

## PAPER SURFACE CHEMISTRY AS A TOOL TO IMPROVE INKJET PRINTING QUALITY

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### SUMMARY

Surface treatment is an important step of papermaking for improving the final product quality. For uncoated printing and writing papers (P&W), surface sizing is becoming a common practice for controlling paper surface characteristics and liquid spreading and absorption.

This work aims at evaluating the potential of assessing and controlling paper surface chemistry as a tool to improve printing quality, by analyzing the impact of the application of different surface sizing formulations in the chemical surface characteristics of the modified paper samples and in the final printing quality. For that, blends of cationic starch and minor quantities (5%, 10% and 20% w/w) of 4 distinct styrene copolymers were used. A sample surface sized only with cationic starch was taken as reference.

Some surface chemical properties of the 13 paper samples were determined, and the inkjet printing quality was also evaluated. The results revealed that the surface sizing treatments used in this study have a substantial influence on the surface energetics and that the chemical properties of the paper surface certainly influence and partially explain the differences detected in the inkjet printing quality.

**Keywords:** Paper, printing quality, surface chemical properties, surface sizing

### INTRODUCTION

At present, there is an increasing demand concerning the printing quality of printing and writing (P&W) paper grades. Printing quality is strongly influenced by the structural and chemical properties of the paper surface, being one of the most important factors concerning customer's evaluation. Thus, all the studies dealing with printing quality, paper-ink interaction and the paper surface characteristics are of utmost importance. Due to this increasing importance this research area is under high development and many related studies have been published in the open literature [1 - 5].

Chemical modification of the paper surface is nowadays a common practice in papermaking, in order to improve printing quality, and surface sizing is a standard operation in many paper mills. Typically - and especially for P&W papers - starch is used for surface sizing, with the main goal of improving paper surface resistance and printability. However, there is an increasing tendency to use blends of cationic starch and synthetic copolymers to enhance surface sizing effects by controlling the paper surface energy, the corresponding hydrophilic character and the affinity towards different types of ink. The main objective of this approach is to improve print quality by optimizing the balance between the absorption and spreading phenomena [2, 4].

The most important function of the starch, when used together with synthetic surface sizing agents, is to act as a binder, in order to produce an even blend. As for the synthetic surface sizing agents, their use is often necessary because the primary raw material of paper and paperboard are the hydrophilic cellulosic fibers. As these synthetic surface sizing agents are usually polymers with some degree of hydrophobicity, the paper surface becomes water resistant, which is crucial for many printing

processes [6]. Typically the chemicals used to produce synthetic surface sizing agents are styrene, maleic anhydride, acrylic acid, ester or polyurethanes. When combined with starch, a thin reticular film is formed at the paper surface, influencing several paper properties such as smoothness, surface resistance, surface free energy and hydrophobicity [4].

In this context, the objective of the present work is to evaluate the potential of paper surface chemistry as a tool to improve printing quality, by analyzing the impact of the application of different surface sizing formulations composed of blends of cationic starch and minor quantities (5%, 10% and 20% w/w) of 4 distinct styrene copolymers, in the chemical surface characteristics of the modified paper samples and in the final printing quality. A sample surface sized only with cationic starch was taken as reference. The main objective of this approach is to improve printing quality by optimizing the balance between the absorption and spreading phenomena.

This study is part of intensive studies on surface sizing undertaken by the authors, where the influence of the surface sizing application into the chemical rather than the physical properties of the paper surface, as well as the impact of the modifications induced by different surface sizing agents applied to the surface of the printing and writing papers in the final inkjet printing quality, are analyzed [5, 6].

Finally, it should be pointed out that the results are of utmost importance to the national paper industry as they relate to its most relevant product – the eucalyptus based printing and writing uncoated papers – for which there are no published results involving the tested formulations. Furthermore, both the copolymers and the formulations used were selected having in mind the feasibility of their application in the paper industry.

## EXPERIMENTAL

### Surface Sizing

A calendered uncoated base paper (80 g/m<sup>2</sup>) produced with a *Eucalyptus globulus* kraft pulp without any surface treatment was surface sized with cationic starch (St) and taken as reference. Additionally, blends of starch with four different styrene copolymers were tested in three different concentrations, as described in Table 1. These surface sized samples were no further calendered.

