Diagnostic sizing-loss problem solving in alkaline systems

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Interaction of precipitated calcium carbonate, size-press starch, and paper additives with alkyl ketene dimer can have devastating effects on sizing. Now we understand their causes and can implement solutions.

For successful operation of an alkaline papermaking system, all components must function harmoniously. It is a delicately balanced system requiring proper chemical selection and control. The experience of several years of alkaline conversions has provided the knowledge to accomplish this goal.

Among the properties desired is uniform, permanent sizing. The mechanism for attaining this has been aptly described in numerous papers and presentations (*1-7*) as retention, distribution, orientation, and anchoring of the size. For alkyl ketene dimer (AKD), the initial concern has been the retention and anchoring (reaction) in the sheet. However, during sizing problem studies, it has been determined frequently that the AKD is retained and reacted (*8*), but sizing is not developed or was developed only to be lost over time.

Studies were initiated to more fully understand these phenomena. We found that the interaction of precipitated calcium carbonate (PCC), size-press starch, and additives and contaminants with the AKD can have a devastating effect on sizing. By working in close partnership with the papermaker, we have developed a working understanding of these interactions.

Additives and contaminants

Additives and contaminants that have a negative impact on sizing are generally surface-active agents. This category includes defoamers, softening agents, surfactants, deinking additives, and lubricating oils. Internal addition of these compounds at the wet end or in the pulp mill will have a negative effect on the process. If placed directly on the surface of the paper at the size press or calender stack, even minute amounts can be devastating.

The most severe effect noted to date has been from glycols, modified glycols, and polyalkyloxylated phenols or alcohols. The typical source is defoamers. A defoamer placed on the paper surface at 50 ppm and having only a few percent glycol can reduce sizing more than 50%, as shown in **Fig. 1**. The typical defoamer level in a size-press starch is 10-100 ppm. Thus, not surprisingly, the effect shown in this lab dipping test has been seen on numerous paper machines. Removal of the defoamer from the system dramatically increases sizing.

In this particular study, the pulp mill defoamers and the recommended substitute size-press defoamer showed no impact on sizing when applied at 50 ppm. However, all the defoamers reduced sizing more than 95% when applied at 500 ppm, as shown in **Fig. 2**. Thus, even acceptable formulations should be used judiciously at all times. **Table I** details defoamer components and order of preference for use in a sized paper grade.

Two other sources of highly oxygenated compounds are worthy of mention. First is the introduction of tissue broke into a sized grade. Tissue typically contains softening agents such as propylene glycol. The result is 100% sizing loss, even at low levels. For mills making both grades, the pulp and water sources must be isolated. The second source is deinking surfactants. As recycled grades become more prevalent, this will emerge as a critical issue. The carry-over of surfactant in the pulp can easily reach 0.1%. At this level, a fatty-acid soap reduces sizing 10-15%, while a polyalkene oxide reduces it 40-50%. This effect should be considered when establishing a deinking system.

The machine water should also be checked for effect on sizing. Organic contamination from press shower dispersants, lube oils, defoamers, etc. can be determined by surface tension measurement. A second concern is the ionic content of the water as measured by conductivity. High ionic content slows the rate of sizing development with the fiber. This reduces the on-machine sizing but does not affect natural aged sizing. If the ionic content is sufficiently high, no on-machine sizing will be obtained. The machine will have poor runnability because breaks will occur continuously at the size press.

This problem occurred at a mill having 0.12% salt concentration and a conductivity of 2300 microohms. The primary ions were profiled as shown in **Table II**. A lab former study showed that all ions, including NaCl, slowed sizing development when present at high levels. The 0.25% level was used on the slow, small lab former because it better simulated the mill experience. The results were similar at pH 7.8 and 9.0, as demonstrated in **Figs. 3 and**

