Effect of hydrolyzed ASA on sizing in calcium carbonate filled paper

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ABSTRACT

Sizing literature shows that the presence of hydrolyzed ASA in paper detracts from sizing. The authors show that the calcium salt of ASA is hydrophobic. In a calcium carbonate filled paper, it does not hurt sizing and can even make some contribution. Paper sized with ASA lost sizing with application of additional hydrolyzed ASA in free acid form but more than regained the sizing when converting the hydrolyzed ASA to its calcium salt form. ToF SIMS surface analysis confirmed the changes in hydrolyzed ASA.

Application:

These results should reduce current concerns about the continued use of ASA in fine paper grades as the trend toward higher levels of fillers continues.

ALKENYL SUCCINIC ANHYDRIDE (ASA) is a synthetic sizing agent widely used in alkaline paper grades. **Figure 1** shows its various structures and that of its salts. ASA is a fast curing size, but it begins to hydrolyze upon contact with water. Hydrolyzed ASA is not a sizing agent in alkaline furnishes. Normal applications therefore minimize ASA hydrolysis.

This paper does not question these facts. Some reports show that hydrolyzed ASA is detrimental to sized paper *(1)* because it acts as a desizing agent like dispersants or surface active agents that interfere with sizing. Because the soluble sodium or potassium salts of hydrolyzed ASA are essentially soaps, they can have this effect. Roberts and Daud *(1)* have applied hydrolyzed ASA from toluene onto pre-sized paper and shown that sizing decreases with increasing dosages of the hydrolyzed ASA size. The hydrolyzed ASA was probably in its free acid or sodium salt form, since the neutral pH paper did not contain filler.

Repeated citings of these data have warned that any ASA that does not react with cellulose will hydrolyze and be detrimental to sizing *(2–7)*. Most alkaline fine paper uses calcium carbonate as filler. The calcium salt of hydrolyzed ASA is not soluble. It is therefore likely that any hydrolyzed ASA in a furnish containing calcium carbonate would be in the calcium salt form or other insoluble salt such as magnesium or aluminum *(8)*. We will show that the calcium salt of ASA is hydrophobic. This is similar to the calcium salt of soap that has use as a hydrophobic source in flotation deinking of newsprint. The question then becomes whether the calcium salt of ASA is detrimental to sizing.

MATERIALS

The ASA used was a sample from commercial production. The precipitated calcium carbonate was commercially available. The paper samples used for tub application were 70 g/m^2 basis weight made on a pilot paper machine from a 70/30 bleached kraft hardwood/softwood blend unfilled and with 20% calcium carbonate in the furnish using 0.5 kg/metric ton of an anionic polyacrylamide retention aid. Handsheets used the same furnish components.

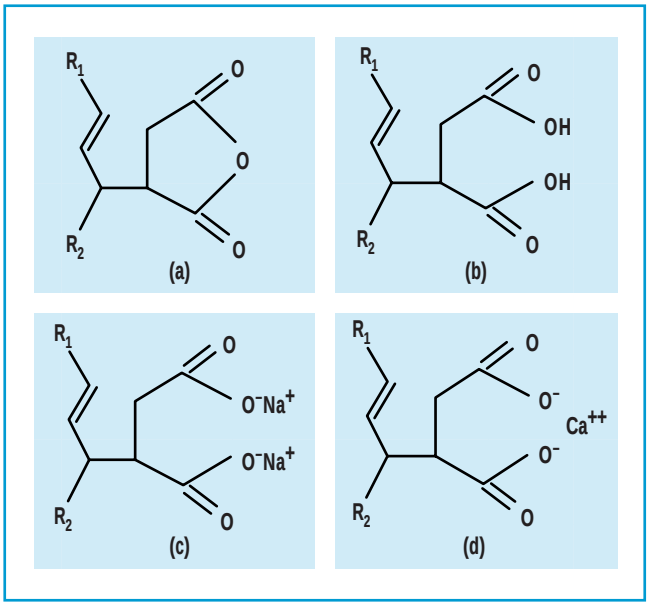
EXPERIMENTAL

Hydrolyzed ASA in acid form was prepared by emulsifying an equimolar amount of water into ASA using a small homogenizer. The water-in-ASA emulsion gradually changed to a clear viscous solution after standing for several days at room temperature as the reaction with ASA consumed water. Infrared analysis showed complete hydrolysis.

