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Influence of Binders on Inkjet Print Quality

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With surface sizing process, the paper surface can be tailored in order to achieve excellent print quality. Present study reports paper surface modifications carried out by surface sizing treatment with formulations composed by different polymer binders systems and subsequent evaluation of inkjet print quality of the produced papers. Binders as cationic starch (used on surface sizing in paper mill) and polyvinyl alcohol (used as binder in coating process) had been used in order to improve the inkjet print quality. These binders systems provide papers with different structure and physical-chemical properties and as consequence differentiated print quality. Parameters, such as, line width, blur, raggedness, inter-color bleed, circularity and dot gain, gamut area and optical printing densities were measured and correlated with the structural and physical-chemistry features of the paper samples. The results revealed higher performance of the paper surface sized with only polyvinyl alcohol. Multivariate analysis demonstrates that hydrophilicity and roughness are properties particularly detrimental for gamut area.

Keywords: inkjet printing, polyvinyl alcohol, print quality, starch, surface sizing.

1. INTRODUCTION

Inkjet printing is a popular low-cost method for producing high quality digital images. Recent developments in printer technology and printing inks lead to an increase in the requirements for paper performance. Most inkjet inks have low viscosity and low surface tension, which set high demands on paper porosity and absorbency characteristics. The inkjet print quality depends on the printer, inks nature and paper characteristics [1, 2]. The finishing of the paper surface is extremely important regarding to the print quality improvement. The surface finishing includes mechanical treatment such as calendering and/or chemical treatments like surface sizing or coating [2, 3]. Surface sizing aims to improve certain paper characteristics as hydrophobicity, surface strength, optical properties, porosity and roughness [3 – 6]. Surface energy, porosity and roughness are properties that greatly influence the spreading and penetration of the inkjet inks and therefore have a decisive effect on print quality.

Surface sizing consists in the application, under pressure, on both sides of the paper, of a formulation essentially composed by binders, wetting or hydrophobizing agents and resins or polymers with a typical dry solids content ranging between 2 % – 15 % [7, 8].

A conventional surface sizing dispersion is composed by cationic starch, which provides stiffness and strength, and a sizing agent that makes the surface hydrophobic to reduce liquids absorption [9]. As an alternative to the conventional surface sizing formulation, it has been developed modified starches [4, 10 – 11]. Other agents such as polyvinyl alcohol, sodium alginate, carboxymethyl cellulose, polyurethane, styrene acrylate copolymers, styrene maleic anhydride copolymers, are also used [2, 5, 6, 11, 12 – 17]. Sporadic use of pigments in surface sizing had been reported, in order to increase the brightness, opacity and smoothness and reduce the porosity, which contributes for the paper printability [3, 18, 19]. In this case, the process is named pigmentation, which corresponds to the application of a film with a grammage ranging from 2 to about 7 g/m^2 per paper side [18].

Zirconium compounds were used to improve the efficiency of various starch modifications and several synthetic surface sizes. It has been reported the positive effect of the application of this compound in the paper quality, machine runnability and total costs [20].

Also, new synthesized products for surface sizing, namely quaternary agents derived from fatty acids, were used to improve print quality [5].

Printability of paper is a generic term, which gives an indication of how paper behaves through printing process. As printing is an interactive process, printability depends on interactions between paper and printing ink and the printing process variables. Good printability means that the paper is not very sensitive to variations in different process variables and consistently gives good print quality. In this sense, the print quality can not be defined in absolute terms; it depends on the optical printing density, print resolution and evenness of the printed image [21].

The printability and print quality parameters are evaluated by specific tests of a printed paper sample, made in controlled conditions and image analysis for the quantification of various parameters such as blur, raggedness, inter-color bleed, circularity and dot gain, mottling and optical printing density. A printer had to be considered with a specific set of influencing variables, namely ink type, drop volume and drop frequency.

