

How to use alum with cationic dispersed rosin size

LEBO XU, JEREMY MYERS, AND PETER W. HART

ABSTRACT: Retention of cationic dispersed rosin size was studied via turbidity measurements on stock filtrate with different alum and dispersed rosin size dosages. Stock charge characteristics were analyzed using both an analysis of charge demand determined via a streaming current detector and an evaluation of zeta potential of the fibers by streaming potential measurement. The results indicated that an optimum amount of alum existed such that good sizing retention was maintained throughout a wide range of dispersed rosin size dosages. However, when an excessive amount of alum was used and fines and colloidal particles were transitioned from anionic to cationic, the cationic size retention was reduced. Laboratory results were confirmed with a paper machine trial. All data suggested that a stock charge study was necessary to identify optimal alum dosage for a cationic dispersed rosin sizing program.

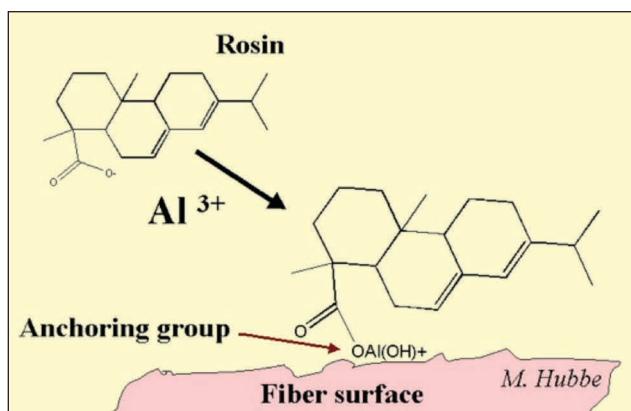
Application: Optimized alum-rosin system interactions on the paper machine wet end can improve product performance and reduce operating cost.

Paper is an engineered cellulosic material. Because cellulose contains a large amount of hydroxyl and carboxylic acid groups, paper is intrinsically hydrophilic. It absorbs water easily and quickly. This property is desirable for some grades, including tissue and towel; however, applications such as offset printing or packaging require that paper resists water absorption to various degrees.

Sizing is a process that enables paper to resist water (or other liquid) absorption and penetration. The purpose of sizing is not to fully prevent liquid from absorbing or penetrating, but to delay the event. Typically, a hydrophobic material is introduced to fiber surfaces during the sizing process. Generally, there are two types of sizing, internal and external. Internal sizing is achieved by introducing a sizing agent into the wet end of the paper machine, universally treating the sheet. External sizing (surface sizing) is generally applied at the size press or later to treat the sheet surface.

In 1807, alum-rosin sizing was invented by Moritz Friedrich Illig in Germany [1]. In this sizing system, rosin (mainly abietic acid or its saponification product) provides the hydrophobic property. Alum helps bond rosin onto the fibers and as such is called a mordant. **Figure 1** shows the molecular structure of rosin and a widely accepted mechanism of how alum sets rosin onto the fiber surface [2]. Rosin may be fortified with malic anhydride, fumaric acid, or both to add two additional carboxylic acid groups to the available reaction sites [3,4]; however, these fortifications typically account for only 10%–25% of the blend, with the rest being rosin [5].

Alum-rosin sizing quickly gained popularity in the paper industry because of its performance and low cost. However, this sizing system was not without issues. The primary issue was that rosin soap could form tacky deposits with calcium ions, affecting machine runnability. Mills using water with high hardness or using calcium carbonate as either paper fill-



1. Schematic of how alum sets rosin on fiber surface [2].

	Rosin Soap Sizing	Dispersed Rosin Size
Major Component	Sodium/potassium rosinate	Rosin acid
Effective Sizing Material	Aluminum rosinate	Aluminum rosinate
Dosing Point	Wet end	Wet end
Mordant	Alum	Alum
Setting Point	Wet end	Dryer section

1. Comparison of rosin soap sizing and dispersed rosin size.

er or coating pigment were particularly susceptible to this problem. As a result, dispersed rosin sizing (DRS) was developed in the 1930s [6,7].

