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Aggregation of Color Pigments by Surface Fixation Treatment

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Abstract. *The quality of a printed image is strongly influenced by the physical and the chemical interactions between the ink and the paper. Print quality can be evaluated either by objective measurements using instruments or by visual assessment studies involving panel of observers judging the final print. In this article, the print quality on commercial papers as well as on non-commercial papers with different amounts of salt for surface fixation has been studied. Perceived detail reproduction depends not only on sharp edge definition but also on the level of color saturation (Chroma). Color saturation and edge definition originate from two different ink and paper interaction processes. Color saturation is heavily dependent on ink penetration while edge definition correlates to ink spreading. In order to gain understanding of the performance of surface treatment by salt, large efforts have been put on splitting up of the increase in color saturation (Chroma) and improved edge definition. The printouts have been made with a desktop printer using pigmented inks. Cross section images have been taken with a light microscope to analyze the ink penetration depth. SEM analysis has been made to analyze the aggregation of the pigments on the surface. The print quality measurements have been both objective measurements such as print density and subjective image evaluation using a test panel of observers in a perceptual study. The perceptual study focused on detail reproduction, and efforts were made to separate the influence of the print density from the edge definition on the detail reproduction. The result from this study shows that an increased level of salt as surface fixation improves the detail reproduction due to aggregation of the pigments on the surface and that the ink penetration depth can be reduced by adding salt as surface fixation resulting in a higher print density. © 2011 Society for Imaging Science and Technology.*
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INTRODUCTION

Ink jet ink is a liquid containing colorants. The colorants can either be dyes dissolved in a solution or particles dispersed in a solution as in the case of pigmented ink.[1] The ink jet printing process can be described as the deposition of a limited amount of liquid onto a paper surface. By thermal and physical interaction at the air/ink and ink/paper interfaces, the carrier fluid evaporates or absorbs into the porous substrate by capillary flow and diffusion.[2,3] During the imbibition process, the carrier fluid should penetrate fast into the substrate or rapidly evaporate in order to avoid color to color bleeding that will impair the detail reproduction.[4] Furthermore, the colorants should stay close to the surface to reproduce a large color gamut and saturated colors.[5] For pigmented ink, the pigments are stabilized with dispersants through steric and electrostatic repulsion.[1] These dispersants usually have a hydrophobic and a hydrophilic part in their structure.[6] The aggregation of the pigments depends on the balance between repulsive and attractive forces and can be described by the DLVO theory.[7] The DLVO theory describes the stability of colloidal particles in a solution by taking the attractive van der Waals forces and the repulsive electrostatic forces of the particles into account. The stabilization and destabilization of particles may however also be affected by other mechanisms such as steric hindrance,[1] hydration and hydrophobic attraction,[8] and polymer bridging.[9]

In paper production, cationic polymers are commonly used as surface treatment for fixating the colorant to the surface and improve print quality.[10] Metal salts can also be used as cationic additives to improve print quality as described in the patent literature.[11] A study by Hamada and Bousfield[10] shows that the print density increases and the ink penetration depth decreases by adding Calcium chloride onto a surface before printing with pigmented ink. A model has also been presented to describe that the cationic ions are able to diffuse upstream of the absorption flow to influence the ink pigment stability.[10]

The main purpose of this work was to study how different levels of salt as surface treatment can lead to aggregation of the pigments and an improved detail reproduction in the final printout. The detail reproduction may be affected by both the color gamut of a printed image and the edge definition. Detail reproduction in terms of edge sharpness and dot gain can be measured objectively, but the impression of a printed image can only be measured subjectively. There are several existing methods for subjective print quality evaluation.[12] As the difference in print quality was relatively small, the pair wise comparison method was chosen in this study.

MATERIALS AND METHODS

Four non-commercial uncoated surface sized papers with varying level of surface fixation, together with six different uncoated surface sized commercial papers with and

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Table I. Papers with and without surface fixation.

