EFFECT OF USING CALCIUM CARBONATE (CaCO₃) IN SURFACE COATING ON LIQUID ABSORPTION OF PAPER AND SOME PRINTABILITY PARAMETERS

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For quality printing results that require detail, the smooth paper surface, absorbency, color and gloss are of great importance. Since the desired surface properties cannot be obtained even in well-polished paper, smooth paper surfaces can be obtained by sizing and coating processes. The aim of this study was to investigate the effect of different amounts of calcium carbonate, added into the surface coating formulation, on liquid absorbency and printability of paper. Paper coating formulations were created by adding 1%, 2.5%, 5% and 7.5% calcium carbonate to an equal amount of cationic starch binder. The obtained coating formulations were applied to the surface of standard pieces of paper with a lab coater. Water absorbency and drop contact angle of all papers (base paper and surface-treated paper) were measured by using the sessile droplet method and then their surface energies were calculated. After the gloss and color changes of the test papers were determined, test prints were applied on their surface with offset printing ink. The effect of surface treatments on the printability characteristics of the paper was examined in detail. It was emphasized that the amount of calcium carbonate used in cationic starch should be optimized with regard to the absorbency and printability of the paper.

Keywords: paper coating, surface chemistry, surface energy, water absorption, printability, calcium carbonate

INTRODUCTION

An improvement in the printability and absorption properties of paper is achieved by controlling the ink–paper interaction. Wetting, spreading and settling of the ink on the printing substrate surface can be achieved in various ways.¹ The structure and fiber characteristics of the paper surface determine the behavior of the liquid phase content of the ink on the paper during the printing process.² The coarser and more macro-porous the paper surface is, the more the printed ink spreads and penetrates into the paper.¹ Thus, paper must have the right hydrophobicity for good printability. In the printing process, a certain amount of ink must penetrate the surface and, at the same time, must remain on the surface of the paper without spreading.³ Surface treatments are important for controlling the penetration rate and lateral spread of ink.

Surface sizing makes paper resistant to liquids and enhances surface durability by adhering the surface fibers of the paper. In addition, this process provides advantages, such as ink retention, abrasion resistance, bursting, tensile and folding resistance. It is used for achieving a high level of water repellency or oil resistance. However, high fluid resistance makes it difficult for the paper surface to absorb liquid ink during the printing process and prolongs the drying time. This leads to increased printing problems, such as strike-through, scumming, contamination and delayed post-print finishing, such as folding and binding.⁴

Printability, high-quality color reproduction and ink gloss are important parameters to be considered in order to achieve uniform appearance or avoid printing problems.⁵ The
paper surface is coated for improving printability and surface properties or for balanced ink absorption. A coating dispersion consists of pigments, binders and additives. Coating pigments are considerably finer than paper fibers. They close the existing pores and cover the surface. Binders act as an adhesive to bind coating pigments to each other, providing adhesion to the substrate and anchor to cellulose fibers. By finishing the coated paper, smoothness and specular gloss are created on its surface.

Coated papers have much denser and more uniform surface than the fibrous structure of uncoated papers. As the coating process changes the contact angle and surface energy of the paper, it affects printability properties, such as dimensional stability, resistance to water, ink setting, paper gloss, print gloss, light scattering, and print density. It is the content and proportions of the coating that determine these properties in the coating process.

The interactions between printing inks and the paper surface, as well as the penetration of the ink vehicle into the coating layer, are to be considered to reach the desired print quality. The ink–paper coating interaction occurs instantaneously upon contact. The absorption process after the initial contact is referred to as ink setting. It is known that ink setting depends on many factors, such as the nature of the substrate, the properties of the coating, and the ink formulation.

The physical structure and chemical properties of the coating layer affect the transfer and setting of the ink. For this reason, the absorbency of the paper/coating surface is a determinant factor for the printing parameters, such as drying process of the ink film, printing gloss and light fastness.

The fundamental interactions between ink and coating components and their influence on the final distribution of multi-component ink on coated paper have attracted some in-depth research works in recent years.

