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INFLUENCE OF THE COATING FORMULATIONS AND BASE PAPERS ON INKJET PRINTABILITY

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ABSTRACT

At the coating were used two substrates, commercial base paper and base paper produced in pilot experimental paper machine. The printing quality varied at both base papers. The coating colours contain commercial silica and precipitated calcium carbonate pigments. As a binder was used polyvinyl alcohol and cationic starch combined with high-cationic polymer SMAI 1000. Colour gamut significantly improved when the inkjet ink contact angle decreased below 14° independently of the base paper. The order of coating colours effect on the base papers was similar. Application of silica pigment in the coating colour provided papers with the largest inkjet ink wetting, the best colour gamut area, print sharpness and smoothness. By using of polyvinyl alcohol, a high colour gamut area was reached but it resulted in a markedly low print sharpness in comparison with cationic starch. Coating of base paper produced in pilot experimental paper machine introduces papers with higher colour gamut and also print sharpness.

KEYWORDS: Inkjet printing, base paper type, coating colour, pigments, binders, printing properties, wettability.

INTRODUCTION

At present time there is an increasing demand concerning the printing quality of printing paper grades. Inkjet quality depends on interaction between ink and the receptive surface. Inkjet print quality can be regarded in a variety of ways, mainly colour reproduction and print sharpness. A coating layer covers base paper fibres to give a uniform surface. It is desirable during printing process that water part of ink absorbs rapidly into the porous structure of paper and dye anchors on the surface layer. It was found that coating with pores up to 0.1 μm absorbs dyes slowly, whereas pores within range 0.1-1.0 μm can cause absorption of the part of dye below coating surface and this may result in a decrease of optical density (Morea-Swift and Jones 2000). A thorough review of absorption of ink into paper as well as the experimental study of connection between various coated surface properties and print quality properties had been published by authors

(Gigac et al. 2015a, b, Stankovská et al. 2016a). We found that the contact angle of ink is a suitable proper parameter for colour gamut prediction of surface sized and coated paper. The study (Gigac et al. 2016) of the coating colour composition (pigments, binders and cationic polymers) influence on surface roughness and porosity, wetting, colour gamut area, water fastness and print sharpness of papers modelled on one commercial base paper had been published. At this work, silica (particle size 5.9 μm, surface area 349 $m^2.g^{-1}$) and precipitated calcium carbonate (particle size 0.5 μm, surface area 17 $m^2.g^{-1}$) pigments, polyvinyl alcohol and cationic starch binders combined with high-cationic polymers were used. As cationic polymer were used poly-DADMAC and styrene maleic anhydride imide copolymer SMAI.

Binders are used to primarily bind pigments together and to anchor the coating to the substrate. The most common used binder is polyvinylalcohol PVOH and cationic starch with a good binding strength. Due to these film-forming agents is dye concentrated in the top region of the binder film layer. However, the polymer film may be regarded also as gamut enhancer (Svanholm 2007). PVOH is an excellent film former and is resistant to wetting by oils, greases and organic liquids. It shows outstanding adhesion to cellulose and provides a high pigment binding strength. Furthermore it provides enhancement of fluorescent whitening agents. PVOH is used within a broad range of paper types to produce release liners, flexible packaging and high brightness papers. The disadvantage of aqueous PVOH solution is its difficult dissolution and high viscosity. Another disadvantage of using PVOH is that it covers the pigment surface and can mask any surface cationicity of the pigment.

Starch is commonly used in paper industry and paper coating, as a widely available and inexpensive agricultural raw material. In native form, it can be used as a sizing agent while after few modifications it can be utilized as a coating agent due to excellent film forming ability. A coating with oxidized starch offers the advantage of good film-forming characteristics and minimal retro-gradation, however, wet-end retention problems occurred during recycling of oxidized starch coated paper because of negatively charged oxidized starch (Rastogi and Samyn 2015). Alternatively, other modified starch such as acetylated starch, cationic starch, and hydroxypropylated starch have been efficiently used as paper coatings. In addition to the binding properties, cationic starch also contributes to the rheological properties of the coating formulation: it acts as a flow modifier and provides water retention.