Paper	Code	Surface fixation	Grammage [g/m^2]
Commercial paper 1	A	Y	81
Commercial paper 1	B	N	81
Commercial paper 2	C	Y	80
Commercial paper 3	D	Y	82
Commercial paper 4	E	N	79
Commercial paper 5	F	N	80
Ref	G	N	78
Low fixation	H	Y	79
Medium fixation	I	Y	79
High fixation	J	Y	79

Figure 1. Test image for subjective print quality evaluation.

without surface fixation, were used in this study. The commercial samples were used as reference point to define the range of interest for this study. The non-commercial paper samples were produced in a full scale paper machine with identical properties except for different levels of surface fixation. The surface fixation used in this study was $CaCl_2$. All samples were characterized by the Bendtsen method for surface roughness and porosity measurements together with the Cobb 60 method to characterize the absorption. The paper samples can be found in Table I.

The printer used in this study was a desktop printer HP Office Jet professional D8000 printer using pigmented, water-based ink. Ethanol was used to separate the pigments from the carrier fluid, and FTIR analysis was used to characterize the pigments. The result from the FTIR analysis indicates that the pigments in the ink consist of organic pigments and carbon black. As it was noticed that the characteristics and the performance of the black ink differed from the others, it was decided to print only with C, M, and Y inks.

Test charts for print quality evaluation were created in Adobe Photoshop™ and Adobe InDesign™ CS3, and all colors were defined in RGB coordinates. The test chart for evaluating the color reproduction contains 11 in. × 7 in. color patches of cyan, magenta, yellow, black, red, green, and blue color in steps of tone values from 0% to 100%.

Spectral reflectance was measured in a spectrophotometer with an optical geometry of 45°/0° and 2° of observing angle. Measurements were made with settings for D50 illumination and with a neutral filter.

For the visual assessment study the RGB GATF 7125 image with a resolution of 1808 × 2280 pixels was selected. This image contains a wide density span as well as many fine details. The perception study was performed on an image in gray scale to reduce the influence of print density on perceived detail reproduction. The gray scale image is depicted in Figure 1.

The gray scale image was printed with composite black ink on paper A–J (Table I). Two additional samples were

Table II. Printed samples used in the perception study.

Paper	Code	Surface fixation	Grammage [g/m^2]
Commercial paper 1	A	Y	81
Commercial paper 1	B	N	81
Commercial paper 2	C	Y	80
Commercial paper 3	D	Y	82
Commercial paper 4	E	N	79
Commercial paper 5	F	N	80
Ref	G	N	78
Low fixation	H	Y	79
Medium fixation	I	Y	79
High fixation	J	Y	79
High fix + low dens	K	Y	79
High fix + blurr	L	Y	79

added to this perception study. One sample was created to resemble the print density and the other to resemble the detail reproduction of an untreated paper. By a look up table (LUT) the amount of color in the grayscale image could be reduced to create an image with a print density similar to paper G. The final image was printed on a paper with a high level of surface fixation (paper J) and is listed as sample K in Table II. The other additional sample was created by applying a 2 × 2 Gaussian-blur filter on the original grayscale image. The filtered image was printed out on paper J and is listed as sample L in Table II.

The perception study was performed in three different laboratories, all neutral gray painted room with controlled illumination. The test panel consisted of 40 participants ranging between 20 and 60 years of age and an equal number of men and women. Most of the participants were experienced in evaluating print samples. The test panels

Table III. Paper properties.

Code	$Cobb_{60}$	Roughness [ml/min]	Porosity [ml/min]
A	27.0	135	960
B	26.0	133	960
C	30.5	263	810
D	30.4	165	1100
E	21.3	187	940
F	68.8	197	940
G	19.4	143	750
H	19.4	150	750
I	19.8	156	750
J	20.7	155	730

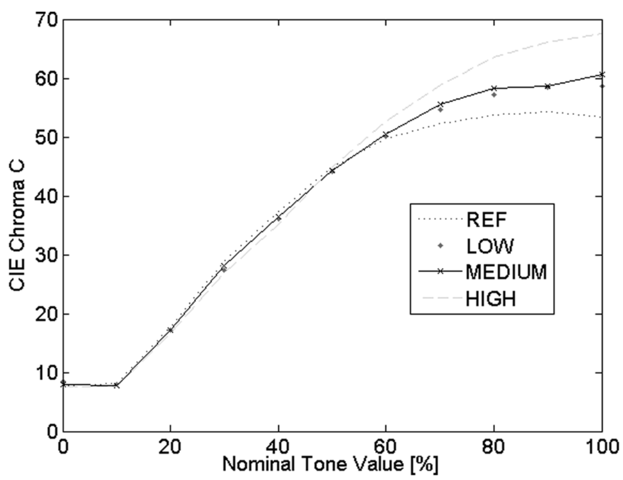

Figure 2. CIE L*a*b* Chroma for papers G–J. The dotted blue curve represents paper G, the dotted red curve represents paper H, the solid black curve represents paper I, and the dashed green curve represents paper J.

were asked to look at the detail reproduction in the images and judge the images in a pair wise comparison.