In this study, first, surface sizing with cationic starch was applied to base paper. Coating formulations were then prepared with cationic starch and different amounts of CaCO₃ used as binder to improve the absorbability properties of paper, as well as to improve the printability properties. The obtained coating formulations were applied to base papers. As a result, the optimum coating formulation, for achieving the best printability and stable liquid absorption, was determined in comparison with the base paper and the sized samples.

**EXPERIMENTAL**

**Material and methods**

In this study, 200 g/m² base (uncoated) paper, cationic starch, CaCO₃ (supplied by BASF Company, China), and process cyan ink (DIN ISO 2846-1) were used.

**Preparation of paper samples and paper coating**

In order to determine the effect of the calcium carbonate ratio on coating and print quality, coatings containing cationic starch and different amounts of calcium carbonate (properties given in Table 1) were prepared and applied on uncoated paper surfaces of 200 g/m².

First, cationic starch-based surface sizing was applied to the base paper. The sizing formulation consisted of 7.5% concentration of cationic starch; it was heated up to 90 °C and then cooled to 60 °C, and finally, applied onto the paper surface using a Mayer rod number 2 in a laboratory-type paper coating machine.

| Table 1
| Calcium carbonate properties |
|---|---|---|---|---|---|
| CaCO₃ | Ph | Humidity | Size | Purity | Shape | Density |
| CaCO₃ | 9 | <0.3 | 2 µm | >99.5 | Cubic | 2.7 |

| Table 2
| Paper coating formulations |
|---|---|---|---|
| Cationic starch (%) | Water (%) | CaCO₃ (%) |
| 12.5 (sized p.) | 87.5 | 0 |
| 12.4 | 86.6 | 1 |
| 12.2 | 85.3 | 2.5 |
| 11.9 | 83.1 | 5 |
| 11.6 | 80.9 | 7.5 |
In the second stage of this study, the same preparation process was applied for the paper coating formulation, but various amounts of calcium carbonate (as given in Table 2) were also added to the first mixture. The formulation was applied to the paper surface, using the Mayer rod in the laboratory-type paper coating machine, under laboratory conditions. The resulting formulations were coated with 0.1 g/m² on one surface.

The papers were conditioned in a coating area for 48 hours before the coating process. Coating was performed with a bar coater (model K303 Multi-coater, RK Print Coat Instruments Ltd., United Kingdom) on 21.0 × 29.7 cm base sheets, with the speed of 2 m/min automatically. Coatings were allowed to dry for 24 h at 20 °C and 65% relative humidity (RH). The coating thickness was 4 µm. The coating amount was adjusted using a number 2 bar. Color (ISO12647-2: 2013), paper gloss (TAPPI T 480 om-09), print gloss (BS EN ISO 2813: 2014), water drop volume change, contact angle (TAPPI T558), surface energy (ASTM D5946) and surface morphologies of the obtained coated papers were determined by a Gretag Macbeth SpectraEye spectrophotometer, Byk Gardner Glossmeter (Sheen Instrument, U.K.), TMI Pocket Goniometer Model PG-X (FIBRO Systems AB Stockholm, Sweden) and Leica optical microscope, respectively. On average, 10 replicates were performed per test. The results of these 10 samples were then averaged.

Printing of surface treated paper

Base paper, sized paper and coated samples (with different coating formulations) were printed with an IGT C1 test printing machine, with an equal amount of process cyan ink (DIN ISO 2846-1). Printing was performed at 0.2 m/s printing speed and 300 N printing pressure. CIE L*a*b* color measurements were carried out on printed and unprinted paper surfaces of differently coated and sized papers, according to ISO 12647-2:2013 standard, with an X-Rite eXact™ Spectrophotometer, in the spectral range from 400 nm to 700 nm (ISO 12647-1: D50 illuminant, 2° observer, 0°/45° geometry, black backing), using a polarized filter. After the completion of L*a*b* measurements, the color differences (ΔE*) of the samples were calculated according to the formula shown below, according to CIE ΔE* 1976 ISO 13655 standards, with an average of ten measurements:

\[ \Delta E^*_{ab} = \sqrt{(L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1)^2 + (b^*_2 - b^*_1)^2} \]

where ΔL*, Δa* and Δb* are differences in L*, a* and b* values, respectively, between the specimen color and the target color.16

Gloss measurements were performed with micro-gloss 75° geometry, according to ISO 8254-1:2009 standard. Print gloss measurements were taken with micro-TRI-gloss 60° geometry and a BYK-Gardner GmbH glossmeter, according to ISO 2813:2014.

