Potential Application of Enzymatically Modified Lignosulfonates as Coating Binders

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INTRODUCTION

Pigment coatings are applied to optimize the surface and printing properties of coated papers (Huang and Lepoutre, 1998). A coating color consists of several components having different functions. To bind the pigments and to fix the coating layer to the base paper, today mainly petroleum based latex binders are used. There are efforts to increasingly substitute these petroleum-based products by renewable binders (Flory et al., 2013; Gosselink et al., 2010). Biopolymers like starch, proteins and lignocellulosic materials are gaining in importance in paper coating applications (Imam et al, 2013). Technical lignins, such as lignosulfonates or kraft lignins, are the major industrial by-products of the pulping industry and are an abundant source of biopolymers, which today are mainly used for energy production. Material applications of technical lignins for special products is only between 1 and 2% (Gosselink et al., 2004), which is mainly due to the heterogeneity of technical lignins. Still more and more applications of technical lignins as building block for polymers, resins or adhesives are being developed recently (Stewart, 2008).

Before this background, the aim of this work was to test the feasibility of the development of a renewable binder based on the lignosulfonates contained in the spent liquor from an industrial source (Mg-sulfite pulp mill) in order to substitute partially petroleum-based SB-latices in pigment coating applications. The potential of enzymatic polymerization of lignosulfonates to enhance the binding properties via modification of the molecular structure was also studied.

Paper coating trials applying the lignosulfonate based binder in top- or precoat on a woodfree base paper were performed on a laboratory coater. We report the results of the first preliminary coating trials using spent liquor (lignosulfonate) directly from the intermediate stage of the black liquor evaporation plant, which demonstrated that ultrafiltration of the black liquor to obtain purer lignosulfonates was - as expected - necessary prior to using them in coatings. Further coating trials applying ultrafiltrated lignosulfonates with and without enzymatic polymerization are presented, which show a potential applicability of such modified lignosulfonates.

MATERIAL AND METHODS

All used chemicals were of analytical grade, purchased from Sigma-Aldrich (Steinheim, Germany), Merck (Darmstadt, Germany) or VWR (Vienna, Austria). Laccase from Myceliophthora thermophila was obtained from Novozymes (Bagsvard, Denmark).
Industrial Mg-sulfite spent liquor containing lignosulfonates from an acid magnesium bisulfite process from the intermediate evaporation stage (approx. 30% solids) and precoated base paper was kindly provided by SAPPI Gratkorn, Austria.

Ultrafiltration of Lignosulfonate

A Memcell unit supplied by Osmo Membrane Systems GmbH (Korntal-Muenchingen, Germany) was used to ultrafiltrate sulfite spent liquor. The sulfite spent liquor having a solids content of 30% was first pre-filtered with a 5µm paper filter to remove solid particles and fibrous material. Another prefiltering step using the Memcell device was performed using a 2µm membrane. Salts, sugars and smaller lignin fractions were subsequently removed using a 150kDa membrane by repeatedly adding water until the permeate was colorless. Afterwards the retentate retained on the 150 kDa ultrafiltration membrane (R150), which had a solids content of around 10-12%, was brought to 30% solids using a rotary evaporator and was used for the experiments.

Enzymatic Lignin Polymerization

A recently described laccase mediated lignosulfonate modification process based on oxygen supplementation was used, which avoids the use of expensive mediators (Ortner et al., 2015; Huber et al., 2016). Enzymatic polymerization of 30% TDS lignosulfonate was carried out in the presence of external oxygen supply.
Lignosulfonates were adjusted to pH 7 using NaOH before enzymatic treatment. During incubation of the lignosulfonate with the Myceliophthora thermophila laccase (MTL), oxygen consumption was monitored using a FireSting-O_2 device from PyroScience GmbH (Aachen, Germany). The sensor was placed in a 100ml glass bottle containing 60 mL of the 30% TDS lignosulfonate sample and then supplied with pure oxygen (100 % saturation) before introducing 233 nkatal ml^{-1} laccase to start the reaction. The thus obtained lignosulfonate was termed "modified lignosulfonate" whereas untreated lignosulfonate was termed "untreated lignosulfonate" (see *Table* 1). Samples were withdrawn after the end of the polymerization (before getting to viscous to process) and the change in molecular weight was measured by using size exclusion chromatography (SEC).

