

# *Sizing variations of dispersed rosin sizes with fortification, hardness, pH, and temperature*

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**ABSTRACT:** Dispersed rosin sizes have been widely used for several decades, but how well they perform is usually accessed only through experience in using them, by trial and error. Therefore, we studied the performance of four cationic dispersed rosin sizes, varying in pH from 5.0 to 7.0, in temperature from 40°C to 60°C, and in water hardness from 135 ppm to 600 ppm CaCO<sub>3</sub>. Three of the sizes were based on fortified rosin, with concentrations of fumaric acid ranging from low to high levels. The fourth size was based on esterified rosin. Data were analyzed by regression, and two polynomial functions fit well, one for the series of fortified rosin sizes and one for the esterified size. Thus, all the sizing data can be represented by these two equations. Increasing the pH decreased sizing for all sizes, but high fortification resulted in the most rapid decline. The esterified size had a relatively flat response to pH, but the esterified size had a greater decline with increasing temperature.

**Application:** The effectiveness of cationic dispersed rosin sizes varies with process conditions and the modification of the rosin used in the size product.

We have studied formulations of dispersed sizes in our laboratory for many years, although we usually evaluate sizes under only a limited range of conditions. Recently we noticed some unexpected trends while studying new sizes, but we also saw unexpected trends for well-established products. These observations led us to a study of the effects of fundamental parameters on sizing. Specifically, we studied the effects of pH, water hardness, and temperature on cationic dispersed rosin sizes, using hand-

sheets made from the same pulp. We chose cationic products because they are popular and are the most versatile type of dispersed rosin size in use today.

## **EXPERIMENTAL**

Handsheets were made with a 60:40 mixture of bleached hardwood and softwood kraft pulp. The pulp was beaten with a Valley beater according to TAPPI T 200 to approximately 330 mL CSE. The basis weight was 100 g/m<sup>2</sup>.

To make the handsheets, we started with pulp at 1% consistency. Under vigorous stirring, dilute NaOH was quickly added to adjust the pH. At 1.5 min after stirring commenced, size and alum were added simultaneously. One minute later, the sheet was formed. Sheets were pressed at 414 kPa for 1 min and were dried on a laboratory drum drier for 2 min at 110–120°C. Sizing was evaluated with a Hercules Sizing Tester (HST), using No. 2 ink, 1% formic acid ink, at 80% reflectance, according to TAPPI T 530.

Sizing response curves were generated for each of four different sizes at pH values of 5, 6, and 7 and at temperatures of 40°C, 50°C, and 60°C. We used three dosage levels to keep the number of handsheets manageable: 0.35% (7 lb/ton), 0.50% (10 lb/ton), and 0.65% (13 lb/ton).

Three levels of hardness were used in our tests: 135 ppm, 270 ppm, and 600 ppm  $\text{CaCO}_3$ . We studied hardness by adjusting the naturally soft water from the city water lines in Pensacola, FL, to 20 ppm equivalent  $\text{CaCO}_3$ .  $\text{CaCl}_2$  was used for the adjustment, but hardness was calculated as ppm  $\text{CaCO}_3$ .

## DISCUSSION

We concentrated on four dispersed tall oil rosin sizes, all cationic. Three of these were fortified rosin, with fumaric acid being the fortifier. Fortified sizes differ in the amount of fumaric acid used and can be classified as having low, medium, or high fortification, with the ratios of fumaric acid to rosin ranging from 3% to 15%. Cationic dispersed sizes were selected for study because they are known to be efficient over a wide range of pH. The fourth size studied is based on an esterified rosin. This size was included because we expected its sizing to be robust at higher pH values [1, 2].

A generalized response curve for rosin sizes, adapted from Keavney and Kulick [3] is depicted in Fig. 1. The curve has an overall sigmoid shape. Almost no sizing is attained until a threshold value of size is added, and the curve thereafter is convex with respect to the  $x$  axis, ending asymptotically.

If cationic resins are added with dispersed rosin sizes, sizing can be achieved at high pH values, as has been known for a long time [4]. Some years after this discovery, it was found that cationic resins can be used to emulsify rosin results and that such cationic dispersed rosin sizes are also effective at high pH levels [5]. The study of cationic rosin sizes is still an active field, as evidenced by many recent investigations [6].

The effects of hardness have been discussed in early works [3], but such comments may not apply to cationic dispersed rosin sizes, a relatively newer type of size. In addition, in our experience, cationic rosin sizes are very toler-

ant of hard water with regard to emulsion properties, whereas anionic dispersed rosin sizes are intolerant.