**Table 1. Samples description.**

Sample	Surface sizing Formulation (% w/w)	Sample	Surface sizing Formulation (% w/w)
St	100% Cationic Starch	StS9-05	95% Cationic Starch 5% Co-styrene-acrylate
StS2-05	95% Cationic Starch 5% Co-styrene-maleic anhydride	StS9-10	90% Cationic Starch 10% Co-styrene-acrylate
StS2-10	90% Cationic Starch 10% Co-styrene-maleic anhydride	StS9-20	80% Cationic Starch 20% Co-styrene-acrylate
StS2-20	80% Cationic Starch 20% Co-styrene-maleic anhydride	StS10-05	95% Cationic Starch 5% Co-styrene-acrylate
StS4-05	95% Cationic Starch 5% Co-styrene-maleic anhydride	StS10-10	90% Cationic Starch 10% Co-styrene-acrylate
StS4-10	90% Cationic Starch 10% Co-styrene-maleic anhydride	StS10-20	80% Cationic Starch 20% Co-styrene-acrylate
StS4-20	80% Cationic Starch 20% Co-styrene-maleic anhydride	-----	-----

The surface sizing formulations were applied using a Mathis laboratory coating device, SVA-IR-B, which operates automatically with different velocities of the applicator roll. A 0.15 mm roll was used and its velocity was adjusted to 6m/min. The drying process was performed in two steps: using an IR drier (1.0 kW drying intensity), coupled to the applicator roll, followed by air drying for at least 10 min. The total surface sizing pick-up was 3.5 ± 0.3 g/m<sup>2</sup>, in each case.

Some of the properties of the compounds used in this work were determined in laboratory, being the results presented in Table 2. The information regarding the monomers proportion was derived from the available product specifications and elemental analysis.

**Table 2. Properties of the compounds used to produce the surface sizing formulations.**

Compound	Monomers proportion**	Solids content (%)	Particles mean diameter***	Surface Tension (mN/m)	pH
St - Cationic starch*	n.a.	12.0	298.8	32.9	5.0
S2 - Co-styrene-maleic anhydride	3:1	15.0	37.2	---	8.4
S4 - Co-styrene-maleic anhydride	2:1	14.6	25.4	38.51	7.6
S9 - Co-styrene-acrylate	3:4	25.7	83.6	49.99	4.3
S10 - Co-styrene-acrylate	1:2	25.5	73.8	64.33	4.7

\* The cationic starch suspension was collected at the paper mill, and includes other process additives, such as optical brightener (OBA) and salt.

\*\* Based on elemental analysis (using the equipment EA 1180 CHNS-O from Fisons Instruments).

\*\*\* Determined using the Coulter N4

### **Contact Angle Measurements**

Contact angle measurements constitute an indirect method to easily assess paper surface energy, being fast, simple and based on easy-to-use equations for the calculation of surface energy components. The fundamentals of this method are well detailed in the literature, and have been previously published by the authors [5, 6]. In this study, the measurements were performed with the DataPhysics equipment OCA20, using the sessile drop method. The initial resting drop image was acquired by a CCD camera and the corresponding contact angle was calculated after fitting the drop contour line. The OWRK (Owens, Wendt, Rabel and Kaelble) theory was applied to the contact angle measurements of five liquid probes: demineralised water, formamide, ethylene glycol, propylene glycol and diodomethane, in order to compute the total surface free energy and its dispersive and polar components [7].