Size Exclusion Chromatography (SEC)

The molecular weights of treated and untreated lignosulfonate samples were determined using size exclusion chromatography (SEC) equipped with degasser, binary pump, auto sampler, a DAD (Diode Array Detector) and a RI (Refractive Index)-detector system (Agilent Technologies 1260 Infinity). A guard column (Waters Ultrahydrogel, 200 Å, 6 x 40 mm, maximum pressure 3.93 MPa) was placed before the two separating columns (Waters Ultrahydrogel 500, 500 Å, 7.8 x 300 mm, 3.93 MPa and Waters Ultrahydrogel 250, 250 Å, 7.8 x 300 mm, 1.96 MPa) connected in series. A 0.1 M $NaNO_3$ solution was used as the mobile phase and a runtime of 120 minutes. The lignosulfonates were diluted with the mobile phase to a concentration of 1 mg*mL^{-1} before loading 100µl onto the column. The Agilent GPC/SEC Software (Version 1.2) was used for analysis of chromatograms. The standards used for size exclusion chromatography (SEC) were Polystyrene Sulfonate Sodium Salts with molecular weights ranging from 208 g/mol – 1,188,400 g/mol.

Coating Color Preparation and Laboratory Coating Process

Topcoating application

Coating formulations (topcoat for a triple coated WFC paper) were prepared using calcium carbonate HC90 from Omya (Oftringen, Switzerland), SB-latex and synthetic thickener from BASF (Ludwigshafen, Germany) and PVOH (Mowiol 4-98) from Kuraray Europe GmbH (Hattersheim am Main, Germany). Latex was substituted partially by untreated and enzymatically modified lignosulfonate in the ratio of 1:2, i.e. latex amount was reduced by 2% and 4% of the ultrafiltrated lignosulfonate was added, either with or without enzymatic polymerization (see *Table 1*). Coating was performed on a laboratory reel-to-reel coater using a stiff blade at a speed of 15 m/min. The base paper was a pre- and mid-coated woodfree base paper provided by Sappi Gratkorn. Target coat weight was 8 g/m² per side.
In the preliminary trials reported in the results the same coating formulations were tested, but lignosulfonate directly from the intermediate evaporation stage, i.e. without ultrafiltration, was used.

Table 1: Topcoat formulations [% dry substance]

	Modified* Lignosulfonate	**Untreated** Lignosulfonate**	**Reference**
Calcium carbonate (HC90)	100	100	100
Modified Lignosulfonate*	4		
Untreated Lignosulfonate**		4	
SB-Latex	6	6	8
PVOH	0,8	0,8	0,8
Thickener	0,25	0,25	0,25
Target solids content	**60**	**60**	**60**

* enzymatically polymerized, ultrafiltrated

** no enzymatic polymerization, ultrafiltrated

Precoating application

Coating formulations (precoat for a double coated WFC paper) were prepared using calcium carbonate HC60 from Omya (Oftringen, Switzerland), SB-latex from BASF (Ludwigshafen, Germany) PVOH (Mowiol 4-98) from Kuraray Europe GmbH (Hattersheim am Main, Germany) and CMC (Finnfix 30) from CP Kelco (Cumberland, USA). Latex was substituted partially by untreated and enzymatically modified lignosulfonate in a ratio of 1:2, i.e. latex amount was reduced by 2% and 4% of the ultrafiltrated lignosulfonate was added, either with or without enzymatic polymerization (see *Table 2*). Coating was performed on a film press (SUMET coater CU5) using a 30µm rod at a speed of 15 m/min. The base paper was an uncoated woodfree base paper provided by Sappi Gratkorn. Target coat weight was 10g/m² per side.

Table 2: Precoat formulations [% dry substance]

	Modified* Lignosulfonate	**Untreated** Lignosulfonate**	**Reference**
Calcium carbonate (HC60)	100	100	100
Modified Lignosulfonate*	4		
Untreated Lignosulfonate**		4	
SB-Latex	6	6	8
PVOH	0,5	0,5	0,5
CMC	0,5	0,5	0,5
Target solids content	**60**	**60**	**60**

* enzymatically polymerized, ultrafiltrated

** no enzymatic polymerization, ultrafiltrated

Coating and Paper testing

Water retention of the coating colors was quantified by measuring the Abo Akademi Gravimetric Water Retention Value (AA-GWR). Furthermore, pH, low shear (Brookfield) and mid shear viscosity (Paar Physica) was controlled. Optical properties were measured using a Technidyne Color Touch 2. Printability parameters (passes-to-fail, set-off, droplet test (ink repellence) were determined using a Prüfbau device and picking resistance using an IGT device.