Cationic charge is a good means to fix the anionic dyes. SMAI being a low molecular weight cationic polymer is supposed to introduce a controlled degree of flocculation in the coating colour and hence can contribute to improving the coating bulk and surface properties. Detailed information about frequently used coating colour components can be reached in many reviews (Grönfors 2010, Wilson 2006, Zhang et al. 2015). Zhang et al. 2015 studied the impact of silica pigment and binder consisted of different ratio of vinyl acetate copolymer VAE and PVOH on print quality and surface properties of paper. The results showed that the best print quality can be achieved when VAE and PVOH ratio is 6:4 as the result of appropriate homogeneity, pore volume and hydrophility.

The quality of print papers is influenced not only by coating composition but also by base paper properties. The uniformity of ink transfer has been often associated with local variations in coat weight which is related to the base paper itself. Mainly, surface roughness, absorbency and sheet matrix formation contribute to the variation in coat weight (Sood et al. 2010). Sheet matrix non-uniform formation affects surface smoothness which is very important factor influencing coat weight distribution along the paper surface under blade pressure of coater. At coating, under adjusted higher blade pressure required for getting desired coat weight on more rough paper, the surface is deformed and a certain irregularities remains as graininess (Sood et al. 2010).

The objective of the present work is obtaining higher quality inkjet papers by application of coating colours. The impact of the application of various coating colour formulations composed of silica or calcium carbonate pigment and two types of binders and styrene maleic anhydride imide copolymer were analyzed in term of surface characteristics as well as inkjet printing quality. The effect of base paper is also considered. Evaluated parameters are surface roughness and porosity, wetting, colour gamut area, water fastness and print sharpness.

MATERIAL AND METHODS

Base paper

Commercial paper from 100 % virgin fibres of basis weight 157 $g.m^{-2}$. Wood-free paper from primary fibres of basis weight 107 $g.m^{-2}$ made at semi-pilot experimental paper machine in our institute, internally sized with 0.30 % of Fennosize 157YC AKD (alkene ketene dimer)and calendered in semi-pilot supercalender KLEINEWEFERS of type K 20/4 (Industrie-Companie, Krefeld, Germany).

Experimentally produced base paper shows a higher surface roughness and a lower free surface energy. The base papers properties are in Tab. 1.

Tab. 1: Physical chemical properties of base papers.

Properties	Commercial base paper A	Experimentally produced base paper B
Basic weight, $g \cdot m^{-2}$	157	107
Apparent density, $g \cdot cm^{-3}$	0.86	0.74
Surface roughness OVSCLINO, %	14.2	18.7
Free surface energy σ, $mJ \cdot m^{-2}$	38.0	33.0

Testing liquid

De-ionized water, 16 % isopropyl alcohol (IPA), water-based inks CMYK and pigmented black ink.

Coating colour and coating

In experiment, the pigment of silica Gasil 23F (PQ Corporation, USA) and calcium carbonate Precarb 800 (Schaefer Kalk) were used. Silica pigment Gasil 23 F has an average particle size 5.9 μm, pore volume 1.6 $ml \cdot g^{-1}$, surface area 349 $m^2 \cdot g^{-1}$ and controlled particle size distribution. Precipitated calcium carbonate Precarb 800 of disc shape has average particle size 0.5 μm and surface area 17 $m^2 \cdot g^{-1}$. As binders were used cationic starch KS (Cerestar SP 05855, Cerestar); pigment was 30 %.

The silica coating colour was prepared from 30 % aqueous solution of Mowiol 28-99, which was mixed with Despumol 7401 and after cooling of this solution less than 40°C, poly-DADMAC was added with required amount of water to get desired concentration of coating colour. GASIL 23 F was gradually dispersed at intense mixing into prepared solution.

The calcium carbonate coating colour was prepared in turbine air stirring apparatus type Dissolver from 60 % aqueous dispersion of Precarb 800 with addition of 0.5 % anionic polyacrylate dispersing agent Polysalz CAL and of 0.1 % NaOH. Into a stirred suspension, Despumol 7401, Mowiol 26-88 and SMAI 1000 (25 % aqueous solution) were added. After 30 min of stirring, the pH was adjusted to 9.5.

