Size reversion in alkaline papermaking

Robert W. Novak and Dominic S. Rende

ABSTRACT: Size response is developed in alkaline papermaking by the formation of an ester bond between the sizing agent and cellulosic hydroxyl groups. Size reversion is the loss of size response with time after the paper has been made. Laboratory data suggest that size reversion increases at higher alkalinity or basicity. We propose that size reversion is, in part, the result of a reverse reaction of the size–cellulosic bond. The rate of reversion is dependent upon the initial size response.

KEYWORDS: Alkaline papers, papermaking, reversion, size.

Size reversion has become a major concern as more companies convert to alkaline papermaking. However, until recently there has been little published information and much speculation as to the cause of reversion *(1–6)*.

Chemical reactions

The two internal sizing agents widely used for alkaline papermaking are alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD). The generally accepted development of size response is through ester formation with cellulosic hydroxyl groups *(7)*. Under alkaline conditions through the forward dryers this reaction occurs relatively fast, and on-machine sizing can be obtained from the slower reacting AKD molecule *(8)*.

A detrimental reaction that takes place during papermaking is the hydrolysis of the sizing agent or reaction with water. ASA hydrolyzes to a dicarboxylic acid. Under alkaline papermaking conditions, the dicarboxylic acid should exist in salt form. Hydrolyzed ASA is a desizing agent, and its salts are very tacky *(9)*. AKD hydrolysis is a two-step process. The first step is formation of a beta-keto acid which, like ASA, under alkaline conditions should exist in salt form. The salt should be quite stable *(10)*, and the rearrangement to the ketone wax should be slow. Little is known about the presence of the beta-keto acid salt or its contribution as a sizing or desizing agent.

Reversion and efficiency

Size reversion is the loss of size response with time after the paper has been made. The phenomenon has been referred to as fugitive sizing. Fugitivity implies that the size response can be recovered by some means; in practice, size response lost during reversion cannot be restored.

Size reversion often has been confused with size efficiency. Size efficiency is the relationship between the size response and the amount of size added to the papermaking system. There are many variables that can affect size efficiency: size retention, filler loading and type, reactivity, and other papermaking additives, to name a few. By far the most important of these variables is size retention. ASA and AKD sizes are emulsified with cationic starches or cationic synthetic polymers which render the size particles cationic. When the size emulsion is added to the paper furnish, it is adsorbed quickly and predominately onto the high-surface-area anionic components of the furnish, in particular the fines and filler. If effective retention programs for filler and fines are not in place, the high-surface-area fines will not be retained; the potential for size hydrolysis increases, and size efficiency will be reduced.

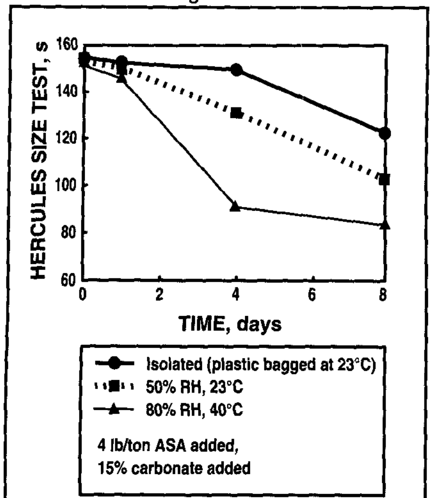
Filler materials are ionic and when included as a papermaking component create more demand for size. Increasing the filler level increases both the demand for size and the difficulty in obtaining fine-particle retention.

The reactivity of ASA and AKD differ dramatically. On-machine size response is easily obtained with ASA over a wide pH range. Alkaline papermaking has made it possible to obtain on-machine sizing response with AKD *(8)*; however, one must still have effective drying before the size press.

Some wet-end additives will interfere with size response. These include surface-active agents such as defoamers, dispersants, and biocides. If these additives are needed for the papermaking process, it is important to screen them and choose the ones that give minimum interference. This also

Novak is group leader R&D and Rende is market development manager for Nalco Chemical Co., One Nalco Center, Naperville, IL 60563-1198.

1. Handsheet storage conditions

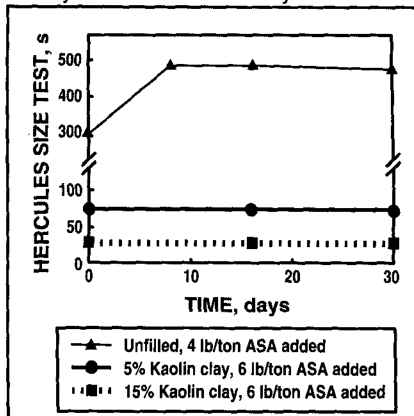


I. Comparison of carbonate fillers

Carbonate source	Hercules size test response, s 1-Day	16-Day
PCC-1 slurry	192	104
PCC-2 slurry	388	265
PCC dry	311	239
GCC dry	295	191
GCC slurry	294	132
European chalk	381	286

PCC = precipitated calcium carbonate
GCC = ground calcium carbonate
4 lb/ton ASA added

2. Clay filled and unfilled study



is particularly true in the size press. Aside from reducing size efficiency by applying excess defoamer in the size press, it is important not to degrade the size-press starch to a point where it acts as a dispersant and increases the hydrophilicity of the paper.

