A NEW ALKENYL-SUCCINIC ANHYDRIDE ALKALINE SIZE

John G. Penniman
President
Paper Chemistry Laboratory, Inc.
Stoneleigh Avenue
Carmel, NY 10512

Maria S. Reichlin
Chief Chemist
Paper Chemistry Laboratory, Inc.
Stoneleigh Avenue
Carmel, NY 10512

ABSTRACT

Papermaking operations which have converted to the alkaline process, utilizing alkenyl-succinic-anhydride (ASA), have experienced one major negative effect. The "hydrolyzate" from the ASA builds up to the point where an unacceptable level of dirt spots appear in the sheet. It is then necessary to stop making paper and boil out the machine. This problem occurs at almost twice the frequency with ASA than when using rosin and alum. Research into alkaline size has led to the development of a new ASA with higher reactivity and correspondingly less hydrolyzate. The new size has twice the reactivity; therefore 1 lb. can replace 2 lb. of the conventional ASA. Because only half as much size is used, the "hydrolyzate" is cut in half. Use of the new ASA can, therefore, overcome the principal residual disadvantage of the alkaline process so that it can be at least as clean as the alum-rosin process.

INTRODUCTION

The use of alkaline size in making fine papers has many well established advantages over the rosin-alum process. Despite the technical, economic and ecological advantages, the market penetration of alkaline size in North American printing and writing paper has been estimated at only about 10%, (1) vs. 50% in Europe.

We recently made a technical audit of several alkaline fine paper operations, each of several years standing, to learn how well the process had been assimilated and how the residual problems were perceived.

In each case top management had made a command decision to adopt the process for cost-saving reasons. The technical problems were surmounted with substantial assistance, in the early stages, from suppliers. After a longer period of time the operating personnel found a handle for the process and were able to control and improve it without substantial supplier assistance. During this period everyone became comfortable with the process and the cost saving objectives were realized. No one any longer looks back ostalgically to the "good old days".

The "Hydrolysate" Problem

Only one major technical problem remains amongst the operations we surveyed: The "hydrolysate" problem. Hydrolysis of ASA occurs on exposure to moisture, and the rate increases at higher temperature and/or pH levels. This is an especially pernicious technical problem because it has been shown that unanchored hydrolysed ASA acts as a desizing agent.(2) It also poses a difficult operating problem because the "hydrolysate" builds up in the system and eventually reaches the point where it causes an objectionable level of dirt spots in the paper. At this juncture the only solution is to shut down the process and boil it out. The principal complaint of the mills in the survey was that the frequency of paper machine clean-ups with ASA was about twice that of the alum-rosin process.

An Approach to Solving the Problem

We have done a great deal of experimental work directed towards improving the efficacy of ASA size. We have learned, for example, that the properties of the olefin used to make ASA plays a critical role in the reactivity of the finished product. Olefin specifications are not in themselves helpful in distinguishing between materials which will produce high activity versus low activity ASA's; the only effective test is to synthesize the ASA and carefully conduct a discriminating laboratory test.

A typical ASA specification is shown in Figure 1. Note that 5-12% is shown as "residue". We distilled this product to eliminate the residue and found that we had approximately doubled the reactivity of the distillate, in comparison with our control, as shown in Table 1.

Figure 1: Alkaline Size #1

Alkenyl-Succinic-Anhydride (ASA)

Specifications

(2,5-Furandion C-16 Alkenyl Dihydro Derivative)

Acid Number	335 - 360
OlefinContent, %, byGLC	0.3 - 1.5
Color, Gardner	13 - 15
Viscosity, cps at 25°C	100 - 160
Residue, % by hplc	5 - 12
Free Acid Content	2% max

CAS No. (listed in TSCA Inventory) (68784-12-3)

Table 1

Variable	Lbs of distilled ASA, (Lab Code T-16) to replace 1 lb ASA	Date
7% Emulsifier A	0.3	6/6/85
7% Emulsifier A	0.6	6/17/85
7% Emulsifier A	0.33	8/6/85
7% Emulsifier B	0.6	10/2/85
1.4% Emulsifier A	0.76	7/26/85
1.4% Emulsifier A	0.64	8/14/85
Average:	0.54	

It is shown that about 0.54 lb. of distilled ASA can replace 1 lb of ASA, when analysed by linear regression, to produce 100 sec HST sizing at 85% reflectance using the 1% green neutral dye dispersion.

The Williams dryer is primarily used in order to show that the conditions exist for self-curing, as opposed to 'force curing' for two hours at 140°C. Williams dryer cure tests show a size requirement higher than would be required on a paper machine, or a lower level of sizing for the same amount of chemical added. See Table 2. The 'force curing' data is more predictive of paper machine performance.