The calcium salt of hydrolyzed ASA was prepared by adding 3 g of hydrolyzed ASA to a dilute potassium hydroxide solution and heating to approximately 70°C to dissolve and form the potassium salt. After cooling and neutralizing with dilute HCl, an equal volume of 4% calcium chloride was added. The precipitate that formed was filtered after standing overnight and washed twice with deionized water before air drying. This was the Time of Flight Secondary Ion Mass Spectrometry (ToF SIMS) standard.

The samples of precipitated calcium carbonate treated with hydrolyzed ASA were prepared by adding 2 mL of 0.1% hydrolyzed ASA dissolved in toluene with approximately 3 mL of toluene to 2 g samples of calcium carbonate powder. After mixing, the toluene was allowed to evaporate.

Tub application of ASA and hydrolyzed ASA mixtures was done by dipping paper in dilute toluene solutions, removing the paper and blotting quickly, and then allowing the toluene to evaporate by hanging in a hood. The ASA and hydrolyzed ASA concentrations were adjusted based on the predetermined toluene pick-up to give the dosages desired. The sheets were post cured in a forced draft oven for 10 min. at 105°C.



1. The chemical structure of ASA (1a), hydrolyzed ASA (1b), the sodium salt (1c), and the calcium salt (1d). (R_1 and R_2 are saturated hydrocarbon chains.).

Two sheets from each treatment were post treated by dipping in a deionized water bath for approximately 10 s, blotting, and drying one pass on a rotary drum drier for 1 min. at 116°C. Two sheets from each treatment for the calcium carbonate filled paper were also exposed to elevated relative humidity levels of 84% and 97% for 3 days. The sheets were reconditioned before testing for ink penetration.

Preparation of handsheets used a 50/50 mixture of bleached kraft hardwood and softwood pulps refined to 500 CSF. One portion of the stock was treated with 15% precipitated calcium carbonate based on the dry fiber. Emulsions of ASA and hydrolyzed ASA were prepared in cationic potato starch at a 4/1 starch to ASA ratio using a small blender. A fixed amount of ASA emulsion was added to batches of pulp with different amounts of hydrolyzed ASA emulsion. Handsheets of 70 g/m^2 grammage were prepared using the filled and unfilled pulps. After conditioning, the sheets were tested for ink penetration using a method similar to TAPPI T530 pm-89 but with an instrument of our own design. The green ink was buffered at pH 7. The post treatment by dipping in deionized water was the same as given above for the sheets sized with ASA from toluene.

Other articles have described ToF SIMS procedures (9). Positive ion spectra detected calcium, and negative ion spectra detected hydrolyzed ASA (9). Note that the intensity of the peaks associated with hydrolyzed ASA in its free acid form are extremely weak for the calcium salt of ASA.

2. A drop of water applied to a powdered sample of the calcium salt of ASA—the high contact angle indicates that the ASA salt is hydrophobic

3. A drop of water applied to a precipitated calcium carbonate treated with 1 kg/ton of hydrolyzed ASA—the high contact angle indicates that the calcium carbonate surface is hydrophobic

RESULTS

Hydrophobicity of the calcium salt of ASA

The calcium salt of hydrolyzed ASA was prepared. **Figure 2** shows a drop of distilled water applied to the powder. The drop displays a high contact angle showing that the calcium salt of ASA is hydrophobic.

Hydrophobicity of treated filler

Figure 3 shows a sample of hydrolyzed ASA applied at 0.1% based on the weight of the calcium carbonate. The contact angle of an applied water drop is high showing that the filler surfaces are hydrophobic. Untreated calcium carbonate readily absorbed the water drop. The hydrolyzed ASA has apparently coated the surface and is sufficiently anchored to make the surface hydrophobic.

Paper treated with ASA and hydrolyzed ASA applied from toluene

Different levels of ASA and hydrolyzed ASA were applied by tub application from toluene solution. Two types of paper were treated. One was unfilled, and the other contained approximately 15% of precipitated calcium carbonate.