RESULTS AND DISCUSSION

Liquid absorption, contact angle and surface energy

In printing, the absorption of printing inks depends on the absorptivity (the total volume of liquid) of the substrate.17 The degree of ink absorption into the printing substrate is important in printing for the contrast formed between the ink and paper.1 The surface topography of the paper is decisive in the process of ink settling and penetration into the paper surface. The amount of coating applied affect the surface morphology, absorbency, contact angle and surface energy. The most important factors affecting the contact angle are the surface energy and roughness of the printing substrate. The surface energy of paper is influenced by the coating composition, and even a small change in the coating composition (surface active chemical, polymer content in binder) could lead to significant differences in paper surface energy, especially regarding its polar part.3 Surface energy plays an important role in the interaction of paper with liquids.

The water absorbency, water contact angle and surface energies of the differently treated paper surfaces were determined according to TAPPI T 458, by the sessile water droplet method. Distilled water was employed as wetting liquid in order to determine the liquid absorbency of the surface-treated papers as a function of time, with a Pocket Goniometer Model PG-X, (FIBRO Systems AB, Sweden), program version 3.4. Images of water droplets were then recorded by using a CCD video camera. Surface energy was calculated according to ASTM D5946 standard test method,14 depending on the water contact angle.

Volume changes of the water drop on the paper surface were measured depending on time and the results are plotted in Figure 1. When examining the water drop volume changes, it can be noted that surface sizing reduced the water absorbency of the paper. This finding is consistent with results reported in the literature.18 Polymer starch, as expected, prevented the water absorption of inorganic fillers and increased the water resistance of the paper surface. With the addition of hydrophilic calcium carbonate to the surface coating, the ability of paper to absorb water was regained. As the amount of inorganic
material in the coating increased, the paper surface became more absorbent.

The contact angles and surface energies of the obtained sample papers are given in Table 3. The data in Table 3 indicate that the largest contact angle and the lowest surface energy were found on the base paper. The contact angle of the base paper decreased after the surface sizing process, which can be explained by the fact that cationic starch formed hydrogen bonds with water, thus allowing its spreading. In the printing process, a low water contact angle is desirable, for avoiding the spreading of ink on the paper surface and for obtaining low ink consumption. Low ink consumption is desired since the optimum print density values can be obtained with less ink, and also because paper printed with low liquid content will be easier to dry.

Table 3
Surface energy and contact angles of test papers

| Paper sample   | Surface energy (mJ/m²) | Contact angle (°) |
|----------------|------------------------|-------------------|
| Base paper     | 40.2                   | 68.6              |
| Sized paper    | 50.7                   | 39.8              |
| 1% CaCO₃       | 49.7                   | 42.5              |
| 2.5% CaCO₃     | 45.7                   | 53.4              |
| 5% CaCO₃       | 45.6                   | 53.9              |
| 7.5%CaCO₃      | 45.2                   | 54.3              |

Surface microstructure

A Leica MZ6 (Veeco Instruments inc., Santa Barbara, USA) microscope was used to visualize the microstructure of the surface treated paper at 90x magnification. A 10 µm x 10 µm displaying area was selected to define the surface microstructure of the paper. Thus, the changes in the surface topography of the papers and the setting of the printed ink film on the surface were displayed and recorded.

Images of the base paper and surface sized paper are presented in Figure 2. It may be noted that, as expected, the porosity of the uncoated paper surface is higher than that of the sized surface, where the gaps among the fibers are filled by the sizing and the surface is smoother. Increased surface irregularity is undesirable when considering the attractiveness of the paper and the printing process, as it will cause refraction. However, increased water resistance due to the surface sizing adversely affects printability and ink absorption. For this reason, it is important that on surface sized paper the prints should not have high ink density.