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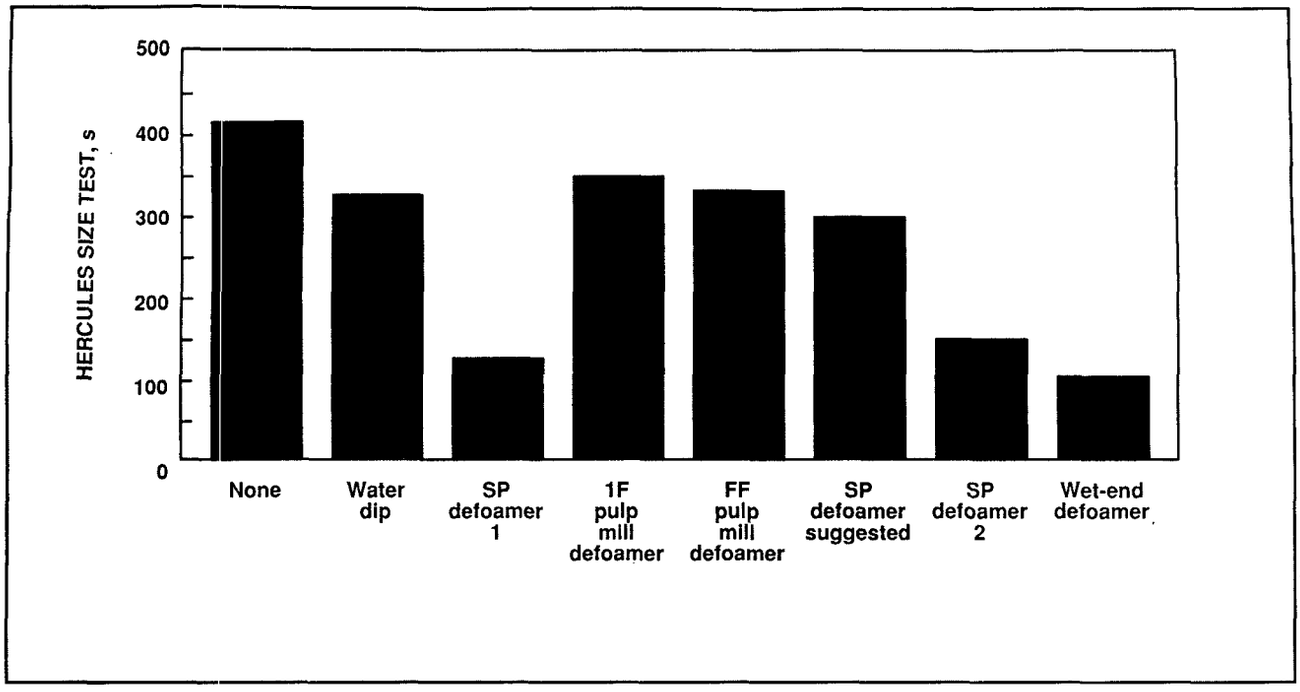
1. Additive effect on sizing at 0.005% concentration



4. The effect can be at least partially offset by using the proper cationic resin system. Two of the systems tested are profiled in **Figs. 5 and 6**. While both resin systems generally improved on-machine sizing, Resin B was significantly more effective.

Precipitated calcium carbonate

Obtaining permanent AKD sizing requires that the dimer react with the cellulose fiber. The portion of the dimer that coats the carbonate gives only a temporary sizing effect. The AKD attaches to the surface of the carbonate with the hydrophobic tails properly oriented. The link may be the formation of a beta keto salt with calcium, but this has not been proven. Regardless of the mechanism, the link will break with time. The dimer is converted to the distearone hydrolyzate. Since this form does not contribute significantly to the hydrophobicity of the paper, sizing drops. The conversion to distearone can be accelerated by moisture and heat. An effective quick test for differentiating permanent sizing from temporary sizing is to dip the paper in water and oven dry the sheet.

The comparison of the water dip to natural aged values shown in **Table III** demonstrates the reliability of this procedure as a predictive test. This table also indicates two of the mechanisms for reducing PCC-AKD interaction. Addition of the PCC to the thin stock well after the AKD addition to the thick stock at the stuff box allowed the AKD to more effectively associate with the fibers. Then, addition of cationic resin helped fix the dimer to the fiber, preventing migration to the carbonate. For this system to be effective, sufficient time between AKD and PCC addition points is needed for dimer distribution and attachment to occur. Conversely, adding the PCC to the pulper or blend chest has been effective in some systems. The carbonate adsorbs anionic trash onto its surface, limiting its ability to attract and react with the dimer. A small loss in opacity and brightness occurs with this method.

