The effects of SMA surface sizes on paper end-use properties

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ABSTRACT: Styrene-maleic anhydride (SMA) surface sizes affect a wide variety of paper end-use properties. This paper examines the effects of various SMA parameters (styrene-to-maleic anhydride ratio, molecular weight, and type of salt) on sizing response, ink-jet printability, offset runnability, coefficient of friction, and Gurley densometer.

KEYWORDS: Anhydrides, end use, hydrocarbons, maleic anhydride, oxygen heterocycles, paper properties, parameters, sizing, styrene, surface sizing, surface treatment.

Although all styrene-maleic anhydride (SMA) surface sizes belong to the same chemical family, there are differences among them that affect their performance in various ways. In order to select a surface size with an appropriate styrene-to-maleic anhydride(S:MA) ratio, an appropriate molecular weight, and the correct type of salt, it is necessary to decide which paper property is to be improved. This paper examines SMA characteristics with respect to five properties: sizing response, ink-jet printability, offset runnability, coefficient of friction, and Gurley densometer.

Sizing response

The type of salt, S:MA ratio, and molecular weight all contribute to sizing response in various ways. We address the type of salt first.

Ammonium salt should be used if sizing response is desired, as shown in **Table I.** In this table, the SMAs (pickups of 0.15%) were applied to an alkaline-base paper with a basis weight of 65 g/m^2 and containing 10% precipitated calcium carbonate (PCC), 0.15% alkyl ketene dimer (AKD), and 0.25% alum. The two SMAs shown in Table I were made from the same copolymer; they are identical except that one is an ammonium salt and the other is a sodium salt. The reason that the ammonium salt was superior with respect to sizing response is that the ammonium group flashed off in the dryer section and allowed the carboxyl groups to coordinate with cationic species in the paper. Sodium does not flash off *(1)*.

Sizing response improves as the S:MA ratio increases, as shown in **Table II.** In this table, the SMAs were applied to an alkaline-base paper also with pickups of 0.15%. The paper had a basis weight of 75 g/m^2 and contained 15% PCC, 0.125% AKD, and 0.25% alum.

The effect of molecular weight on sizing response is not clear. To see this, compare Table II with **Table III.** In Table III, the SMAs were applied to an alkaline-base paper with pickups of 0.10%. The paper had a basis weight of 70 g/m^2 and contained 3% ground calcium carbonate (GCC), 8% clay, 0.025% alkenyl succinic anhydride (ASA), and 0.25% alum. The high molecular weight of the 1:1 SMA apparently helps it to overcome its styrene deficiency (when compared to the 2:1 SMA). However, in Table II, the molecular weight does not appear to be important when compared with the S:MA ratio. The major difference between Tables II and III is in the base papers employed in the studies. Both base papers were poorly sized (0–2 seconds). The base paper in Table II had a Gurley densometer of 50 s/100 cm^3, while the base paper in Table III was quite porous (16 s/100 cm^3).

Given the data in these two tables, we may draw two general conclusions. First, higher-molecular-weight SMAs may help improve sizing response on poorly sized, porous-base papers, but this appears to be a threshold effect. Second, if the molecular weight of the SMA is

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I. Effect of type of salt on sizing response

SMA salt	*S:MA ratio*	*Molecular weight*	*Sizing response, s*
Ammonium	1:1	120,000	124
Sodium	1:1	120,000	4

II. Effect of S:MA ratio on sizing response

SMA salt	*S:MA ratio*	*Molecular weight*	*Sizing response, s*
Ammonium	3:1	58,000	122
Ammonium	2:1	38,000	41
Ammonium	1:1	120,000	27

III. Ink jet printability (IJP) as a function of various SMA properties

SMA salt	*S:MA ratio*	*Molecular weight*	*Sizing response, s*	*IJP (1=Best)*
Ammonium	3:1	58,000	120	1
Ammonium	2.7:1	80,000	141	1
Ammonium	2:1	38,000	87	2
Ammonium	1:1	120,000	115	3
Starch	-	-	2	4

IV. Ink jet printability (IJP) as a function of various SMA and half-ester properties

SMA salt	*S:MA ratio*	*Molecular weight*	*Sizing response, s*	*IJP (1=Best)*
Ammonium	3:1	58,000	120	1
Ammonium	2.7:1	80,000	141	1
Ammonium	2:1	38,000	87	2
Ester	1.18:1	180,000	126	3
Ammonium	1:1	120,000	115	4
Starch	-	-	2	5

at least 50,000, a further increase in molecular weight will have little effect on sizing response, when compared to the effect of S:MA ratio.