Images of half tone dots were taken with light microscopy at 210 × magnification (top view). An image analysis routine was used for calculating the printed area covered by ink representing the final spreading of the droplets. The number of pixels resembling ink coverage was calculated by using a threshold value of 33% of the maximum intensity of the printed dots. Cross section images of the ink penetration were taken with a light microscopy and 430 × magnification to analyze the ink penetration into the paper. A scanning electron microscope was used for analysis of the ink distribution on the surface both with 150–-350 × magnification (top view) to see the ink distribution on the surface and 10–12000 × magnification to see the pigments on the surface. SEM analyses were made on 100% full tone surfaces printed out on a paper without applied surface fixation (paper G) and with a high level of surface fixation (paper J).

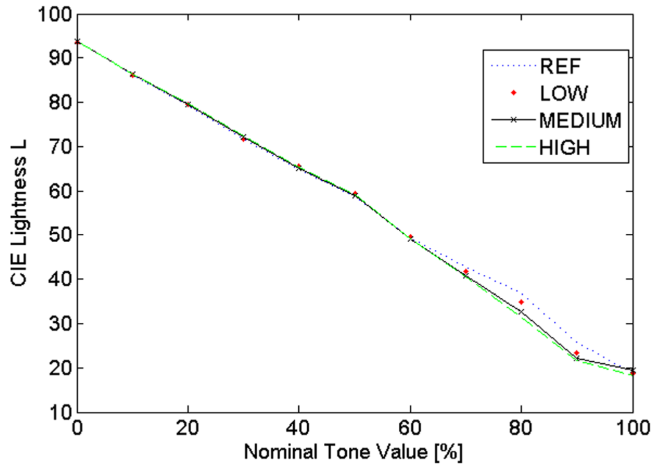

Figure 3. CIE L*a*b* lightness for papers G–J. The dotted blue curve represents paper G, the dotted red curve represents paper H, the solid black curve represents paper I, and the dashed green curve represents paper J.

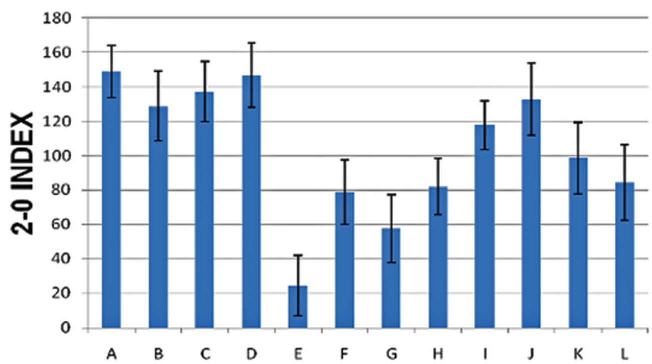

Figure 4. Results from the perception study on the grayscale image.

III. RESULTS

Results from the measurements of paper properties, ink penetration depth, and analysis of aggregation of pigments on top of the surface with SEM together with print quality evaluation are presented below.

Paper Properties

The content of the commercial papers (A–F) and the difference between them were not known in detail although some properties were measured and are shown here. Differences in printability can therefore only partly be derived from knowledge about the papers. The difference between the four non-commercial papers (G–J) was the level of surface fixation only, and the study focuses therefore on the non-commercial papers. The results from the measurements of the Bendtsen porosity and surface roughness together with the Cobb 60 value are listed in Table III. The data indicate that applied surface fixation does not largely affect the porosity and the surface roughness. This can be seen by studying papers G–J in Table III where the amount of surface fixation increases from G to J. The commercial paper F exhibited the highest Cobb 60 value revealing that this paper is more hydrophilic and absorbs more water