### **Inverse Gas Chromatography (IGC)**

IGC has also proved to be a powerful and reliable tool for the characterization of solid surfaces, like fibers or paper. IGC differs from conventional chromatography since the material under analysis is not the one injected into the column but the surface of the stationary phase contained in the column. The principle of IGC is simple: an inert carrier gas elutes a minute quantity of a probe (solute) molecule through a column packed with the stationary phase under analysis, which in this case is paper. Due to the thermodynamic interactions between the two phases, the probe molecules are retained for a certain time, which is used to derive not only the dispersive components of the surface energy and their variation with temperature but also the acid-base character of the surface, based on the Lewis concept (i.e., the ability to accept and donate electrons). The methods for the calculation of the dispersive component of the surface energy ( $\sigma_s^d$ ) and of the Lewis acid/basic constants ( $K_a$  and  $K_b$ ) are well described in the literature [8, 9]. IGC experiments were performed using a DANI GC 1000 chromatograph, equipped with a flame ionization detector (FID). The experiments were carried out at oven temperatures between 35 and 60°C using 5°C intervals at infinite dilution. To determine the dispersive component of the surface energy, a series of n-alkane probes was used (n-hexane, n-heptane, n-octane, n-nonane, n-decane), while to assess the acid-base properties five polar probes were tested (trichloromethane ( $\text{CHCl}_3$ , acidic), dichloromethane ( $\text{CH}_2\text{Cl}_2$ , acidic), acetone (amphoteric), ethyl acetate (ETA, amphoteric) and tetrahydrofuran (THF, basic)). Natural gas (83.7 % methane) was used to determine the dead retention volume [8, 9].

### **Printing Quality Evaluation**

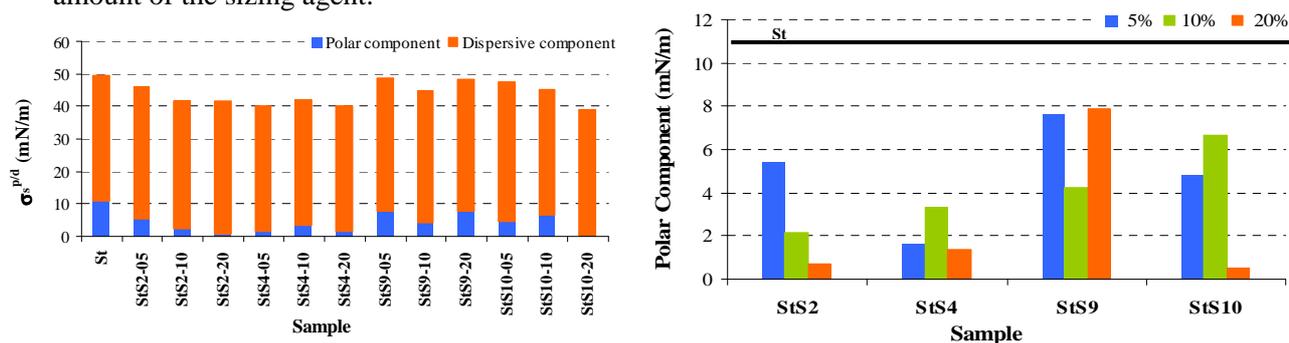
To evaluate the printing quality all the samples were printed with a specific mask using the inkjet printer HP5652. Inkjet printing quality was assessed by quantitative measurements, which include: Optical Density, measured by the spectrophotometer Gretag D19C; Gamut Area, determined through the CIE Lab colour coordinates obtained for six colours by using the AvaMouse spectrophotometer

(Avantes); and Line quality, evaluated using the Personal Image Analysis system PIA BASF – 8042319 for a black line with yellow background. The results from the printing tests were correlated to those obtained from the characterization of the paper surfaces by using the Partial Least Squares tool.

Taking into account that surface is a small part of a paper sheet and the fact that the differences between the samples tested have a small magnitude, all the data were submitted to an analysis of variance (ANOVA) and Principal Component Analysis (PCA), in order to validate the relevance of all the results, by analyzing inter and intra-samples variability.

