Neutral/alkaline Sizing of Paper with Fortified, Saponified Wood Rosin Premixed with Alum and Retained Using Cationic Polymer

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Abstract

Rosin, as a traditional internal sizing agent, has not been extensively used under neutral or alkaline pH due to the ineffectiveness of aluminum sulfate (alum) under such conditions. Rosin has some inherent advantages relative to the cellulose-reactive agents alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA). Rosin is generally not subject to problems with paper-surface slipperiness, sizing reversion, or hydrolysis. Rosin products are widely used on account of their favorable price, but they are pH-sensitive and their emulsions can become unstable and lose homogeneity during storage. Developing a rosin-sizing system from domestic sources is a primary objective of this study. Crude rosin was obtained from mixed pine stumps by hexane extraction. Fortification was carried out with maleic acid anhydride to alter the structure of the rosin. The material was then saponified until reaching an acid number of 26. Part of the rosin with premixed with alum, using a blender. To make the alum-premixed sizing formulation positively charged, a high-charged cationic polymer (poly-DADMAC) was added. Each sizing agent formulation was tested with three pulp types. Charge demand values of bleached chemical pulp, unbleached kraft pulp and recycled pulp were determined, and the sizing behavior of the resulting paper was compared. For comparison, paper was also sized conventionally with alum and rosin. Greater sizing performance was obtained with the pre-mixed rosin formation than with the conventional sizing. Moreover, it was observed that the yellowish coloration of the paper was decreased with increasing pre-mixed rosin sizing agent usage in the case of the bleached furnish.

Key Words: Internal sizing, rosin sizing, pre-mix rosin, sizing treatment, crude wood rosin.

Introduction

The rosin market has been widening over the past decade. According to the rosin market data of Trademap, rosin and rosin acid imports to the dominant market of China were 55 million tons, together with domestic production of 450,000 tons. Paper product applications involving rosin soaps have experienced significant expansion over the years [1]. Internal sizing agents provide water resistance to the paper products. Traditional internal sizing agents are rosin products, alkyl ketene dimer (AKD), alkenyl succinic anhydride (ASA) and copolymer products [2, 3, 4]. Rosin sizing products are supplied mainly as either emulsions of rosin acids or as rosin soap [5, 6, 7].
There is not any domestic production of rosin sizing agents in Turkey yet. Turkey’s consumption of rosin sizing agent is 1.178 tons. Approximately 960 tons of crude wood rosin, 41 tons gum rosin, and 1500 tons crude tall oil were produced in 2017. The produced amount of rosin would barely meet the demand even when using all of the crude rosin production as sizing material. The total paper production was 4,360,000 tons in Turkey according to the same source. An amount of 3,480,000 tons of it is suitable for rosin sizing applications. The domestic rosin sizing products can be preferred over other kinds of sizing agents due to various advantages such as an affordable price, less friction and waxy deposits problem, and better printability [8, 9]. Rosin is not subject to the kinds of hydrolysis problems faced by users of ASA and AKD [10, 11]. However, rosin-sizing agents require a greater addition amounts than ASA and AKD to increase paper’s resistance to water [12]. Fortification of crude wood rosin is necessary because rosin is sensitive to oxidation and biodegradation, which is important for its storage stability [13]. Subsequently, the simplest method of forming a rosin product suitable for sizing is saponification by treatment with alkali such as NaOH.

In order to achieve effective rosin sizing there is a need for a positively charged fixative (sometimes called a mordant) to anchor the rosin size to the fibers. The most widely used mordant to precipitate rosin soap products onto the surfaces of fibers is aluminum sulfate, which is known as papermakers’ alum [14, 15, 16, 17]. For a high-efficiency of rosin sizing, the pH should be in the range between 4 and 5.5 [14, 18]. There has been intensive interest in rosin not only for acidic systems but also for neutral sizing conditions. In the case of rosin products with the addition of alum or polyaluminum chloride (PAC), the further addition of polyethylene imine (PEI) or poly DADMAC [19], as well as supplementary treatment with fatty acids [20, 21] can further improve the sizing effect under neutral sizing condition.

A novel feature of the present work was to employ cationic demand titrations as a means of adjusting the formulation of sizing treatments based on partially fortified rosin size, alum, and the high-charge cationic (quaternary ammonium) polyelectrolyte poly-(diallyldimethylammonium chloride) (poly-DADMAC). Response variables included the stability of the sizing formulation and the water resistance of the resulting paper. There are many instabilities in paper production that can reduce paper sizing effectiveness [22, 23, 24]. Unbleached kraft pulp furnish often contains variable levels of lignin and hemicellulose residues that can lead to instabilities in paper machine operations. Recycled fibers and fines, as well as a wide range of contaminants are sources of instability in the production of recycled paper products. Compared to unbleached kraft and recycled furnish, bleached chemical pulp has less colloidal substances. The charge demand of different pulps needs to be compared to obtain effective sizing performance.