Most published studies regarding paper surface treatments focused on the examination of the contribution of coating structure to inkjet print quality [12, 22 – 28]. Fewer studies have been published on open literature concerning

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surface sizing and their impact on inkjet print quality [5, 6, 16, 17]. Formulations composed by starch and quaternary agents derived from fatty acids (EPK2) were used in surface sizing. Such formulations showed better print quality of lines and dots when compared with others made by blend of starch and synthetic agents (styrene acrylate latex or styreic maleic anhydride) [5, 17]. This behavior is assigned to the low surface energy of the papers sized with EPK2, which prevents the ink spreading. However, regarding color reproduction, the results were poor due to the high acid component exhibited by those papers, which can change the ionization state and the absorption spectra of the dye molecules [17]. Moutinho *et al* [6] observed that the paper surface sized with a blend of cationic starch and co-styrene-maleic anhydride originated high gamut area and optical printing densities, compared to the paper modified with cationic starch and co-styrene-acrylate. Nevertheless, concerning line and dot print quality, trends were not evident.

This work reports the influence of various surface sizing formulations designed with different binders compositions on paper properties (structural and physical-chemical), and relates them to inkjet print quality parameters.

2. EXPERIMENTAL DETAILS

2.1. Materials

The base paper used for surface sizing treatments was produced from bleached softwood and hardwood mix kraft pulp and was internal sized (grammage 74.4 g/m^2). The binders used in surface sizing were cationic starch suspension and a fully hydrolyzed polyvinyl alcohol (PVA). The test liquids employed on contact angle measurements for surface energy evaluation, were distilled water, methylene iodide (Aldrich, 99 % purity) and ethylene glycol (Merck, > 99.5 % purity).

2.2. Sizing preparation and application

Table 1 shows the surface sizing formulations (composition and solids content). The base paper without any surface treatment was designed for B. The cationic starch suspension used in this work was collected at the paper mill and includes other additives such as optical brightener and a sizing agent.

The PVA solution was prepared at 25 % solids by adding the required amount of dry PVA powder to cold water under agitation and heating the mixture up to 85 ºC. The solution was maintained at this temperature for the period of 40 min to assure complete dissolution of the PVA.

Table 1. Formulations description

Paper	Composition	Solids content,%
B	No surface treatment	–
S	100 % starch	11.8
SP80:20	80 % starch + 20 % PVA	11.8
SP50:50	50 % starch + 50 % PVA	11.8
P0.6	100 % PVA	6.0
P1.7	100 % PVA	8.0
P3.6	100 % PVA	11.8

The surface sizing was applied with a laboratory reverse roll coater (Mathis Type RRC-BW) at room temperature, only in one side of the base paper. The operating conditions of the coater were maintained constant: pressing power between applicator roll and transport roll at 3.5 bar, the distance between dip roll and applicator roll was –125 μm and rolls speed was 20 m/min. All surface sized sheets were dried on an IR drier during 2 minutes reaching a final temperature of 100 ºC. The papers were then conditioned at 23 ºC and 50 % relative humidity during 24 hours, before physical characterization and printing.

2.3. Surface sized sheets characterization

The pick up of sizing formulation applied was determined by the increased weight, after sizing. Bendtsen air permeability and Bekk smoothness of the paper sheets were determined according to ISO 5636-3:1992 and T 479 om-91 standards, respectively.

The 3D topographical parameters were obtained from data acquired on an Altisurf 500 optical profilometer that subsequently were treated in the PaperMap 4.0 software. Each reported value represents the average of six scannings of the 4.8 mm × 4.8 mm surface area. Several parameters had been computed, being considered only the average roughness (Sa), maximum peak height (Sp), maximum valley depth (Sv), skewness (Ssk), kurtosis (Sku) and the interfacial area ratio (Sdr), in order to describe the treated papers surface topography.

The surface free energy and corresponding dispersive and polar components of treated paper samples were also evaluated. Contact angle measurements were carried out on OCAH 200 Dataphysics Instruments by means of sessile drop method using distilled water, methylene iodide and ethylene glycol as test probe liquids. The surface free energy and its dispersive and polar components were obtained using the geometric mean according to Owens, Wendt, Rabel and Kaelble approach [29].

2.4. Print evaluation

The surface sized papers were printed on an HP Deskjet F370 printer with a specific printing target, using plain paper and normal printing as printer settings. Subsequently, inkjet print quality was evaluated in terms of gamut area, optical printing densities and line and dot quality parameters.

Color essays were carried out in an Avamouse Spectrocam handheld reflection spectrophotometer under the following conditions: D65 illuminant, observer 2º, instrument geometry 45º/0º and Status I as density spectral response. Gamut area, which represents the range of reproducible colors, was calculated as the area of hexagon (a*,b*), where a* and b* are the CIE L*a*b* coordinates obtained for each of the 6 colors: cyan, magenta, yellow, red, green and blue. Optical printing density of the black, cyan, magenta and yellow was calculated by the difference between optical density of the printed spot and paper.

