by emulsion polymerization, despite both oligomers having the same backbone composition. A possible explanation for this difference will be discussed later. Overall the level of anti-knot bleeding is a true step-change compared to when traditional waterborne primers are used. In fact, the knot bleeding performance matches that of solvent borne two component isocyanate curing systems while SO1 contains much less solvent and needs no crosslinking.

Cationic oligomer-polymers – preparation and properties

Oligomers EO1 and SO1 were used in an additional emulsion polymerization step. In doing so one has to realize that the amount of cationic oligomer in the final composition is reduced significantly. Therefore a negative effect on the anti-knot bleeding properties, for which the cationic oligomer is the active ingredient, could be expected. The specifications and the anti-knot bleeding properties of these two oligomer-polymer systems are compared in Table 2. SOP1 contains 9.7% solvent whereas EOP1 contains no solvent. When this amount of solvent was added to EOP1 coagulation occurred. The amount of cationic oligomer in EOP1 and SOP1 was the same. For the anti-knot bleeding test either SOP1 or EOP1 was used as primer and NeoCryl XK-90 (a sequential polymer available from DSM NeoResins⁺) was used as topcoat.

Table 2. Specifications of EOP1 and SOP1.

	Cationic emulsion oligomer-polymer EOP1	Cationic solution oligomer-polymer SOP1
Solid content (%)	40.0	42.5
Solvent (%)	0.0	9.7
pH	4.5	4.6
Viscosity at rt (mPas)	25	421
Particle size (nm)	74	200

Anti-knot bleeding		
# cycles to rating 3	1 (blisters)	> 40
# cycles to rating 0	2 (blisters)	n.d.

Two important conclusions follow from Table 2. First of all, the oligomer-polymer based on the solution oligomer shows superior anti-knot bleeding properties. Even after more than 40 cycles (> 960 hours) only a slight discoloration is observed for SOP1 while the system based on EOP1 already after two cycles is strongly discolored. As also observed for SO1 (Table 1), the level of anti-knot bleeding is a true step-change compared to using traditional waterborne primers and the knot bleeding performance of a solvent borne two component isocyanate curing system is matched. Again, this is achieved using a waterborne system and without the need for crosslinking. Secondly, despite the fact that the oligomer-polymer SOP1 contains approximately half of the amount of the cationic oligomer compared to the cationic oligomer dispersion itself, the anti-knot bleeding are as good as that of the pure cationic oligomer itself. Thus, diluting the active ingredient by half did not negatively affect the knot bleeding properties at all. Dilution however significantly reduces the amount of solvent present in SOP1.

The results of the anti-knot bleeding test for SOP1 are shown in Figure 1. In this particular test, the knot bleeding of a coating system comprised of two layers of NeoCryl XK-90 (as primer and topcoat) was compared to that comprising SOP1 as primer and NeoCryl XK-90 as topcoat.

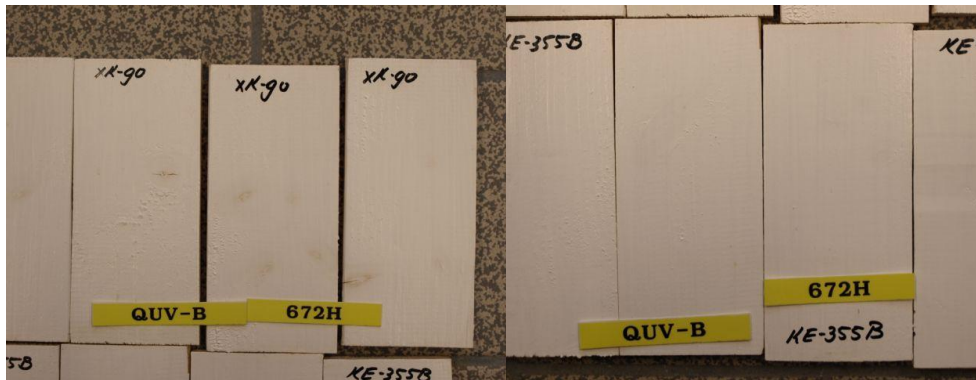


Figure 1. The anti-knot bleeding results of a system based on NeoCryl XK-90 (left) and SOP1 (right) after 672 hours QUV (28 days).

The panels coated with the two layers of XK-90 showed clearly brownish discoloration around the knot areas whereas the system based on SOP1/XK-90 showed no discoloration at all. After 1008 hours exposure (42 days) the difference is even more pronounced (Figure 2) and the system based upon SOP1 shows no discoloration at all.



Figure 2. The anti-knot bleeding results of a system based on NeoCryl XK-90 (top) and SOP1 (bottom) after 1008 hours QUV (42 days).