Coating colours were applied on the paper surface by the laboratory coater DOW CHEMICALS (system Trailing Blade) with the knife of thickness 0.3 mm. The deposit of coating was regulated with air pressure at the knife 60-120 kPa, with the rate of supporting roll 60 m.min-1 depending upon corresponding viscosity of coating colour. Coated paper was dried in a laboratory owen with air circulation at temperature 140°C within time 3 min. After drying coated papers were loaded for cockle elimination, occurring at one-side coating. The coat weight of coating layer on the base papers were within 10.7-13.1 g.m^{-2}. The composition and properties of coating colours are in Tabs. 1 and 2.

Tab. 2: The composition and properties of silica coating colour.

Materials (*% per pigment*)	**G1**
Gasil 23F	100
PVOH (Mowiol 28-99)	30
Poly-DADMAC	2.5
Despumol 7401	0.02
Solids, %	20.4
Viscosity Brookfield (100 rpm, at 23°C), mPa.s	1525
pH	5.28
Coat weight, g.m^{-2}	13.1
Specific charge density, μeq.g^{-1}	+ 11

Tab. 3: The composition and properties of calcium carbonate coating colours.

Material (*% per pigment*)	**P3**	**P3-S**
Precarb 800	100	100
NaOH	0.1	0.1
Polysalz CAL	0.5	0.5
PVOH Mowiol 26-88	30	0
Cationic starch (Cerestar SP 05855)	0	30
Despumol 7401	0.01	0.01
SMAI 1000	2.0	2.0
pH	8.51	8.68
Solids, %	30.8	42.8
Viscosity Brookfield (100 rpm, at 23°C), mPa.s	1566	1710
Coat weight, g.m^{-2}	10.7	11.3
Specific charge density, μeq.g^{-1}	- 32	+ 407

Inks properties

At the inkjet printing of coated papers and base papers in the printer Canon PIXMA i7250, original dye-based inks CLI-521 Y, CLI-521 C, CLI-521 M, CLI-521 BK and pigmented ink PGI-520-BK were used. Their properties are shown in Tab. 4.

Tab. 4: Inks properties.

Liquids at 23 °C	Cyan C	Magenta M	Yellow Y	Black K	Black pigmented
Specific charge density, μeq·g^{-1}	-91	-112	-115	-229	-740
Surface energy σ, mJ·m^{-2}	37.4	37.7	38.2	39.8	43.6
Concentration, %	0.30	0.28	0.30	0.28	0.04
Density ρ, g·cm^{-3}	1.08	1.06	1.07	1.07	1.09

Dynamic of water and 16 % isopropyl alcohol absorption

Water and 16 % isopropyl alcohol absorption was measured by the ultrasound analyzer PDA C.02 (Emtec, Radnor, PA, USA) with frequency 2 MHz within time of 43 ms-60 s. De-ionized water has free surface energy of 72 mJ·m^{-2} and 16 % IPA has 44 mJ·m^{-2}. A higher IR intensity corresponds to slower liquid penetration. For evaluation of fine pores content on paper surface was used the time at which 95 % IR (t_{95}^{IPA}) is reached. A higher value corresponds to higher fine pores content. The principle and procedure of measurement and the evaluation have already been described in scientific literature (Stankovská et al. 2016b).

Specific charge density of coatings

Polarity positive or negative and specific charge density (μeq·g^{-1}) of coating colours, dye-based inks and pigmented inks was determined by polyelectrolyte titration using the Streaming Current Detector (Waters Associates, Inc.). A cationic standard of 0.001 mol·l^{-1} poly(diallyldimethylamonium chloride) solution and an anionic standard of 0.001 mol·l^{-1} sodium polyvinyl sulphate (PVSNa) solution were used.

Wettability

Contact angle of water and inkjet cyan ink colour of base paper and coated papers was measured by „Sessile drop" method using the optical tensiometer (OCA 35, Dataphysics Instruments GmbH, Germany). Within this experiment, the dynamic contact angle in time of 5 s (CA_5^{water}, CA_5^{Cyan}) was used. The higher contact angle corresponding with reduced surface wetting.

The evaluation of surface topography by photoclinometry

The surface of coated papers was pictured by the CCD camera Coolpix E4500. The measurement process as well as image treatment was published in Wood Research (Gigac et al. 2006). The surface roughness is evaluated as the surface optical variability (OVS_{CLINO}, %).

Inkjet printing

Coated papers and base paper were printed at the inkjet printing of papers in Canon PIXMA i7250 printer within the mode Matte. Original dye-based inks CLI-521 Y, CLI-521 C, CLI-521 M, CLI-521 BK and pigmented ink PGI-520-BK were used.

