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# THE EFFECT OF SURFACE SIZING ON PAPER WETTABILITY AND ON PROPERTIES OF INKJET PRINTS

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## ABSTRACT

The work is aimed at control of physical and chemical properties of paper by surface application of water based polymer dispersions. The polarity and specific charge density as well as hydrophobic effect of alkylketen-dimer, styrene-acrylate copolymer, styrene-butadiene latex, copolymers of styrene and dimethyl aminopropylamine maleimide and styrene-acrylic ester on printing properties of modelled papers was studied. All papers were printed with thermal inkjet printer using dye and pigmented water-based inks. Print quality was evaluated in terms of optical density, water fastness and print sharpness. The necessity to modify and to optimise sizing solutions in order to create a cationic and simultaneously sufficiently and adequately hydrophilic paper surface is emphasized.

KEYWORDS: Contact angle, inkjet printing, optical density, print sharpness, surface sizing, water fastness.

## INTRODUCTION

Surface sizing is a way how the penetration of liquids into the paper can be controlled. Improvement of the printability and absorption properties of the paper is achieved by controlling liquid – paper interaction. Surface sizing is modified by combination of several factors such as composition of sizing agents (chemical composition, viscosity, temperature, pH) and paper properties (basis weight, internal sizing, water content, porosity, surface energy and surface roughness).

The base paper must have the right hydrophobicity for good inkjet printability. This prevents the ink from penetrating inside the paper. Certain amount of ink must penetrate to the surface and the same time ink must stay on the surface of the paper without spreading (Kilpalainen and Manner, 2000). Important is the equilibrium between internal and surface sizing for controlled penetration rate and lateral spreading of ink. Surface sizing markedly influences the unwanted penetration of one ink to another. In achieving specific printing applications, the whole printing system should be evaluated, namely the print head, inkjet ink and the substrate onto which ejected droplets are placed. Additional considerations include image/information processing, speed, print quality etc. In the case of graphics printing, the optical properties of the colorant play an essential role in the final perception of the image. The image is actually combination of process colours – cyan, magenta, yellow and black. Placement of each ink drop and the order of placement as well as bleeding issues, play significant roles in the print quality (Pond et al. 2000).

There is no such thing as a universal ink. Therefore the development of jettable materials is increasing. In each case, many issues have to be considered, among them: application performance (functional), print quality (bleed, surface wetting), adhesion, image robustness (water fastness, light fastness), jetting characteristics (viscosity, dynamic surface tension). The drop impact on the substrate converts the spherical drop into a flat dot, its size depending on the physicochemical properties of both substrate and ink. The behaviour of ink drops on substrates depends on wetting substrates and the flow of ink during the wetting process. Print quality at application of low viscosity water soluble printing inks is evaluated by several methods such as measurement of surface optical density, unevenness, sharpness, mottling, penetration outside of required surface, quality of dots and lines and extent of colours.

Porosity and topology of pores, chemistry of surface together with surface tension and viscosity of liquids are playing an important role in surface paper interaction with liquids. Liquids can penetrate paper by action of external pressure forces or internal forces spontaneously sucking liquids into paper through capillary system. By applying of liquid droplet on paper surface a different mechanisms of liquid reception occurs in relation to contact angle formed by liquid on paper surface. Instantaneous capillary penetration occurs only at initial contact angle under 90°. Capillary penetration is described by Washburn-Lucas-Rideal equation

$$x = \sqrt{\left(\frac{R\gamma}{\eta}\frac{\cos\theta}{2}\right)t} \qquad (1)$$

where: penetration depth (x) depends on square root of penetration time and on absorption coefficient of the porous body (Daub et al. 1986, Alava and Niskanen 2006). The absorption coefficient is a function of time, (t), pores diameter (R), surface tension (γ), dynamic viscosity of the liquid (η) and of contact angle between the liquid and porous wall (θ).