In making general comments on the effect of fortification, Watkins states that fortified size usually gives more efficient sizing in bleached pulp, but the higher the pH, the less advantageous is the use of fortified size [7]. In our results, higher pH values led to severe declines with higher fortification.

## DATA ANALYSIS

The experimental data were divided into two subsets. The dosage of size, the temperature, pH, and hardness were independent variables, and the HST time was the dependent variable in both subsets. In the first subset, the percent fortification was considered an additional fifth independent variable. The second subset consisted of data pertaining to esterified rosin only, and there were only the four independent variables.

Multivariate linear regression was performed using the software packages Microsoft Excel and Mathcad 2000 Professional. The results in both cases were identical in that both programs gave the same coefficients  $c_i$  for the following fit to the data:

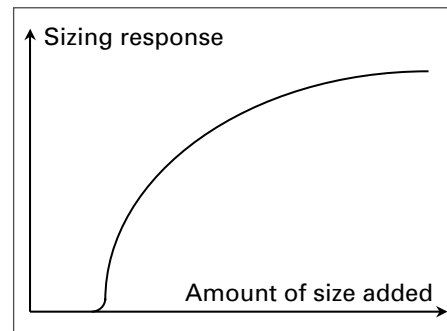
$$f_{\text{linear}}(x_1, x_2, x_3, x_4, x_5) = c_0 + c_1x_1 + c_2x_2 + c_3x_3 + c_4x_4 + c_5x_5 \quad (1)$$

where  $f_{\text{linear}}$  is the function that fits the experimental data, and

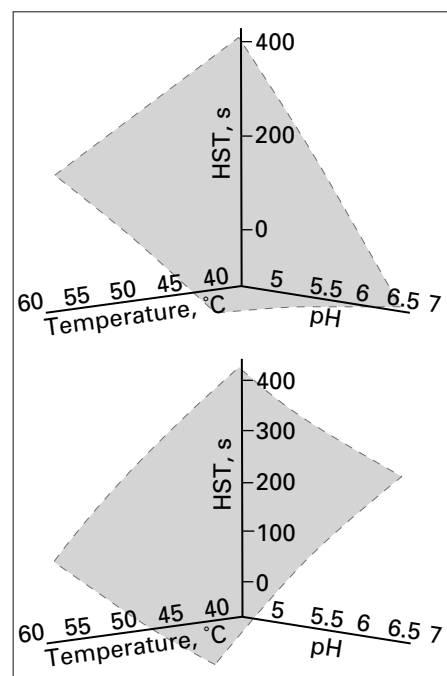
- $x_1$  = temperature, °C
- $x_2$  = dosage, %
- $x_3$  = pH
- $x_4$  = hardness, ppm
- $x_5$  = percent fortification, % (used when applicable).

Multivariate polynomial regression was performed with Mathcad only. In this case, the coefficients  $c_i$  are desired for a second-order polynomial fit to the data:

$$f_{\text{2nd order}}(x_1, x_2, x_3, x_4, x_5) = c_0 + (c_1x_1 + c_2x_2 + c_3x_3 + c_4x_4 + c_5x_5) + (c_6x_1^2 + c_7x_2^2 + c_8x_3^2 + c_9x_4^2 + c_{10}x_5^2) + (c_{11}x_1x_2 + c_{12}x_1x_3 + c_{13}x_1x_4 + c_{14}x_1x_5) + (c_{15}x_2x_3 + c_{16}x_2x_4 + c_{17}x_2x_5) + (c_{18}x_3x_4 + c_{19}x_3x_5 + c_{20}x_4x_5) \quad (2)$$



1. Generalized sizing response curve for rosin sizes, showing its overall sigmoid shape.



2. Effect of pH and temperature on sizing for medium fortification (upper graph) and esterified resin (lower graph).

The residual  $r$  is a measure of the goodness of the fit and is defined as

$$r = \frac{1}{n} \sum_{j=1}^n (f_{\text{linear},j} - \text{data}_j)^2 \quad (3)$$

where  $n$  is the total number of data points and  $f_{\text{linear},j}$  is the fit to the  $j$ th data point  $\text{data}_j$ . The lower the value of  $r$ , the better the fit. For both data subsets, the residual obtained for the second-order function is less than half of the residual for the linear function, indicating that the second-order equation provides a better fit to the data, as expected.