Colour gamut area

The colour gamut area CGA was calculated as the pentagram area from a* and b* colour coordinates of the C, M, Y, G (green) and O (orange) blocks. Colour coordinates were measured by using the Elrepho spectrophotometer (Lorentzen & Wettre, Sweden).

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 without agitation and allowing the immersed prints to dry for 24 hours at room temperature. Optical density was measured by densitometer QUIKDens 100. Water fastness (WF) was calculated as optical density of prints before (OD_1) and after (OD_2) exposing them to water:

$$WF = 100 - 100 \times ((OD_1 - OD_2)/OD1) \quad (\%) \quad (1)$$

Print sharpness

The print sharpness was evaluated as deformation of the letter "s" in the text. The digitalized image of the printed surface area was captured using a CCD Coolpix E4500 camera with an adapter for homogenous lighting. For calculation of print object deformation, the method BOX Counting of the harmonic and fractal analysis HarFA 5.3 software was used as we introduced in our previous work (Gigac et al. 2016). Print object deformation POD was evaluated from the ratio rp/ra, where rp is perimeter radius of the object and ra is area radius of the object. Reduced print object deformation corresponding with improved print sharpness according to equation:

$$\text{Print sharpness} = 100 \times POD_{IDEAL} / POD_{MEASURED} \quad (\%) \quad (2)$$

where: POD_{IDEAL} - 3.5 for inkjet gloss paper (photo quality) printed in the printer Canon PIXMA i7250.

RESULTS AND DISCUSSION

Since the reception of the coating as well as uniformity of coating spreading on the paper surface is significantly influenced by the base paper surface and permeability. Physical and printing properties of base paper and matt coated paper are shown in Tabs. 5. and 6. By measurement, too low specific charge density (+11 $\mu eq.g^{-1}$) silica coating colour G1 was found. It is the result of cationic standard poly-DADMAC adsorption on the structured silica pigment with a high specific surface area and using of the titration method for determination of specific charge density with higher molecular polyelectrolyte.

Tab. 5: Coated papers and the commercial base paper properties.

Labelling	Base paper A	A-G1	A-P3	A-P3-S
Specific charge density of coating colour, $\mu eq.g^{-1}$		+11	-32	407
Porosity Gurley, s	53	102	557	132
Roughness OVS, %	14.2	10.1	15.7	12.8
Wetting CA_5^{water}, °	78	13	47	20
Wetting CA_5^{cyan},°	35	10	27	29
Penetration t_{95}^{IPA} , s	0.07	0.41	0.05	0.06
Penetration IR_5^{IPA} , s	0.22	9.99	5.40	12.66
Colour gamut area CGA	4402	9888	7009	6287
Print sharpness, %	27.5	79.2	24.3	66.0
Water fastness WFC, %	38	103	22	94

Tab. 6: Coated papers and the experimentally produced base paper properties.

Labelling	Base paper B	B-G1	B-P3	B-P3-S
Specific charge density of coating colour, μeq.g^{-1}		+11	-32	407
Porosity Gurley, s	12	34	248	35
Roughness OVS, %	18.7	10.7	18.9	12.8
Wetting CA_5^{water}, °	113	18	57	87
Wetting CA_5^{cyan},°	65	14	18	22
Penetration t_{95}^{IPA} , s	0.15	1.15	0.05	0.06
Penetration IR_5^{IPA} , s	3.91	47.84	11.84	21.68
Colour gamut area CGA	4 987	10 208	7509	7236
Print sharpness, %	19.75	81.21	32.59	63.87
Water fastness WFC, %	46	102	14	95

Porosity

By coating, porosity of papers decreased, markedly at base paper A (Gurley 102-557 s). The most significant effect on both base papers was indicated with coating colour P3 of calcium carbonate pigment combined with PVOH (Gurley 248 and 557 s). Porosity of surface treated base paper A decreased in the order: G1 > P3-S > P3 and surface treated base paper B: G1 = P3-S > P3.

Surface roughness

The surface roughness OVS_{CLINO} of the base paper B (18.7 %) was higher as of base paper A (14.2 %). By coating it decreased (10.1-12.8 %) excepting the application of coating colour P3 (15.7 and 18.2 %). The roughness increasing is the result of fibres swelling in aqueous solution of lower polymerized PVOH (Mowiol 26-88) at coating process when the surface structure could be opened.