RESULTS AND DISCUSSION

Preliminary trials with lignosulfonates containing spent liquor

First coating trials using lignosulfonate containing spent liquor directly from the intermediate evaporation stage at 30% TDS, only filtered through a 5µm paper filter to remove solid particles and fibrous material, showed dusting already right after coating drying of the reel-to-reel coater indicating a very low binding force of the lignosulfonates. Extremely poor IGT picking tests verified this observation. For lignosulfonate containing samples, no values could be determined, because the first signs of picking were evident below 2 cm under the lowest loading.

As the water retention values (AA-GWR) of 975 g/m² (see also *Figure 3*, left bar) of this coating was very poor, binder penetration into the base paper was measured for this coating applied directly on an uncoated base paper using a method developed by Hofer et al. (2015), which makes use of the autofluorescence of lignosulfonates. In the BF and GFP images on the left side of *Figure* 1, a cross-section of a coated paper with untreated lignosulfonate containing spent liquor (no ultrafiltration, no enzymatic polymerization) is illustrated. The BF (visual light) image shows the coating layer appearing darker, whereas the GFP image (UV light) shows the green fluorescing lignosulfonate; the white lines in the GFP image indicate the segmented coating layer from the BF image. A clear lack of lignosulfonate binder in the coating layer is obvious; the lignosulfonate is penetrating deeper into the base paper and depletion of the lignosulfonate binder in the coating layer is clearly visible. Almost all of the binder penetrated into the porous system of the base paper and binding force of the coating layer is too low.

To overcome this excessive penetration of lignosulfonates contained in the spent liquor into the base paper by an increase in molecular weight, enzymatic polymerization of the lignosulfonates with a laccase mediated modification process based on oxygen supplementation (Ortner et al., 2015; Huber et al., 2016) was tried. First trials with industrial spent liquor containing lignosulfonates originating directly from the intermediate evaporation stage, only filtered through a 5 µm paper filter, showed a significant increase in average molecular weight after 6h of enzymatic polymerization (*Figure* 2).

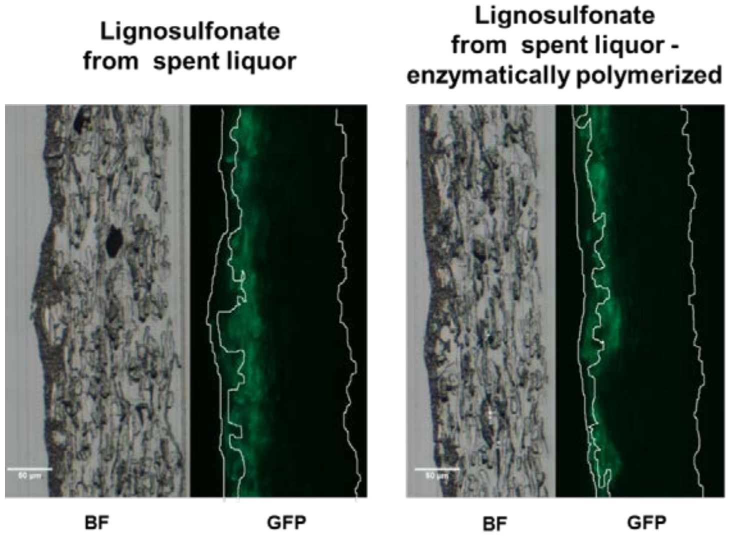
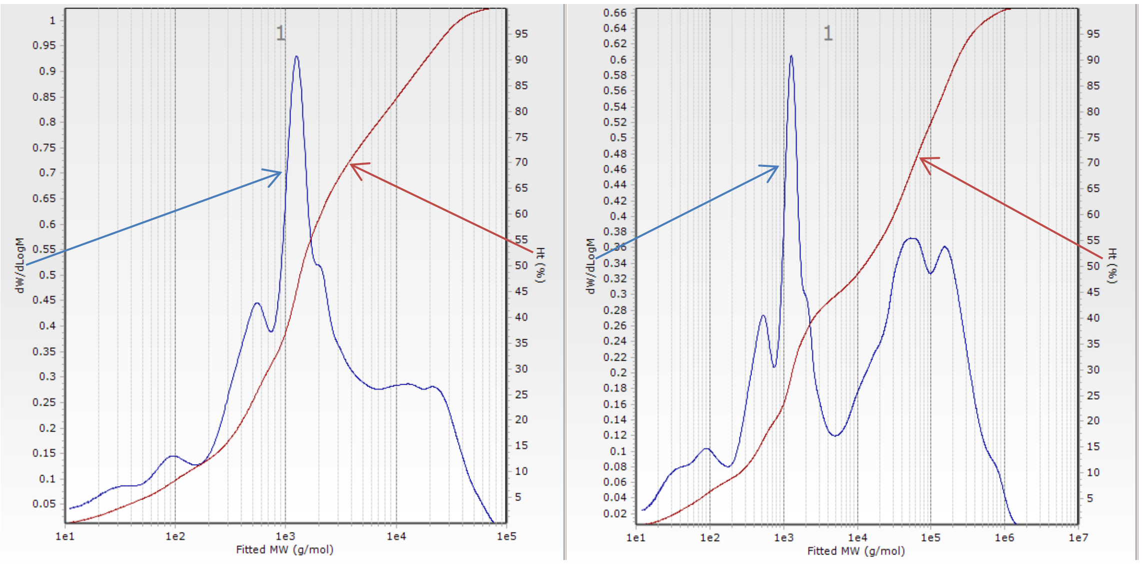