Ink-jet printability

In another paper presented at the TAPPI 1994 Papermakers Conference *(2)*, it was shown that ink-jet printability (IJP) can be quantified by the measurement of optical densities and through the use of image analysis. In this study, IJP was determined semi-quantitatively.

The template used to evaluate IJP is shown in **Fig. 1.** IJP ratings were obtained by considering a combination of factors: quantitative measurement of the width of text letters (the narrower the letters, the better, as this indicates little ink spreading); a subjective evaluation of the degree of feathering on the leading edge of the letters in the text; a quantitative measurement of showthrough in the 100%-print-coverage areas (i.e., percent brightness reduction on the back of the 100%-print-coverage areas); and a subjective evaluation of ink spreading in the 50%-print-coverage area. The subjective evaluations were performed by a panel, and the printed samples were not identified as to the type of SMA applied, if any.

The results for SMAs are shown in Table III. Of the SMA properties considered, the S:MA ratio is the only property that correlates with IJP. Further evidence to this effect is given in **Table IV,** which includes an ammonium salt of an SMA half-ester. The general conclusion is that IJP improves with increasing S:MA ratio.

Offset runnability

In this study, we consider only one aspect of offset runnability: a condition known as milking, piling, linting, or dusting. This problem, perhaps the most troublesome that offset printers face, is due in part to the nature of the offset printing process and in part to the increased use of filler in alkaline printing papers.

During the lithographic offset printing process, the nonimage areas of the printing plate are covered with an aqueous fountain solution. The image areas of the plate are covered with a greasy, tacky ink. Both ink and fountain solution are transferred from the plate to the offset blanket and then to paper. The fountain solution can loosen fines, fillers, and loosely bonded particles (such as dirt) in the paper. When these materials are freed from the paper surface, they can transfer to the blanket or the plate, requiring a press shutdown for cleaning.

Since filler does not bond to the cellulose in paper, it is not surprising that linting has become more of a problem as paper filler levels have increased. Many variables affect linting, including blanket material, blanket wash, fountain solution, press speed, printing nip pressure, and ink coverage *(3).* Due to the large number of variables involved, a given lot of paper may run well on one press but poorly on another, or run poorly on one day but run well the next on the same press and the same job.

The papermaker has no control over the printing press variables, and economic considerations may prevent him from reducing filler level. Given these considerations, the following question arises: How does the papermaker measure and reduce the milking tendency of paper? The literature outlines many laboratory and on-line tests for milking and linting *(3-7).* A test for milking tendency is best done with an offset press, although this is time-consuming and expensive. Several commonly used paper tests were recently investigated for their abilities to predict the milking tendencies of various papers. The papers used in these tests were machine-made samples whose milking and linting characteristics had been determined at a commercial offset printer to be “good” or “bad.” **Table V** lists a typical set of results.

V. Tests for milking and linting

Paper	Sizing results, s	Sizing results, g/m²	Wet rub, % pickup, Water	Wet rub, % pickup, IPA	Gurley densometer, s/100 cm³
Good	77	31.9	0.79	0.42	16
Bad	177	33.9	1.31	0.68	17
Bad	234	31.0	1.23	0.68	15
Bad	45	47.3	1.76	0.80	16

There were no correlations between milking and either sizing or densometer. But in all of our investigations, we have found that the wet rub test, using either deionized water or 15% isopropanol (IPA) as the test liquid, correlates best with on-press performance; lower-percent pickups indicated less milking problems. We used the wet rub test in the following work to indicate the milking tendency of paper.