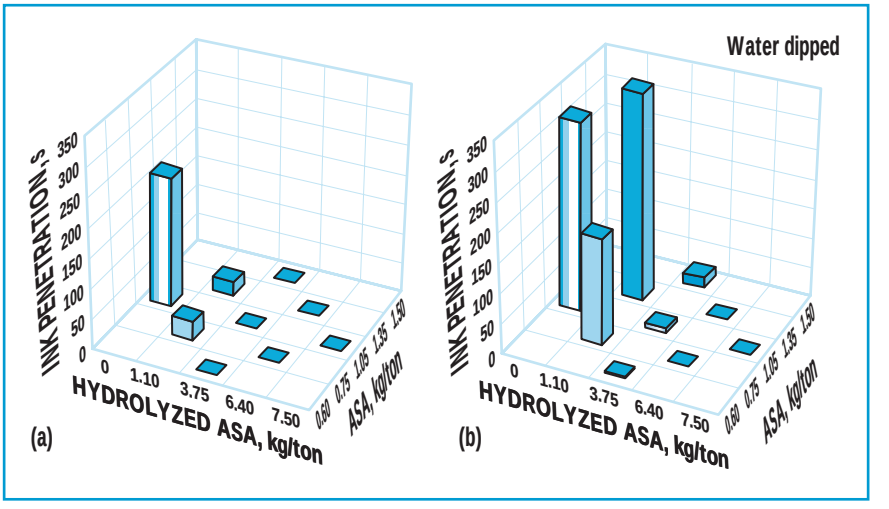
The results of sizing tests for the unfilled paper in **Fig. 4a** show that sizing decreases with increasing levels of hydrolyzed ASA in agreement with prior reports *(1)*. A decrease also occurred with the paper containing calcium carbonate as Fig. 4a shows.

When the same treated papers used in **Figs. 4a and 5a** were moistened by dipping in water for a few seconds and redried, the results in **Figs. 4b and 5b** showed dramatic differences. Figure 4b shows that the water dip produced no appreciable change in the sizing of the unfilled paper. Figure 5b shows that the sizing of the filled paper was restored and even increased to a level higher than that of the paper containing no hydrolyzed ASA. Restoration of the sizing in the calcium carbonate filled paper is probably due to the formation of the calcium salt of hydrolyzed ASA. If so, this shows that the calcium salt can contribute to sizing. Note that the calcium salt alone does not give sizing. Filled paper treated with hydrolyzed ASA only and without ASA showed no sizing before or after a water dip (data not shown). Perhaps the calcium salt of ASA does not sufficiently anchor to the fiber surfaces to give sizing by itself.

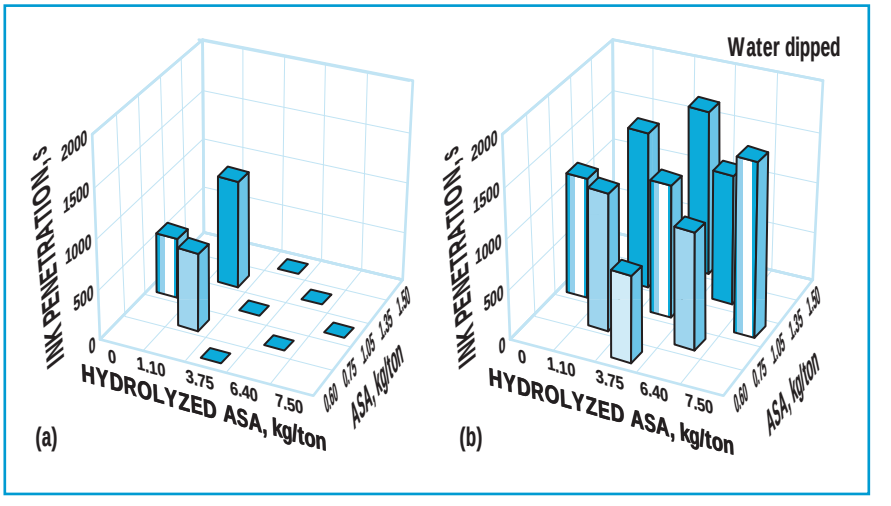
The restoration of sizing for the calcium carbonate filled paper also occurred when exposing the paper to high humidity. **Figures 6a and 6b** show results for the filled paper after being held for three days at 84% and 97% relative humidity.