Horizontal black line width, raggedness and blur were measured, and inter-color bleed was calculated from black over yellow and yellow over black line sections. From a matrix of black dots, gain and circularity were also measured. The parameters related with the line and dot quality analysis were performed on a QEA, personal image analysis system (PIAS II).

2.5. Statistical methodology

Multivariate analysis was performed using the Unscrambler® 9.5 software. Principal Components Analysis (PCA) was made on a data matrix based on six samples and seven print quality variables: gamut area (Gamut); optical printing density of the black (PD_Bk); black dot circularity (Dot_circ); blur, raggedness and width of the horizontal black line (L_Blur, L_Rag and L_Width, respectively); inter-color bleed (ICB). The Partial Least Squares Regression (PLS) methodology was used to predict the structure and physical-chemistry properties effects on the print quality parameters. The structural and physical-chemistry variables used in PLS construction are the following: sizing pick up (P_up); Bendtsen air permeability (B_air_p); Bekk smoothness (Bekk_s); Sa; Sp; Sv; Ssk; Sku; contact angle with water (CA_w); total, polar and dispersive components of the surface free energy (SE_t; SE_p; SE_d, respectively).

3. RESULTS AND DISCUSSION

3.1. Surface sized papers sheets characterization

Paper properties are presented in Table 2. The sizing pick up range from 0.6 g/m^2 to 3.6 g/m^2, depending on the formulations viscosity and solids content. In the formulations with only PVA, the solids content was varied purposely in order to obtain different pick up and assess the impact of the PVA amount on print quality.

Table 2. Values of sizing pick up, Bendtsen air permeability, Bekk smoothness and topographical parameters of papers

Paper	Pick up, g/m^2	Air perm., ml/min	Bekk, s	Sa, µm	Ssk	Sdr, %
B	__	337	23.80	3.03	–0.26	12.00
S	3.5	247	5.75	3.21	–0.09	(a)
SP80:20	1.8	291	16.17	3.09	–0.22	13.80
SP50:50	1.8	290	16.00	3.17	–0.20	(a)
P0.6	0.6	312	22.30	3.05	–0.26	(a)
P1.7	1.7	289	20.30	3.12	–0.20	12.80
P3.6	3.6	125	19.70	3.03	–0.24	12.30

(a) Value not measured by the equipment.

In Table 2, it is also possible to observe that all surface sized paper have similar low air permeability values, indicating that the papers have a much closed structure. This low air permeability comes from the base paper. However, increasing the amount of PVA provides papers with even lower air permeability. Comparing papers sized with starch and PVA at the same pick up level, we observe that PVA creates a more closed structure than starch. This is because PVA has a good binding strength and good film-forming capacity [12, 13, 30].

Concerning Bekk smoothness, all surface sized papers presented lower smoothness, relating to base paper. A possible explanation for this result is the re-humidifying of the paper during the sizing process and the subsequent drying with lower tension, resulting in greater fibers freedom reorganization. The paper surface sized with starch showed less smoothness. According to Maurer and Keraney [10], drying conditions for starch binder in a coating must be carefully controlled in order to avoid non-uniform porosity. Furthermore, starch is a less efficient binder on a basis weight than PVA. Starch is composed mainly by amylopectin (branched fraction) and a lesser amount of amylose (linear polymer chain) [31]. The linear polymer fraction contributes more toward film formation on paper surface comparatively to amylopectin [32]. Thus, the lower effectiveness of the starch in terms of film formation may explain the lower smoothness of the paper surface sized with starch against PVA. Moreover, Bekk smoothness decreases with the increase of the PVA pick up possibly due to rise of formulations viscosity. The amount of PVA deposited was controlled by changing the solids content; the higher solids content of the PVA formulations the higher the viscosity. At the nip applicator roll, during transfer of formulation onto the paper surface, the film is split into two layers; one is deposited on the paper web and the other remains on the roll surface. Film splitting may be responsible for patterns on the paper surface. Key variables affecting these patterns are the rheology of the sizing formulation and film thickness [10, 32].