Paper surface energy is influenced by coating composition when even a small change in coating composition (surface active chemical/detergent, polymer content in binder) could have a significant influence on paper surface energy mostly on its polar part (Zilles 2001). A liquid with a lower surface tension as well as a higher portion of non-polar component does not bypass the hollows but immediately is wetting the surface. Differences of surface in chemical and morphological condition are causing hysteresis of contact angle values. As a result of roughness and porosity variability as well as of changes of hydrophilic and hydrophobic areas in paper the value of the static contact angle is between the receding contact angle (when air displaces liquid) and the advancing contact angle when air is displaced by liquid (Radvan and Skold 1966).

Good inkjet print quality means sharp print and intense colours. Relatively a new approach to describe natural structures is the application of fractal geometry (Bunde and Havlin 1994). Imaging photometry is a way for evaluation the printing quality in terms of optical and geometric increase in printed point (Nežádal et al. 2000). Image fractal analysis of digitalized printed structures is obtained with the help of HarFA 5.3 (Harmonic and Fractal Image Analyse) software. HarFA can be used to determine the basic parameters of print quality of printed structures (the lightness of printed material, the quality of print, homogeneity of printed material and printed area, the quality of printed edges and so on).

The objective of this work was to evaluate influence of surface application of water based dispersions of polymers on structure, wettability and inkjet print quality of surface sizing papers.

## MATERIAL AND METHODS

### Paper samples

Base paper: commercial wood-free offset (100 % primary fibres) of base weight 157 g.m$^{-2}$.

### Sizing agents

The trade sizing agents were used in experiments. AKD is alkylketen dimer (Kemira); SA is styrene-acrylic acid copolymer (Kemira); SB latex is carboxylated styrene-butadiene-acrylonitrile copolymer (EOC Belgium Latex Division); SMAI 1000 is styrene maleic anhydride copolymer with styrene/maleic anhydride ratio 1/1 (Cray Valley); SMAI 3000 is styrene maleic anhydride copolymer with styrene/maleic anhydride ratio 3/1 (Cray Valley); SAE is amphoteric styrene-acrylic ester (AkzoNobel).

### Testing liquids

De-ionized water, water-based dye and pigmented inks.

### Surface sizing

Modelled papers were prepared by surface sizing of base paper in a laboratory size press Werner Mathis AG at constant speed of paper 5 m.min$^{-1}$ and pressure 980 kPa in the nip. Subsequently paper was dried 3 min at temperature 105°C. Sizing agent properties: concentration 1-7 %, viscosity 11-12 s (Ford cup No. 4), pH was in range 3.5-7.8. The content of sizing agent in modelled papers was 0.1-0.5 % SOF (percent of solid chemical on fibre solids).

### Surface tension and viscosity of liquids

The surface tension of 16 % aqueous solution isopropyl alcohol and inkjet inks PIXMA (dye inks CLI-521 Y, CLI-521 C, CLI-521 M, CLI-521 BK and of a pigmented ink PGI-520-BK) by optical tensiometer OCA 35 (DataPhysics) was determined. The „Pendant drop“ method was used for determination of surface tension. In Table 1 is presented surface tension of tested liquid and inks. The surface tension of the ink is a primary factor determining droplet formation and spreading on the substrate upon contact (Magdassi 2010). The surface tension can be controlled by using surfactants and by selecting proper solvent compositions. For example, adding propanol to water will cause a large decrease in surface tension, from 72.8 mN.m$^{-1}$ to below 30 mN.m$^{-1}$, depending on the propanol concentration.

The viscosity of 16 % isopropyl alcohol (IPA), cyan, magenta, yellow and black dye-based and black pigmented water-based inks was determined by the rotational viscometer Brookfield LVDV+II+Pro. The results are in Tab. 1.

### Specific charge density of liquids

Polarity and specific charge density of sizing agents, dye-based inks and pigmented inks was determined by polyelectrolytic titration using the Streaming Current Detector (Waters Associates, Inc.). A cationic standard of 0.001 N polydialyldimethylamonium chloride (PDADMAC) solution and an anionic standard of 0.001 N sodium polyvinylsulphate (PVSNa) solution were used. The measured data are in Tab.1.