Based on these results a more in-depth investigation was started into the reason behind the difference in knot bleeding performance of the oligomer-polymer systems based on cationic oligomers made by solution or emulsion polymerization.

Cationic oligomers – characterization

First of all the surface tension of the cationic oligomers were measured. The surface tension for the EO1 oligomer was 40.8 mN/m, while that of SO1 oligomer was 33.4 mN/m. The lower surface tension of the solution oligomer can be explained by the fact that this solution still contains solvent, which has a lower surface tension than water.

The isoelectric point (IEP) of EO1 was measured to be 8.35, while that of SO1 was 9.01. Since both oligomers have a pH between 4 to 5, both oligomers are cationically charged.

The weight average molecular weight of both oligomers is within the same range, 27 kDa for EO1 and 35.3 kDa for SO1. However, the chemical composition distribution (CCD) as determined by HPLC was quite different. This can be seen in Figure 3. The oligomer prepared by emulsion polymerization EO1 has a broader compositional distribution than the oligomer prepared by solution polymerization SO1, despite the fact that the chemical composition is identical for both oligomers. The broader distribution may be caused by the heterogeneous nature of emulsion polymerization.

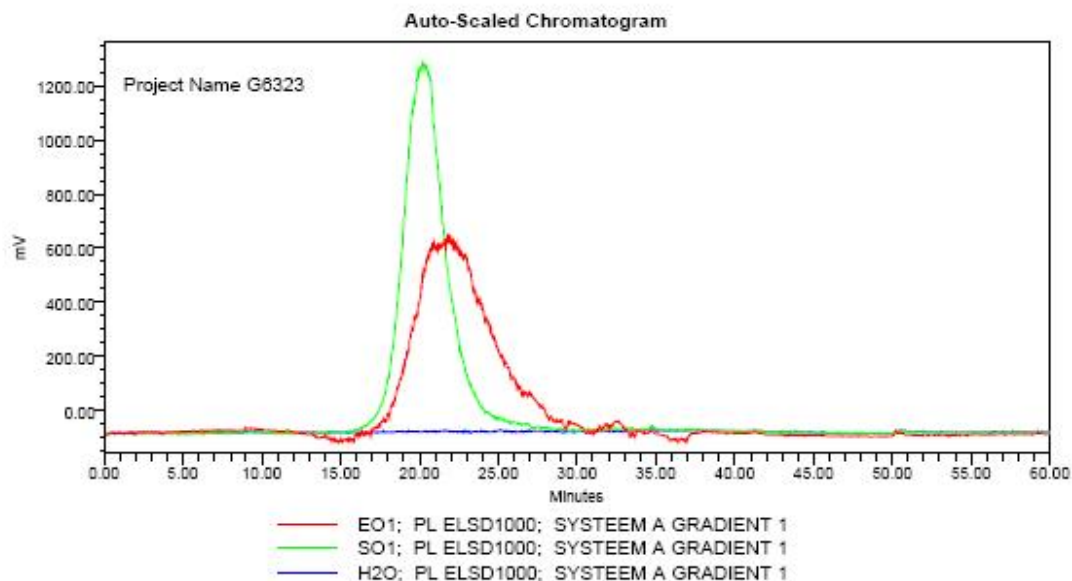


Figure 3. Chemical composition distribution of cationic oligomers prepared by emulsion (red line) and solution (green line) polymerization.

Addition of formic acid

When adding formic acid/water to EO1 dispersion with a particle size of about 200 nm, the particles dissolve and an almost clear solution remains. This is accompanied by a viscosity peak. For SO1 during the addition of water/formic acid solution no viscosity peak was encountered (Figure 4).

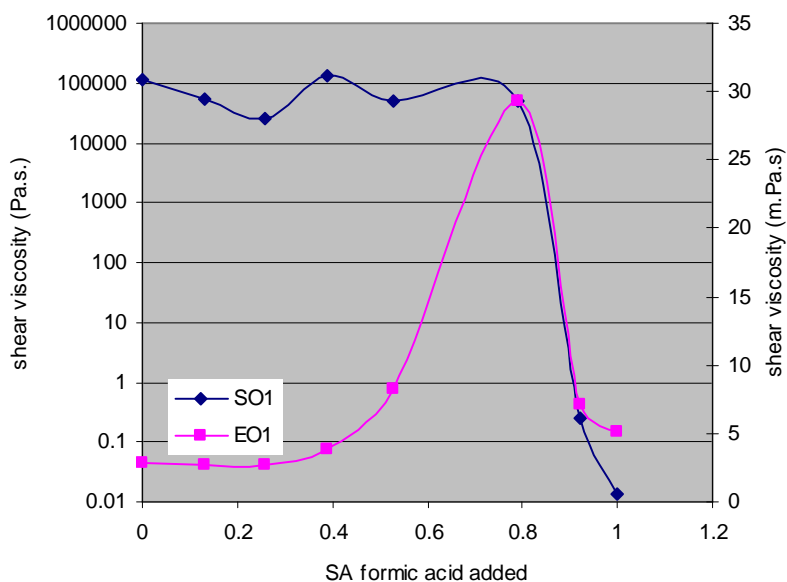


Figure 4. Viscosity as function of the amount of formic acid for the solution oligomer SO1 (left axis) and emulsion oligomer EO1 (right axis).