Figure 1: *Penetration of lignosulfonates from spent liquor into the base paper. Brigthfield (BF) and green fluorescent (GFP) images of blank (untreated lignosulfonate from spent liquor) (left) compared to BF and GFP image of enzymatically polymerized lignosulfonate from spent liquor (right).*



	Mn	Mw	Mz	PD
Blank	277	5714 Da	23445	20.63
Enzymatically polymerized	423	76453 Da	370387	180.7

Figure 2: *Molecular weight distribution (SEC) of enzymatically polymerized lignosulfonate from spent liquor with 30% TDS (right) compared to blank (untreated lignosulfonate) at 30% TDS (left, no enzyme treatment) and their average molecular weights (table below figure)*

Penetration of lignosulfonates into the base paper could be reduced dramatically by enzymatic polymerization (see GFP image on the right side of *Figure 2*). Three-dimensional evaluation of 100 cross sections as the ones depicted in *Figure 1* (image length > 5mm) resulted in the penetration depth illustrated in *Figure 3*. Due to enzymatic polymerization, the penetration depth was decreased by around 10µm. The penetration depth for the SB-latex reference was not determined because SB-latex needs to be stained by a fluorescent dye and the results are not directly comparable to the lignosulfonate coatings.

The observations regarding penetration depth were confirmed by measuring a more than 50% higher water retention (low AA-GWR) for the enzymatically polymerized lignosulfonates compared to untreated samples. As can be seen in *Figure* 3, the modified lignosulfonates were in the same AA-GWR range as the reference.