The surfaces of the obtained coated papers were examined by an optical microscope (Fig. 3). It was determined that the calcium carbonate was distributed homogeneously on the surface, but agglomeration occurred as its amount was increased. Surface roughness increased with the addition of inorganic
material. These results are consistent with those reported in the literature.\textsuperscript{20,21}

Figure 2: Microscopic images of base paper and sized paper

Figure 3: Microscopic images of coated paper surfaces (with different amounts of CaCO\textsubscript{3})

Figure 4: Microscopic images of cyan solid tone printed surfaces (magnification 90x)
Offset prints were made on the differently surface-treated papers and their surface properties were examined again (Fig. 4). It can be noted that fibers are clearly visible on the uncoated paper, even after printing. As regards the sized sample, its surface was smooth due to surface sizing, and its surface roughness was significantly reduced, because the natural polymer sizing makes the cellulose fibers adhere to each other and fills the gaps among them. In the samples coated with calcium carbonate containing formulations, it may be seen that surface fibers still adhered to each other, due to the starch in the composition of the coating, and the surface was smooth. However, in the coatings containing 5% and 7.5% calcium carbonate, agglomeration could not be prevented and undesirable blistering formed on the surface. After a while, under the effect of friction, these blisters fall apart and the white paper surface is exposed in the middle of the print. Thus, the integrity of the ink film on the surface is deteriorated.

Paper gloss change with coating

When examining the gloss of the paper samples (Fig. 5), it may be observed that the lowest gloss was recorded for the untreated base paper, and this gloss value increased 10 times after the sizing process. The cationic starch applied to the paper surface filled the gaps among the fibers and formed a film on the surface, which reduced the diffuse reflection from the fibers and increased gloss. The addition of calcium carbonate to the coating formulations increased the roughness of the film formed on the surface, thus reducing the gloss slightly, compared to the surface sized papers. As the amount of calcium carbonate was increased, paper gloss decreased. However, even in the coatings containing the highest amount of calcium carbonate, the gloss value was 7 times higher than that of the base paper. The results obtained were consistent with those found in the literature.

Paper color change with coating

CIE \(L^*a^*b^*\) (CIELAB) colorimetry of the treated papers was assessed with an X-Rite eXact™ Spectrophotometer and color differences \((\Delta E^*_{ab})\) versus the values for the base paper were calculated for each sample. It was found that the major color difference, compared to the base paper, was recorded for the sized paper (Fig. 6). The chromophore groups in the cationic starch caused the surface of the paper to turn slightly yellow after the sizing process. It is thought that this yellowing increases the color difference on the paper surface. However, with the addition of calcium carbonate, the color change in the blue part, the opposite of yellow on the axis, decreased the yellowing and the \(\Delta E^*_{ab}\) value decreased. Similar results are available in the literature.

Relationship between paper coating and print quality

Print color characteristics

The base paper and surface treated papers were printed using an IGT C1 printability tester, with process cyan color ink, at standard density value. The color differences \((\Delta E^*_{ab})\) between the cyan color printed base paper and surface-treated papers were then calculated. The results are given in Figure 7. It is noted that the color differences follow the same trend as those for unprinted paper, but they reach higher values. In other words, the color change on the unprinted paper was increased even more after printing and, as a result, the color difference \((\Delta E^*_{ab})\) value increased. Despite this, the delta e values obtained were within acceptable limits, according to ISO 12647-2. The investigation revealed that cationic starch and calcium carbonate applied to the paper surface do not affect adversely the printing color.