## RESULTS AND DISCUSSION

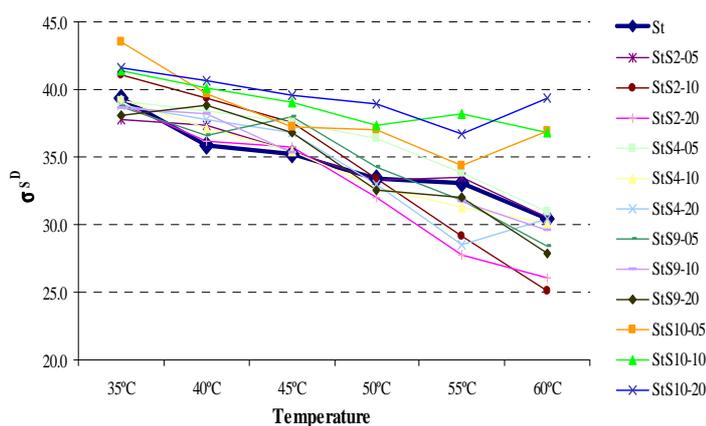
Surface free energy and the corresponding dispersive and polar components of the paper samples were determined, according to OWRK method, as indicated in the experimental section. The knowledge of these parameters is essential to assess the impact of the various sizing agents on the samples surface properties. The results obtained are plotted in Figure 1 –a). As it can be seen, the surface free energy of the paper samples is mainly dispersive. Moreover, the addition of the synthetic surface sizing agents to the cationic starch tends to decrease the total surface energy mainly due to the decrease of its polar component rather than the dispersive one, leading to more hydrophobic surfaces. This effect was expected, since the surface sizing agents added are mainly non-polar compounds. Since the major effect of the addition of the synthetic surface sizing agents is detected in the polar component of the surface energy, the values of this component are detailed in Figure 1-b), regarding the influence of the amount of the sizing agent.



**Figure 1 – a) Graphical representation of the polar and dispersive components of the surface energy for the various samples tested; b) Polar component of the surface free energy for all the samples tested.**

As Figure 1-b) reveals, the addition of the various synthetic agents significantly reduces the polar component of the surface energy. Concerning the concentration of the sizing agent, all types of behaviors are observed, as a consequence of the distinct molecular orientations of these agents at the surface of the paper samples. For instance, samples StS2 (co-styrene-maleic anhydride) present a consistent decrease in the values of the polar component with the sizing agent concentration, suggesting that the molecules of the co-polymer are oriented at the paper surface with the styrene monomer towards the exterior. On the contrary, the oxygen containing monomers are pointing inwards, i.e. towards the fibrous matrix, probably as result of some attraction from the -OH groups of cellulose. For Samples StS9 the polar component exhibit a minimum for 10 %, probably because for the intermediate concentration the molecules (larger than the ones of co-styrene-maleic anhydride) nearly fill the available sites and the increase in concentration leads not only to the accumulation of the molecules but also to their reorientation, the acrylate group (more polar) reorients outwards leading to an increase in the polar character of the surface.

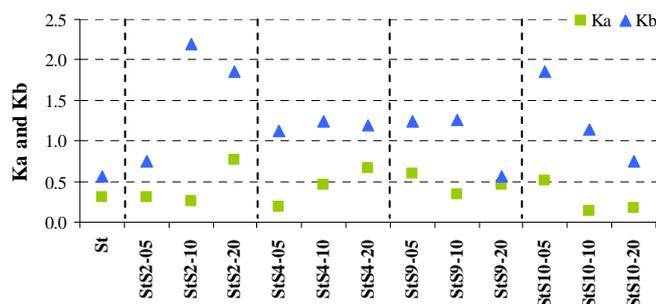
As mentioned before, with IGC it is also possible to determine the value of the dispersive component of the surface free energy ( $\sigma_s^D$ ) of the paper samples, by using the retention times determined for the n-alkane series at different temperatures. The results are presented in Figure 2 for all the samples tested.



**Figure 2 –  $\sigma_s^D$  determined by IGC at different temperatures.**

Regarding temperature, a decrease of  $\sigma_s^D$  with the temperature increase is noticed for all samples. Concerning the effect of the synthetic surface sizing agents' addition to the cationic starch, it was found that, in general, higher values are obtained for the sizing blends than for the reference sample (St). This indicates that the sizing agent generally increases the surface ability to establish dispersive interactions, probably due to the higher surface tension of the sizing agents compared to that of the cationic starch

As mentioned before, besides the dispersive interactions investigated using the n-alkane probes, the acid- base interactions, based on the Lewis concept, can be studied by IGC by injecting polar probes. The values of Ka and Kb obtained for all samples are plotted in Figure 3.