Again, size reversion is the loss of size response with time. Size reversion is not the loss of response in passing through the size press. Further, size reversion is not the failure of natural aging in meeting an oven cured test. It is possible to over-cure paper or paperboards, and a proper oven test should be constantly monitored.

Laboratory studies

An experimental laboratory procedure was developed to simulate the size reversion phenomena observed commercially. The procedure allowed for the study of variables that might affect reversion, to understand the mechanism of reversion, and to attempt to reduce or eliminate reversion.

Handsheets of 60 lb/3000 ft^2 basis weight were prepared using a semiautomatic British sheet mold with 50/50 bleached hardwood/softwood kraft fibers and 15% filler added (based on fiber). The water used for stock preparation, sheet formation, and all dilutions contained 100 ppm total hardness and alkalinity. The fiber slurry was stirred at 1000 rpm to which was added, at 15-second intervals, filler (if present), cationic starch, papermaker's alum, coagulant, size emulsion, and flocculant. The furnish then was stirred for an additional 30 seconds prior to handsheet formation. Handsheets were pressed and dried on a rotary-drum dryer set at 220°F. Standard drying was 106 seconds, which produced a moisture content of about 1.2%. The handsheets were allowed to equilibrate to room temperature for at least five minutes before an immediate size test was run. A Hercules size tester, using Hercules No. 2 ink (1% formic acid), set at 80% reflectance was used for all experiments.

Initial variables studied

The initial variables studied were handsheet moisture, storage conditions, and size emulsification medium (cationic starch vs. synthetic cationic polymer). Using commercial precipitated calcium carbonate, size reversion to some degree was observed in every experiment. The most stringent storage condition (80% RH and 40°C) showed the greatest degree of reversion, as shown in **Fig. 1**. The forced aging condition (80% RH and 40°C) was used for subsequent studies because it showed the most reversion in the shortest time.

Carbonate filler

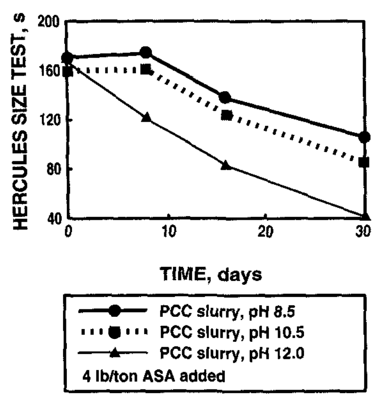
A number of commercial calcium carbonates were evaluated. In all cases, reversion to some degree was observed (**Table I**).

Mechanism

A plausible mechanism for size reversion can be forwarded. When size emulsion is added to the papermaking process,. it can readily adsorb on filler and fiber. As the paper is dried, the size on the fiber can flow and react, forming the aforementioned ester bonds. Filler chemistries do not afford potential chemical bonding, and, therefore, size adsorbed on filler begins to hydrolyze. In the case of ASA size, the hydrolyzed ASA is a known desizing agent; in the case of AKD, although not known, the beta-keto acid salt may function as a desizing agent in a similar fashion as the hydrolyzed ASA. With time, these materials can reorient and cause a loss in size response.

This mechanism should apply to paper containing any filler or even no filler at all. When size reversion experiments were conducted using clay filler and no filler, reversion was not observed to any degree under forced aging conditions (**Fig. 2**). An emphasis toward understanding size reversion in carbonate filled papers was undertaken.

3. Carbonate pH study



II. Effect of increasing alkalinity

Filler type	Alkalinity, ppm	Hercules size test response, s 1-Day	7-Day
None	100	749	1160
Kaolin	100	24	47
PCC	100	272	100
None	1150	209	3.1
Kaolin	1150	125	0.4

15% filler added
10 lb/ton cationic starch added to 4 lb/ton AKD size
Standard retention scheme of alum, coagulant, and flocculant

III. Effect of coagulant on size response

AKD dose, lb/ton	Coagulant dose, lb/ton	Hercules size test response, s Immediate	33-Day
2.0	0.0	100	3
3.0	0.0	297	158
4.0	0.0	409	265
2.0	2.0	91	3
3.0	2.0	297	156
4.0	2.0	379	253

15% precipitated calcium carbonate filled
10 lb/ton cationic starch with AKD size

Commercially prepared precipitated calcium carbonates of widely varying bulk pH were studied. **Figure 3** shows the reversion response. We found the greatest degree of reversion occurred with the precipitated carbonate having the highest bulk pH. Later work, using a second set of precipitated carbonates of varying bulk pH, showed an identical trend.

In later work, we found by increasing whitewater alkalinity, reversion could be induced in a system where no reversion had previously been observed. Under standard papermaking conditions employing clay filler and no filler at all, we continued to observe no reversion. However, increasing the alkalinity from 100 ppm to 1100 ppm as $CaCO_3$ produced a complete loss of sizing response within the first seven days at the forced aging condition (**Table II**).

