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SIZING WITH ROSIN SIZES

AE Pais, Regional Manager
Hercules, Incorporated 101, Thomson Road,
05-01, United Square,
Singapore 1130

Abstract

The chemistry and application of soap and dispersed sizes in papermaking is discussed. Rosin-based sizing agents have been developed that function efficiently over the pH range of 4.0-6.5, thus enabling the papermaker to achieve the benefits of near-neutral papermaking. Because a large number of chemical and physical variables affect sizing performance, good process control is essential to minimize qulity variability.

Introduction

Sizing of paper and paperboard is carried out to control the rate of penetration of liquid into the sheet. The liquid penetrant most often controlled is water. Occasionally it is desirable to control penetration of other liquids such as oils, alcohols, acids or alkalies. Rosin sizing will only give resistance to aqueous penetrants.

Sizing can be accomplished through internal and/or surface addition of chemical additives. Rosin sizes are used almost exclusively as internal sizing agents.

Internal sizing agents are used to control both end use properties of the paper and the pick-up of chemicals applied to the surface of the sheet at the size press or calendar stack. Internal sizing has the advantage of developing water repellency throughout the entire sheet.

Types of Rosin size

Since rosin itself is water insoluble, it is first necessary to convert the rosin to a form that is dispersible in the aqueous papermaking system

Two major methods exist to ensure rosin dispersibility.

1. saponify the rosin with alkali to an alkaline salt resulting in a rosin salt. Soap Sizes
2. disperse or emulsify the rosin as a finely divided particle of submicron dimension in an aqueous medium. (dispersed size).

In determining what type of rosin based sizing agent to use, the key considerations are:-

* optimum operating pH of the papermachine.
* cost efficiency of the sizing agent.
* handling

Before discussing the advantages and disadvantages of each type of size with respect to the above consideration, we will briefly review how these sizes work.

There are four major steps in any internal sizing process (1):

1. Size retention
2. Uniform distribution
3. Proper orientation of the hydrophobic group.
4. Anchoring of the sizing particle to the fiber.

Reaction of rosin with alum to form an aluminium resinate is a critical step in successfully carrying out the internal sizing process. The chemistry of sizing development is essentially the same for both types of rosin size, but the mechanism of sizing is somewhat different for the two forms.

Mechanism of sizing

Soap Sizes

Soluble soap sizes or resinate ions are reacted with soluble aluminium ions to form a positively charged, insoluble size precipitate. The size precipitate is retained on the negatively charged cellulose fiber by electrostatic attraction.

Rosin soap sizing systems are most efficient in the pH range of 4.2-4.6, where Al^{+3} is thedominantaluminium species and there is little absorption of alum by the pulp fibers (2).

Drying the wet paper at elevated temperatures enhances the distribution of the precipitate and properly orients it to provide a low energy hydrophobic surface. Cross-linking of aluminium resinates by a process known as olation may further anchor the size precipitate.

Dispersed sizes

In dispersed rosin size systems, the size is added to the slurry in the form of discrete, submicron particles consisting predominantly of free resin acids. The particles are retained in the sheet in this form. In the dryer section the free resin acid particles spread over the fiber surfaces. Sizing is effected by the reaction of free resin acids with aluminium species adsorbed on the fibers.

The retention of dispersed size particles is by a combination of factors, including electrostatic attraction, bridging with hydroxy alumina polymer or cationic retention aid. Optimum retention of dispersed size particles occurs with optimum first-pass retention on the paper machine. This usually occurs at pH 4.6-5.0, the pH of maximum formation of hydroxy alumina polymer.

The free resin acids in dispersed size have a much lower sintering temperature than does the aluminium resinate precipitate of soap size. Therefore, distribution of dispersed size particles during drying is easier and more uniform and this is thought to account for the enhanced efficiency over that of soap sizes.

While the free resin acids in dispersed sizes are uniformly distributed over the fiber, reaction with alum is necessary to anchor the resin acids in the proper orientation. Marton and Marton [5+4] concluded that dispersed rosin sizes react primarily with aluminium species adsorbed on the fiber surfaces.

Arnson([5],[6]) and Crow([7]) showed there is little adsorption of aluminium ions on cellulose fibers below pH 4.5. Arnson found the adsorption of aluminium on cellulose fibers to increase at the pH at which the soluble polynuclear species A18 (OH)10 (SO4)5 $^{+5}$, forms. Crow observed the increase in aluminium adsorption to coincide with the pH of precipitation.

Thus, the optimum pH range for anionic dispersed sizes is above pH 4.6 and occurs usually at the point of maximum first pass retention between 4.6-5.0. Although dispersed size can be effective up to a 6.0 pH with proper retention system and pH control.

To summarize, soap sizes work best at low pH between 4.2 and 4.5, whereas the dispersed sizes function best at higher pH levels, between 4.6-5.0.

Choosing the sizing agent

Earlier, it was mentioned that there are three key considerations in choosing a sizing agent.

Paper Machine PH

For most of the history of sizing and papermaking, it was necessary for the papermaker to control his papermachine at the pH which allowed him to size with soap sizes. With the development of dispersed sizes that can function up to near-neutral pH, the papermaker now has the flexibility to run the machine at the pH level that gives maximum productivity or optimum finished product properties. The significant advantages to running a paper machine at pH levels higher than 4.5 are:

Lower Cost Better Productivity

-- less alum

-- less corrosion

-- greater degree of whitewater closure from less sulfate ion buildup.

-- better retention, cleaner machine, less felt filling, fewer deposits.

-- improved strength, fewer wet-end breaks

-- easier drying, less energy

-- better drainage.

Improved quality.

-- better sheet strength, less interference from alum in fiber-to-fiber bonding.

-- less acidic degradation.

-- more permanent sheet.