Even when a well functioning system is established, intermittent problems can occur. Generally, any condition that causes over-flocculation of the carbonate also increases the size interaction and subsequent reversion. Three reasons for this occurrence have been identified to date:

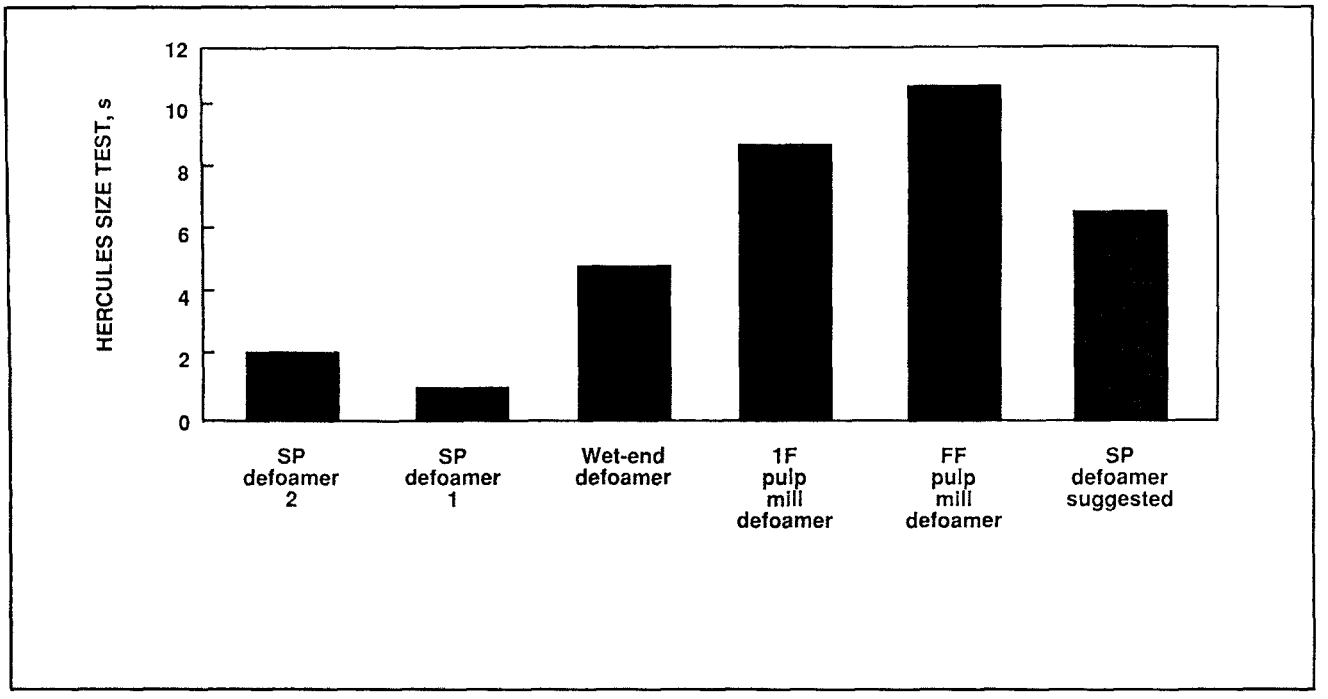
1. Contamination of PCC with grit of an inorganic nature
2. Insufficient laminar flow in the carbonate addition line
3. Use of chilled water (northern river) for PCC dilution.

Starch

Addition of starch to the paper surface should enhance sizing by closing up the sheet. However, we have experienced cases in which the starch caused permanent reduction of sizing by 50-100% in alkaline systems. This had not occurred when the mill was using rosin sizing. Thus, the mechanism is more complex than starch penetration into the sheet.

One hypothesis of the mechanism for sizing loss requires an understanding of starch composition. The sizing loss has been documented with corn and wheat starches. It does not occur with waxy maize, even under the same cooking conditions. The difference between these starches is the amylose content. Corn and wheat have 25-30% amylose fraction, while waxy maize typically has 0-5%. Amylose is the unbranched to slightly branched fraction of the starch. When amylose fragments are broken from the starch matrix, they first exist as random coils. However, they have the ability to coil into a helical structure. This helix can coil around molecules with hydrophilic end groups attached to long, straight-chain hydrocarbons.

2. Additive effect on sizing at 0.05% concentration



I. Defoamer components

Preferred
Silica
Silica oils
EBS
Most nitrogen components
Wax
Acceptable
Hydrocarbon oils
Modified hydrocarbon oil
Fatty acids/esters/alcohols
Avoid
Glycols
Modified glycols
Polyalkylated phenols or alcohols
High oxygenated acids/esters

II. Water ionic content

Low	*Synthetic KLF water, ppm*	*Machine water, ppm*
Calcium	40	180
Sodium	23	300
Chloride	40	170
Sulfate	44	100

Molecules such as fatty acids and alcohols are included in this class.