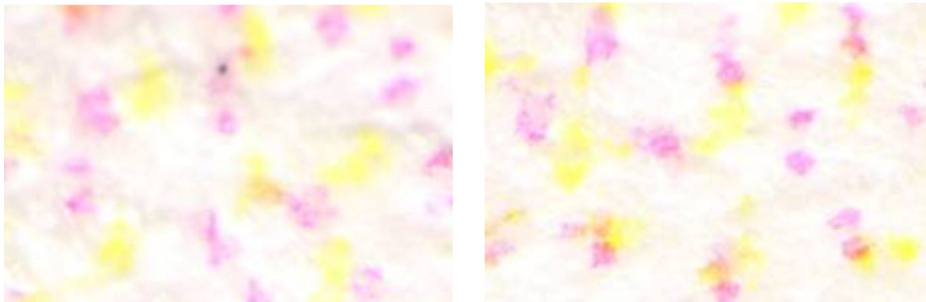

Figure 5. Microscopy images of a 10% red surface printed out on paper with a low (left) and high (right) amount of surface fixation.

than the other papers. Paper D exhibited the highest porosity value, whereas the difference in measured porosity was relatively small among the non-commercial papers G–J.

Print Quality

The CIE L*a*b* Chroma for all colors and lightness for black color were calculated for all papers. It was observed that an increased level of surface fixation increases the Chroma for higher tone values. Papers A, C, and D exhibited higher Chroma than papers B, E, and F at 100% tone value for cyan, magenta, red, green, and blue (data not shown). The result for red color printed out on papers G–J is depicted in Figure 2. The result for the red color is representative for all colors tested. It can be noticed that for lower tone values (<40%), an increased amount of surface fixation slightly reduces the Chroma. Although the absolute value of the Chroma may depend on the experimental setup and the experimental conditions, a lower Chroma at the lower tone values for samples with a higher degree of surface fixation could be confirmed by a large number of measurements, where all measurements showed this trend.

Only small differences in lightness for printed black color were found for papers with applied surface fixation compared to papers without surface fixation. The result for black color printed out on papers G–J is depicted in Figure 3. The result is representative for all papers tested.

Perception Study

The detail reproduction of a printed image may increase not only by improved edge definition of a printed sample but also as a result of an increase in the Chroma, where an increase in the Chroma may give differences between colored areas that become more readily distinguishable from each other. Therefore, efforts were made to minimize the later effect in the perception study by using a gray scale image (Fig. 1) printed with composite black ink. The results from the perception study at three different labs all correlated and were therefore added together. The result is presented in Figure 4. It can be observed that an increased level of surface fixation improves the detail reproduction (samples G–J). These results may however be related to changes in both print density and in edge definition.

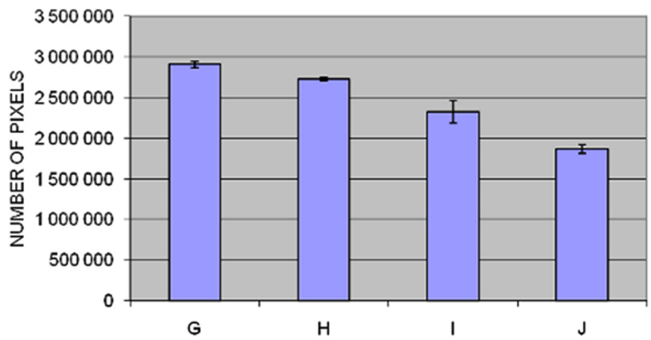

Figure 6. Droplet spreading for a 10% surface printed on papers G–J.

However, by comparing sample K and G in Fig. 4 it can be seen that the image with a lower print density printed out on a paper with a high level of surface fixation (sample K) resulted in a better detail reproduction than for the paper with a low level of surface fixation (sample G). This indicates that an increased level of surface fixation not only improves the color reproduction but also improves the part of the detail reproduction in a printed image that is related to the edge definition. Comparing sample L (high level of surface fixation and blurred image) and sample G (low level of surface fixation and original image) an improved detail reproduction for sample L compared to sample G can be observed. It shall also be noticed that sample G exhibited a lower Chroma than sample J (Fig. 2).

Among the commercial papers, it can be observed that papers E and F (without any surface fixation) reproduced a lower detail reproduction than the other commercial papers. On the other hand, paper B, without surface fixation, exhibited a detail reproduction which was close to the detail reproduction of the commercial papers with surface fixation (papers A, C, and D).

An example from the light microscopy images of a 10% red printed surface on samples with varying amount of surface fixation is depicted in Figure 5. The printed dots appeared to be smaller and more distinct for the paper with higher amount of surface fixation (right image).