A comparison of rosin soap sizing and DRS is provided in **Table I**. Both soap sizing and DRS are added at the wet end and need alum as a mordant to form strong bonds with fibers. The primary difference between the two sizing mechanisms

is the location of the reaction between the rosin agent and alum. For soap sizing, the reaction happens at the wet end. Alum reacts directly with rosin soap and then bonds with the fibers. Rosin acid in DRS is well protected as an emulsion and will not react with alum until sufficient energy is transferred to the sheet in the dryers. Upon heating, the emulsion is destabilized, releasing the rosin acid, to spread and react with alum on the fiber surface. Therefore, for DRS application, sizing retention and sizing development are two separate phases, while they happen simultaneously in soap sizing. The difference in the setting location means that sizing retention is more challenging for DRS. Before setting, DRS is merely associated with fibers via ionic bonding, which is not very strong in aqueous solutions. The separation of DRS and fibers (loss of the sizing material) might occur before the majority of the water is removed. In addition, DRS particles are much smaller than fibers and voids between fibers, making it difficult to physically trap them in a wet web.

Alum, often referred to as the papermaker's friend, is a versatile material for papermaking. It is widely used for many purposes beyond sizing, such as improving drainage and retention, pH adjustment, and deposit control [8]. In practice, machines that use cationic DRS sizing also use alum. The function of alum, in this DRS sizing program, is mainly to develop sizing with retained DRS in the dryer section to provide the final liquid-repelling property [9].

Because both alum and cationic DRS are positively charged in the wet end (especially for the acidic papermaking process), will additional alum hurt DRS retention because of repulsion between like charges? In this study, the effect of alum dosage on cationic DRS retention was explored. Retention was evaluated at different alum and DRS dosages. Charge demand analysis by use of a streaming current detector (particle charge demand [PCD]) and streaming potential (system zeta potential [SZP]) were also conducted to help identify the mechanisms associated with the interactions between DRS and furnish (fibers and fines and particles). Among the findings was a critical alum dosage, beyond which the charge of fines and particles was reversed, that significantly impaired DRS retention. A mill DRS application case study was also conducted and reviewed.

EXPERIMENTAL

Hardwood (HW), pine, DRS, and alum samples were all collected from a mill making solid bleached sulfate (SBS) paperboard. A generic testing stock was prepared by mixing 80 wt% HW and 20 wt% pine pulp. The stock consistency was adjusted to 0.7 wt% and the alum and DRS were diluted to 1 wt% with deionized water. Alum was diluted immediately before use, thus minimizing its hydrolysis in the dilute solution. The generic stock had pH 4.4. The pH decreased as more alum was added. The pH range in study was 4.1–4.4. The cationic DRS was received as an emulsion at about 40 wt% solids. Optical microscopic images showed the diameter of DRS particles to be approximately 1.5 μm .

Turbidity, NTU		Dispersed Rosin Size, lb/ton				
		0	4	8	16	32
Alum, lb/ton	0	0.0	6.8	15.0	16.9	23.4
	10	6.5	12.2	1.6	3.6	17.9
	20	1.7	7.9	8.8	13.5	29.8
	40	9.5	14.2	18.9	40.5	67.9
	80	2.4	13.5	23.7	31.3	78.7

II. Tested alum and dispersed rosin size dosage and associated turbidity.

For the DRS retention study, 3 L of 0.7 wt% stock was placed in a bucket. The alum was added and well mixed. Progressive amounts of DRS were added until the completion of the cycle. At each DRS dosage, a 50 mL sample was collected and passed through a strainer. The filtrate was collected for turbidity measurement on a LaMotte 2020e turbidity meter (LaMotte Co.; Chestertown, MD, USA), which used a 2300°C tungsten lamp as a light source. The light wavelength was 0.6–2.3 μm , with peak intensity at around 1.3 μm . Because the DRS particle size (1.5 μm) was bigger than the wavelength at peak light intensity, the turbidity meter was sensitive to the existence of DRS particles in solution and therefore able to evaluate DRS retention. Turbidity baseline data were collected using filtrate from the original stock before any additives. The baseline value was subtracted from final turbidity measurements to quantify the DRS contribution to the final turbidity. The turbidity values were used to quantify the retention of DRS. The entire series was repeated at each alum dosage. The adjusted turbidity values were reported as the average of three measurements.