What kind of mechanism is consistent with these observations, and what is known about ester chemistry? Reversion is the loss of size response with time. Any unreacted size that ends up in the sheet, especially ASA, should hydrolyze relatively quickly after the paper is made. We know that hydrolyzed ASA is a desizing agent, yet no reversion was seen using ASA in clay or unfilled handsheet studies.

Ester hydrolysis is accelerated with increasing pH *(11)*. The strongest observation concerning ester hydrolysis is the fact that complete ester bond breakage takes place by stirring ASA-cured paper overnight at room temperature in an aqueous sodium hydroxide-tetrahydrofuran mixture. This procedure is used for quantitative detection of ASA *(12)*. Calcium carbonate itself is a basic salt; that is, it is the salt of a weak acid and a strong base.

What we now believe can cause size reversion is a slow loss of the ester bond with time and that higher levels of basic materials remaining in the finished paper will accelerate the ester cleavage.

Coagulants and size reversion

Coagulants (highly cationically charged, low-molecular-weight synthetic polymers) play an important roll in fine-particle retention, especially in alkaline papermaking. Coagulants have been hypothesized to cause reversion under commercial papermaking practices.

A number of coagulant chemistries have been investigated as a cause of size reversion. They include epichlorohydrin dimethylamines (Epi-DMA) and diallyldimethyl ammonium chlorides. These coagulants were used as part of the primary fine-particle retention schemes employed in the unfilled and clay filled handsheet studies previously discussed where no reversion was observed.

Field experience has shown that there are numerous instances of size reversion during alkaline papermaking where no coagulant was used. Also, in systems where coagulant was used (and still is used), different degrees of reversion were observed within the same reel of paper from no reversion to extensive reversion. Laboratory experience has shown that size reversion was inversely proportional to the initial size response; that is, the higher the initial size response, the less the degree of reversion with time (**Table III**). The retention program in this example was kept constant while varying both the AKD-size and coagulant dosages. Similar sizing responses with and without coagulant yielded similar degrees of size reversion for both chemistries cited earlier.

Industry practices

What have papermakers done to retard size reversion? A higher initial size response produces less reversion, and papermakers have taken advantage of this by targeting higher size specifications and using more internal size. This practice, however, introduced the potential for machine deposits, higher sizing costs, and created some end-use problems. Some papermakers have reduced internal size by using surface sizing to maintain a given size specification. Since the introduction of satellite precipitated carbonate plants, carbonate quality and bulk pH have been better controlled. These attempts to control reversion have only been band-aids and have not eliminated the problem.

Conclusion

We came to the following conclusions:

- All carbonate filled handsheets show some degree of size reversion. The most size reversion was observed with precipitated carbonate.
- Clay filled or unfilled handsheets show no reversion.
- Reversion could be induced in clay and unfilled handsheets by increasing the alkalinity of the papermaking system.
- The extent of size reversion was a function of the precipitated carbonate pH.
- In experiments where no reversion was observed (clay filled and unfilled handsheets), the Epi-DMA coagulant was used.
- We believe that size reversion in alkaline papermaking is, in part, the result of a slow reverse reaction, that is, cleavage of the size ester bond. TJ

Literature cited

1. Moyers, B. M., Tappi J. 75(1): 112(1992).
2. Colasurdo, A. R. and Thorn, L., TAPPI 1992 Papermakers Conference Proceedings, TAPPI PRESS, Atlanta, p. 135.
3. Harvey, R. D., TAPPI 1992 Papermakers Conference Proceedings, TAPPI PRESS, Atlanta, p. 143.
4. Patton, P. A., TAPPI 1992 Papermakers Conference Proceedings, TAPPI PRESS, Atlanta, p. 415.
5. Gill, R. A., TAPPI 1992 Sizing Short Course Notes, TAPPI PRESS, Atlanta, p. 75.
6. Strutz, M. D., TAPPI 1992 Sizing Short Course Notes, TAPPI PRESS, Atlanta, p. 81.
7. Crouse, B. W. and Wimer, D. G., Tappi J. 74(7): 152(1991).
8. Reynolds, W. F., The Sizing of Paper, 2nd edn., TAPPI PRESS, Atlanta, 1989, p. 40.
9. Scalfarotto, R. E., Pulp & Paper 58(4): 126(1985).
10. Brown, B. R., Quat. Rev. Chem. Society 5: 131(1951).
11. Sykes, P.A., Guidebook to Mechanism in Organic Chemistry, 4th edn., Longman Group, 1975, p. 234.
12. Unpublished, Quantitative Determination of ASAs, Nalco Chemical Co., Naperville, IL, 1988.

The authors gratefully acknowledge the assistance of Kerrie Johnson, Victor Klausner, and Mark Dille for obtaining size reversion laboratory data and those technical service representatives throughout the world for useful technical discussions.

Received for review Jan. 8, 1993.

Accepted Feb. 18, 1993.

Presented at the TAPPI 1993 Papermakers Conference.