Surface analysis using ToF SIMS

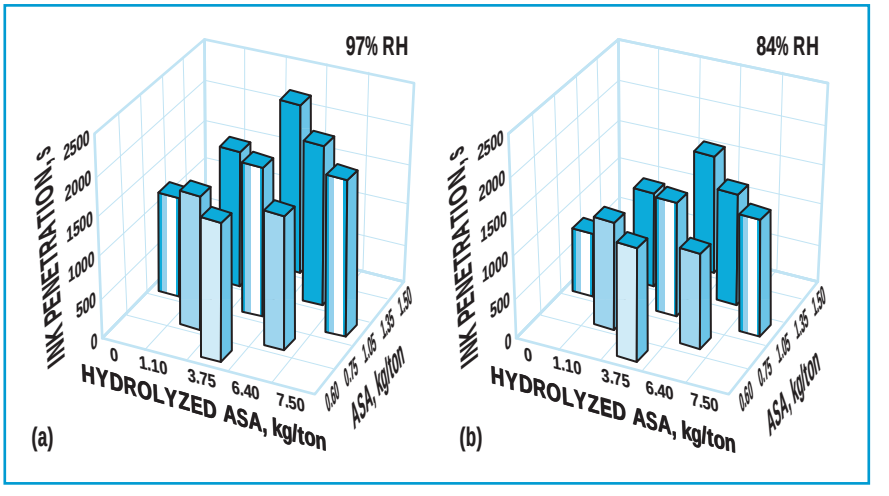
Evidence that the calcium salt of the hydrolyzed ASA is contributing to sizing came from surface analysis of



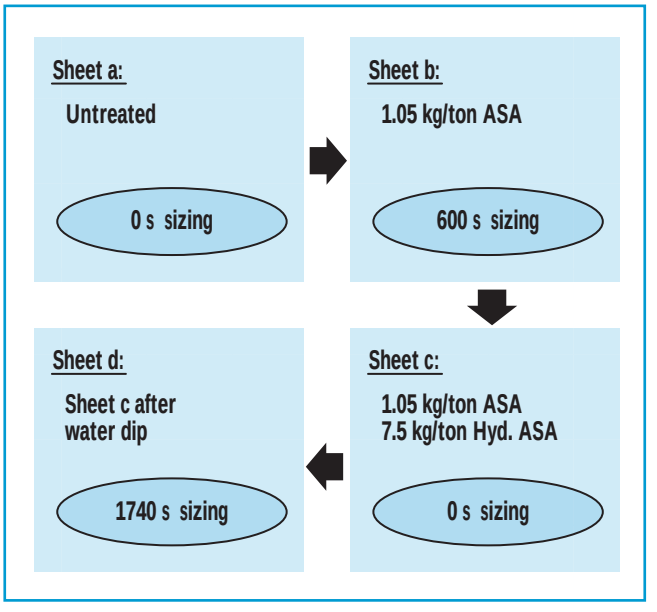
4. Ink penetration of unfilled handsheets treated with ASA and hydrolyzed ASA blends applied from toluene and cured (a) and the same paper after a water dip and redrying (b)



5. Ink penetration of handsheets filled with calcium carbonate treated with ASA and hydrolyzed ASA blends applied from toluene and cured (a) and the same paper after a water dip and redrying (b)

