MODIFIKACIJA GCC ZA KAKOVOSTNEJŠI IZPIS KAPLJIČNEGA TISKALNIKA

GCC MODIFICATION FOR BETTER PERFOMANCE OF INK-JET PRINTS

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IZVLEČEK

Navkljub negativni medijski publiciteti papir ohranja vodilno vlogo med uporabljenimi grafičnimi materiali. Razlog je v tem, da je papir izjemno odporen proti okoljskim vplivom in predvsem je tudi biorazgradljiv. Premazi, narejeni iz naravnih sestavnih delov, lahko nadomestijo ekološko manj prijazne in cenovno dražje sintetične materiale. Posebne lastnosti lahko zagotovimo s površinsko aktivnostjo, to je kemijsko ali s spremembo geometrije pigmentnih delcev, ki se jo doseže bodisi z granulacijo bodisi z razporeditvijo različnih velikosti pigmentnih delcev oziroma njihovo obliko. Naravni kalcijev karbonat (GCC) se vse pogosteje in vse širše uporablja v papirni industriji. Poleg zadostitve ustreznih optičnih lastnosti je trend v izdelavi lažjih, z uporabo nanomaterialov, to je materialov nižjih gramatur oziroma tako imenovanih NMP. Zahteva po nižji specifični energiji in proizvodnih stroških sili proizvajalce grafičnih papirjev k povišani uporabi pigmentov. Vendar je, tako kot pri vsaki stvari, tudi v tem primeru uporaba pigmentov do neke mere smiselna. Tako je nastala pri inženirjih ideja o prilagoditvi delcev pigmenta, ki bi razširila krog uporabnosti in namembnosti. Modificirani GCC pigmentni delci, to je TCC (treated calcium carbonate), zagotavljajo prav široko uporabnost. V prispevku so predstavljeni ustrezni tehnološki postopki obdelave surovega GCC in učinek, ki jih modifikacija geometrije pigmentnih delcev, kateri obenem zvišajo funkcionalne lastnosti, kot so struktura papirja in površina le-tega, doprinese. Rezultati raziskave slikovito predstavijo, kako inženirsko zasnovana modifikacija GCC pozitivno učinkuje na v osnovi zastavljeno končno namembnost tako premazanega papirja, to je potiskljivost papirja s kapljičnim tiskalnikom z barvami na vodni osnovi.

Ključne besede: GCC, modificirani pigmenti, premazan papir, kapljični tisk, bleeding, wicking.

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] Overall, paper industry is in a transition situation, where its main goal is not just basic paper production, as it was in the past, but producing additional products, i.e. coated paper for specific purposes. Paper filler and paper coatings in the form of GCC, has become essential in making paper and are the most significant portion of used additives, in terms of weight percent, e.g. in range from 3 to 38 %. [4, 5, 6, 7]

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. [8, 9] 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. [10] 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). [11, 12] Liquid transfer on/in

paper surface is represented *with Young-Laplace equation:*

$$\Delta p = 2\gamma_{\lambda} \cos\left(\frac{1}{r}\right) \quad (1)$$

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_{λ} – 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.

The Lukas-Washburn equation (eg. Equ. 2) 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 EXPERIMENTAL PART

In laboratory scale some trials of preparing and coating colour with modified GCC pigment were done in company Calcit. 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 m²/g (i.e. Table 1).

3 RESULTS

Results of the investigation were outcome of the research work, namely grounded on the bases of preliminary idea of creating such a paper coating formula that ink-jet printouts would meet the final demand towards the highest possible quality. Therefore we have included SEM and image analysing software ImageJ.

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.

Table 1: Modified pigment preparation.
Preglednica 1: Priprava modificiranega pigmenta.

Trials, No.	Modification procedure	Addition		BET [m²/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 main differences between used materials, like specific surface area and mean particle diameter are shown in the Table 2.

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.

Table 2: Pigments characteristics.
Preglednica 2: Karakteristike pigmentov.