The aim of this study was to investigate the influence of different treatment conditions of a pre-mixed rosin/fixative system and a conventional (reserve sizing) rosin treatment on charge demand and sheet formation variables. A further goal was to establish effective rosin sizing treatments for some contrasting fiber sources.

**Experimental**

**Crude Wood Rosin**

Crude wood rosin samples were obtained from IVA Resin Biomass Inc. The isolation method was hexane extraction from pine stumps. The chemical composition of Crude Wood Rosin (CWR) was as follows:

88% Wood Rosin (Levopimaric acid, Abietic acid, Neoabietic acid, etc.)
9.5% Turpentine (alpha pinene, beta pinene, myrcene, etc.)
1% Pine oil (alpha terpineol, etc.)
1% Pine tar
0.5% Aliphatic hydrocarbons

Specimens of both the unsaponified and saponificated rosin were analyzed with gas chromatography-mass spectrometry (GC-MS). The results were as shown in Figures 1 and 2. As shown, there were changes in the details of retention times, indicating changes due to saponification. Rosin acids were abundant in the saponificated material, as it gave rise to between 20 and 30 peaks [25].

Fortification and Saponification of Rosin
Only levopimaric acid from the abietadienoic class is capable of undergoing Diels-Alder (fortification) reactions, but thermal isomerization occurs between abietadienoic acids [26]. Levopimaric acid has hydrophobic character but it also contains a carboxylic acid group. Increasing this single carboxylic group by fortification with maleic or fumaric anhydride (a Diels-Alder reaction) in the range between 2% and 8% enhances the performance of rosin sizing in papermaking [18] and provides durable storage characteristic of soap or emulsions [5]. Fortification of a small proportion of the levopimaric acid molecule instead of the entire amount of levopimaric acid has been shown to provide better results [20]. Whether the rosin just has its own carboxyl groups or added carboxyl groups, it has to be neutralized using an alkali metal hydroxide. Therefore, the partially fortified rosin product had a lower requirement of NaOH to bring about saponification.
As the first step of the process, the separation of turpentine was accomplished at 230°C for 2 hours. This separation prevents the binding of alum to turpentine during the sizing. After decreasing the temperature to 120°C, fortification was carried out with maleic anhydride. Finally, saponification was done with NaOH. 302.45 g of crude wood rosin and 30.245 g of maleic anhydride were charged to a flask equipped with a condensor and the mixture refluxed for three hours. The reaction product is dark amber color maleated rosin intermediate. The reaction is shown in Figure 3. For the saponification step, 33 g of NaOH and 100 g of H2O were mixed in a beaker. The mixture was added to whole maleinated rosin sample under mechanical stirrer and then 297 g of water was added before the process was terminated. 763 g of fortified rosin soap (default rosin) was obtained with 48% solid content. The crude wood rosin had a 219 acid number. After the saponification process, the acid number was 26 according to ASTM D465-15.

![Levopimaric Acid Fortified with Maleic Acid Anhydride](image)

**Fig. 3.** Levopimaric acid fortified with maleic acid anhydride by Diels-Alder reaction

The temperature/time diagram of the reaction is given in Figure 4. After saponification, the cooling step can be shortened according to the state of the process. Dry matter content was 48% of the final products. Sizing agent was diluted to 20% solids content as a stock solution.

![Temperature-Time Diagram](image)

**Fig. 4.** Reaction diagram of rosin sizing agent
Charge Demand Analysis
Charge demand analysis, measured by titration to a streaming current endpoint, is widely used to determine optimal balances in the papermaking process [26]. Near-zero charge demand is sometimes expected in an optimized system because of favorable drainage and retention of fine particle at that point [27, 28, 29]. 10 mL of pulp was titrated with 0.001N poly-DADMAC (Yixing Cleanwater Chemicals Co.). The charge demand for these experiments was analyzed using a Mutec streaming current detector (BTG Corp.) at the Kartonsan Mill Laboratory.

Formulation of Rosin by Premixing
Under acidic conditions, rosin soap sizing agent becomes anchored in the presence of the alum. The rosin soap reacts with the alum, yielding aluminum dirosinate, along with some unreacted free rosin [5, 20]. Aluminum monorosinates can also subsequently form by reacting with any rosin molecules still in their protonated form at elevated temperature as the paper is being dried [6].

When the rosin size is being used under neutral or alkaline conditions, it is necessary to reduce the contact time of rosin products and aluminum [10] to make an adjustment in the rosin size content. Researchers have shown that the premixing of aluminum products with rosin and then adding the blend to the fiber suspension could be beneficial [30, 31, 32]. In the present work the alum was added directly to the fortified and saponified rosin sample. The alum was prepared as a 2% solid content of aluminum sulfate. The alum was slowly added to 10 mL of rosin sizing agent that had a 2% solid content, and the pH changes were observed (Figure 5).