Figure 4 reveals two things. First of all the viscosity of EO1 is much lower than that of SO1 up to 0.8 stoichiometric amount (SA) of formic acid added. Secondly, the viscosity of the solution

oligomer SO1 remains constant until 0.8 SA formic acid and then drops significantly. This is in strong contrast to the viscosity profile of EO1. For this oligomer, upon adding formic acid a clear viscosity peak is observed. This is a significant difference between the two oligomers. SO1 is prepared in solution and remains a solution upon adding formic acid, until some small particles are formed. In contrast, for EO1 upon adding formic acid the particles are protonated and swell with water and this increases the viscosity. After 0.8 SA formic acid was added the swollen particles dissolve and the viscosity drops. The picture below visualizes this dissolution process.

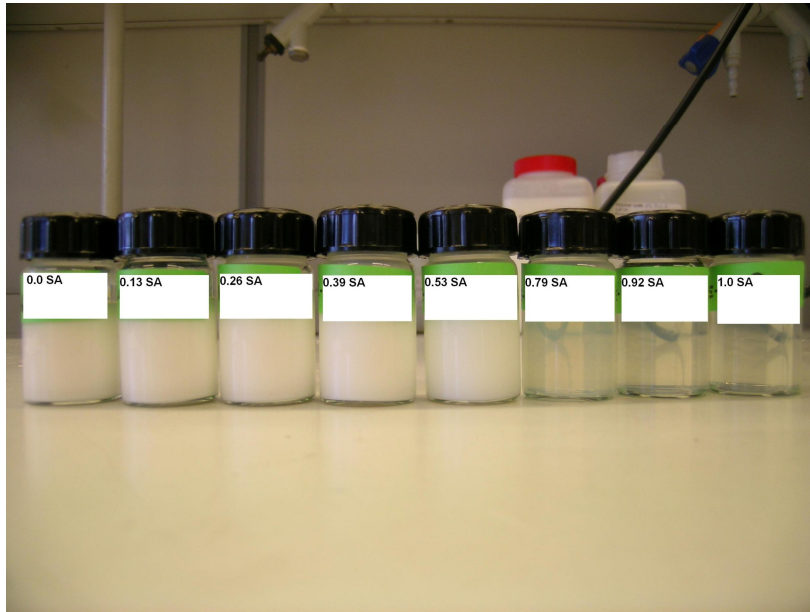


Figure 5. EO1 samples at various amount of formic acid added. From left to right 0.0, 0.13, 0.26, 0.39, 0.53, 0.79, 0.92 and 1.0 SA formic acid was added.

Rheology measurements confirm the solution behavior for the two oligomers. Both EO1 and SO1 show over a very wide shear range a Newtonian behavior and have a phase angle of 90° , indicating Newtonian fluid like behavior. SO1 shows a very slight shear thinning behavior at very low shear rates.

For SO1, up to a solid content of 30 wt% the viscosity is high. Only when the solid content dropped below 30 wt% the viscosity decreased six orders in magnitude over a solid content range of only 5 wt, probably due to the formation of some small particles.

Oligomer-polymers – characterization

The iso-electric point (IEP) of EOP1 was measured to be 8.45 and with the pH being between 4-5 this means that EOP1 is cationically stabilized. Particles with zeta potentials more positive than +30 mV or more negative than -30 mV are normally considered stable.⁴ Zeta potential measurements for EOP1 indicate that below pH 6.8 EO1 is stable (data not shown). The IEP of EO1 and EOP1 are almost identical (8.35 versus 8.45) indicating that the surface of the polymer particles is covered by the cationic oligomer EO1.

For SOP1, the IEP was 9.01. Since the pH was typically 4 to 5, the IEP indicates that cationic oligomer is adsorbed onto the particles. The IEP of SO1 was 9.01, identical to that of SOP1 indicating that SO1 is present at the particle surface. Zeta potential measurements indicate that SOP1 is stable at a pH below 7.8.