Water wetting and dynamic penetration of water

The base paper B is internally more porous but has more hydrophobic surface due to calendering. The coating increased the water wettability of papers surface treated on both base papers. Wetting contact angle in time 5 s decreased from 78° (base paper A) to 13-47° and from 113° (base paper B) to 17-87°. The lower contact angle and thus a higher wetting, the faster ink solvent penetrates under the coating layer. The highest wetting was obtained with silica pigment G1 (CA_5^{water} 13 and 17°). The effect of calcium carbonate coating colours varied depending upon the base paper. The water wetting of surface treated base paper A decreased in the order: G1 > P3-S > P3 and base paper B in the order: G1 > P3 > P3-S. Time course of ultrasound signal intensity IR at the contact of water with base papers and coated papers is shown in Fig. 1. Ultrasound signal intensity IR of the base paper increased at the beginning phase as the consequence of time-limited surface hydrophobicity. In this case, at first the steady surface wetting and fibres swelling occurred and later the water penetration happened. The same process occurred at base paper A coated with P3. Other coated papers have a hydrophilic surface, where the immediate wetting and water penetration take place. In the case of base paper coated with G1, the immediate wetting and penetration occurred only in the beginning stage up to 0.5 s.

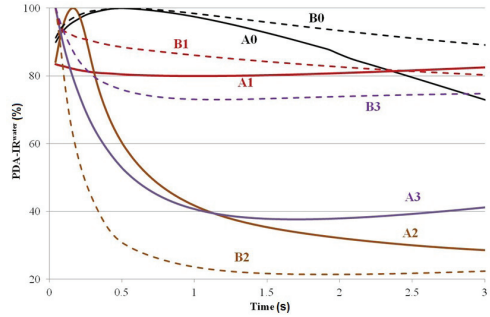

Fig. 1: Time course of ultrasound signal at the contact of coated papers and base papers A and B with water. Sample labelling: 0) base paper; 1) G1; 2) P3; 3) P3-S.

Dynamic penetration of isopropyl alcohol

The fine pores content on paper surface was tested by the interaction of coated papers and base papers with aqueous 16 % isopropyl alcohol solution (IPA). An aqueous solution of IPA has a lower surface energy (44.24 $mJ \cdot m^{-2}$) which helps to eliminate the effect of paper hydrophobicity. Its surface energy is similar to water-based inks (37-40 $mJ \cdot m^{-2}$). The base paper B has more fine pores content on surface as the result of calendering. By coating, the surface with a higher fine pores content was achieved only when using G1 (t_{95}^{IPA} 0.41 and 1.15 s) in comparison to both base papers (t_{95}^{IPA} 0.07 and 0.15 s). Surface of paper coated with silica pigment has markedly larger pores but also more micropores in comparison to surface coated with calcium carbonate pigment determined by SEM analysis (Gigac et al. 2016). Silica coating colour did not decrease coated paper porosity as markedly as calcium carbonate coating colours but formed a closed surface structure. This structure together with a uniform distribution of pores and particles of pigments causes a fast absorption of solvent from the ink. The result is an uniform anchoring of dye at the surface due to its smoothness, as confirmed by the measurement of printing properties, mentioned below.

Inkjet cyan ink wetting

Coating increased the inkjet cyan ink wettability of papers (CA_5^{cyan} 10-29°) against of the base paper A (CA_5^{cyan} 35°) and B (CA_5^{cyan} 65°). The highest wetting was obtained with G1. Calcium carbonate pigment markedly improved the wettability at the application on the base paper B (CA_5^{cyan} 18 and 22°). The significant effect of binders was not found.

Colour gamut area

Colour gamut area shown to be influenced by both, type of coating colour and base paper. By coating, the colour gamut area CGA increased. The two-fold higher colour gamut area was reached at the papers coated with G1 against base papers. The colour gamut area of coated papers on both base papers was increased in order: P3-S < P3 < G1. The application of coating colour with starch binder has not been as effective as with film-forming PVOH binder. The film forming effect leads to a poor penetration of dye and the dye is concentrated in the top region of coating. Fig. 2 shows the dependence of colour gamut area from dynamic inkjet cyan (A) and water (B) contact angle of coated papers and the base papers. For a good CGA, a highest inkjet cyan wettability of paper surface is required. The higher CGA and better inkjet cyan wettability was reached by coating of base paper B. A more hydrophobic base paper B with higher fine pores

content on the surface reduces the penetration of the binder from coating colour. This is the reason for reducing the penetration of inkjet dye to coating colour and CGA improvement.