The inkjet ink dye typically coutains a functional group, like sulphonic or carboxylic acid groups, that make them water-soluble and cellulose loving. Cationic polymers are often added to coating color to chemically fix the dye at the surface of coating to increase the dye density or print density and water fastness (Ruyz 1999).

*Tab. 1: Specific charge density, surface tension and viscosity of dye and pigmented water-based inks.*

| Liquids at room temperature 23°C | IPA 16 % | Magenta | Black | Yellow | Cyan | Black pigmented |
|---|---|---|---|---|---|---|
| Specific charge density, μeq.g$^{-1}$ | - | -289 | -259 | -191 | -137 | -16 |
| Surface tension γ, mN.m$^{-1}$ | 41.6 | 36.5 | 39.5 | 37.1 | 37.6 | 41.2 |
| Dynamic viscosity η, mPa. s | 1.10 | 2.67 | 2.61 | 2.46 | 2.43 | 2.46 |
| Density ρ, g.cm$^{-3}$ | - | 1.11 | 1.09 | 1.09 | 1.10 | 1.07 |

## Static contact angle

Contact angle of modelled papers as well as base paper was measured by the "Sessile drop" method by the OCA 35 (DataPhysics) optical tensiometer. Wetting time was recorded by a CCD camera at the sequence 20 frames per second. Contact angle was calculated as the average of ten parallel measurements. De-ionized water was used for contact angle measurements. In our study we used static contact angle in time 5 ms for surface paper hydrophobicity evaluation.

## Inkjet printing

Papers were printed by the Canon Pixma i 4700 thermal printer in the mode Plain paper. The print contains a full colour areas C, M, Y and K of dye inks; text printed by yellow dye ink on black background and text printed by black pigmented ink in yellow background.

## Optical density and water fastness of inkjet prints

The water fastness was measured by immersing the printed samples into de-ionized water for 5 min (Vikman and Vuorinen 2005) without agitation and allowing the immersed prints to dry for 24 hours at room temperature. Optical density was measured by the densitometer QUIKDens 100. Water fastness (WF, %) was calculated as optical density of prints before ($OD_1$) and after ($OD_2$) exposing them to water:

$$WF = 100 - [100 * (OD_1 - OD_2) / OD_1] \tag{2}$$

## Print sharpness

Digitalized image of the printed surface area was captured using a CCD Coolpix E4500 camera with an adapter for homogenous lighting. The print sharpness was evaluated as deformation of the letter "s" in the text. Dimension of the analyzed image was 274 x 460 pixels. For calculation of print object deformation the fractal analysis of the harmonic and fractal analysis HarFA 5.3 software was used (Nežádal et al. 2000). Digitized data were transformed for further processing into gray-level images (256 gray levels, I = 0.299R + 0.587G + 0.114B) and afterwards thresholded. This procedure is called masking. Masked images were subsequently thresholded. For the selected GL grey colour shade to darker colours 0 value (black) and to brighter colours 255 value (white) was assigned. Thus the fractal structure originated. The Box Counting Method was used to assess area filling enabling determination dependence of squares number covering the object on their dimension. Thresholded image segmentation is expressed by two parameters of K fractal measure and D fractal dimension. The fractal dimensions and fractal degree computation is following: Number of white (NW), partially black (NBW) and black squares (NB) are determined. The fractal dimension D characterizing filling of white (DW) and black (DB) area, as well as interface size of DBW thresholded image and fractal measure K was determined (Fooley et al. 1997). The object deformation is calculated from ratio of radius for perimeter and radius of (rL/rS) letter area. Deformation of yellow letter on black background (Y on K) and black letter on yellow background (K on Y) were evaluated. Image thresholding was performed in broader range and dependence of letter „s“ deformation on GL was evaluated. GL level for evaluation was selected in the field of small deformation changes (plateau). GL = 130 was selected for image Y on K and GL = 100 for K on Y. The decreasing deformation of printed object indicates improved print sharpness.