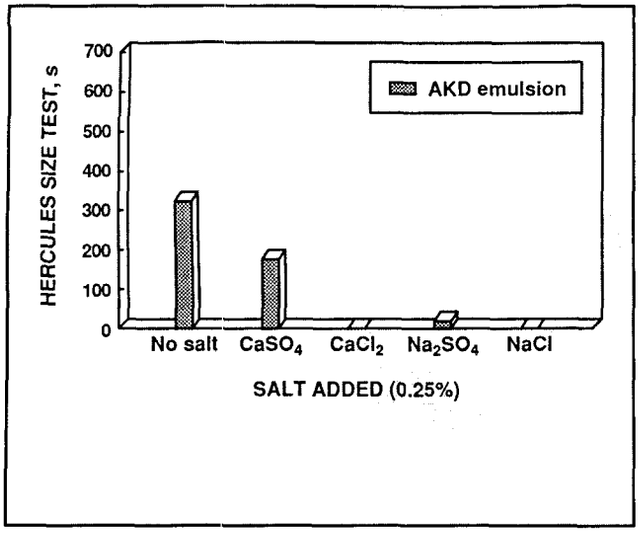
Extensive studies have been made of this interaction. The inclusion of the organic molecule is known as a clathrate. The complex is made by the cage structure enclosing the organic molecules, with weak adhesive bonds holding it in place (*9, 10*). The occurrence is more frequent in the solid phase rather than in solution, but it can occur in either (*10-12*). The diameter of the coil is 4-10 A, which limits the interaction to linear molecules.

The alkyl ketene dimer molecule is two linear hydrophobic tails joined by the di-ketene group. It is in a solid paper matrix, making the interaction more probable. It is not possible to directly prove that a clathrate between cycloamylose and AKD is formed in the sheet, but indirect evidence leads us to this supposition.

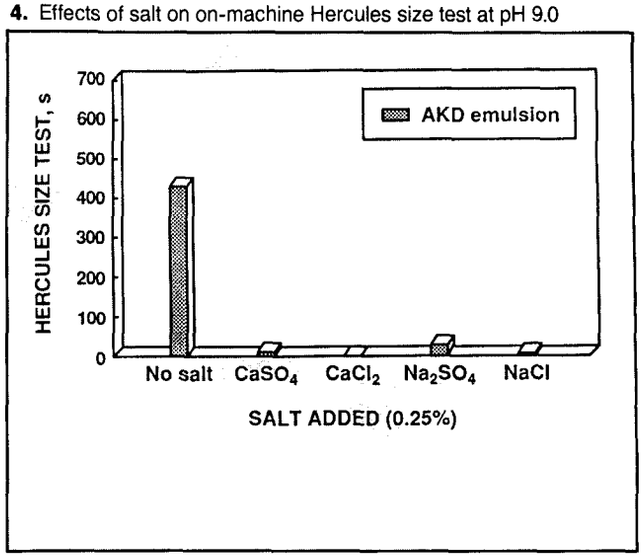
A measurement of the cycloamylose (fragmented amylose) content has been developed using an iodine spectrophotometric method (*13, 14*). Correlation of this measurement with AKD-starch sizing loss has been made. No problems are experienced when cycloamylose content measures 0-4%, 5-8% shows significant sizing loss, and more than 8% essentially loses all sizing permanently.

Solutions to the problem have been based on assumptions that the theory is correct. Mill results have shown the solutions to work. The use of waxy maize with its low amylose content or quaternized starch, which inhibits tight coiling of the amylose, eliminates the problem. Ethoxylated starch reduces but does not eliminate the effect. Presumably, its smaller side group is less effective than the quaternary at blocking the coiling mechanism. Addition of calcium stearate to the starch gives it an alternative molecule to coil around. The amount of addition must be controlled to a level that will not cause slip problems. Controlling or changing the cooking procedure pH, temperature, and additive level to prevent significant