Next, we added aliquots of n-decane solvent to the distilled size and again conducted activity testing. In one case the sized sheet was cured on the Williams Dryer, resulting in a low level of sizing; in the other case the sheets were cured at 140° for 2 hours, resulting in about one order of magnitude greater sizing. In both cases, the 80% distilled size : 20% n-decane solvent showed a level of sizing equivalent to the 100% distilled product. See Tables 2 and 3.

Table 2 **3.5 lb/T Distilled ASA Size**

Paper dried on Williams Dryer:

Hercules Sizing Test (HST); Seconds, 1% neutral dye, 85% reflectance.

Distilled ASA (T-16)	T-16+10% n-decane	T-16+20% n-decane	T-16+30% n-decane	T-16+40% n-decane	T-16+50% n-decane
26	28	47	21	8	3
24	28	32	24	5	4
26	36	31	20	8	3
Seconds, Average:					
25	31	37	22	7	3

Oven dried paper; 140° C

Hercules Sizing Test (HST); Seconds, 1% neutral dye, 85% reflectance.

Distilled ASA (T-16)	T-16+10% n-decane	T-16+20% n-decane	T-16+30% n-decane	T-16+40% n-decane	T-16+50% n-decane
212	362	315	133	124	73
173	166	136	64	62	42
183	179	123	106	75	52
Seconds, Average:					
189	236	191	101	87	56

Table 3 **5 lb/T Distilled ASA Size vs. Competitive Product "A"**

Paper dried on Williams Dryer

Hercules Sizing Test (HST); Seconds, 1% neutral dye, 85% reflectance.

Distilled ASA (T-16)	T-16+10% n-decane	T-16+20% N-decane	T-16+30% N-decane	T-16+40% n-decane	T-16+50% n-decane	Competitive Product "A"
1000+	879	1000+	160	67	34	625
1029	859	831	324	68	16	551
1000+	1000+	1000+	397	67	21	524
						916
						1135
						374
						482
						1500
Seconds, Average:						
1000+	1000+	1000+	294	67	24	763

Conclusion

The distilled, diluted ASA should provide a major reduction in hydrolysate in routine mill usage, for the following reasons:

1) The "residue", which can amount to 5-12%, has been completely eliminated as a possible source of paper machine contamination.

2) The efficacy of the ASA has been increased. This in turn reduces the amount of ASA required for a given level of sizing and reduces the hydrolysate contamination problem commensurately.

3) Reducing the ASA with 20% of solvent again, as in 2 above, results in an additional effective decrease in potential hydrolysate contamination of 20%.

Experimental

I. Preparation of ASA Emulsion:

1. Cook cationic starch (Cato F) at 3% solids.

2. Cool to room temperature.

3.* Pre-blend ASA with 7% emulsifier by weight and mix for 15 minutes. When a solvent such as N-decane is used, it is added at the same time as the emulsifier.

4. Add 167g cool starch to blender; blend for 5 seconds.

5. Add 2.7g ASA/emulsifier to blender.

6. Emulsify at high speed for 30 seconds.

7. Rinse walls of blender with water.

8. Dilute to 500 ml in graduated cylinder with distilled water. This gives 0.5% ASA, 1% starch for a total of 1.5% solids.

9. Dilute to 0.15% solids. This gives 0.05% ASA and 0.1% starch.

10. Make fresh every 2-3 hours.

II. Evaluation of Efficacy

Objective: To evaluate various experimentally synthesized ASA samples for sizing efficiency.

Pulp: Bleached kraft hardwood pulp is dispersed in tap water using Waring blender. When calcium carbonate filler is added, it is allowed to condition overnight in order to reach electrokinetic equilibrium.

Handsheets: Make Dynamic Paper Chemistry Jar^{tm} handsheets, 3 per sizing agent addition level. See Operating Manual for detailed procedure. (3)

Basis weight of Dynamic Paper Chemistry Jar^{tm} handsheets was about 200 g/m^2; caliper was about 6.2 x 10^{-5} meters (2.4 x 10^{-3} inches).

Dry For: 5 minutes in Williams Dryer or two hours at 140°C in drying rings.

Conditioning: In drying rings, overnight, at 70°F and 50% relative humidity.

Dry End Parameters to Measure: Hercules Sizing using 1% Neutral Dye at 85% reflectance. Analyze by linear regression to determine the amount of distilled ASA which provides sizing equivalent to 1 lb of ASA Size No. 1.

Chemical Addition: Various addition levels were used, in the range of 1-8 lb/T ASA to dry weight of pulp.

Mixing Time: 5 seconds

Literature Cited

1 Laufman, Max, PTS "Chemical-Technological Problems of Papermaking" Munich, Germany September 25-27, 1984.

2 Wasser, Richard B., TAPPI Short Course on Alkaline Papermaking, Denver, CO, April 17-19, 1985.

3 **Dynamic Paper Chemistry Jar**[tm] Mark III, Operating Manual, supplied by Paper Chemistry Laboratory, Inc.