**Figure 3 – Values of Ka and Kb computed from the IGC measurements for the different sizing agents and different concentrations.**

From this plot, it is possible to observe that all the Ka and Kb values determined by IGC have the same order of magnitude, and the Kb values are superior to those of Ka. This indicates that the surface of the papers is predominantly amphoteric with a slight tendency to donate electrons (i.e. with a moderate basic character). In comparison to the sample sized with cationic starch alone (St), it is possible to see that the largest impact of the addition of the synthetic surface sizing agents is noticed on the values of Kb.

The surface acid-base character, evaluated by the Ka and Kb values, is ruled by the availability of functional groups at the paper surface. Thus, and taking into account previously published studies stating that the availability of the hydroxyl groups (-OH) at the surface strongly relates to the surface acidity [9- 10] it is possible to elaborate further about the composition and orientation of the molecules of the sizing agents

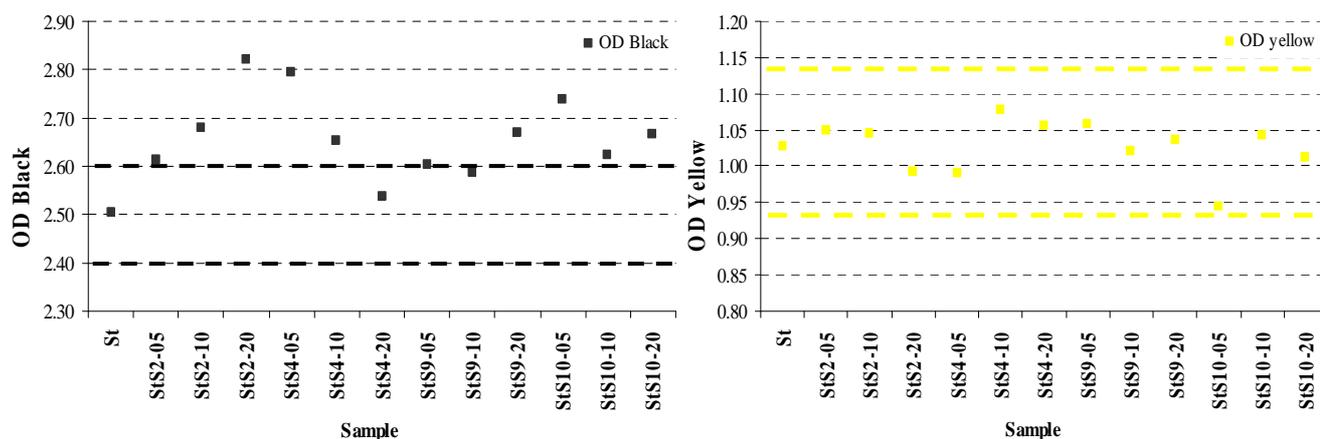
Regarding surface sizing agent S2, the IGC results are in agreement with the ones of contact angle measurements, indicating that the molecules are probably oriented so that the styrene monomer is turned to the exterior and the oxygen of the maleic anhydride monomer points inwards for all concentrations. The increase of the Kb values in comparison to the reference sample (St) is certainly due to the presence of the electronic cloud of the styrene monomer. In addition, when the amount of sizing agent is increased to 20% the electron accepting effect of the oxygen atoms of the maleic anhydride monomer is strongly enhanced, as detected by the increase in Ka. Analyzing now S4, which differs from the sizing agent S2 in the styrene/maleic anhydride ratio, the increment in Kb is smaller than that found for sample StS2, in agreement with the also smaller styrene amount.

As for the sizing agent S9, some assumptions regarding the orientation of its molecules at the paper surface were anticipated when analyzing the contact angle results for 5 and 10% of incorporation. As explained, the styrene monomer was the one oriented outwards, and only for 20% incorporation, and the acrylate monomer was the one predominantly turned out. The IGC results confirm this analysis but

reveal that at 5% incorporation the amount of styrene and acrylate groups oriented outwards is similar, while at 10% the orientation of the styrene towards the exterior is the dominating one. The results obtained by IGC for sample StS10 are inconclusive with regard to the orientation of the copolymer molecules at the paper surface.