|                     | FORTIFIED | ESTERIFIED |
|---------------------|-----------|------------|
| <b>Coefficients</b> |           |            |
| $c_0$               | 1487.732  | 1147.632   |
| $c_1$               | -5.67833  | -16.6348   |
| $c_2$               | 842.2058  | 764.5556   |
| $c_3$               | -200.32   | -78.8889   |
| $c_4$               | -0.11693  | 0.009059   |
| $c_5$               | -13.7558  | ...        |
| <b>Residuals</b>    |           |            |
| $r$                 | 14,550    | 4247       |

**I. Coefficients for multivariate linear regression for fortified and esterified rosin sizes.**

|                     | FORTIFIED               | ESTERIFIED              |
|---------------------|-------------------------|-------------------------|
| <b>Coefficients</b> |                         |                         |
| $c_0$               | 1952                    | -11.254                 |
| $c_1$               | -41.279                 | 20.826                  |
| $c_2$               | 3480                    | 2441                    |
| $c_3$               | -298.483                | -125.721                |
| $c_4$               | -0.869                  | -0.493                  |
| $c_5$               | 38.923                  | ...                     |
| $c_6$               | -0.03791                | -0.21422                |
| $c_7$               | 477.531                 | 1028                    |
| $c_8$               | -8.235                  | 9.389                   |
| $c_9$               | $1.017 \times 10^{-3}$  | $8.948 \times 10^{-4}$  |
| $c_{10}$            | -2.972                  | ...                     |
| $c_{11}$            | -5.459                  | -33.600                 |
| $c_{12}$            | 7.029                   | 0.384                   |
| $c_{13}$            | $-2.917 \times 10^{-3}$ | $-4.607 \times 10^{-3}$ |
| $c_{14}$            | 0.101                   | ...                     |
| $c_{15}$            | -386.586                | -173.315                |
| $c_{16}$            | -0.343                  | 0.04729                 |
| $c_{17}$            | -44.876                 | ...                     |
| $c_{18}$            | 0.04212                 | $4.820 \times 10^{-3}$  |
| $c_{19}$            | 2.714                   | ...                     |
| $c_{20}$            | $4.824 \times 10^{-3}$  | ...                     |
| <b>Residuals</b>    |                         |                         |
| $r$                 | 6815                    | 2182                    |

**II. Coefficients for multivariate polynomial regression for fortified and esterified rosin sizes.**

Figure 2 presents plots of the second-order polynomial fit equation, showing, as an example, the effect of temperature and pH on sizing. The positive effect on sizing of simultaneously increasing pH and temperature is clearly seen in the top graph. Temperature and pH act individually to decrease sizing efficiency, since the coefficients  $c_1$  and  $c_3$  are negative in both fitting equations. However, since the coefficient  $c_{12}$  in the 2nd order polynomial fit is positive, there appears to be a synergistic effect between these

two variables. That is, a simultaneous increase in the value of  $x_1$  and  $x_3$  will yield a larger value of the term  $c_{12}x_1x_3$ , contributing to longer HST times. Sizing decreases with increasing pH due to saponification of rosin and also due to its effect upon alum [8].

The coefficients for the regression of HST data and the corresponding residuals are presented in Tables I and II.

## INTERPRETATION OF RESULTS

Some trends exhibited by the data are well known. For example, sizing increases strongly with dosage and generally decreases with increasing pH and with increasing temperature. However, there are also some other notable trends. Sizing by the esterified size is maintained well as pH is raised, but only at the lower temperature. This relative flatness of sizing vs. pH is similar to the findings of Ito [2] and is ascribed to the stability of the size emulsion particles in near-alkaline conditions. However, the rosin ester product drops off strongly in sizing effectiveness as temperature is increased, and this effect is more pronounced as pH increases. These trends can be seen in Fig. 2.

The fortified sizes decrease strongly in sizing effectiveness as pH is raised. At the higher temperatures, however, there is an unexpected increase with temperature, although the increase is small. As a partial explanation, there are three phenomena involved that are rate dependent, where the rates increase with temperature. These three are the interaction of the size with alum, the saponification of the carboxylic acid groups, and changes in the aluminum species.

An interesting trend is the decrease in sizing with increasing levels of fortification. Results show that fortification has little effect on sizing at low pH, but as the pH is raised, high fortification becomes detrimental. This outcome is at least partly due to saponification of the carboxylic acid groups that begins at about pH 6.