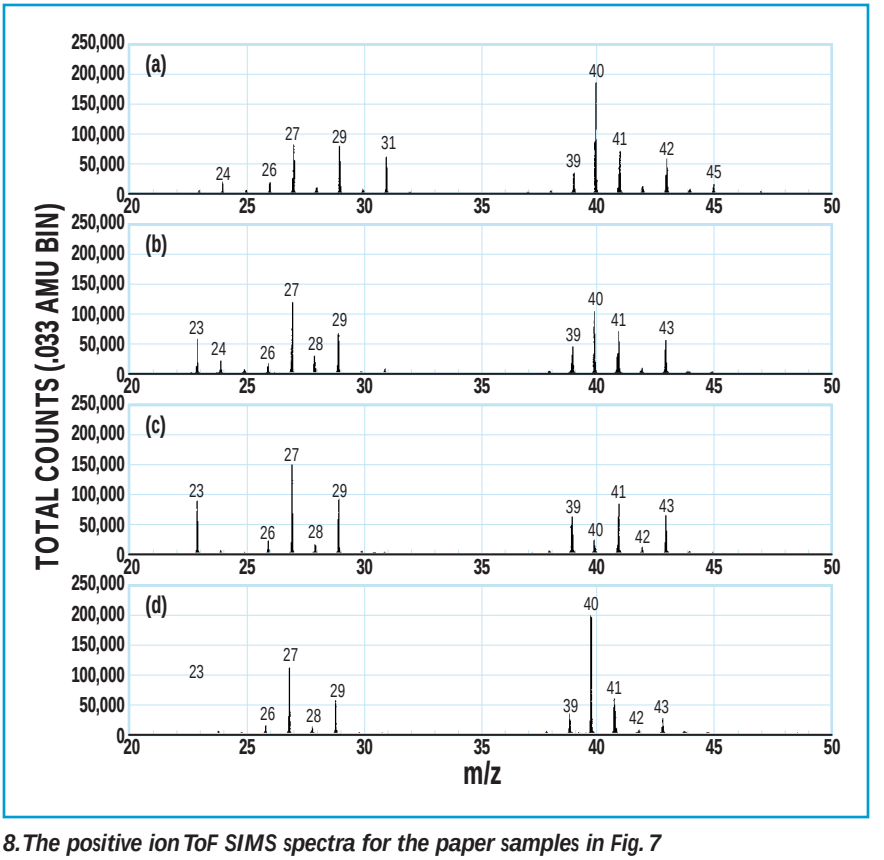


6. The same handsheets described in Fig. 5 exposed for three days to 97% RH (a) and 84% RH (b) before measuring the sizing level



7. The treatments for four calcium carbonate filled sheets selected for ToF SIMS surface analysis

these papers using ToF SIMS. **Figure 7** shows the four samples of filled paper selected for surface analysis. Note the differences in sizing. The hydrolyzed ASA inhibits sizing in sheet 7c, but the sizing is more than restored after a water dip as sheet 7d shows.