The negatively charged sizing material was cationized with varying amounts of 0.001N poly-DADMAC. It was hypothesized that the most suitable dosage would coincide with reversal of the surface charge to a positive sign. Accordingly, the selected addition amount is illustrated as a circle (Figure 6). It was found during preliminary testing that the conditions corresponding to the circled point in Figure 6 gave the most efficient rosin acid sizing. The formulation represented by the circle will be referred to in this article as “pre-mixed rosin sizing”. Thus, a cationic sizing material was obtained.
For comparison, another specimen of fortified and saponified rosin was not pre-mixed with alum. Instead, following the conventional industry practice, it was used for rosin sizing with alum added to the furnish ahead of the rosin addition (see later). This condition was called “default rosin sizing”.

**Fibers for Paper Preparation**

Three types of fibers used in this work were supplied from various sources. The pulp types were bleached chemical pulp (a 50:50 mixture of hardwood and softwood), recycled pulp from the Kartonsan carton mill, and unbleached kraft cellulose from a local company. The unbleached kraft pulp and bleached cellulose were beaten with a Valley beater according to ASTM 1048-36. The beating process was continued until a freeness of °SR 45 was reached. Furnishes were diluted 0.5% consistency and kept in the containers. Na₂SO₄ was added until the electrical conductivity reached 1000 μS/cm.

Paper samples were prepared at 60 g/m² basis weight using a British sheet mould (T205 sp-02). The sizing with pre-mixed rosin treatment and default rosin sizing treatment to prepare the handmade paper was performed in Istanbul University, Forest Product Chemistry and Technology laboratory. Handsheets were dried at 105°C for 20 minutes after 48 h of conditioning in dry air. The standard pulp characteristics are given in Table 1. Tests were conducted at 23°C. Testing the pulp with the SR rates, turbidity and charge demand evaluated besides, the pH-value, the turbidity, the conductivity of the each furnish. Rosin addition amounts were constant (2%). The abbreviations, as given in Table 1, represent W. as bleached, K. as Kraft, and R as recycled pulp.

<table>
<thead>
<tr>
<th>Base Paper Characteristics</th>
<th>White (W)</th>
<th>Kraft (K)</th>
<th>Recycled (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drainability °SR</td>
<td>45</td>
<td>47</td>
<td>48</td>
</tr>
<tr>
<td>Conductivity [μS/cm]</td>
<td>1003</td>
<td>1010</td>
<td>1027</td>
</tr>
<tr>
<td>Ash Content [%]</td>
<td>0.2</td>
<td>0.1</td>
<td>10.29</td>
</tr>
<tr>
<td>pH-value</td>
<td>7.05</td>
<td>6.25</td>
<td>6.49</td>
</tr>
<tr>
<td>Turbidity [NTU]</td>
<td>560</td>
<td>522</td>
<td>624</td>
</tr>
</tbody>
</table>
Different additive programs were employed for the two formulations of rosin considered. In the case of the rosin that had not been pre-mixed with alum, 1% aluminum sulfate was added to the pulp suspension prior to addition of the rosin. This is an example of a reverse sizing addition sequence. The reverse sizing was carried out due to water hardness, which can lead to the agglomeration of rosin soap and formation of calcium or magnesium rosinate [18]. Water hardness was 78 mg/L according to measurements taken in the mill. In the case of the rosin that had been pre-mixing with alum during its formulation, the corresponding wet-end additive was poly-DADMAC, as described earlier.

Table 2 summarizes the chemical additives that were employed in preparing the paper specimens considered in this work. The word “Yes” below the heading (Na₂SO₄) means that a sufficient amount of Na₂SO₄ was added to reach an electrical conductivity of 1000 μS/cm during mixing of the furnish with the sizing agent. The “1% alum” was added prior to addition of rosin (so-called “reverse sizing”). The poly-DADMAC was added to the rosin after the alum premixing of the rosin soap size.