Dispersed size efficiency is affected by the emulsion system and several physical properties.

Dispersed sizes are generally more efficient than soap sizes. On a dry basis, dispersed sizes are approximately twice as efficient as fortified soap sizes and three times as efficient as mill-made soap sizes (except in systems or grades where sizes requirements are low, i.e., less than 3 lbs/ton).

The primary reason for better cost efficiency of dispersed size is the lower melting point of the high free resin acid particle resulting in easier and better distribution of the size over the fiber.

In addition, substantially lower alum requirements help reduce costs.

Handling

Next to filler and fiber, sizing agent costs can be one of the most expensive ingredients added to the papermaking process. There are shipping costs, labour costs associated with loading and unloading, cooking and storage costs. Most important is the ability to get the product to the machine in a usable form with a high degree of control. Variability in soap size make-up and addition rate means variability in finished product properties, as well as variability in sizing cost.

Soap sizes are alkaline in nature, non-corrosive and can be stored in carbon steel storage tanks. However, tile or stainless steel is recommended due to eventual iron scale formation in the vapour space of a mild steel tank. All soap sizes of similar type are usually compatible with each other.

Dispersed sizes. Dispersed sizes are usually sold as 30-50% solids, liquid emulsions. Since they are approximately three times as efficient as mill-made sizes, on a dry pound basis, there is usually no change in freight costs. Dispersed sizeds can be shipped by the manufacturer in tank trucks, tank cars, and drums. The product should be protected from freezing during transit. Dispersed sizes are stored at room temperature and heating is never recommended or required.

Dispersed sizes are mildly acidic, therefore, stainless steel, tile, plastic, or epoxy-lined tanks and equipment are recommended.

Dispersed sizes can be metered in the dilute or in concentrated form. Some, but not all, dispersed sizes require low hardness, low-alkalinity water to produce a stable dilute dispersion. Because of different manufacturing processes all dispersed sizes are not necessarily compatible with one another.

Application considerations

Wet End

Soap sizes are usually added in dilute form to pulp that has been adjusted to pH 7.0-7.5. The dilute size may be added batchwise at the beater or pulper, or continuously to the pulp at the machine chest or stuffbox. Alum is added after the size to a final headbox pH of about 4.2-4.5. A minimum of 1% alum, based on fiber, is recommended.

Under some adverse sizing conditions, such as high hardness, alkalinity, or interfering ions in the stock, it is preferable to add the alum first to ensure the rosin size reacts with alum rather than with hardness or other interfering ions. This is known as reversed sizing procedure. Total acidity is an ideal control test to ensure alum is not over used. Alum tends to buffer at pH levels not significantly less than 4.0 and it becomes very easy to end up with high levels of acidity without much change in pH. This can result in paper-strentgh deterioration, poor sizing, and paper machine deposits and Dispersed sizes are usually added at the same point (simultaneous addition) as alum or after (reverse addition) the alum. the machine chest outlet, stuffbox, or fan pump are ideal points of addition. A minimum alum level of 0.75% is usually recommended in conjunction with headbox pH of 4.6-5.2 for dispersed sizes.

A suitable cationic retention aid is usually required in printing and writing paper production with all rosin sizes due to filler content.

Factors affecting sizing

High stock temperature and long hold times, adversely affects sizing efficiency. For this reason it is beneficial to continuously add the sizing agent, close to the machine. the type of pulp furnish affects the degree of size receptivity. The amount and type of filler affect efficiency. filler contributes significant surface area to the system. Different types of fillers have different surface areas.

Retention probably has the most significant impact on sizing efficiency and machine performance of any of the wet-end variables. Poor retention causes foam, felt filling, foil and wire deposits, wet-end breaks, and holes, and poor sizing. Poor internal sizing affects size press pickup and drying.

Moderate levels of refining may improve sizing efficiency because of improvements in the formation of the final sheet. High levels of refining reduce sizing because of the increased hydrated surface area of the fiber that must be covered with sizing material.

Other additives at the wet-end such as defoamers, slimicides, surfactants, wetting agents, dyes, optical brighteners, etc., may have a negative effect on sizing efficiency depending on quantity, point of addition and ionic charge.

Starches, wet-strength chemicals, retention aids, or other additives that improve first pass retention will generally improve rosin sizing efficiency.

Increased wet pressing generally improves sizing especially at low levels of sizing. Drying temperature affects the degree of mobility or migration of the sizing agent after the sintering temperature has been reached. Not only does the amount of internal size affect the amount of size press pick-up, especially on slower machines, the size press pickup and formulation in turn affect the degree of sizing of the finished sheet. Calendering may have a beneficial or negative impact on sizing.

Measuring sizing

Finally, the degree of sizing attained is that amount of resistance to wetting, penetration or adsorption imparted to the paper or paperboard as measured by a sizing test. Over the years, many size tests have been developed. There is no one universal sizing test. The only meaningful one is the one that tells you whether your product will meet your customers' end use requirements. All mill control sizing test should also:-

* be senistive to changes in sizing level.
* be reproducible from tester to tester.
* have short test times.
* be usable on a wide range of basis weights.

Summary

Rosin based sizes are available as soap sizes, or high free-resin, acid-dispersed sizes. The development of dispersed sizes has extended the pH range to 4.0-6.0 in which efficient sizing with rosin can be achieved. A review of the advantages and disadvantages of each type with respect to machine operating pH, cost effectiveness, and handling, generally indicate significant benefits when the lower melting point dispersed sizes are used.

The major chemical and physical factors impacting rosin sizing efficiency affect soap sizes and dispersed sizes similarly. However, the impact of the sizing agent type on machine performance is not the same. The use of reduced quantities of size and alum in the wet-end results in a stronger sheet, a cleaner machine, and better productivity.

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