For charge testing, 15 L of 0.7 wt% stock sample was placed in a 5-gal bucket. Various dosages of alum were added. Then, a 400 mL sample was collected for determination of particle charge demand (PCD) analysis by use of a streaming current detector and an evaluation of system zeta potential (SZP) of the fibers by use of streaming potential testing. A Müttek PCD-03 (BTG Eclépens S.A.; Eclépens, Switzerland) was used to measure the charge demand. The stock sample was passed through a strainer and the filtrate was collected for PCD testing. A Müttek SZP-05 was used to measure the streaming potential. The collected testing stock was directly measured by the testing device. All PCD and SZP data were reported as the average of three measurements.

A paper machine trial was conducted, making virgin coated solid bleached sulfate (SBS) board. The typical machine furnish was a mixture of HW and pine pulp. Target machine pH was 4.5 for the DRS sizing program. The paper machine runs were conducted in a pH range of 4.1–4.4. Alum dosage had less effect on the machine pH because of the practice of controlling the machine pH though the use of sulfuric acid and caustic. Sizing of the final paperboard product was evaluated by

the Hercules size test (HST) using TAPPI Standard Test Method T 530 om-02 “Size test for paper by ink resistance (Hercules-type method).” The test was conducted at room temperature using green dye ink with 10 wt% formic acid.

RESULTS AND DISCUSSION

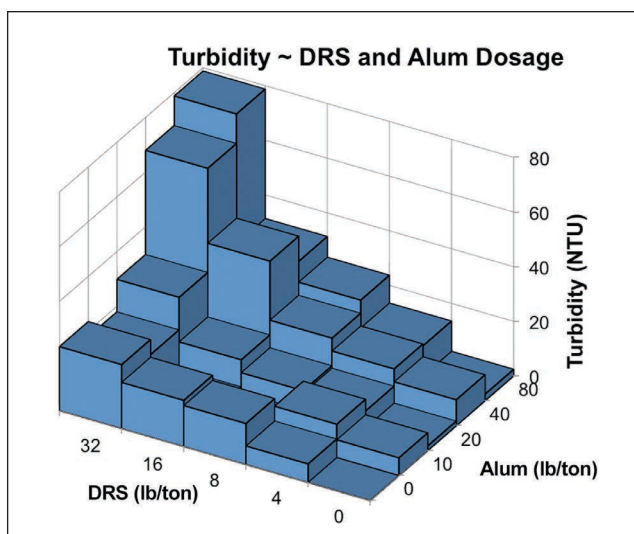
Dispersed rosin size retention was evaluated by measuring the turbidity of the stock filtrate with varying amount of alum and DRS. Briefly, a mixture of stock, DRS, and alum was passed through a strainer to mimic the drainage in the forming section of a paper machine. Turbidity of filtrate (TurbidityFinal) was measured. Turbidity of original, untreated stock with no alum addition (TurbidityStock), before any additives, was also measured as a baseline. The additional DRS in the filtrate was

responsible for the difference in the initial and final turbidity (reported Turbidity = TurbidityFinal - TurbidityStock). High turbidity indicated that more DRS was present in the filtrate, suggesting poor DRS retention.