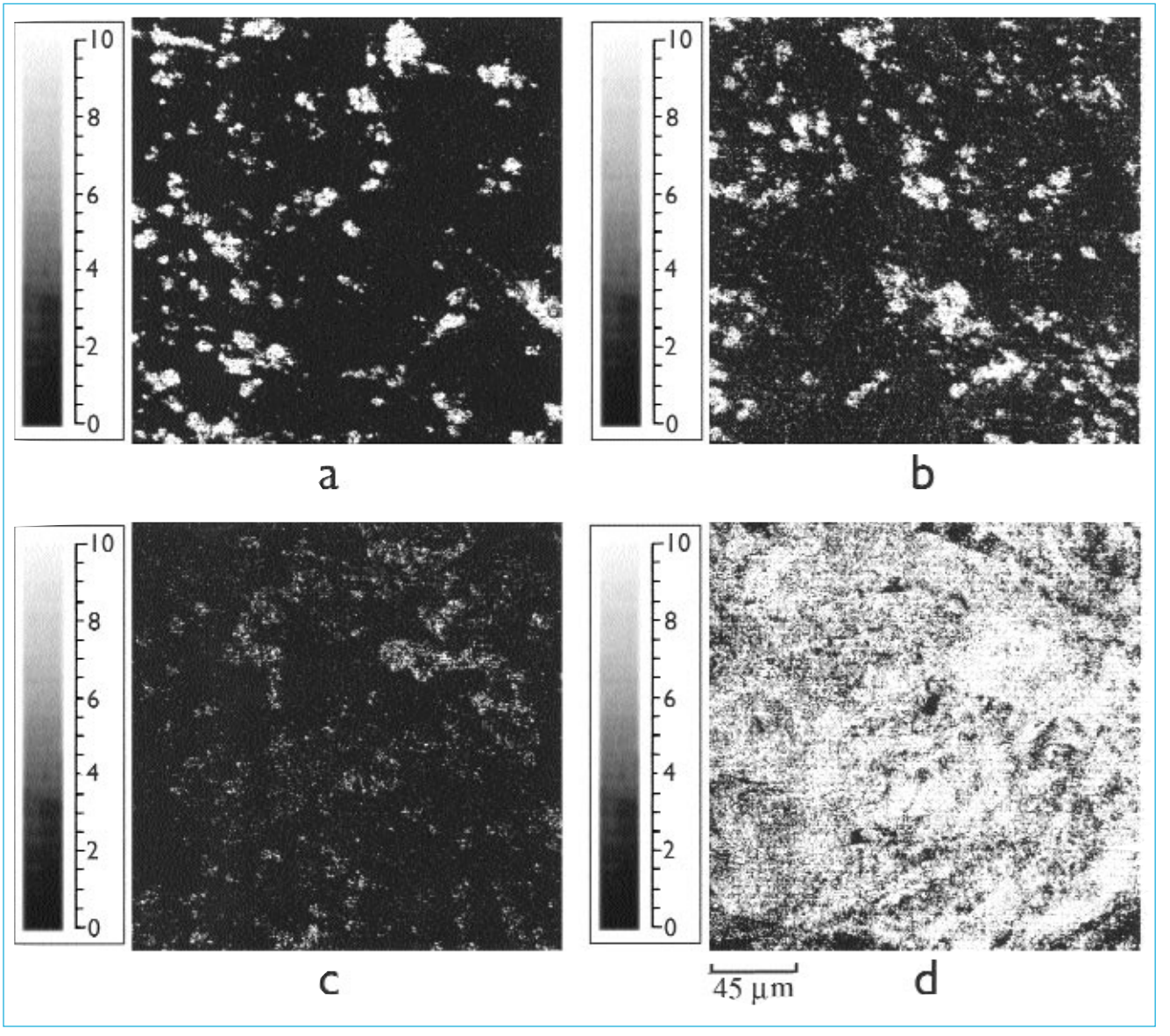


8. The positive ion ToF SIMS spectra for the paper samples in Fig. 7

Detection of calcium in the positive ion spectra. **Figure 8** shows the positive ion ToF SIMS spectra for the four samples. A strong calcium peak (40 m/z) was evident for the untreated sheet 6a as expected. Treatment with 1.05 kg/metric ton of ASA only, 6b, reduced the intensity presumably because the ASA covers some calcium carbonate surfaces. Treatment with an additional 7.5 kg/metric ton of hydrolyzed ASA, 6c, almost eliminated the calcium peak. After the water dip, 6d, the intensity of the calcium peak is even higher than the untreated sheet. The difference before and after the water dip suggests that the calcium after the water dip has moved closer to the surface. Formation of the calcium salt of the hydrolyzed ASA is consistent with this data.

Perhaps even more revealing are the ToF SIMS images of the calcium distributions for the four samples that **Fig. 9** shows. Figure 9a shows the distribution of calcium in the untreated calcium carbonate filled sheet. The distribution is very prominent and nonuniform as expected with filler particles exposed. After treatment with ASA only, the intensity of the calcium on the surface decreases as Fig. 9 b shows. The distribution is similar. With ASA and hydrolyzed ASA present, Fig. 9c shows that the calcium on the surface decreased greatly as noted above. The distribution was still mottled. When the sheet was dipped in water and redried, Fig. 9d shows that the paper surface again showed high levels of calcium but with a more even distribution. One would expect such a distribution if the detected calcium was that associated with the hydrolyzed ASA.