The number of pixels in the printed area was calculated for 10% half tone values of cyan, magenta, and

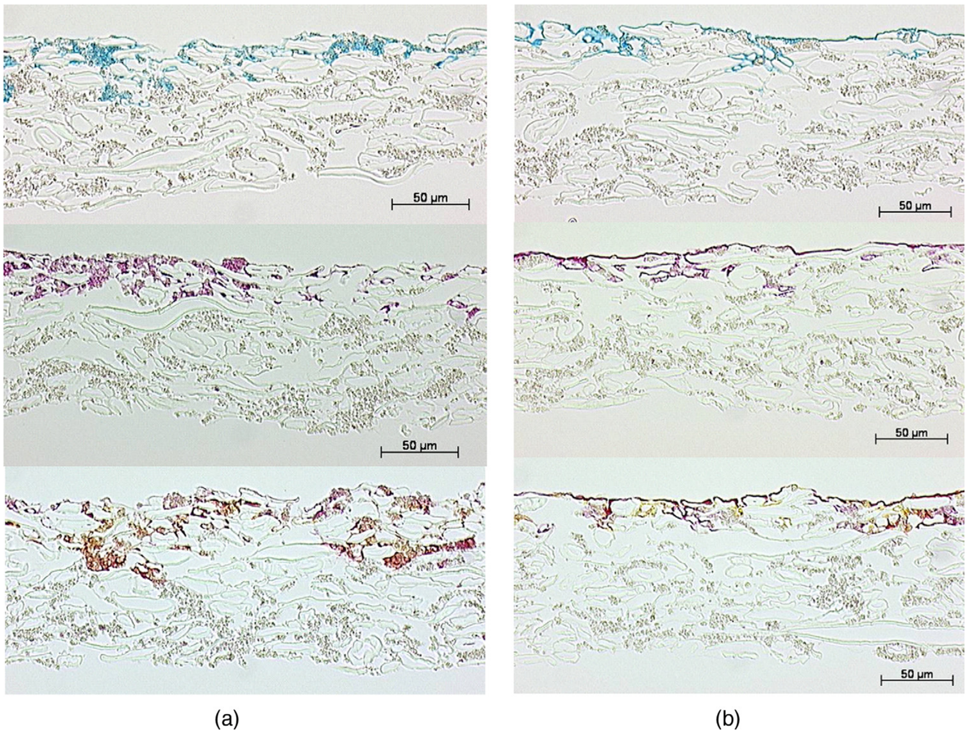

Figure 7. Cross section images of 100% printed fulltone surfaces on paper without surface fixation (left images) and a high level of surface fixation (right images). Cyan, magenta, and red from the top to the bottom.

yellow printed on papers G–J. The result shows that an increased level of surface fixation decreases the ink spreading of the droplets. The result for cyan printed out on papers G–J is depicted in Figure 6. The result is representative for 10% surfaces of cyan and magenta. The resulting smaller dots on the samples with a higher level of surface fixation can be expected to give the possibility to print finer details and thereby improve detail reproduction. This correlates well with the data from the perception study presented in Fig. 4.

Ink Penetration

Light microscopy cross section images are depicted in Figure 7 for 100% full tone surfaces of cyan, magenta, and red printed out on papers G and J. The left images show the ink penetration for a paper without surface fixation (paper G), and the right images show the ink penetration for a paper with a high level of surface fixation (paper J). It can be seen that the pigments stay closer to the paper surface for the paper with a high level of surface fixation for all colors. Only small differences in penetration depth were observed for black color (not shown).

SEM Analysis

In Figures 8 and 9 examples of SEM pictures of an unprinted surface for a paper with a low level of surface fixation (Fig. 8) and a high level of surface fixation (Fig. 9) are presented. No important difference can be observed between the two unprinted surfaces on papers G and J.

In Figures 10 and 11 examples of SEM images is depicted with 350 × magnification of a 100% magenta printed surface on paper G without surface fixation (left image) and on paper J with a high level of surface fixation (right image). The magenta printed surface on paper G without applied surface fixation (Fig. 10) differed from the printed surface on paper J with surface fixation (Fig. 11) in that the printed surface on paper J appeared denser than on paper G.