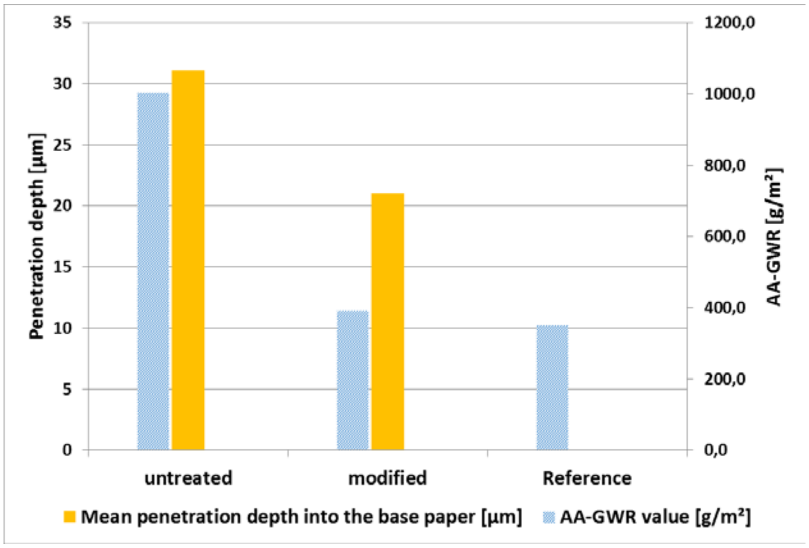


Figure 3: *Penetration depth of lignosulfonates into base paper (measured according to Hofer et al. (2015)) and AA-GWR water retention of coatings containing lignosulfonates from spent liquor compared to the reference (untreated… lignosulfonate from spent liquor, no treatment; modified… enzymatically polymerized lignosulfonate from spent liquor)*

Although binder penetration was significantly reduced using enzymatically polymerized lignosulfonates from the spent liquor, binding force was still insufficient, which we attributed to a large amount of impurities contained in the industrial lignosulfonates, as e.g. salts, sugars or extractive. Therefore, ultrafiltration was applied in all further trials to eliminate the impurities, which were assumed on the one hand not to contribute to the binding function and on the other hand to hinder the lignosulfonate binder to form a continuous film.

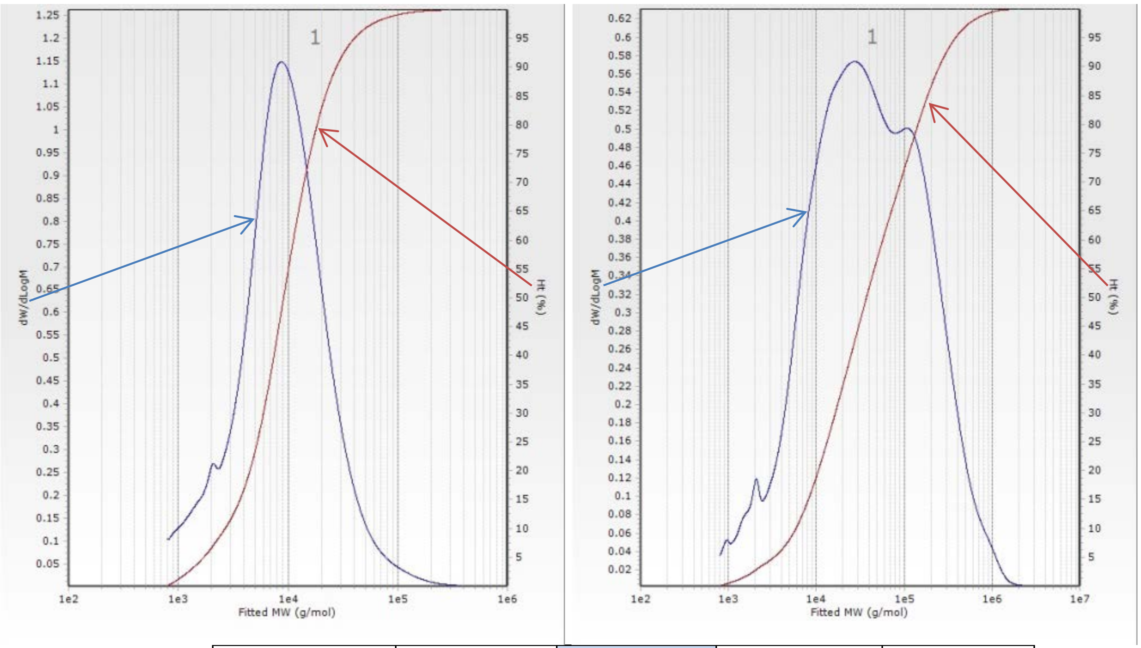
Trials using ultrafiltrated lignosulfonate

Ultrafiltration pre-trials identified a pre-filtration using a 2 µm membrane and final filtration using the retentate of an ultrafiltration through a 150kDa membrane as the most suitable raw material for coating applications. Using such ultrafiltrated lignosulfonate samples, the incubation time in enzyme polymerization could also be reduced from 6 to 2 hours to reach a similar molecular weight increase compared to non-ultrafiltrated samples. Lignosulfonate content also was increased from around 40% in the spent liquor to more than 70% after ultrafiltration.