SMAs have been used to reduce the milking and linting tendency of offset paper *(8).* There are, however, a wide variety of SMAs to choose from, and some of them affect milking in different ways. For example, **Table VI** indicates that an 80,000-molecular-weight, 2.7:1-S:MA ammonium salt outperforms a 38,000-molecular-weight, 2:1-S:MA ammonium salt. This study was performed with a low-viscosity oxidized starch, which is less effective than a medium- or high-viscosity starch in reducing milking.

VI. SMA properties vs. wet rub

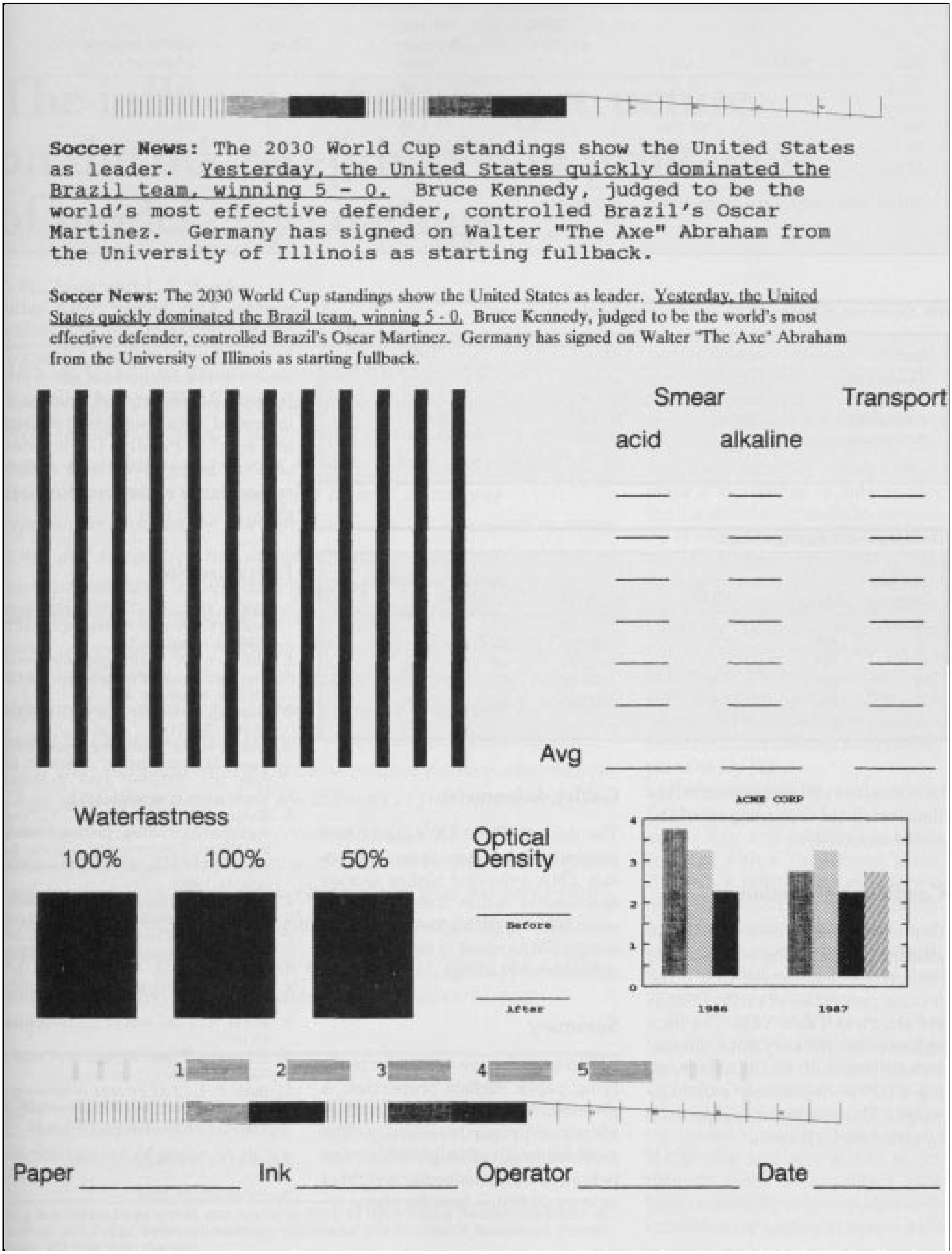
Salt	S:MA	MWT	SMA addition, %	Wet rub, % pickup water	Sizing, s
None	-	-	0	3.09	0
Starch	-	-	5.6*	1.12	1
Ammonium	2:1	38,000	0.15	1.12	39
Ammonium	2.7:1	80,000	0.15	1.05	96
Ammonium	2:1	38,000	0.30	1.07	172
Ammonium	2.7:1	80,000	0.30	0.87	244