By studying SEM images of the magenta printed surfaces with a higher resolution (10000×) in Figures 12 and 13, it can also be seen that the pigments aggregate on the paper surface with a high level of surface fixation (Fig. 13), resulting in larger particles as compared to a paper without surface fixation (Fig. 12).

Differences could be observed in the SEM analysis for black color printed on papers G and J. An example from the result from the SEM and 10000 × magnification for black color printed out on papers G (left image) and J (right image) is presented in Figures 14 and 15.

DISCUSSION

Although surface fixation treatment with salt on uncoated papers can improve the print quality, the quality of the detail reproduction on the various papers studied in this work may be affected by variations in paper properties and paper content other than just different levels of salt as surface treatment. Paper F, reproducing a higher detail reproduction than paper E, also exhibited a higher Cobb 60 value as

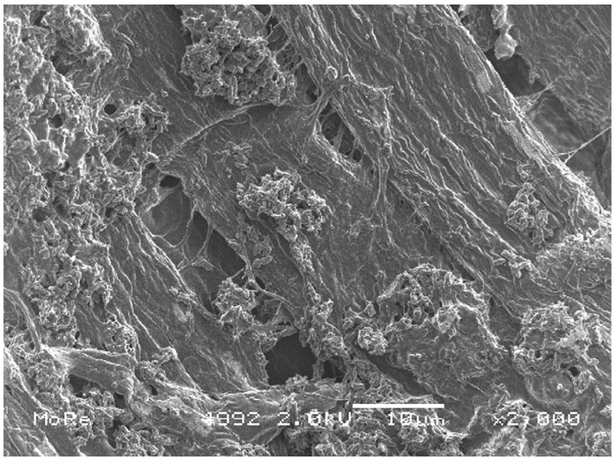

Figure 8. SEM image of an unprinted surface for a paper without surface fixation (paper G).

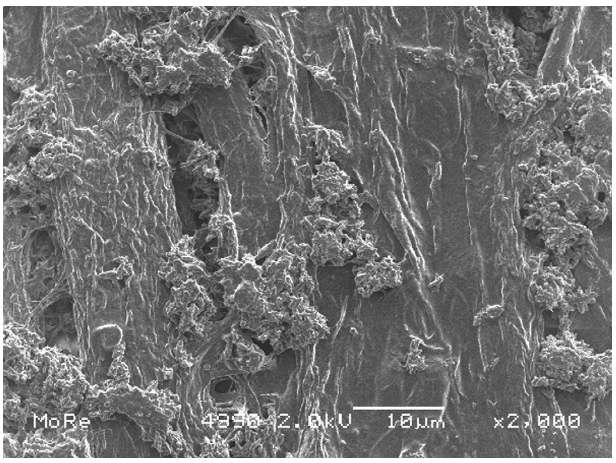

Figure 9. SEM image of an unprinted surface for a paper with a high level of surface fixation (paper J).

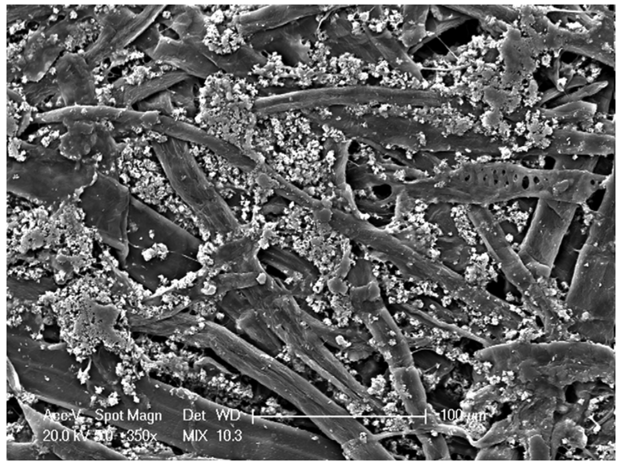

Figure 10. SEM image of a magenta printed fulltone surface printed out on a paper without applied surface fixation (paper G).