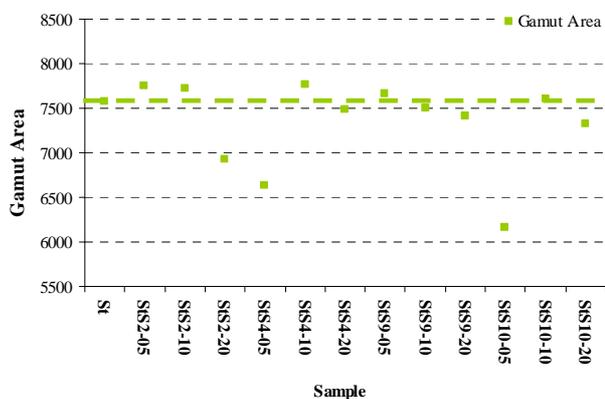
Several printing quality parameters were accessed in the context of this study. However, after using the Principal Component Analysis (PCA) tool the variables remaining as the most relevant to evaluate ink jet printing quality are the optical density for black and yellow ink, gamut area and line gain.

The values achieved for the optical densities are presented in Figure 4 for the black yellow colors. The dashed lines limit an interval of 0.2 units of magnitude (in this case relative to the reference sample, St) usually stated and accepted as distinguishable by the human eye in terms of optical density differences [11].

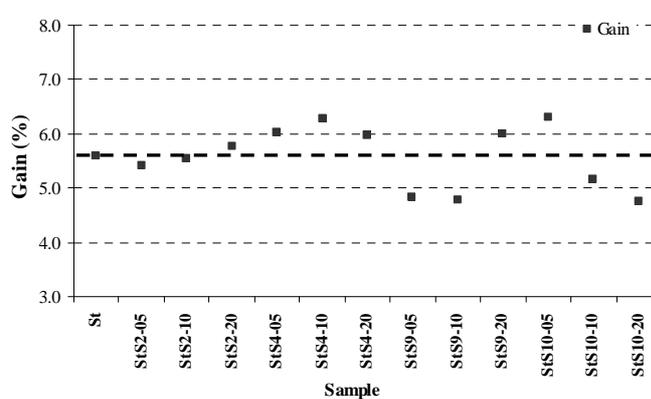


**Figure 4 – Optical density values achieved for black and yellow color. The lines delimit the range in which it is considered that the samples can not be clearly differentiated from the St sample.**

The black optical density values generally increase with the addition of the synthetic surface sizing agents to the surface sizing formulation. As for the yellow optical density a slight increase relative to the reference sample is detected only in some situations and the measurements do not allow differentiating the samples within the limits considered. The increase of the optical density values is probably influenced by the increase of the surface hydrophobicity of the samples due to the addition of the synthetic surface sizing agent, and it is more visible when using the black ink because it has as surface tension value more close to the one of the water than the one of the yellow ink. It is important to emphasize that, in spite of the small differences, for both black and yellow colors, the optical density values of all samples are acceptable in terms of printing quality (values superior to 2 for black ink and 0.9 for the yellow ink). As mentioned before, while the optical density values report the color intensity achieved for specific colors, the gamut area is used to evaluate the paper ability to reproduce a wide range of colors. The results obtained for this parameter are plotted in Figure 5.



**Figure 5 – Gamut area values. The dashed line corresponds to value achieved for sample St.**



**Figure 6 – Gain values. The line refers to the value achieved for the St sample.**

For most of the samples the gamut area values are satisfactory (values superior to 7000 are usually accepted for this kind of papers and printing process). Using the St sample as reference, the samples with an improved performance are StS2-05, StS2-10, StS4-10, StS9-05 and StS10-10. Regarding gain (Figure 6) is possible to see that most of the sizing formulations improve the printing performance in terms of image definition.

As previously mentioned, the printing quality parameters refer to different aspects of the printed image (mainly color saturation or image definition) and thus they must not be analyzed separately. In this context, combining the results obtained for the four parameters (black optical density, yellow optical density, gamut area and gain), the samples with the best printing performance are StS2-05, StS9-05 and StS10-10.