Detection of hydrolyzed ASA in the negative ion spectra. Hydrolyzed ASA is detectable in the negative ion spectra as peaks at 339 and 367 m/z corresponding to ASA from the C16 and C18 olefins. **Figure 10** shows the negative ion spectra for the four samples. No hydrolyzed ASA was detected in the untreated sheet, 10a, as expected. Some was found in the paper treated only with ASA, 10b. This was unexpected, because any ASA that does not form covalent ester bonds with the cellulose should hydrolyze with the water vapor present on exposure to air. (The SIMS tests were made several days after the treatments.) The paper treated with hydrolyzed ASA, 10c, showed very high levels of hydrolyzed ASA as expected. After the water dip, 10d, the peaks for hydrolyzed ASA were extremely low. The negative ion spectrum obtained



9.The same spectra as Fig. 8 showing the calcium distribution over a 500 x 500 micron area

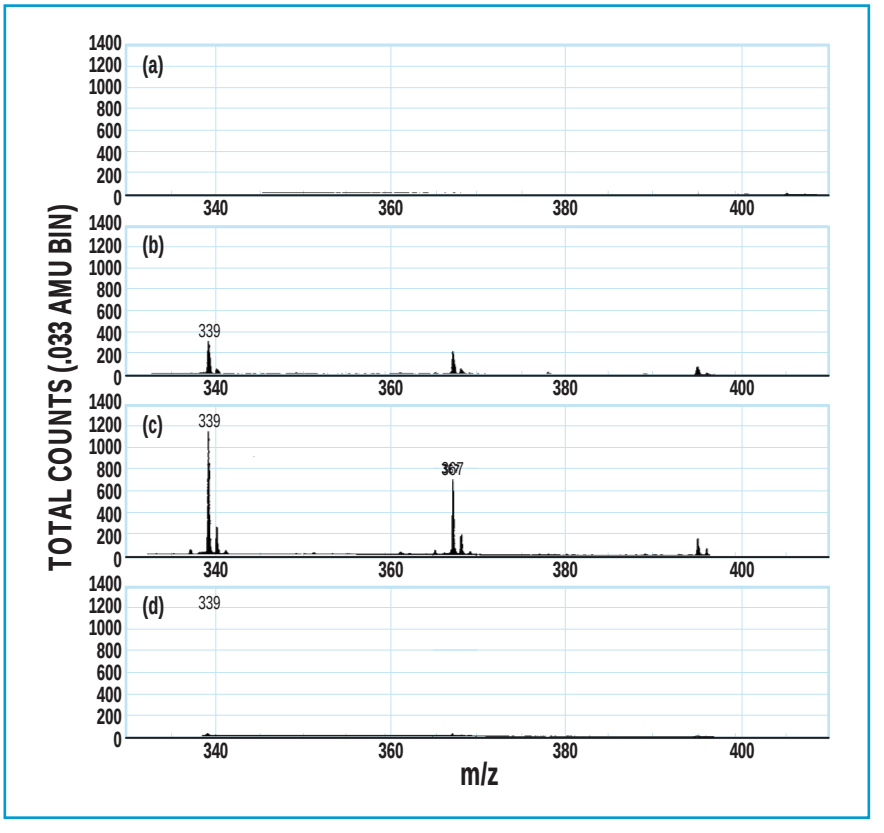
from the calcium salt of hydrolyzed ASA shows only very weak peaks at these masses. Disappearance of these peaks is therefore consistent with the formation of the calcium salt of ASA after the water dip.

In summary, the sizing results combined with the ToF SIMS analysis suggest that the hydrolyzed size applied from toluene remains in the free acid form. ToF SIMS can detect it. Little calcium is present on the surface due to the covering of hydrolyzed ASA. Water application allows the calcium salt of the hydrolyzed ASA to form. ToF SIMS now shows the presence of calcium evenly distributed on the surface. The separate experiments that showed that the calcium salts of ASA are hydrophobic suggest that the corresponding increase in sizing on water exposure is due to this salt formation.