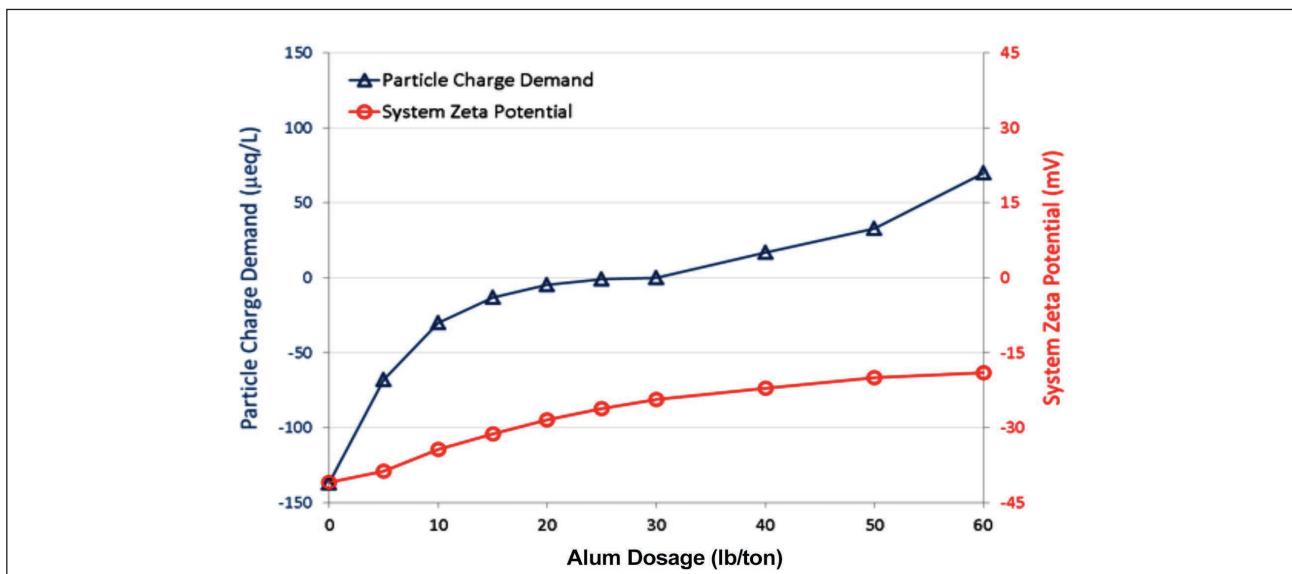
The alum dosage, DRS dosage, and resulting turbidities were reported in **Table II**. The turbidity data were plotted against alum and DRS dosage in **Fig. 2**. Column height indicates the turbidity value, which infers the level of DRS retention. At low alum dosages (0, 10, and 20 lb/ton), columns height increased because increased DRS dosage was not rapid, which indicates that good DRS retention is maintained over a wide range of DRS dosages. However, at high alum dosages (40 and 80 lb/ton), turbidity increased rapidly when high DRS dosages were used. This suggests that excessive alum dosage impairs DRS retention. A critical alum dosage for the tested system was located between 20 and 40 lb/ton, above which DRS retention dropped significantly when its dosage was increased.

A slowly increased column height at a certain alum dosage suggests that DRS retention is not sensitive to its dosage. Sizing results will be expected to maintain a relatively linear relationship with sizing dosage. A consistent sizing efficiency is advantageous for paper machines that change grades often because a single parameter (sizing dosage) can be manipulated to dependably achieve the desired sizing of paper product. Figure 2 also shows that the lowest turbidity with added DRS was not obtained at the lowest alum dosage (0 lb/ton). In this particular example, about 10 lb/ton alum gave the lowest turbidity, which showed that a certain amount of alum actually helped retain sizing, especially at high DRS dosage.