The measurements acquired from air leak instruments such as obtained from Bekk smoothness are denominated macro roughness. However, one of the disadvantages of this technique is the lack of sensitivity at small scale, enough to be relevant for printing evaluation. Therefore, profilometry measurements are selected to evaluate microtopography of paper surface. The results presented in Table 2 show that surface topography parameters for the different papers are very similar, but papers surface sized with starch presenting slightly higher roughness values. The negative value of Ssk parameter indicates the preponderance of valley structures on the surface of all papers. Interfacial area ratio is not conclusive due to the absence of some values provided by the equipment. Large values of this parameter indicate higher percentage of additional area contributed by the texture when compared to an ideal plane. Thus, the analysis of measured values evidences that all treatments increase the texture of paper surface. Despite the differences in the methods principles, this result is in agreement with that found from the analysis of the Bekk smoothness.

From a physical-chemical point of view, the papers sized with different formulations showed somewhat similar values for surface free energy but with distinct characteristics of polarity, as can be seen in Fig. 1.

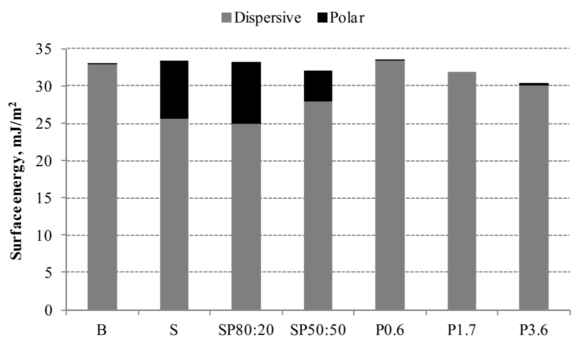

Fig. 1. Dispersive and polar components of surface energy

The base paper is practically non-polar due to internal sizing that made it hydrophobic. The paper surface sized with starch presents a significant polar component. Starch formulation, although composed by a mixture of several additives, mainly contains starch. This is a hydrophilic polymer that binds to cellulose fibers through hydrogen bonds [10], providing a noteworthy polarity. The addition of 20 % PVA practically does not change the physical chemistry of the paper surface when compared with the starch treatment. Only at a higher level of PVA addition (50 %) there has a significant decrease of the polar component, maintaining however a similar paper surface free energy. Paper treated only with PVA, independently of the pick up, exhibit a polar component close to zero. Higher applied amount of PVA causes a slight decrease of the surface free energy. Despite the PVA polymer being hydrophilic [33], the paper surface sized with this polymer has a hydrophobic nature. Schuman et al. [33] found that the PVA fully hydrolyzed, exhibited lower moisture absorption when compared with other grades, being considered more water resistant than a partially hydrolyzed PVA. The same author explains that this trend is due, presumably, to the larger number of hydrogen bonds between the hydroxyl groups in PVA fully hydrolyzed, making them less accessible to the water molecules [33]. The PVA used in this experimental work is fully hydrolyzed and the possible establishment of hydrogen bonds within polymer chains may also explain the non-polar nature of the paper surface treated with pure PVA.

3.2. Print evaluation

In order to evaluate the color reproduction performance of the produced papers, optical printing density and gamut area results are plotted in Fig. 2.

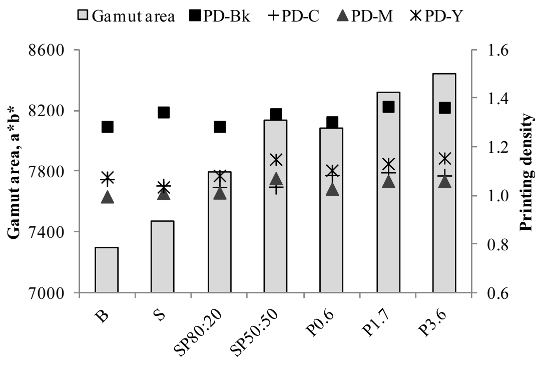

Fig. 2. Gamut area and optical printing density of the black, cyan, magenta and yellow

We observe that all formulations have a positive effect in the color reproduction capability. Increasing the PVA content in the formulation enhances the gamut area, being the lowest value for the starch treatment and the highest for the PVA surface sizing. The excellent capacity of color reproduction obtained with PVA, even at low pick up levels, is due to the good film-forming characteristics as already stated.

