Styrene maleic anhydride imide resin (SMAI): a novel cationic additive in paper coating for ink-jet printing

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Abstract: A good image reproduction in ink-jet printing requires high print/dye density at the surface of coated sheet. A cationic polymer is normally used in coating color to chemically fix the anionic dye at the surface. Though considered to be a good dye-fixing agent, the commonly used Poly-DADMAC significantly retards coating runnability. In this work, SMAI - a multifunctional resin, is investigated as a cationic additive. SMAI as cationic additive significantly improved the print quality.

EXPERIMENTAL

Materials
In this work, precipitated calcium carbonate (PCC) was used as the pigment, as PCC is an emerging commercial alternative to silica. Partially hydrolyzed PVOH [5] was used as the binder and SMAI as a cationic additive. The SMAI resin used in this study had styrene to maleic anhydride ratios of 1:1, 2:1, and 3:1 and is named SMA1000I, SMA2000I and SMA3000I respectively. The charge densities of these cationic polymers increase as the m/n ratio increases.

A typical formulation contained 100 parts pigment, 7pph binder and 1 - 4 pph cationic additives. Formulations containing poly-DADMAC and those with no cationic additive were used as control samples. Solids content of coating formulations were limited to 25% and 30% due to high coating color viscosity at high solid levels.

Methodology

Coating and Calendaring
Commercial fine paper with a basis weight between 60 and 100 g/m² was targeted as the coating base throughout the investigation. The basis weight of the base papers used in this investigation was found to be within 75 ± 1 g/m². The base sheets were C1S coated (coated on one side) using a standard laboratory drawdown coater. Coat weight of the samples for print quality analysis and surface gloss measurements were between 8-9 g/m².

To understand the effect of concentration of SMAI’s on print quality and surface gloss, PCC based coating color formulations at 30% solids were prepared with varying concentrations of SMAI’s (SMA 1000I, SMA 2000I and SMA 3000I) from 1 to 4 pph and coated on the standard base sheets.

The coated sheets were dried in an oven at 100°C for 5 minutes. The coated sheets were then conditioned in a controlled temperature and humidity room at 25°C and 50% RH for 24 hours. The conditioned sheets were then conditioned in a controlled temperature and humidity room at 25°C and 50% RH for 24 hours. The conditioned sheets were then cut into 4-inch sections and were calendared using a laboratory calendar at a line load 300 kn/m and at 100°C. These calendared sheets were once again placed
in the conditioning room for 24 hours prior to printing for print quality analysis.

**Print Quality Analysis**

A Canon BJC - 4300 color bubble jet printer with new ink cartridge and new print head was used to print the pure black text for print quality analysis. “Inkjet Print Test” in 12pt Times New Roman font was the text analyzed. The print images were captured using a digital camera in fine mode as .JPG files. The image illumination, selected image quality (fine) and size settings remained the same throughout the image capturing section. The images were then analyzed using the Optima 6.0 software that calculated the grey intensity of the image with the image area and perimeter. The image background was set to pure white and the print grey intensity was measured on a scale of 0 to 255 where 0 represented pure white and 255 represented pure black.

**Water fastness**

The printed images from the print quality analysis were then analysed for water fastness. The coated sheets containing the images were immersed in a trough containing distilled water at 25°C and left for 4 minutes. The sheets were then dried at 100°C for 5 minutes. The retained optical density of the image, along with the area and perimeter, were again determined as described in the print quality analysis.

**Surface gloss**

The surface gloss of the coated sheets was measured using Novogloss, a statistical gloss meter in which a value of 99 represented a perfect glossy surface. The measurements were done at a light incident angle of 75°.

**RESULTS AND DISCUSSIONS**

A good paper coating formulation is expected to exhibit good coating quality and good coating runnability [8]. Coating quality is the quality of the coated surface itself, like surface smoothness, gloss and printing properties. A good print quality can be attained only if the coated surface can produce images with a high grey scale density and good image sharpness.

Grey scale, shown as in Fig. 2, was chosen for the study, and is based on a gradient of 0 to 255. The closer the image mean grey is to 255, the better the print density, and the lower the values for image area and image perimeter, the better the image sharpness. A representative character “t” which was distributed through the line of the text was chosen for analysis. An analysis of the entire text line was also done to confirm the findings, and showed similar results to the analysis of the single character.

An analysis of mean grey values attained with a different cationic additive, as shown in Fig. 3, indicates that the addition of a cationic additive in the coating formulation improved the image mean grey considerably, and there is a positive contribution from the SMAI to the print quality. The mechanism of the dye fixation is similar in poly-DADMAC and SMAI and is a result of the ionic interaction between the cationic site on SMAI and the anionic sites associated with the dye in ink-jet ink. The image grey values attained on coated sheets with SMAI’s as the cationic additive were either higher or comparable to those attained with poly-DADMAC. Although there is a difference in charge density, the contribution by different grades of SMAI’s to print quality seems statistically similar. The error bars here represent the variation in the measured parameter for the letter “t” in one print.