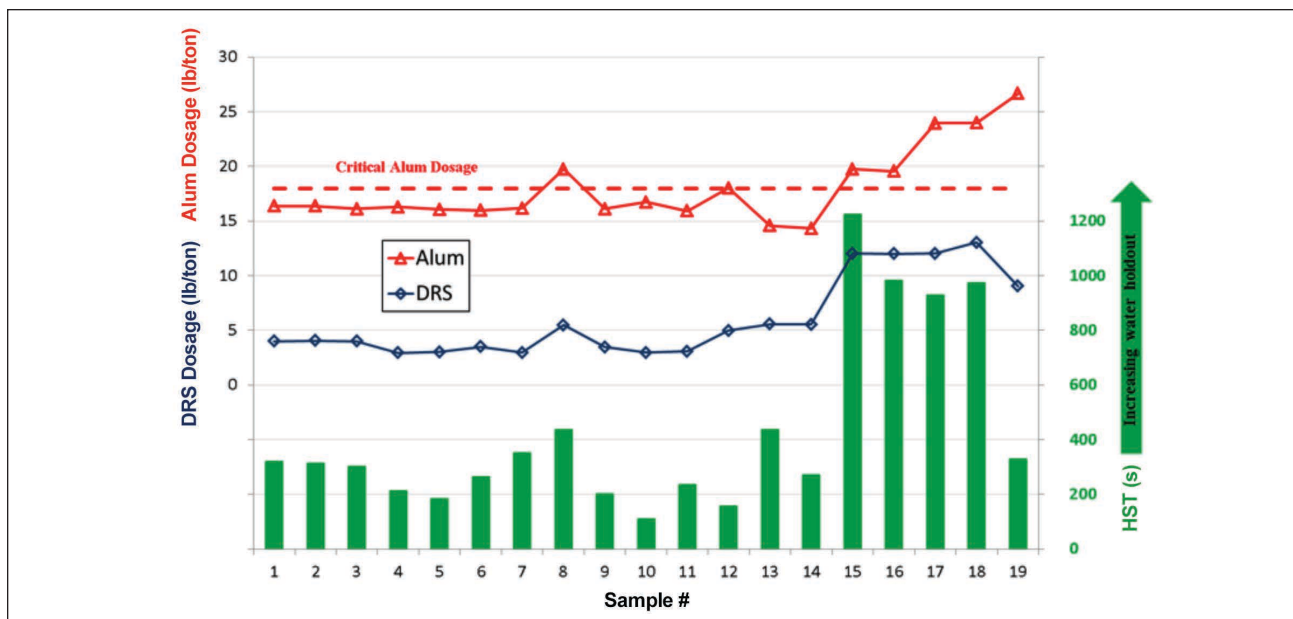
Because no starch or retention aid was used in the experiment to provide the bridging effect for sizing retention, electrostatic interaction was likely the only mechanism to retain DRS. In this case, charge characteristics are important for the



2. Plots of turbidity versus dispersed rosin size (DRS) alum dosage. Point of origin is lower front corner.



3. Plots of charge demand analysis by use of a streaming current detector (PCD) and zeta potential of fibers by use of streaming potential measurements (SZP) versus alum dosage.



4. Plots of alum and dispersed rosin size dosages and Hercules size test values.

DRS retention. Charge demand analysis and streaming potential of testing stock were measured at different alum dosages to better understand sizing retention. The results are shown in **Fig. 3**; PCD data indicate charge demand of the fines and colloidal material and SZP data show the surface charge of fibers. The figure shows that the original stock (both fibers and fines) was negatively charged. When alum was added, negative charge on both fibers and fines was reduced. The pH of the stock during testing was 4.1–4.4. In this pH range, most alum was in the Al^{3+} form [10]. Therefore, it is logical to expect that adding alum will neutralize negative charge on both fibers and fines.

The rate of negative charge reduction was different between fines and fibers. Fiber streaming potential measurements (SZP data) remained negative for all tested alum dosages; however, charge transition from negative to positive was observed on the fines (PCD data) when alum dosage was higher than 25–30 lb/ton. This was probably because fines have a larger relative surface area than fibers to absorb more alum [11]. In addition, a study has shown that such charge differences can also be explained by the mesoporous nature of the cell walls of kraft fibers [12]. The fact that aqueous solution can flow through the cells walls of these fibers means that when steaming potential is used to measure meta potential, it is not just measuring the zeta potential at the fiber surfaces. Rather, the signal is a composite value that is also affected by the interior of the fibers, including very small pores that are less likely to be affected by any wet-end additives such as alum, and the zeta potential may continue to appear negative even if the fiber surface has become positive [12]. In other words, absorbed small aluminum ions may diffuse into mesoporous fibers and not contribute to the fibers' surface charge. When the charge on the fines was flipped to positive, fines would

repel cationic DRS to reduce overall sizing retention. This was consistent with the increased turbidity data at high alum dosage. In Fig. 2, when the alum dosage was higher than 20 lb/ton, the turbidity increased rapidly with increased DRS dosage, suggesting poor sizing retention.