The optical printing density of the black is superior to those of the other colors, as expected. This difference may be due to three factors; first, the drop volume of color inks is much lower (5 pl) than the drop volume of black ink (16 pl); second, the surface tension of color inks is inferior to the black ink; and finally the black ink of the printer used was pigment-base while color inks are dye-base. Thus, the distinct interaction behavior of the black and color inks with the paper surface may explain the differences in optical printing density values.

There are no obvious trends with respect to optical printing density among samples; nevertheless, there is a tendency for the samples treated only with PVA or with high content of PVA, to show slightly higher values. This result is in agreement with trends found for the gamut area. Once more, the good film-forming nature of PVA contributes to achieve the excellent performance for the color reproduction. The PVA film prevents the deep ink absorption, keeping the dye/pigment at the surface contributing to the higher optical printing density and gamut area. This can be observed in Fig. 3.

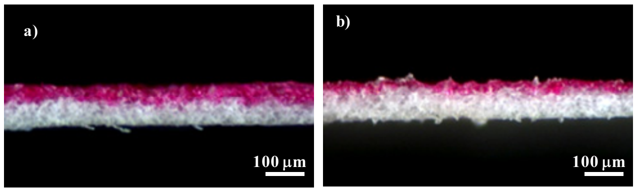

Fig. 3. Cross section of base paper (a) and PVA sized paper (b) after magenta printing

The results of the line and dot print quality parameters are listed in Table 3. The analysis of these parameters is quite difficult, since there are no clear trends. The assessment of the parameters separately shows that the paper treated with starch presents highest blur, i. e., poorer sharpness. Concerning raggedness, a measure of the contour irregularity, it appears that all formulations improve the line contour. This parameter depends on the ability of the paper to spread the ink from its initial position, due to the phenomena of capillarity. The papers surface sized only with PVA, exhibits in general lower line width in relation to the papers treated with formulations containing starch. However, all the papers show ink spreading with elevated line widths comparatively to theoretical printed value (350 µm). There is not necessarily a direct relationship between line width and blur, since a line can expand, but at the same time having well-defined contour. With regard to inter-color bleed, a comprehensive analysis of the results shows that base paper presents the highest value and consequently the poorest performance. The surface sizing improves the inter-color bleed, especially when using only PVA.

Dot circularity and dot gain do not present any trend for the treated papers. We can assume that the circularity and dot gain values are fairly similar for the different papers in analysis. However, the paper surface sized with the lowest pick up of PVA present the best circularity and dot gain (corresponding to the lowest values of these parameters), providing some evidence that there is an optimal range for the PVA addition level. Regarding to the formulations composed with only PVA, the improvement of the gamut area with pick up observed from PVA0.6, PVA1.7 until PVA3.6, and the deterioration in the line and dot quality is mainly due to the fact of ink being contained at the surface level. This situation can be explained by the decreasing of the air permeability, due to a more closed surface paper structure. The ink carry fluid (water) having a slower absorption rate, tends to stay at surface, worsening the line and dot quality but increasing color strength by the dye molecules/pigments resting at surface.

Table 3. Line and dot print quality parameters

Paper	Horizontal black line, µm			ICB	Black dot	
	Blur	Rag.	Width		Circ.	Gain, %
B	163.75	22.75	491.50	49.13	1.91	24.10
S	182.00	18.75	512.00	40.25	1.90	28.70
SP80:20	171.50	18.00	515.00	45.75	1.95	26.70
SP50:50	170.00	16.00	521.50	45.13	1.92	29.35
P0.6	165.75	15.75	498.00	36.81	1.86	22.35
P1.7	163.75	18.00	489.00	36.19	1.94	24.95
P3.6	175.00	19.75	501.00	38.50	1.91	24.90

The paper surface sized with starch presents poor color reproduction properties and weak line and dot quality when compared to the others. These poor results may be related to the higher surface roughness and simultaneously higher polarity that contributes to ink spreading. Starch and PVA blends generates intermediate properties between starch and PVA pure formulations, closer to the results obtained with starch or PVA depending of the properties considered. Comparatively to sizing formulations studied by other authors [5, 6, 17], the formulations composed with only PVA present as an advantage a good balance between color reproduction and print quality of the line and the dots.

From the analysis of Fig. 3 and Table 3 it is possible to conclude that are competing variables that determine the color reproduction capability and the line and dot print quality parameters. This can be assessed in detail through multivariate analysis.