Good image sharpness is an indicator of the effectiveness of the cationic additive in limiting the lateral spread, or motting, of the ink dye. The image sharpness details, seen in Fig. 4, reveal that the area of the image produced is smaller with SMAI as the
Cationic additive in coating formulations, compared to the reference coating, i.e. coating with no cationic additive and with poly-DADMAC as additive. SMA1000 I produced the smallest image area compared to other cationic additives. The image area produced by SMA 2000I, SMA 3000I and poly-DADMAC were comparable.

The image perimeter, which is also an indication of the lateral spreading of the ink, is shown in Fig. 5. Image perimeter produced with poly-DADMAC was the lowest, with SMAI's showing comparable values, which indicate the effectiveness of SMAI as a cationic additive in improving the image sharpness.

The water fastness test is an important method of confirming the dye fixing property of a cationic additive in a coating formulation. A good printed image should retain almost all dye, or print density, after a brief exposure to water. This aspect of the print quality is important in outdoor applications of the image printed. The value of the image mean grey retained by coatings containing SMAI was significantly higher, compared to that retained with poly-DADMAC, as shown in Fig. 3. The dye density retained was over 95% with SMAI as additive, which is quite promising for outdoor or humid environment applications. This is a clear indication that the dye in the ink is chemically fixed on the surface of the coating and that the contribution of SMAI to print quality is better than that of poly-DADMAC. The dramatic increase in water fastness can be partly due to the styrene present in the SMAl, which helps in good film formation.

As expected, the area of the image increased after the water fastness test, this is due to the lateral spreading of the dye upon contact with water. Coatings containing poly-DADMAC and SMAI have shown almost similar increases, nearing the value attained with a control sample without a cationic additive. While the perimeter of the image is expected to show an increase, Fig. 5 shows that there was a decrease. This is because upon exposing the print to water, the curly cost lines of the image can merge into one another due to lateral spreading of the dye, bringing down the perimeter. Figure 6 shows the details of the digital images of the test prints after the water fastness test.

An effort is made here to understand the extent of the interaction exhibited by cationic additives at different solid loading on print quality. The print quality, including image grey value, image area and image perimeter, was evaluated for coating at 25%. The print quality at 30% solid loading was found to be superior to that at 25% solid loading. The data presented and discussed here is only of 30% solid loading. The combined contribution of high solid loading [1,8] and cationic additive has significantly improved the image grey value. The binder and cationic additive being the same, this better value of image mean grey can be attributed to better interaction and surface properties (improved surface smoothness and increased porosity of a coated surface at a given coat weight) obtained at high solid loading.

An investigation to understand the effect of the concentration of cationic additive on print quality was also carried out.

**TABLE I. Coated surface gloss with different cationic additive.**

<table>
<thead>
<tr>
<th>Coating Formulation</th>
<th>Cationic additive @1pph</th>
<th>Gloss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pigment: PPC</td>
<td>SMA 1000I</td>
<td>59.51</td>
</tr>
<tr>
<td>Binder: PVOH</td>
<td>SMA 2000I</td>
<td>51.91</td>
</tr>
<tr>
<td>Partially Hydrolyzed</td>
<td>SMA 3000I</td>
<td>51.60</td>
</tr>
<tr>
<td>Poly-DADMAC</td>
<td>Poly-DADMAC</td>
<td>48.36</td>
</tr>
<tr>
<td>None</td>
<td>None</td>
<td>50.88</td>
</tr>
<tr>
<td>Base sheet</td>
<td>Base sheet</td>
<td>8.00</td>
</tr>
</tbody>
</table>
Coating formulations with different concentrations of cationic additives (1pph - 4pph at 25% and 30% solid content) were prepared, coated and analyzed for print quality. The results showed that concentration of cationic additive does not seem to affect the print quality at 30% solid loading, while at 25% solid level, although not significant, print quality showed a slight improvement. The highest mean grey value attained at 25% solid loaded coating is only 231.2, whereas that attained with 30% solid loaded coating is 238.58, and in both the case the cationic additive is SMA 1000I.

The surface gloss of the coated sheet is an important property that can contribute to improving print quality. Table I indicates that use of SMAI as cationic additive also has the effect of improving the surface gloss, while an additive like poly-DADMAC had very little or no effect. SMA 1000I attained the highest gloss at 1pph. The surface gloss showed a small increase with increasing concentrations of SMAI (data not given here). The improvement in surface gloss of the coating can be attributed to the good film forming properties of these SMAI polymers when added as cationic additives.

**CONCLUSIONS**

The study clearly demonstrates the basic contribution of SMAI as a cationic additive in improving the print quality in a paper coating formulation for inkjet printing. Chemical fixation of the anionic dye at the surface of the coated paper has led to higher print density and better image sharpness. The water fastness of the printed image has improved dramatically when using SMAI as cationic additive, confirming the strong dye fixing property of SMAI. The good film forming nature of SMAI has contributed to improved surface gloss and hence better print gloss. To conclude, SMAI can substantially contribute to improving the inkjet print quality compared to poly-DADMAC and hence demonstrate the possibility of employing SMAI as an efficient and commercially viable cationic additive in paper coating formulations for inkjet printing.

**ACKNOWLEDGEMENT**

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**LITERATURE**