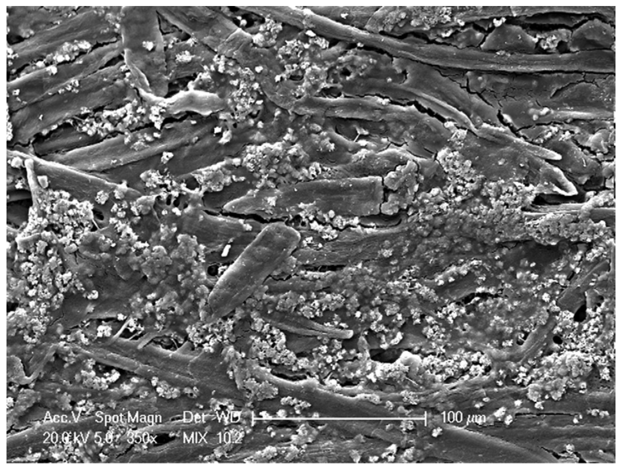

Figure 11. SEM image of a magenta printed fulltone surface printed out on a paper with applied surface fixation (paper J).

compared to paper E, and the difference in detail reproduction between these two papers might be explained by a faster absorption of the aqueous solution due to the hydrophilic characteristics of paper F. Another parameter that can impair the detail reproduction is surface roughness. Measurement data on the non-commercial papers presented in this work show however only negligible variations in surface roughness when applying salt as surface fixation. The same holds for the porosity measured on the non-commercial papers.

An earlier study of the line quality[13] shows that no measurable improvement in edge sharpness was found for a paper with surface fixation treatment (paper A), as compared to the paper without surface fixation treatment (paper B). This is consistent with the subjective measurements of detail reproduction, which show only small differences between sample A and sample B. Therefore, the commercial paper B deviates slightly from the reasoning in this article by exhibiting a detail reproduction which is better than expected for a paper without surface fixation treatment. Results from the perception study show that papers E and F, without any surface fixation, reproduced a lower detail reproduction compared to the other papers. For the non-commercial papers J and G, with a high and low level of surface fixation, respectively, the edge sharpness measurements and the results from the perceptual study show that the surface fixation treatment improves the line quality[13] and the detail reproduction.

It may be objected that applying salt onto a surface may increase the surface energy and thereby typically increase the droplet spreading. If so, this could worsen the detail reproduction in the final printout, especially for hydrophobic, slow absorbing surface sized papers. Optical microscopy images show however that a high level of surface fixation decreases the droplet spreading, reproducing more distinct printed dots. This is consistent with the finding that the increased level of salt as surface fixation improves the detail reproduction in a printout made with pigmented ink. It furthermore explains the finding that a high level of surface fixation slightly reduces the Chroma at the lower tone values ($<40\%$) since the contribution from

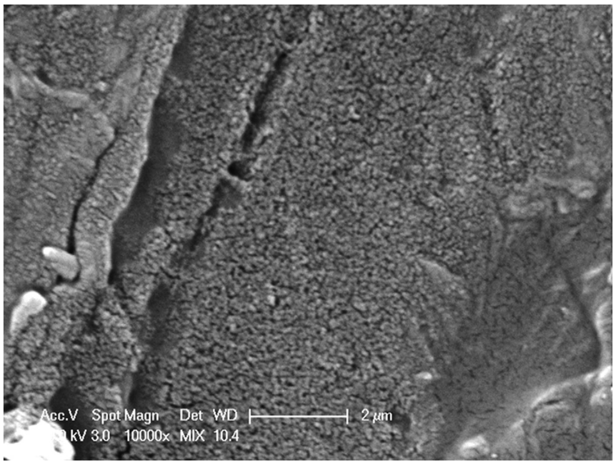

Figure 12. SEM image of a magenta printed fulltone surface printed out on a paper without applied surface fixation (paper G).

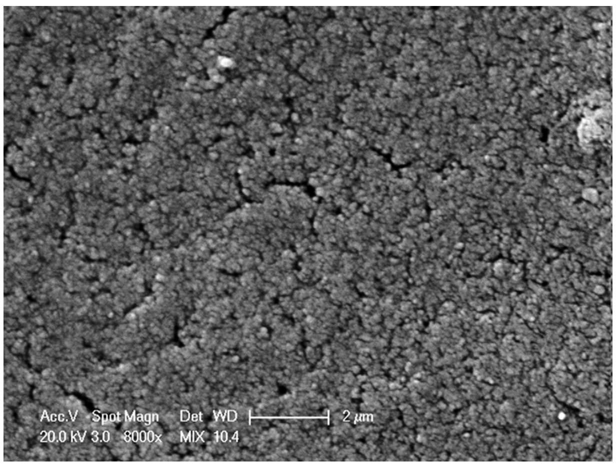

Figure 13. SEM image of a magenta printed fulltone surface printed out on a paper with a high level of applied surface fixation (paper J).