3.3. Multivariate analysis: relationships within print quality parameters and structural and physical-chemistry properties

PCA could help in building a rank of the papers tested based on their structural and physical-chemical variables and print quality properties. The PCA analysis separates the paper samples into two different groups: P3.6, P1.7 and P0.6 form a cluster of papers sized only with PVA in different amounts, and S, SP80:20 and SP50:50 form the second cluster of papers composed by pure starch and blends with PVA at different parts. In addition, P0.6 differentiated from the other two PVA samples, since it has the lowest gamut area, black optical printing density and dot circularity values.

Concerning to print quality parameters, PCA shows a strong positive correlation between the line width and inter-color bleed. The blur of the line and dot circularity as well as raggedness of the line and black optical printing density are also much related.

The SP80:20 and SP50:50 papers have high values of ICB and L_Width and low values of L_Rag and PD_Bk. On the other hand, P1.7 and P3.6 have low values of ICB and L_Width, and show a high gamut area, black optical printing density and line raggedness values.

PLS analysis was based on inter-color bleed, raggedness and gamut area. These properties have been found to be the most important to explain the variation of data (PCA analysis). The analysis was performed only with the six samples under study and for that reason the results should not be used as a predictive purposes.

It was found that 73 % of physical-chemical properties variation explains 96 % of gamut area values for a correlation factor of 0.98. According to the weighted regression coefficients, the model suggests that a decrease in SE_t, SE_p, Sv and Sku, and an increase of CA_W, SE_d and Bekk_s, are particularly beneficial for gamut area. In general, it can be said that the elevated hydrophilicity and roughness generates lower gamut area; this is probably due to the higher absorption and spreading of the ink, getting a lower ink film thickness on paper surface and consequently a minor gamut area is observed.

The PLS model shows that 63 % of structure and physical-chemistry properties variation explains 91 % of the difference observed on inter-color bleed property, for a correlation factor of 0.76. The model separates the papers into two main groups, but in this particularly case the values of this parameter are very similar on papers sized with only PVA than on papers sized with starch and with blend starch/PVA. According to the weighted regression coefficients, the model suggests that an increase in SE_d, CA_w, Sp, Ssk and Sku and the decrease in SE_p would be especially beneficial. The physical-chemistry properties have a great influence on inter-color bleed, particularly a certain hydrophobicity seems have a positive effect on this property. Additionally, a surface composed by a plane with lot of peaks (higher Ssk) and the presence of high peaks / deep valleys (elevate Sku) appears to create a barrier to spreading of the inks, thus reducing the inter-color bleed.

The PLS model shows that 73 % of structure and physical-chemistry properties variation explains 85 % of the difference observed on raggedness line property. It was found that a closed structure and a surface with lower deep valleys have a detrimental effect on the raggedness.

4. CONCLUSIONS

In the present work, the paper surface was modified by application of different formulations composed by cationic starch, PVA and a mixture of them in two proportions in order to evaluate the performance of these sized papers on inkjet print quality. The papers sized only with PVA exhibited lower Bendtsen air permeability and higher Bekk smoothness. On the other hand, the physical-chemical properties showed that modified papers display similar surface free energy, but different polarity. Papers sized with starch showed significant polar component, while the modified papers only with PVA presented a non-polar surface.

PCA analysis revealed the formation of two papers clusters related to the binder under study; one group constituted by the paper surface sized with starch and starch/PVA mixtures and another constituted by the papers treated with only PVA with different pick up. Contribute to this differentiation, the gamut area, the black optical printing density and the line properties width, raggedness and inter-color bleed.

The existence of competing variables that determine the color reproduction and the line and dot printing parameters were clearly shown in the current study. It has been demonstrated that high hydrophilicity and roughness originates lower gamut area, resulting probably of the higher absorption and/or spreading of the ink. The paper modified with starch follows this trend. Certain hydrophobicity and a surface formed by a plane with lot of peaks seems a positive effect at inter-color bleed level possibly due to barrier effects created by the presence of peaks. Moreover, a closed structure and a surface with lower deep valleys are accompanied by pronounced raggedness, i. e. the contour irregularity of the line deteriorates.

A higher performance was obtained when the surface sizing was carried out with only PVA. These papers demonstrate a better balance between color capacity reproduction and line and dot print quality.

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