Table 2. Test conditions in preparation of handsheets

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Pre-treatment</th>
<th>Sheet preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alum pre-blend</td>
<td>Poly-DADMAC</td>
</tr>
<tr>
<td>White bleached pulp-blank</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>White bleached pulp-Default rosin sizing</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>White bleached pulp- premixed rosin formulation</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Kraft- blank</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Kraft-Default rosin sizing</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Kraft- premixed rosin formulation</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Recycled-blank</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Recycled-Default rosin sizing</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Recycled- premixed rosin formulation</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Results

Cationic Demand of Papermaking Furnish

The results obtained from cationic demand titrations of the furnish showed that the unbleached kraft pulp had lower charge demand than bleached and recycled pulp. The cationic demand of pulp furnishes treated with the pre-mix rosin-alum-poly-DADMAC system was slightly lower than conventional rosin-treated samples. In both cases the furnish before addition of sizing-related additives had the highest cationic demand (Figures 7-9). These findings indicate that both of the sizing systems (the rosin acid with alum, as well as the pre-mix rosin-alum-poly-DADMAC system) had a net positive charge character.
Fig. 7. Cationic demand of bleached furnish for blank, 2% default rosin and 2% Pre-mix rosin addition

Fig. 8. Cationic demand of recycled furnish for blank, 2% default rosin and 2% Pre-mix rosin addition

Fig. 9. Cationic demand of kraft furnish for blank, 2% default rosin and 2% Pre-mix rosin addition

**Cobb₆₀ Sizing Results**
Sizing results were obtained with same amount of default rosin vs. pre-mix rosin with various types of furnish. The Cobb₆₀ results are given in Figure 10. Previous research had shown that threshold level of sizing effect of recycled fibers could be below than virgin fiber because of sizing in a prior cycle [33]. Less sizing agents was sufficient sizing level for recycled furnish than previous studies [23, 34]. Papers Cobb₆₀ tests were evaluated according to ISO 535.

![Fig. 10. Cobb₆₀ Results of Handmade Paper. Notes: K = kraft; W = bleached; R = recycled furnish; default rosin = rosin acid emulsion size with alum; Pre-mix rosin = partially fortified rosin soap with poly-DADMAC](image)

Residual rosins in kraft fibers make the paper more hydrophobic compared to bleached chemical pulp. This can be explained based on the tendency of the fibers migration of the surface of the paper [35]. It was observed that the pre-mix rosin had more sizing capacity in all experiments. In addition, the premixing of the rosinate sizing agent with the alum (pre-mix rosin treatment), followed by use of poly-DADMAC during sheet preparation made it possible to achieve sizing with no further alum addition.

**Optical properties**
Optical properties have vital importance for paper products, especially the printing papers. Sizing conditions as well as the drying section have detrimental effects on paper, particularly recycled paper [36]. Sizing treatment with rosin agent have some risk to give yellowness to the printed paper. Rosin soap and pre-mix rosin treatment treated paper were compared for this reason. In this study the optical properties of white paper from bleached chemical pulp tested. Yellowness and \(L^*, a^*, b^*\) color space values were evaluated using Elrepho spectrophotometer with D65, 10° illuminant. As shown in Table 3, the default rosin sizing yielded only minor effects on paper color, mainly increasing the yellowness when used at the highest dosages. In the pre-mix rosin treatment case, the change in yellowness was low to negligible compared to the blank untreated sample.
Table 3. Standard characteristics of furnish

<table>
<thead>
<tr>
<th>Rosin Addition Amount</th>
<th>Yellowness</th>
<th>Color Space Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L*</td>
<td>a*</td>
</tr>
<tr>
<td>Blank</td>
<td>14.72 (0.32)</td>
<td>92.09 (0.19)</td>
</tr>
<tr>
<td>1% Default Rosin</td>
<td>15.90 (0.34)</td>
<td>90.90 (0.21)</td>
</tr>
<tr>
<td>2% Default Rosin</td>
<td>16.44 (0.28)</td>
<td>91.16 (0.26)</td>
</tr>
<tr>
<td>2% Pre-mix rosin</td>
<td>15.09 (0.34)</td>
<td>92.08 (0.25)</td>
</tr>
<tr>
<td>5% Default Rosin</td>
<td>18.10 (0.33)</td>
<td>90.89 (0.27)</td>
</tr>
<tr>
<td>10% Default Rosin</td>
<td>18.19 (0.36)</td>
<td>91.02 (0.29)</td>
</tr>
</tbody>
</table>

Note: Values shown in parentheses are standard deviations.

Conclusions
Two systems of rosin sizing were formulated and shown to be effective for three different furnish types under neutral/alkaline pH conditions. In particular, a partially fortified rosin soap size, formulated by pre-blending with alum and with sufficient poly-DADMAC to give a net positive charge to the sizing mixture, gave the paper effective resistance to water without further usage of papermaker’s alum during sheet preparation. Favorable sizing results also were achieved by conventional use of alum and rosin (conventional rosin soap sizing using a reverse order of addition). In both cases the sizing agent was prepared from crude rosin extracted from softwood stumps with hexane. Both sizing treatments decreased the cationic demand of the furnish, which is consistent with a net positive charge, resulting from the cationic agents used during size formulation. The sizing results were in order of the cationic demand for the different furnish types; the unbleached kraft furnish had the lowest cationic demand and gave to lowest Cobb sizing values under the conditions of testing.

References


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