Pigment sample	D50 [%]	BET [m²/g]
standard quality	0.686 μm	12.24
TCC 2	1.241 μm	32.93
Ref.	1.353 μm	60.74

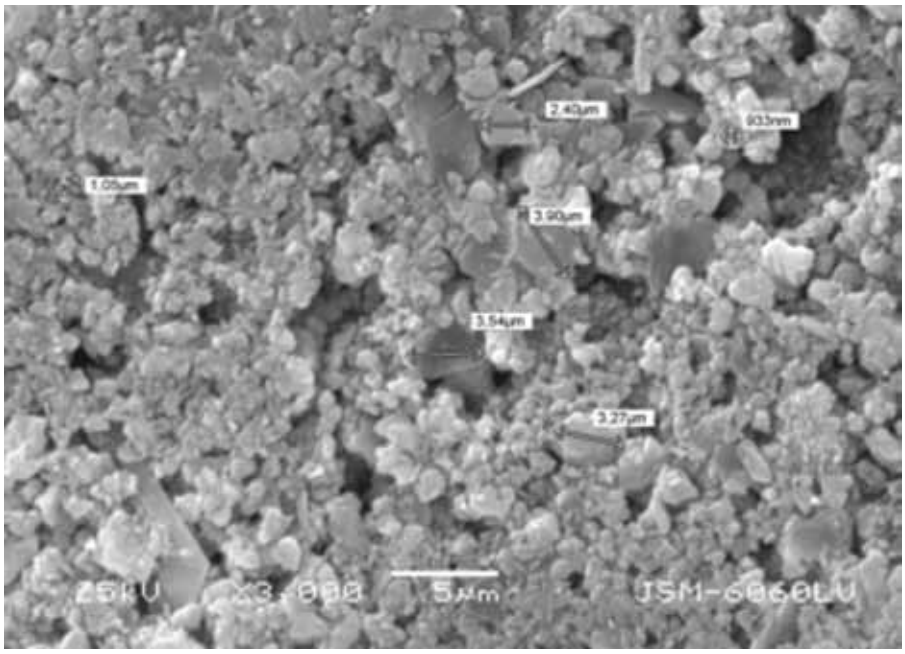

Figure 1: Standard product.
Slika 1: Standardni proizvod.