Theoretically the charge density of SO1 and EO1 is 0.96 meq/g. From titration experiments it was calculated that the actual charge density was 0.76 meq/g for EO1 and 1.06 meq/g for SO1. This indicates that for EO1 less DMAEMA is incorporated and that probably some is present in low

molecular weight material that is not titrated by the titration experiment. For SO1 all DMAEMA seems to be built in. This was to be expected because of the completely different nature of the polymerization methods used for both cationic oligomers. The solution polymerization is a homogeneous process whereas the emulsion polymerization is a heterogeneous process. It is well known that in a typical emulsion polymerization process hydrophilic, water-soluble monomers to a certain extent are incorporated in low molecular weight species. This can also be seen in Figure 3 showing that the EO1 has a broader chemical composition distribution. This means that in the solution system not only all of the DMAEMA is incorporated but also all chains will contain this functionality. This makes this oligomer much more effective in scavenging the water-soluble extractives.

Film formation

The large differences between the two cationic systems were expected to result in differences in film formation and wood penetration as well. A first indication was obtained by light microscopy of the knot areas coated with either SO1 or EO1 (Figure 6). This showed that the filing power of the oligomer prepared by solution polymerization was much higher than that of the oligomer made by emulsion polymerization.

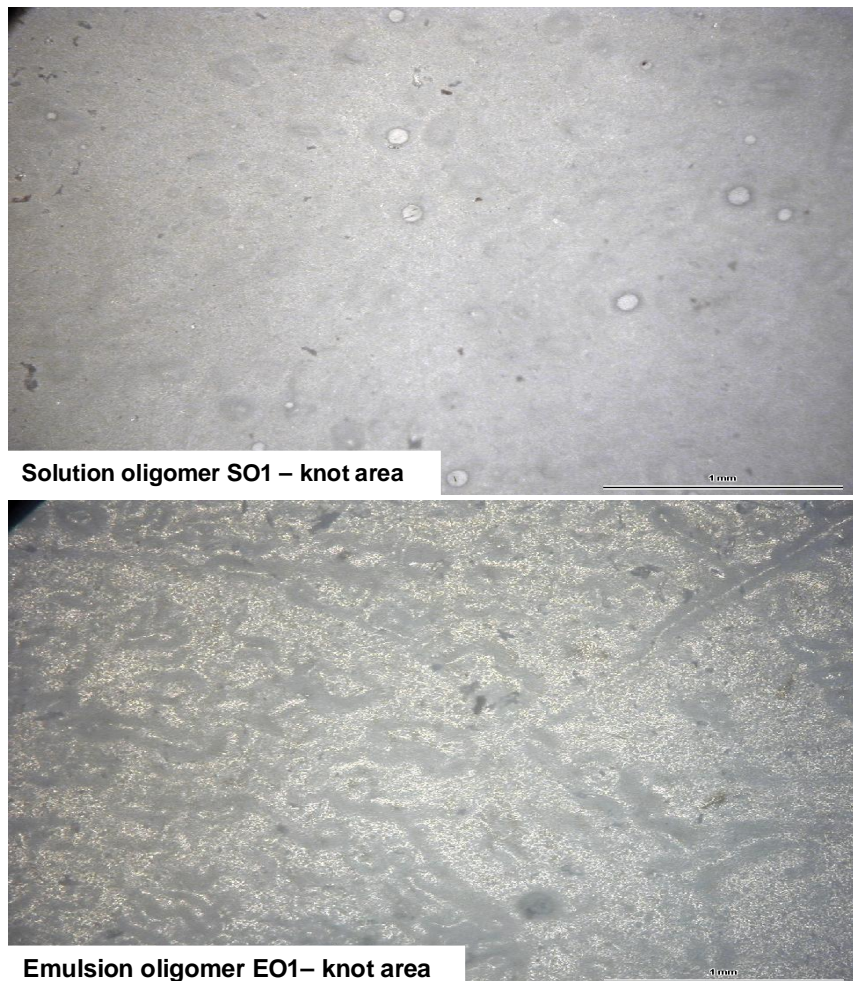


Figure 6. Light microscopy pictures of the knots for SO1 (top) and EO1 (bottom).

Conclusion

We have shown that cationic oligomers prepared by solution polymerization showed excellent anti-knot bleeding properties. Moreover, when these oligomers were used for a following emulsion polymerization process the resulting cationic oligomer-polymer system also showed excellent anti-knot bleeding properties. These systems outperform currently available waterborne primers and show a performance level comparable to that of solvent borne two component isocyanate curing systems while using much less solvent and no crosslinkers.

Detailed investigations indicated that this difference is caused by the different behavior of the two cationic oligomers, despite their identical composition. The fact that SO1 was prepared in solution resulted in a more homogeneous incorporation of the cationic charges resulting in an oligomer with a higher charge density. This makes the cationic oligomer SO1 much more effective in scavenging wood extractives. All in all, this explains the superior knot bleeding of SOP1, not only when compared to EOP1 but also when compared to traditional waterborne primers.

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