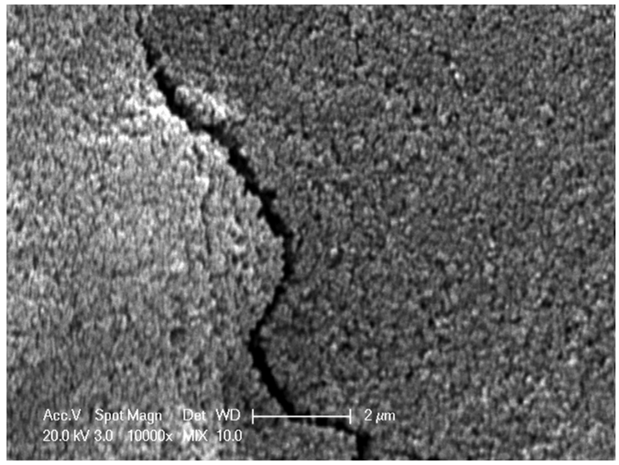

Figure 14. SEM image of a black printed fulltone surface printed out on a paper without applied surface fixation (paper G).

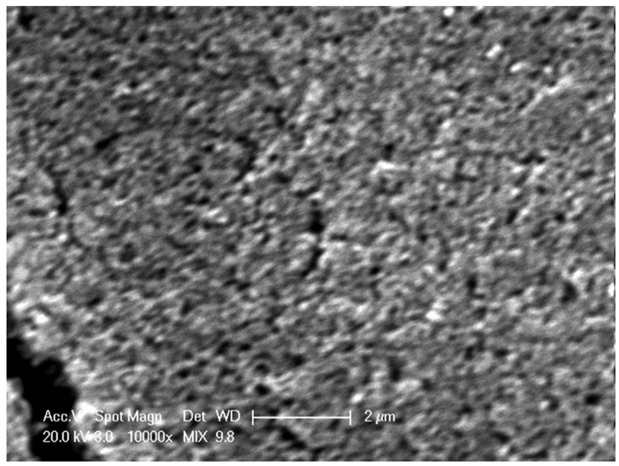

Figure 15. SEM image of a black printed fulltone surface printed out on a paper with a high level of applied surface fixation (paper J).

the white paper background is included in the spectral measurement. Smaller dots lead to a larger uncovered paper area, i.e., reduced physical dot gain. Although the dots may contain pigments that have aggregated close to the surface and therefore effectively absorb light, the total reflectance of light may still be slightly larger at the lower tone values. At the higher tone values, when the dots cover most of the paper, the pigments at the surface effectively absorbs the light and thereby decreases the total reflectance, as compared to an untreated paper. The decrease in droplet spreading may be explained by changes in electrostatic interactions between the pigments at the paper–ink interface, possibly yielding a faster aggregation of the color pigments on papers having a high level of surface fixation.

It was shown in previous work that surface fixation with salt can improve the color gamut volume of the print.[14] This study confirms that, for the higher tone values, a high level of surface fixation does indeed increase the Chroma. Cross section images show that the ink penetration depth decreases with an increased level of surface fixation. The color pigments stay closer to the paper surface where they are able to more effectively absorb spectral parts of the incoming light, thereby yielding more vivid and saturated colors.

The presented findings in this paper may be explained by aggregation of the color pigments due to the applied salt as surface fixation. Anionic surfactants are commonly used as dispersants in pigmented ink to avoid undesirable aggregation of the pigments and to stabilize the ink.[1] Within the framework of the DLVO theory, the addition of salt decreases the electric double layer around each particle and the energy barrier that has to be overcome in order for particles to aggregate. The SEM images presented in this work illustrate the aggregation of pigments on top of the surface as an effect of the surface treatment.

CONCLUSION

The detail reproduction in a printed image is an interplay between the print density and the edge definition originating from surface spreading of the droplets. In this study, it was shown by subjective measurements that the edge definition in a printed image can be improved by using paper treated with a salt solution for surface fixation for printouts with pigmented inks. It was shown by objective measurements that the surface fixation can reduce the penetration depth and make the pigments aggregate at the paper surface.

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