GCC MODIFICATION FOR BETTER PERFOMANCE OF INK-JET PRINTS

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Abstract
Paper is still the most common graphical material because of its traditional sustainability and biodegradability. Coatings and surface treatment with natural components and additives can replace unfriendly and more expensive synthetic materials, normally with special properties. However, special properties can be obtained with surface functionalization by chemical or pigment particle geometry modification. Surface geometry modification can be achieved with the application of the pigments and coating formulations with apparel properties, e.g. granulation, particle size distribution and particle shape. The natural ground calcium carbonate (i.e. GCC) usage in papermaking industry is more and more widely used. Beside optical properties, the trends of lightweight materials, i.e. reducing grammage by using nano materials and products (i.e. NMP), lower specific energy requirement and costs, forces increasing of pigments usage. After all, as everything has its own limits, the resemblance also happens with GCC pigment. Following the stated above, the pigment engineering appears with the idea of particles modification to increase its applicability and particularity. Modified GCC particles, e.g. TCC (i.e. treated calcium carbonate) enable wide range spectrum of the GCC raw material application. In the article, the right technological procedure to treat wet grinded GCC and the effect on the changes of the particle geometry, that are at the same time influenced on increasing functional properties, i.e. paper structure and its surface, are presented. Results of survey showed that properties of GCC coated printing paper, required for ink-jet printing with water-based inks had significantly improved.

Key words: GCC, modified pigments, coated paper, ink-jet printing, bleeding, wicking

1 Introduction
The paper industry has realized high-speed inkjet printing as a vast new business opportunity. To provide high goals the R&D activities are going into a new, i.e. modified coating pigments, mostly on the bases of GCC development with special properties as the answer on the increasing market demands. [*1, 2, 3*] Ink-jet printing is non-contact printing technique. The only contact is in the moment of ink transfer on the paper surface. For good reproduction and print quality, the coated papers are used, where the coated layer serves as micro-porous substrate. Dye in ink penetrates into the micro-porous substrate along the capillaries and the depth of the penetration is the criteria for the printout quality. [*4, 5*] An ink-jet printing test for the vaterite-coated papers resulted in high print quality, without bleeding or wicking problems because of the good wettability tendency (similar with silica). In the paper coating substrate, the

fixing agent, i.e. poly-DADMAC was added. [*6*] For liquids, e.g. ink or printing color, their penetration into the paper is more important than flow through the paper structure. Liquid penetration takes place by capillary flow in capillaries between particles in coated layer structure. The penetration flow is expressed by the Lukas-Washburn (Equation 1) and Young-Laplace equations (Equation 2). [*7, 8*] Liquid transfer on/in paper surface is represented with *Young-Laplace equation*:

$$\Delta p = 2\gamma_l \cos(\theta)\frac{1}{r} \quad (1)$$

while wettability or liquid penetration is expressed by *Lukas-Washburn – equation*:

$$h^2 = \frac{r^2 t}{4\eta}\left(\frac{2\gamma\cos\theta}{r} + \Delta p\right) \quad (2)$$

where is:
Δp – external pressure difference, γ_l – surface tension, θ–contact angle between the liquid and the capillary wall, r – pore radius, η– fluid viscosity, p – liquid pressure in the nip, and h – distance travelled.

Solely surface tension and gravity effects drive the flow of the liquid. In printing and converting processes the nip pressure forces liquid to penetrate into the paper. Regarding printing process, we can talk about liquid transfer and wettability of the printing substrate. On the other hand, in printing and converting processes the nip pressure forces liquid to penetrate into the paper. Further, surface tension is small compared to external pressure. *Lucas-Washburn* equation (e.g. Equation 2) can be rewritten in Equation 3, where, *p*, is liquid pressure in the nip.

$$h^2 = \frac{2r^2 tp}{k\eta} \quad (3)$$

The Kozeny constant, *k*, is included to account for irregular and tortuous pores. *Kozeny-Carman* equation (e.g. Equation 4) gives us a quantitative relation between permeability and porosity. The model assumes a uniform bed of packed particles that have an effective particle diameter (d_{eff}).

$$K_n = \frac{\Phi^3 d_{eff}^2}{36(1-\Phi)^2 k} \quad (4)$$

where is:
Φ–porosity, d_{eff} – effective diameter (influence on pore volume and shape), and k – Kozeny constant.

Equations 3 and 4 express the phenomena of liquid transfer in to the printing substrate. The Lukas-Washburn equation predicts the depth of liquid penetration. In converting process, e.g. calendaring, paper surface, mostly coated surface, the external pressure compresses paper structure, which reduces pore volume and consequently reduces liquid penetration.

2 Results

In laboratory scale some trials of preparing and coating colour with modified GCC pigment were done. The main purpose of all trials was to find out the procedure of pigment modification to encounter the market demands for the ink-jet printing papers and paperboards. Cationic treatment captures the anionic dye and keeps it from spreading and wicking. The GCC, with special production procedure, the charge as well as the shape and size of the pigment particles were also modified. The specific surface area increased and at the same time, the particles charge increased from 17 to 12 mV at pH 7.85. With the addition of weak and/or strong acids, we changed the specific surface area from 8 to 33 m^2/g (i.e. table 1).

Table 1. Modified pigment preparation.

Trials, No.	Modification procedure	Addition		BET [m^2/g]
/	raw material – dry			8.10
5	material with 10 % s.c. + weak acid	$Ca(OH)_2$	CO_2	29.10
8 – TCC2	material with 10 % s.c. + weak acid	$Ca(OH)_2$	CO_2	32.93

The trials of coating base wood free paper with three coating colours, with standard wet grinded GCC pigment quality, modified pigment TCC2 and reference pigment, were done. The main differences between used materials, like specific surface area and mean particle diameter are shown in the table 2.