Thus a sufficiently reproducible high degree of polymerization was achieved already after 2 hours of incubation at an oxygen supply rate of 15cm^3 leading to an increase of the average molecular weight from 14092 to 97574 Da (see *Figure 4*). It is also to be noted that ultrafiltration alone also leads to a higher molecular weight of the lignosulfonates (compare blank in *Figure 4* to blank in *Figure 2*).

Ultrafiltrated and enzymatically polymerized lignosulfonates as binder in topcoat application

Combination of ultrafiltration and enzymatic polymerization of lignosulfonate resulted in good water retention values (AA-GWR) of 120 g/m² of the thus produced coatings.



	Mn	Mw	Mz	PD
Blank	5853	14092 Da	40793	2.408
Enzymatically polymerized	13493	97574 Da	365735	7.231

Figure 4: *Molecular weight distribution (SEC) of enzymatically polymerized lignosulfonate (ultrafiltrated 2µm > x > 150kDa) with 30% TDS (right) compared to blank (untreated ultrafiltrated lignosulfonate) at 30% TDS (left, no enzyme treatment) and their average molecular weights (table below figures)*

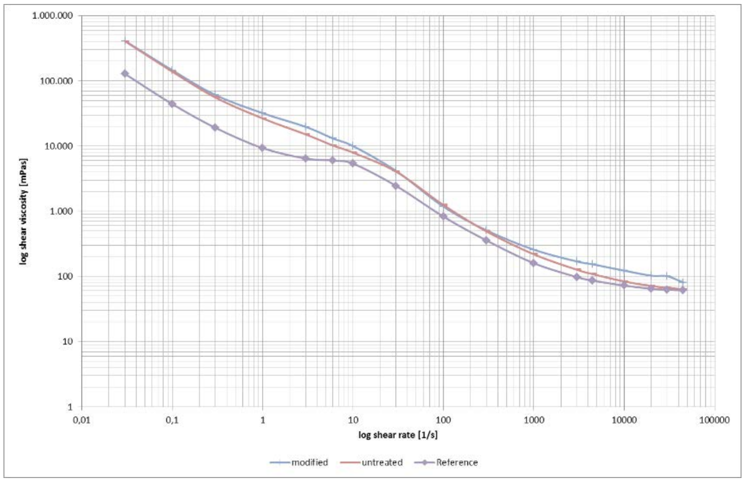


Figure 5: *Rheological behavior of untreated (ultrafiltrated, no enzyme treatment) and modified (ultrafiltrated, enzymatically polymerized) lignosulfonate containing coatings in comparision to reference coating*

In *Figure 5* the rheological behavior of the produced pigment coatings (recipes see *Table 1*) is illustrated. In comparison to the reference coating, the lignosulfonate containing coatings are slightly higher in viscosity. At higher shear rates the coating containing the modified lignosulfonate (ultrafiltration and enzymatic polymerization) showed the highest viscosity at a level still acceptable for blade coating. In *Table 3*, the BF viscosities are shown and again, the formulation containing enzymatically polymerized lignosulfonate showed slightly higher values.

Table 3: Additional viscosity measurements

	Modified Lignosulfonate	Untreated Lignosulfonate	Reference
BF 100 [mPas]	2850	2288	2324
BF 20 [mPas]	10500	8580	8560
Spindle number	5	5	5

The applied coat weights are shown in *Table 4*. Because of the rather low solid contents of the lignosulfonates of 30% the coatings only reached a solids content of 60 % and thus only rather low coat weights could be achieved. The solids of the lignosulfonates were not further increased due to economic reasons, as more water would have to be evaporated given the solid contents of only around 10-12% after ultrafiltration. Based on the rheology of the coating formulations it is unclear why lower coat weights in comparison to the reference were achieved for the lignosulfonate containing coatings.

Table 4: Applied coat weights at the laboratory blade coater

	Modified Lignosulfonate	Untreated Lignosulfonate	Reference
Coat weight [g/m²]	6,6	7,3	10,6

The coated papers were tested regarding optical and offset printing properties. Printing test showed promising results (see *Table 5*). Possibly due to the higher coat weight applied for the reference, the ink setting is a bit slower compared to the lignosulfonate coatings. Modified and unmodified lignosulfonates almost showed the same ink setting, but the modified lignosulfonate reached higher offset suitability values which were slightly higher than the reference. Also the droplet test results as a measure for water repellence showed similar results for all coatings.