*Starch pickup held constant at 5.6% for surface-sized samples

The effect of salt type on wet rub was also investigated, as shown in **Table VII.** These data point to two conclusions. First, a high styrene content contributes to reduced milking. Second, the ammonium salt of an SMA is preferable to the sodium salt of an SMA for controlling milking. Note that there are other approaches used to control milking and linting. Research in this area indicates that these problems are reduced if the surface size and starch are retained on the surface of the paper, as opposed to penetrating into the body of the paper *(8).* This implies that increasing starch viscosity and solids should help, as this retards penetration. It also implies that a good film-forming starch, such as hydroxyethylated starch, should be effective.

Regarding paper machine operation, results indicate that milking and linting tendency has some relationship to the level of sheet formation *(9).* Linting is generally reduced with improved formation. Therefore, good mixing and dispersion of filler, minimization of floc formation, and improved first-pass retention all work together to minimize linting. Work with newsprint *(10)* indicates that linting is reduced when fines are maximized at the paper surface. This implies that wire pit foaming should

1. Ink jet printability template



VII. Effect of salt type on wet rub

Salt	S:MA	MWT	SMA addition, %	Wet rub, % pickup water	Sizing, s	Gurley densometer, s/100 cm^3
None	-	-	0	2.96	0	4.9
Starch	-	-	4.0*	1.30	0	5.0
Na	1:1	120,000	0.12	1.26	1	5.5
Na	2.7:1	80,000	0.12	0.86	9	5.5
NH_4	2.7:1	80,000	0.12	0.55	202	5.4

*Starch held constant at 4.0% for surface-sized samples

VIII. Coefficient of friction (COF) as a function of molecular weight

Salt	S:MA	MWT	COF
Ammonium	2:1	38,000	0.47
Ammonium	3:1	58,000	0.44
Ammonium	2.7:1	80,000	0.43
Ammonium	1:1	120,000	0.43

IX. SMAs and Gurley densometer

Surface size	Salt	S:MA	MWT	Gurley densometer, s/100 cm^3
Starch	-	-	-	59
1	NH_4	3:1	58,000	67
2	NH_4	1:1	120,000	68
3	Na	1:1	120,000	82
4	Na	1:1	350,000	97

be minimized and wet-end additives that contribute to foaming should be added cautiously.

Coefficient of friction

One of the major uses of SMA in alkaline papermaking is to increase the coefficient of friction (COF). The friction properties of various SMAs are shown in **Table VIII.** The data indicate that the only SMA characteristic that contributes to increasing COF is decreasing molecular weight. This conclusion is supported by other work *(1, 11)*.

Gurley densometer

The data in **Table IX** suggest two general conclusions: (a) the sodium-salt SMA provides higher Gurley densometer values than the ammonium salt and (b) higher-molecular-weight SMAs result in higher Gurley densometer readings.

Summary

SMAs are effective agents for modifying paper surface properties. A given SMA, however, does not affect all paper properties equally. The ammonium salt of a high-S:MA ratio polymer, with a molecular weight of at least 50,000, is best for sizing response. Also, higher S:MA ratios provide better ink-jet printability. For controlling milking, a high-styrene-content ammonium salt is preferred. Coefficient of friction is improved with decreasing molecular weight. Finally, Gurley densometer is improved with a high-molecular-weight, sodium-salt SMA.

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