Print gloss

Print gloss is a measurement of light reflection and is significantly affected by paper smoothness. Print gloss values of the surface treated paper can be seen in Figure 8. Examining the results, it can be remarked that the printing gloss increased due to the polymeric film formed on the sized paper surface. The addition of calcium carbonate to the surface coating has reduced the printing gloss of the paper, compared to that of the surface sized paper. However, it has been found that the printing gloss on papers coated with calcium carbonate is about 9 times higher than the printing gloss on the base paper. As the amount of calcium carbonate in the paper coatings was increased, it is observed that both paper gloss (Fig. 5) and printing gloss (Fig. 8) gradually decreased.
**Light fastness**

In ink light fastness, in addition to the color pigment, the printed substrates also have a role to play. For this reason, in printing processes, the printing substrate should be taken into account in terms of its sensitivity to light fastness. The light fastness measurements of the printing test samples were carried out according to ISO 12040:1997 (R2016). Color differences between the printed surface treated and untreated samples were expressed as CIE $L^*a^*b^*$ and $(\Delta E^*_{ab})$. The results obtained (Fig. 9) reveal that all the surface treatments applied to the paper decreased its resistance to light. It was determined that the surface treated papers changed their color against the light more significantly than uncoated paper. This was caused by the degradation of the double bonds in the structure of the cationic starch used in the coating and sizing processes, upon exposure to light, and therefore the color shifted to yellow. In addition, the calcium carbonate in the coating formulations was converted into calcium oxide by the heat generated in the environment during the light test, and therefore the color difference increased slightly as the amount of calcium carbonate was increased. Examining the light fastness values of cyan color printed uncoated paper and surface treated papers, it can be concluded that the surface treatments had a positive effect on the light fastness of the ink. This is thought to be due to the fact that the cationic starch fastened the ink film more to the paper surface, and therefore the color was affected less by light. As the amount of calcium carbonate was increased in the surface coating formulation, there was a gradual decrease in the light resistance of the ink. This is explained by the low light resistance of calcium carbonate itself. The light fastness results found for the printed test papers were found to be consistent with those reported in the literature.

**Ink consumption**

Paper–ink interaction is extremely important in printing. Ideal printing outputs should be achieved with minimal ink consumption. It should not be supposed that visual printing quality will increase as the amount of ink increases.
In this study, equal density prints were made on treated and untreated papers. The amount of ink used to achieve uniform density during printing was weighed and the amount of ink required to print 1 square meter of area was calculated. It has been found that much more (about twice) ink is consumed to achieve the same print density on the untreated paper (Fig. 10). The reason is that the ink spread forward in the spaces between the cellulose fibers. Therefore, more ink was needed to form the same ink film on the paper surface. Also, an equal amount of ink was spent on all the coated papers.

CONCLUSION

In this study, coatings containing different amounts of calcium carbonate, in addition to polymeric starch, were prepared and applied, and the effects of these coatings on the gloss, color, absorbency, water contact angle, surface energy and printability of the paper substrates were examined.

According to the results obtained, the gloss of the treated papers increased, compared to that of the untreated paper, as polymer starch decreased the liquid absorbency of the paper, whereas calcium carbonate increased the water absorbency back. Accordingly, it can be concluded that the setting and drying rate of the ink on the paper surface can be balanced with the coating containing polymer starch and different amounts of calcium carbonate.

Since the calcium carbonate agglomerates and cannot be distributed uniformly, the use of 5% or more calcium carbonate in the coating formulation causes irregular printing results. For this reason, the content of calcium carbonate should not exceed 2.5% in the paper coating.

It was determined that the yellowing of the paper color can be eliminated by adding calcium carbonate into the coating. When the printing results were examined, it was concluded that the color differences remained average.

Polymer starch increases the gloss of paper and print, while the addition of calcium carbonate decreases the gloss proportionally with the increase in its content in the coating. Therefore, the use of calcium carbonate should be limited, especially in products where printing gloss is desired.

Any surface treatment increases the light fastness of the ink film on the printed paper surface. However, as the calcium carbonate content in the coating increases, the light fastness of the ink film decreases. Therefore, the amount of calcium carbonate in paper coatings to be used in printed products, especially for outdoor applications, should be kept at a low level.

It has been determined that the treatments applied to the paper surface reduce the ink consumption by an increase in the amount of coating. From an environmental point of view, this means that less volatile organic compounds are released.

When all the results are examined, it can be concluded that the coating formulation containing 2.5% calcium carbonate leads to optimum printability parameters on paper substrates.

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