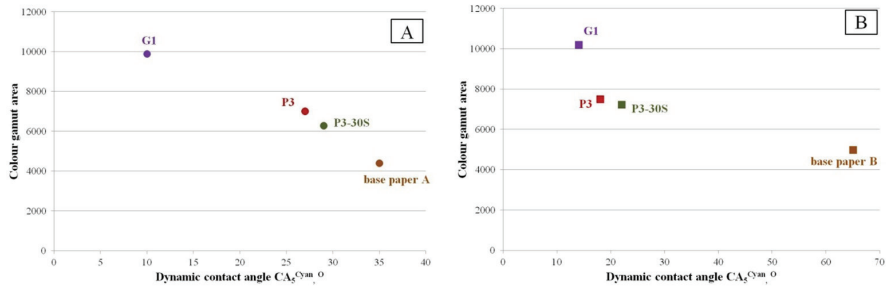

Fig. 2: Colour gamut area depending upon inkjet cyan dynamic contact angle of coated papers, base paper A and B. Sample labelling: 0) base paper; 1) G1; 2) P3; 3) P3-S.

Print sharpness

Print sharpness was influenced mainly by coating colour and base paper properties shown to have a small effect. Print sharpness of base paper B is worse due to higher roughness and more microporous surface. At printing of paper surface with extend of fine pores the better colour gamut can be achieved (dye of ink remains on surface), however, too slow absorption of solvent ink leads to edge raggedness, line broading and colour bleeding and also to reduced print sharpness. However, by coating the print sharpness improved, even better values are achieved than at coating of base paper A. Coating with G1 and P3-S improved print sharpness of both base papers. Print sharpness decreasing at application of coating colour P3 on the base paper A relates with a higher surface roughness and negative specific charge density of coating colour (-32 $\mu eq.g^{-1}$). The best print sharpness and smoothness of paper were obtained with coating colour G1.

Water fastness of inkjet cyan ink

Water fastness was influenced mainly by coating colour and base paper properties shown to have a small effect. The result of coating was a high water fastness of cyan printed area (WFC 94-102 %), excepting paper coated with coating colour P3 which has a negative specific charge density. In this case, WFC is lower (14 and 22 %) compared to the base papers alone (38 and 46 %). The highest WFC was reached with coating colour G1 as the result of structured pigment surface. There have been some publications aimed at the effect of specific charge density of surface treating agents on water fastness of inkjet printed area (Stankovská et al. 2016 a, b).

CONCLUSIONS

In this work, inkjet print quality was evaluated by parameters as colour gamut, print sharpness, porosity and surface roughness, water and inkjet ink wettability and water fastness of cyan printed area. At comparison of two base papers, print sharpness of experimentally produces base paper is worse due to higher roughness and more microporous surface but colour gamut is higher. The coating led to hydrophilic surface of papers, excepting the application of calcium carbonate pigment combined with PVOH at commercial base paper. By coating of both base papers with silica based coating colour, the best colour gamut area, print sharpness and water

fastness was reached due to a good water and cyan ink wettability of surface. Also, silica coating colour provides a uniform pores and particle distribution and together with prevalence of large pores enables rapid absorption of the ink solvent. The smoothed surface enables a uniform spreading of inkjet dye.

Calcium carbonate coated papers did not achieve such colour gamut area and print sharpness as silica coated paper. Paper coated with coating colour of film-forming polyvinyl alcohol as binder has better colour gamut area. On the other side, PVOH causes a higher surface roughness resulting in a weak print sharpness of papers coated at commercial base paper and due to negative specific charge density a weak water fastness of both coated base papers.

The results shows that colour gamut area is influenced by coating colour as well as base paper properties. A high colour gamut area of one type of base papers was achieved due to its higher surface hydrophobicity and slower liquid penetration. On the other hand, print sharpness and water fastness was influenced mainly by coating colour and base paper properties shown to have a minimal effect.

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