Consider the results displayed in Fig. 3. All curves are for 50°C and a hardness of 270 ppm. Along the  $x$  axis, the pH varies from 5 to 7, and the percent fortification on the  $y$  axis varies from 0% to 15%. The vertical  $z$  axis is the HST value in seconds. At low dosage and high fortification (left curve), the HST value drops

from about 150 s to almost 0 s. At medium dosage and high fortification (middle curve), the HST drops from approximately 300 s to 0 s. At high dosage and high fortification (right curve), the HST drops from about 450 s to 0 s. Thus, if the size dosage is increased, the drop-off in HST value at high pH is greater for fortification at a higher percent.

## LIMITATION ON APPLICATION OF RESULTS

The sizes tested are similar to the NeuRoz family of rosin size dispersions. Because of the limited scope of this study, other aspects of sizing performance were not measured. For example, high fortification was seen to be detrimental to sizing as measured by the HST at high pH. However, high fortification is usually useful for achieving good boiling boat tests. TAPPI T 819 is similar to the way some paper mills conduct the boiling boat test except that the water temperature is near boiling.

## CONCLUSIONS

Sizing results versus pH, fortification level, water hardness, temperature, and size dosage can be represented well by a second-order polynomial function. Sizing data for the esterified size are represented by a separate polynomial. The results show sizing decreasing with increasing pH, but the effect is particularly severe for the size with the highest fortification. Esterification ameliorates the decline with pH but accentuates the decreases with temperature. The combination of higher hardness and higher temperature resulted in small increases in sizing for low and moderate levels of fortification.

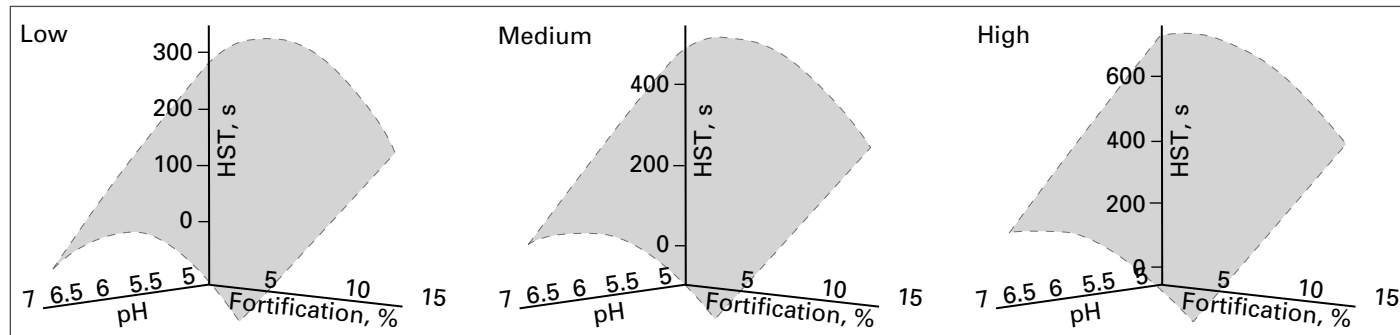
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## INSIGHTS FROM THE AUTHORS

At Plasmine Technology, we perform handsheet studies all the time, but they have always been limited in scope. In this study, we carried out a comprehensive, systematic study of many variables at one time. Many researchers have done sizing studies before, but to the best of our knowledge, this work represents the first time sizing can be predicted over a range of process variables with a mathematical expression.

Some aspects of this work were difficult. The sheer magnitude of the handsheet work was overwhelming. Fortunately we had two dedicated laboratory workers who labored for months to collect the data. Another difficult part of the study was the assessment of the relative importance of the variables, which was not easy because the units of measure for the variables are not related.

That a mathematical expression could be used to summarize the volume of sizing information collected was gratifying to us as researchers. If process engineers can use a mathematical equation to predict sizing behavior, they can consider more closely how changes in conditions on the paper machine may affect sizing.

Our results showed several interesting physical phenomena. The esterified size performs very well as pH is raised, but only if the temperature is low. As both pH and temperature are raised, performance drops off dramatically. By contrast, fortified sizes can perform better at a higher pH as the temperature is raised, a real surprise. The effect of rosin fortification is more influential as pH increases.

We intend to use the knowledge gained to help develop better sizing products for high pH values and high operating temperatures. The effect of water hardness is complicated and may be worthy of a study all by itself.

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