## RESULTS AND DISCUSSION

On Fig. 1 water fastness of printed yellow area of base paper and modelled papers in relation to sizing agent content is shown. Water fastness of base paper was 61 % (yellow mark). Surface sizing increased water fastness of all sized papers in comparison to base paper. Water fastness improved with increasing charge density of sizing agent. Specific charge density values are presented in Tab. 2. The highest water fastness showed a paper sized by SMAI with specific charge densities +2166 and +2764 μeq.g$^{-1}$. These results are in accordance with the work of Rich et al. 1999 who stated that cationic polymer additive enhances dot resolution and water fastness by associating with the anionic inks to form an immobilized colorant that retards bleeding and resists washing off with water. The lowest water fastness have papers sized by SA and SB latex having a higher negative charge density. Despite of a high positive charge density of AKD (+1750 μeq.g$^{-1}$) water fastness reached only the level of SAE with negative charge density (-7.5 μeq.g$^{-1}$) due to the fact that the surface of modelled paper had a high hydrophobicity with a contact angle 134-136°. Similar results were also obtained with other dye inks (cyan, magenta and black).

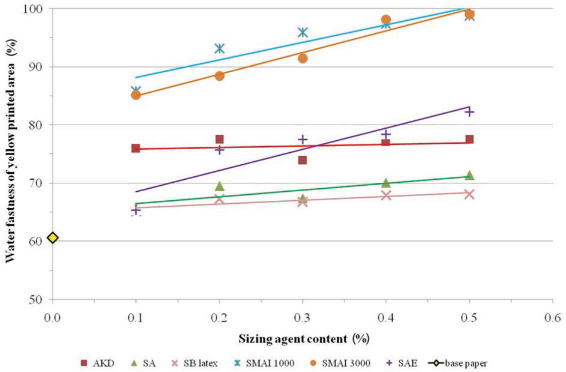


*Fig. 1: Water fastness of yellow printed area of base paper (yellow mark) and modelled papers with 0.1–0.5 % SOF sizing agents.*

*Tab. 2: Specific charge density of sizing agents.*

| | AKD | SA | SB latex | SMAI 1000 | SMAI 3000 | SAE |
|---|---|---|---|---|---|---|
| Specific charge density, μeq.g$^{-1}$ | + 1750 | - 92 | - 177 | + 2764 | + 2166 | - 7.5 |

Deformation of the yellow letter on black background of base paper was 5.8 (Fig. 2). With the exception of sizing agent AKD, yellow letter print sharpness was increased by surface sizing. Sizing agents of SMAI type with a higher positive charge density increased yellow letter print sharpness. A similar improvement was observed even with SAE agent with a lower negative charge density. Despite of the high charge density of AKD, due to increased hydrophobicity, yellow letter print sharpness deteriorated in comparison to base paper in consequence of poor paper surface wetting.

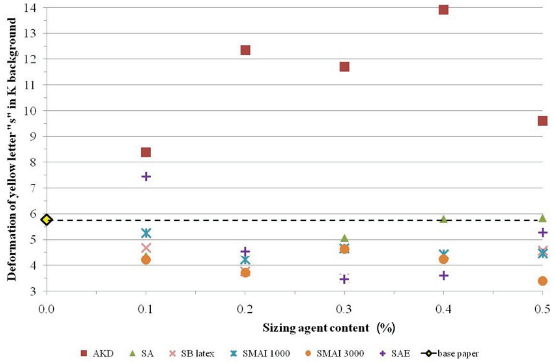
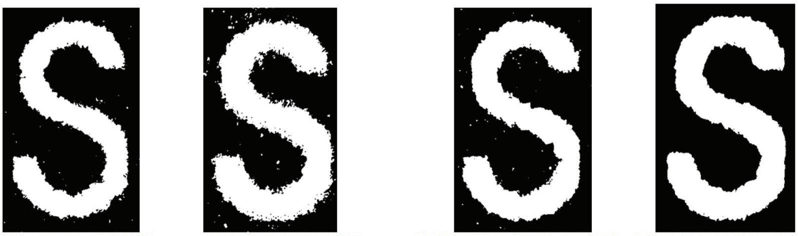