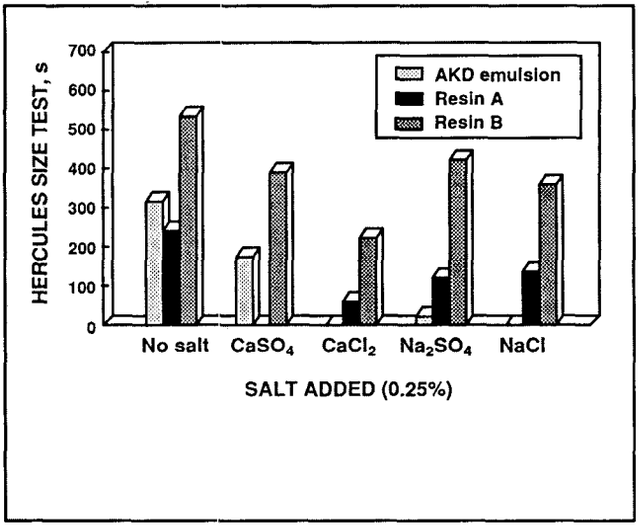
3. Effects of salt on on-machine Hercules size test at pH 7.8



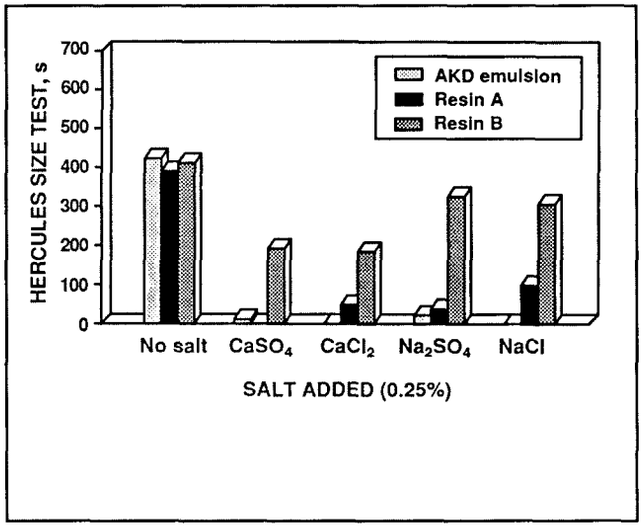
4. Effects of salt on on-machine Hercules size test at pH 9.0



5. Effects of cationic resin on the on-machine Hercules size test at pH 7.8



6. Effects of cationic resin on the on-machine Hercules size test at pH 9.0



III. AKD-PCC interaction

Condition	On-machine	Cured	Water	NA
PCC to machine chest	2	4	...	0
PCC to FP	110	119	19	11
	120	147	25	30
PCC to FP	72	97	70	72
Plus resin	76	129	54	51

AKD SBX
Starch SBX

amylose breakout also helps, though the ability to do this is often limited by the equipment available.

Summary

When a sizing problem is encountered, a series of diagnostic tests can be performed at the mill site. These tests define whether the problem is with the pulp, water, PCC, starch, additives, or contaminants. Care must be exercised in interpreting the results since multiple problems may exist. One source of interference may mask underlying problems.

The general scheme for isolating sources of problems is:

1. Obtain paper with good sizing. Test additives and starch on the paper surface. Change additives and starch if a negative impact is seen.
2. Check water system for conductivity and surface

tension. Track down and limit inorganic and organic contamination sources if necessary.

3. Check PCC-AKD interaction using the water dip test. Change addition points and resin usage. Use a promoter resin.
4. Look for contamination in pulp broke and recycle composition, and in machine lubrication, press, and felt washing components.

The order of investigation may vary according to what is known or suspected about the system. However, to obtain the optimum system, all sources of sizing loss should be identified and minimized.

Experimental

First, secure the following materials as specified in the tests: water (must be clean, distilled, and deionized, if possible), additives, SP starch (without additives, if possible), and paper (BSF preferred, second choice reel).

For the additive study, dilute the additive to 0.005%. Accuracy is not critical since the test is a relative measure. Then dip the paper into the additive solution (do each additive separately). For the starch study, dilute starch to 1% TS with water and dip paper in starch. For the carbonate study, dip paper in clean water.

For the control sample (additive/starch), dip paper in clean water, allowing water to soak through. For the carbonate control, use the paper sample as is.

For all papers, allow excess water to drip off for 5 s, place papers in oven at 105°C for 5-10 min, and complete Hercules size test under appropriate conditions.□

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