After the laboratory study, a paper machine trial was conducted to validate the effect of alum dosage on DRS sizing efficiency in a manufacturing environment. Data were first collected under normal machine conditions. Blend chest samples (before any additive) were titrated with alum to determine the critical alum dosage. The titration was performed by gradually adding alum into the stock and monitoring charge demand by a streaming current detector. The critical alum dosage was determined to be the amount of alum required to bring the charge demand close to zero. At the time of trial, the critical alum dosage was determined to be 18 lb/ton. Then, both the alum and DRS dosages were varied while other machine parameters were held constant. The HST was conducted on final board samples to evaluate sizing efficiency. The alum dosage, DRS dosage, and corresponding HST values are plotted in **Fig. 4**. The critical alum dosage is marked as a dashed line in Fig. 4.

For samples 1–7, alum dosage was held constant and below the critical value. HST values showed good correlation with the DRS dosage during this period. Then both the DRS and alum dosages were varied but the alum dosage was maintained near or below the critical value (samples 8–14). In this case, HST results were still able to follow the DRS dosage. For samples 15–19, the alum dosage was raised higher than the critical value. On the basis of the previous laboratory study, charge on the fines and particles would be flipped at this alum dosage and result in reduced size retention. The machine data showed that, although high DRS dosage was maintained, a

gradually decreased HST value was obtained. When comparing sample 19 and sample 14, HST results were similar, although DRS dosage for sample 19 was 50% higher than that of sample 14. The machine data confirmed that when the charge of the fines and particles was flipped because of over-dosed alum, sizing efficiency of cationic DRS was reduced. Because the same drying conditions (sizing developing conditions) were maintained, the decline in sizing efficiency was most likely caused by reduced sizing retention.

CONCLUSIONS

Dispersed rosin sizing retention at various alum and sizing dosages was studied using turbidity measurement on stock filtrate. The charge of the stock was characterized through charge demand analysis by use of a streaming current detector and streaming potential measurements. The results suggested that additional alum in a cationic DRS program changed the stock charge to affect sizing retention. The proper amount of alum could maintain high sizing retention within a wider DRS dosage window. However, over-dosed alum flipped the charge of fines and particles to affect sizing retention. Data from a machine trial agreed with observations obtained from the laboratory study. The critical alum dosage was dependent on stock components and would vary in a case by case manner. For a particular furnish at a paper mill, a charge study is essential to guide alum usage to obtain the best results from cationic DRS sizing. **TJ**

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LITERATURE CITED

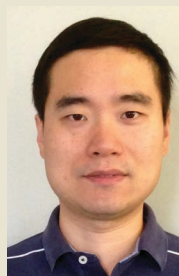
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ABOUT THE AUTHORS

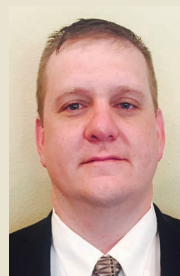
Properly applied, an alum-rosin system under typical industrial conditions can result in reduced operating costs and improved product performance. While the current work is relatively fundamental, it extends the understanding obtained in the laboratory into actual practice on the paper machine.

The most difficult part of this research was running the machine trial. A thorough understanding of the potential operation improvements had to be balanced by potential lost production scenarios on the paper machine. Operating personnel had to be convinced to risk the trial. On the other hand, the laboratory findings rather easily translated into real work application.

This work can help mills make proper use of alum with cationic dispersed rosin size, potentially improving performance and reducing operating costs. As the alum-rosin system is highly pH dependent, repeating the current work at a higher



Xu



Myers



Hart

pH would help extend our fundamental and application-based understanding of the system.

Xu is a research chemist at WestRock Co., Richmond, VA, USA. Myers is a paper machine engineer at WestRock Co., Evadale, TX, USA. Hart is director of Fiber Technology and Innovation, WestRock Co., Atlanta, GA, USA. Email Hart at peter.hart@westrock.com.