*Fig. 2: The effect of sizing agents on dye yellow letter deformation on black background.*

Fig. 3a presents the thresholded image of yellow dye letter on black background. Even the lowest sizing agent content of AKD made a significant deterioration of print sharpness in comparison to base paper (letter deformation increased from 5.8 to 8.4). On the contrary, in case of sizing agents SMAI, the print sharpness improved (to 5.3 and 3.4) depending upon the type as well as its content in modelled paper. In case of pigmented black letter on yellow background (Fig. 3b) a considerably higher letter sharpness on base paper was reached (4.1) without a markedly improvement at any used sizing agent. The reason is a different mechanism of water-soluble and pigmented ink interaction with paper surface.



Base paper, rL/rS 5.8 AKD 0.1 %, rL/rS 8.4 SMAI 1000 0.1 %, rL/rS 5.3 SMAI 3000 0.5 %, rL/rS 3.4

*Fig. 3a: The thresholded image of yellow dye letter on black background of base paper and modelled papers.*

Base paper, rL/rS 4.14 AKD 0.1 %, rL/rS 10.0 SMAI 1000 0.1 %, rL/rS 3.97 SMAI 3000 0.5 %, rL/rS 4.12

*Fig. 3b: The thresholded image of pigmented black letter on yellow background of base paper and modelled papers.*

Surface sizing of base paper changed the structure, porosity as well as paper surface roughness which is in accordance with another works (Hallamaa et al., 1997, 1999; Mesic et al. 2013). In Tab. 3 besides wetting contact angle with water, resistance to air permeability (Gurley method) of base paper and modelled papers with 0.1-0.5 % sizing agent content are presented. Papers with higher resistance to air permeability have a lower porosity.

*Tab. 3: Surface properties of base paper and modelled papers.*

| | **Base paper** | **AKD** | **SA** | **SB latex** | **SMAI 1000** | **SMAI 3000** | **SAE** |
|---|---|---|---|---|---|---|---|
| Static contact angle (water), ° | 83 | 134-136 | 95-110 | 95-102 | 89-96 | 97-102 | 103-117 |
| Resistance to air permeability, s | 53 | 49-66 | 55-65 | 53-78 | 51-59 | 50-63 | 51-66 |

Increased porosity was not observed at papers sized by SB latex and by SA (Fig. 4). Increased porosity (decreased resistance to air permeability) was found at a lower content (0.1-0.2 %) of other sizing agents. These modelled papers have a higher porosity as well as higher surface roughness. The reason is fibre swelling in a paper due to vapour diffusion through fibre pores, so called fibre sorption.

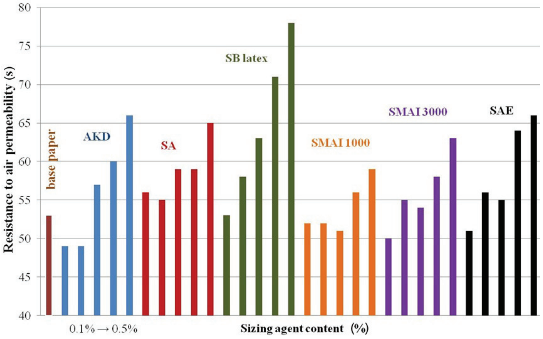


*Fig. 4: Resistance to air permeability of base paper (brown marked column left) and modelled papers with 0.1-0.5 % SOF sizing agents.*

Fig. 5 shows the influence of sizing agent type on contact angle with water reflecting paper surface hydrophobicity. Due to a higher surface roughness of modelled papers with low sizing agent content higher contact angles were reached. On Fig. 5 can be observed that paper roughness decreases wetting (increases contact angle) more markedly in comparison to increasing sizing agent content on paper surface. The highest hydrophobicity was reached with AKD and the lowest hydrophobic effect has SMAI 1000. Sizing agent SMAI 3000 had a higher hydrophobic effect in comparison to SMAI 1000. This is related to increased ratio of styrene to maleic anhydride in accordance to another works (Batten 1995, Valton et al. 2004).