In order to relate this printing quality performance with the results of the previous analysis regarding the interactions at the paper surface and the effect of each surface sizing agent into the surface properties of the paper samples, partial least squares (PLS) numerical models were used. Considering the number of variables and groups that were used in this process, a large number of models were considered. Table 3 summarizes the results of those presenting the larger degrees of explanation.

From Table 3 is visible that the explanation percentages as well as the correlation coefficients are in general quite small. However, it is possible to verify for instance that the gamut area values are quite well explained by the contact angle values, while the values of Ka and Kb consistently contribute to a relevant explanation percentages of the printing quality parameters.

**Table 3 – Results achieved by PLS models using the variables corresponding to the paper surface characterization for the explanation of the quantitative quality results, divided in groups.**  
\*Total % (1st component; 2nd component)

Dependent Variables Set (yy)	Independent Variables Set (xx)	Explanation %*	Correlation Coefficient
Gamut Area	ContactAngles (CA)	23 (15; 8)	0.39
Gamut Area	Surf. Tension+Polar and Disp. components by CA	13 (13; 0)	0.36
Gamut Area	CAWater + Ka + Kb	12 (12; 0)	0.35
ODBlack	CA	10 (8; 2)	0.28
ODBlack	CAWater + Ka + Kb	10 (10; 0)	0.31
ODYellow	CA	17 (6; 11)	0.23
Gain	Disp Comp by I GC +Ka+ Kb	16 (16; 0)	0.40
Gain	Ka + Kb	12 (12; 0)	0.25
Gain	Polas Comp by CA +Ka+ Kb	17 (16; 1)	0.40
Gain	CAWater + Ka + Kb	18 (18; 0)	0.42

## CONCLUSIONS

As expected, this study confirms that the addition of the copolymers to the cationic starch increased paper surface hydrophobicity in different degrees according to the respective composition and concentration. As for the derived surface energetics results, it was shown that the P&W papers surface is predominantly dispersive, meaning that the polar and acid-base interactions have a smaller influence on paper behavior. However, these secondary interactions allow detailing the influence of the surface modifications, since they are more specific than the dispersive ones. In fact, the values of the polar component of the surface free energy obtained for different copolymer concentrations enabled to present solid hypotheses concerning the orientation of the molecules at the paper surface, namely regarding the different functional groups.

The IGC analysis of the dispersive interactions has not only confirmed but in some cases also complemented the hypotheses raised for the molecules orientation based on the contact angle measurements. Furthermore, it was verified that the papers dispersive component of the surface free energy decreases as the temperature increases. As for the acid-base character it was found that the

paper surface is amphoteric with a slightly basic character ( $K_b$  values always higher than those of  $K_a$ ) and that the addition of the synthetic surface sizing agents to the traditional sizing formulation increases the surface ability to establish acid-base interactions due to a general increase of  $K_a$  and  $K_b$  values (more relevant for  $K_b$ ).

As for the distribution of the surface sizing agents on the surface, it was verified that they stay at the paper surface in layers, and the amount necessary to complete each layer depends on the size of the copolymer molecules. Moreover, the functional groups of the sizing agent turned towards the air interface are those that mostly influence the paper surface properties, as expected

The final inkjet printing performance, evaluated through the determination of several parameters related to color reproduction and image definition confirmed that for better inkjet printing performances the predominance of non-polar rather than polar groups turned outwards is desirable. The predominance of these polar groups can not be excessive since they must also be accessible for paper-ink interactions in order to allow the ink to dry fast.

The differentiation between samples in terms of printing performance and the detail of the analysis did not reach the same level obtained with the surface characterization techniques. Therefore, the use of more precise printing quality evaluation techniques to detect and quantify the differences between the samples is desirable. Nonetheless it is possible to state that the addition of synthetic surface sizing agents to the surface sizing formulation improves printing quality parameters, and the samples with an overall better performance are samples StS9-05 and StS10-10, which include co-styrene-acrylate copolymers in the sizing blend.

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