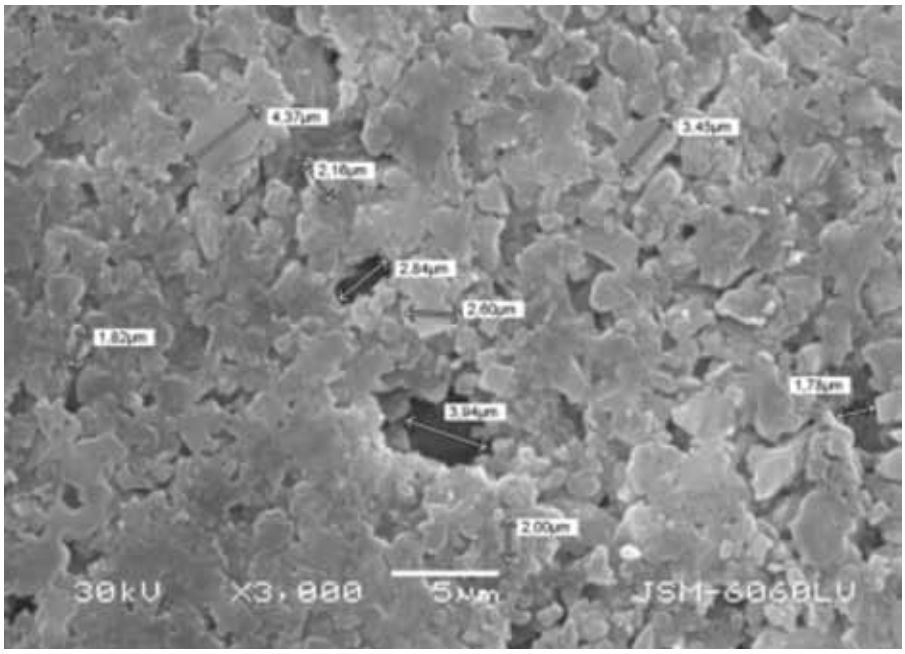

Figure 2: Modified product – TCC2.
Slika 2: Modificiran proizvod – TCC2

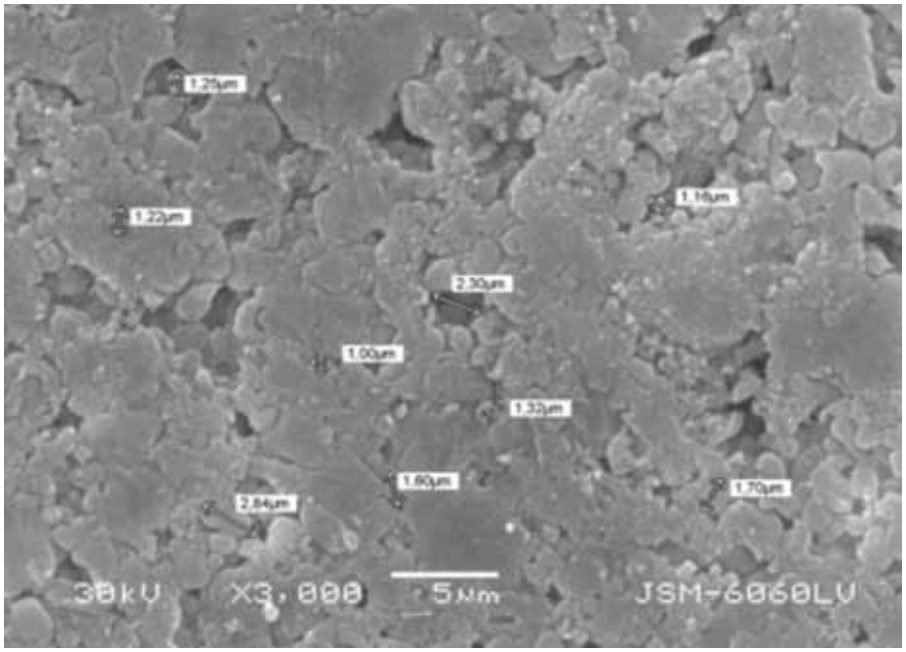

Figure 3: Reference product.
Slika 3: Referenčni proizvod.

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.

Coated papers were tested on inkjet printing. Pre-presses were done on the printer HP Officejet 6000 Printer (thermal 4800 × 1200 dpi, dye-based inks, min 1.3 pl). In the Table 3–5 are presented results of bleeding and wicking, determined by image analyzing software ImageJ. 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. In Table 3 are presented results of bleeding of black 8 on yellow background. TCC2 has an increment over 10 %, which is not well enough and it is something to work on in the future researched.

From Table 4 is well seen the tendency towards lower increment of TCC2, which is just 0.07 %. However, same trend of lowering wicking can be seen from Table 5, where TCC2 has increment of perimeter in just 0.63 mm or exactly 1.00 %. Mentioned results of image analyzes clearly indicate, how well were pigment particles modified and that our research is going in the right direction. Not simply grounding pigment particles of GCC into the nano size particles, but modifying them on such way, that surface is after treatment correctly charged, which will have an impact on the capturing water based printing ink of inkjet printer and hold the dye particles on the coated paper surface, which results in color satiation and has the end effect on clear picture and text reproduction as well as on the readability.

Table 3: Bleeding of black 8 on yellow.
Preglednica 3: »Krvavenje« črne 8 na rumeni podlagi.

Specimen	Picture of bleeding	Area [%]	Increment [%]	Share [%]
standard	8	38.95	– 5.72	12.24
TCC2	8	55.56	10.89	32.93
reference	8	44.68	0.01	60.74
ideal	8	44.67		

Table 4: Bleeding of yellow 8 on black.
Preglednica 4: »Krvavenje« rumene 8 na črni podlagi.

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.
Preglednica 5: Sivenje.

Specimen	Picture of wicking	Area [mm²]	Perimeter [mm]	Increment of Perimeter	Share [%]
standard		38.16	1.86	– 2.80	5.12
TCC2		36.37	0.07	0.63	0.19
reference		36.29	– 0.01	0.56	– 0.03
ideal		36.30			

4 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 outcome of the study, how does modified GCC pigment impact on micro-porosity of the coated paper surface and how it effect on capturing anionic dye in ink-jet printing technique. As presented in Table 4 and 5, 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.e. 10–12 pt, are.

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