Negative effect of sizing agents on optical density of yellow, cyan and magenta colour areas was found. The effect of surface sizing on decreasing of yellow area optical density is shown in Fig. 6. The most markedly decreasing of optical density was at paper sized by AKD which increased base paper contact angle from 88° to 136°. The best results were obtained by application of SMAI 1000 which has the lowest hydrophobic effect. By increasing of its content in modelled papers (0.1-0.5 %) the contact angle increased to 89-96° (Tab. 3 and Fig. 5). The extend of structural change as well as porosity and surface roughness change by water and aqueous solutions is subject to physical-chemical base paper properties such as wettability, swelling and water retention value of fibres.

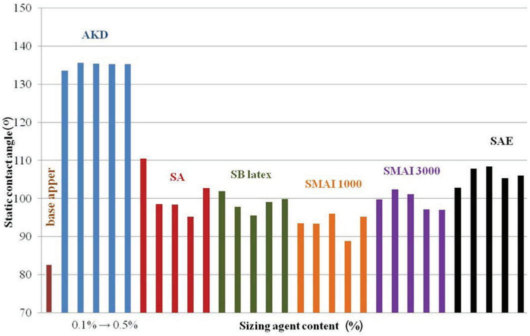


*Fig. 5: Static contact angle (surface hydrophobicity) of base paper (brown marked column left) and modelled papers with 0.1-0.5 % SOF sizing agents.*

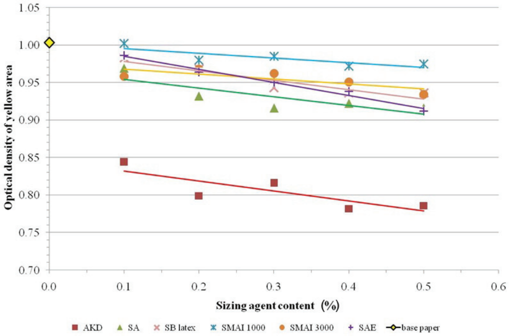


*Fig. 6: Optical density of yellow printed area of base paper (yellow mark) and modelled papers with 0.1-0.5 % SOF sizing agents.*

Optical density of black coloured area was significantly increased at all modelled papers (including high hydrophobic papers sized by AKD) in comparison to base paper. Hydrophobic effect of sizing agents on optical density of black coloured area is fundamental and has a similar trend as presented at other (C, M, Y) coloured areas.

## CONCLUSIONS

An inkjet substrate must demonstrate several unique properties to produce high quality images with inkjet inks. A significant effect was found related to polarity, specific charge density and hydrophobic effect of sizing agents on printing parameters of modelled papers: a) water fastness, b) print sharpness c) optical density.

By increasing of polymer cationic charge and decreasing of its hydrophobic effect the printing parameters improved. Cationic and hydrophilic paper surface improves separation of dye and water from dye water-based inkjet inks.

For water fastness as well as print sharpness, the fixation of anionic dyes is important by forming of complex with cationic polymer. Simultaneously it is necessary for improving optical density to increase the wetting and absorption rate (retain sufficient hydrophilic surface). Both these conditions are accomplished by styrene maleic anhydride copolymer sizing agents. Increase of paper roughness reduces wettability of paper surface more markedly than increase of sizing agent content.

Alkylketen dimer and higher contents of other sizing agents with a higher hydrophobic effect are unacceptable as this cause a significant retardation of inkjet inks drying.

Improvement of print quality and of sizing agents' surface impact is assumed by using a base paper with a lower tendency of surface roughness increase. The content of recycled fibres with reduced swelling ability, more intensive base paper sizing followed by increase of surface hydrophility by using styrene maleic anhydride copolymer in a combination with polymers of hydrophilic character could provide high-grade type of uncoated inkjet paper.

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