Table 2. Pigments characteristics.

Pigment sample	D50 [%]	BET [m^2/g]
standard quality	0.686 μm	12.24
TCC 2	1.241 μm	32.93
Ref.	1.353 μm	60.74

The following SEM pictures (i.e. Fig 1–3) of calendared coated paper surface show how coating structure is organized, especially on the micro and macro scale. The effect of the particles shape and size on micro porosity of the coating layer is well seen from Fig. 1–3, where modified product TCC2 is in well relation with the reference one. GCC particles are more or less equally distributed on the surface, with as little as possible low number of micro and macro pores.

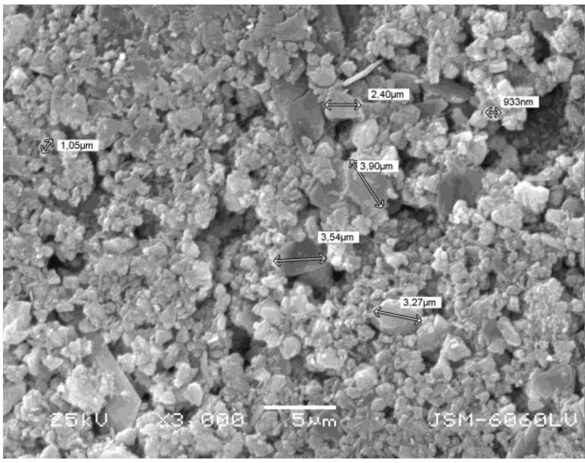

Fig 1. Standard product.

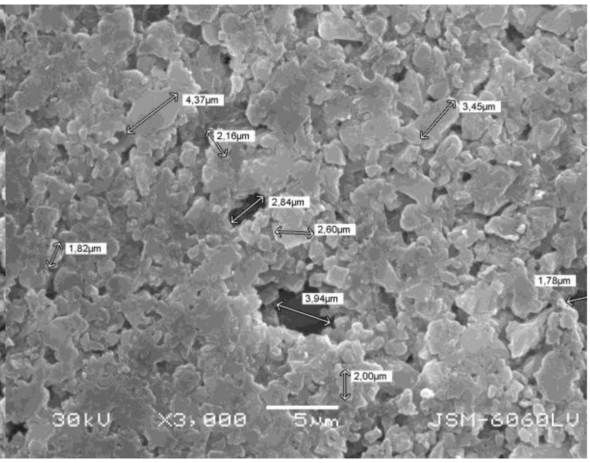

Fig 2. Modified product TCC2.

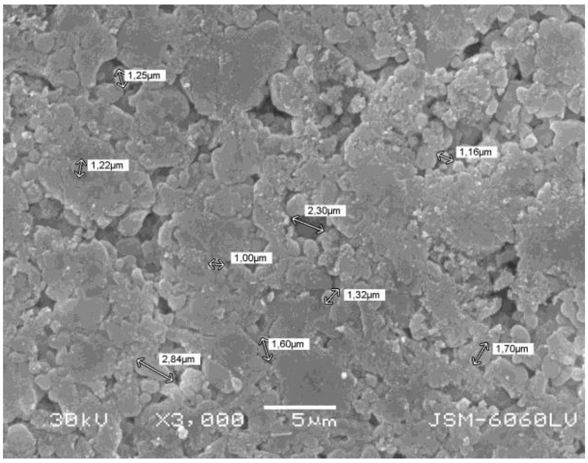

Fig 3: Reference product.

Coated papers were tested on inkjet printing. Pre-presses were done on the printer HP Officejet 6000 Printer (thermal 4800 x 1200 dpi, dye-based inks, min 1.3 pl). In the table 3–5 are presented results of bleeding and wicking, determined by image analysis. The effect of the pigment particles modification on micro porosity and successful capturing anionic dye showed significantly clear, so spreading and wicking, evaluated by image analysis was minimized.

Table 3. Bleeding of black 8 on yellow.

Specimen	Picture of bleeding	Area [%]	Increment [%]	Share [%]
standard	8	38.95	− 5.72	− 12.81
TCC2	8	55.56	10.89	24.38
reference	8	44.68	0.01	0.02
ideal	8	**44.67**		

Table 4. Bleeding of yellow 8 on black.

Specimen	Picture of bleeding	Area [%]	Increment [%]	Share [%]
standard	8	38.16	1.86	5.12
TCC2	8	36.37	0.07	0.19
reference	8	36.29	− 0.01	− 0.03
ideal	8	**36.30**		

Table 5. Wicking.

Specimen	Picture of wicking	Area [mm^2]	Perimeter [mm]	Increment of Perimeter [mm]	Share [%]
standard	E	21.82	60.50	− 2.80	− 4.42
TCC2	E	24.68	63.93	0.63	1.00
reference	E	24.13	63.86	0.56	0.88
ideal	E	**23.30**	**63.30**		

3 Conclusions

Ground calcium carbonate (GCC) is the main component in the coating color. The successful pigment engineering, like finer particle size distribution, effective dispersing system and other procedures that are reflected in modified specific area, charge etc., provide a satisfactory high values of significant properties of the coated paper surfaces that are used as a main graphic material in many different printing technics. Results of development work are studying the impact of modified GCC pigment on micro-porosity of the coated paper surface and effect on capturing anionic dye in ink-jet printing technique. As presented the results are significantly well and the printouts are of high-resolution quality with very low bleeding/wicking. Information printed on such coated paper is clear and could be used also for smaller text/pictures as the standard, i.e10–12 pt, are.

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4 Literature

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