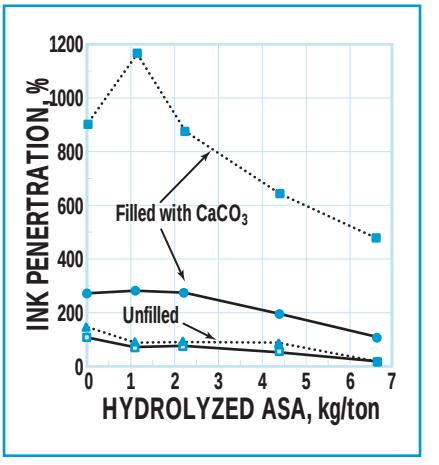
Wet-end addition of ASA and hydrolyzed ASA emulsions

The experiments described above applied the ASA and hydrolyzed ASA to pre-formed paper. What happens with application as emulsions using the normal wet-end addition technique? To find out, we made handsheets from pulp treated with ASA and hydrolyzed ASA emulsion blends. The dosage of ASA remained constant while using different levels of hydrolyzed ASA. In one case, no calcium carbonate was present. Another case used 15% calcium carbonate based on the fiber weight. Results in **Figure 11** for unfilled paper show that sizing decreased as the level of hydrolyzed ASA increased for a fixed dosage of ASA. Water dipping of the sheet as a post-treatment did not make a significant change in sizing levels. This agreed with the results obtained by tub application from toluene. For pulp containing calcium carbonate filler, the detrimental effect of hydrolyzed ASA was smaller. Subsequent water dipping produced a large increase in sizing levels.

One might expect that the initial sizing for the carbonate containing



10. The negative ion ToF SIMS spectra for the same paper samples as Figs. 8 and 9



11. Application of ASA and hydrolyzed ASA by internal addition to furnishes with and without calcium carbonate filler with dashed lines indicating the effect of a subsequent water dip on sizing

paper would have been high and largely independent of the hydrolyzed ASA, because the hydrolyzed ASA could have formed calcium salts with the calcium present in the water. The subsequent water dip would not be necessary to form the calcium salt. A likely explanation for the large increase following the water dip is that the hydrolyzed ASA was present during handsheet formation as an emulsion and did not have direct exposure to the calcium present in the water. Only after removal of the water in the dryers would the emulsion particles break and allow the hydrolyzed ASA to spread on the fiber and filler surfaces. With little water present, salt formation would be inhibited. The subsequent water dip then exposed the hydrolyzed ASA to the water and allowed the calcium salt to form.

This suggests that the rewetting that occurs on a paper machine in the size press aids in converting any hydrolyzed ASA into its calcium salt to enhance sizing. This is a mechanism that we believe is new.

Note that the calcium carbonate filled handsheets made with only ASA added also showed a large sizing increase after the water dip. This may be due to some hydrolysis of the ASA during handsheet formation. After the water dip, the ASA forms the calcium salt that then contributes to the sizing of the paper.

CONCLUSIONS

If hydrolyzed ASA is present in paper as the calcium salt, it is not detrimental to sizing generated by ASA itself. It may even contribute to the sizing. The calcium salt of ASA is hydrophobic. When present on the surface of calcium carbonate filler particles, it makes them hydrophobic as well. TJ

KEYWORDS
Succinic anhydride, internal sizing, size, water repellence, calcium carbonate, filled papers, hydrolysis, fine papers, surface sizing, calcium compounds

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LITERATURE CITED

1. Roberts, J. C. and Daud, W. R., *Proceedings of the 10th Cellulose Conference*, Wiley, New York, 1988, p. 1531.
2. Hodgson, K.T., *Appita* 47(5):402(1994).
3. McCarthy, W. R. and Stratton, R. A., *Tappi J.* 70(12):117(1987).
4. Roberts, J. C., in *Paper Chemistry* (J. C. Roberts, Ed.), Chapman and Hall, New York, 1991, p. 127.
5. Bobu, E. and Cimpoesu, G. H., *Cell. Chem. Tech.* 27:225(1993).
6. Roberts, J. C., in *Pira Reviews of Pulp and Paper Technology*, Pira International, Surrey, 1992, pp. 1–57.
7. Novak, R. W. and Rende, D. S., *TAPPI 1993 Papermakers Conference Proceedings*, TAPPI PRESS, Atlanta, p. 438.
8. Scalforotto, R. E., *Pulp and Paper* 59(4):126(1985).
9. Brinen, J. S. and Kulick, R. J., *1996 International Paper and Coating Chemistry Symposium Proceedings*, CPPA, Montreal, p. 125.