Table 5: Offset printability results Prüfbau

	Modified Lignosulfonate	Untreated Lignosulfonate	Reference
Offset suitability dry [passes to fail]	6,5	6	6
Offset suitability wet [passes to fail]	5,5	4,5	5
Ink setting after 30 s	0,5	0,45	0,57
Droplet test [%]	54,0	53,2	53,7

Optical brightness of coatings containing lignosulfonates showed as expected significantly lower values compared to the reference (see *Table 6*). Difference in brightness values, measured without UV, were around 5 points and measure with UV around 10 points. Enzymatic polymerization of lignosulfonate caused a shift in color to a more reddish appearance and a lower brightness.

Table 6: Optical brightness

	Modified Lignosulfonate	Untreated Lignosulfonate	Reference
R457 +UV	82,24	84,24	95,74
R457 -UV	77,18	78,75	83,95

Ultrafiltrated and enzymatically polymerized lignosulfonates as binder in precoat application

Ultrafiltrated and enzymatically polymerized lignosulfonates were also tested in the application in a precoat (recipes see *Table 2*). There precoats were applied with a film press in single sheet mode, which also allows better adjustment of the coat weight. The results of the IGT pick test of the pre-coated samples are listed in *Table 7*. Untreated (ultrafiltrated, no enzyme treatment) lignosulfonate showed a slightly lower picking resistance than modified (ultrafiltrated, enzymatically polymerized) lignosulfonates and both showed clearly lower values than the reference.

Table 7: Coat weight and IGT Picking of pre-coatings

	Modified Lignosulfonate in PC	Untreated Lignosulfonate in PC	Reference
Precoat weight [g/m²]	10,4	9,9	9,6
IGT pick test [cm/s]	118	109	141

The three precoated papers were topcoated using a standard topcoat taken directly from the coating machine SM9 in Gratkorn. In *Table 8,* the Prüfbau printing results for the topcoated papers are shown. Again, the offset suitability of all three samples is comparable, with a slight advantage for the reference in passes-to-fail wet. Ink setting of the modified lignosulfonate containing precoat is comparable to reference, untreated lignosulfonate containing precoat shows slower ink setting. The droplet test as a measure for water repellence shows significantly better values for the lignosulfonate containing samples compared to the reference.

Table 8: Printing tests of pre-coatings containing lignosulfonate plus standard top-coating

	Modified Lignosulfonate in PC	Untreated Lignosulfonate in PC	Reference
Offset suitability dry [passes to fail]	3	3	3
Offset suitability wet [passes to fail]	2	2	2,5
Ink setting after 30 s	0,38	0,48	0,36
Droplet test [%]	81,3	84,3	62,9

The brightness level of the double coated samples is listed in *Table 9*. Again brightness measured with and without UV is significantly lower compared to the reference.

Table 9: Brightness of pre- and top-coated samples

	Modified Lignosulfonate in PC	Untreated Lignosulfonate in PC	Reference
R457 +UV	83,23	81,7	92,38
R457 -UV	79,34	78,02	85,56

SUMMARY AND OUTLOOK

Ultrafiltrated and enzymatically polymerized lignosulfonates were applied as partial replacement of SB-latex in woodfree coated paper coating formulations (precoat and topcoat). Lower penetration depth of lignosulfonate based binder into the base paper was achieved by ultrafiltration and enzymatic polymerization of the spent liquor containing the lignosulfonates. This also led to a significant improvement in water retention of the coating formulations containing lignosulfonates. The coated papers containing a lignosulfonate based binder showed promising results regarding offset printability, which justifies further research.

As expected brightness values are significantly below the reference and need to be improved. Therefore, trials to bleach the lignosulfonates via ozone or hydrogen peroxide are currently in progress with promising first results. Also it will be necessary to increase the solids content of the ultrafiltrated lignosulfonates, which is a challenge from the economic side. In general the economics of upgrading lignosulfonates contained in spent liquor using the described processes are presently under evaluation.

Enzymatically polymerized lignosulfonates also might be interesting in size press applications for packaging papers, where brightness not of an issue. First results in such applications have also shown promising results.

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