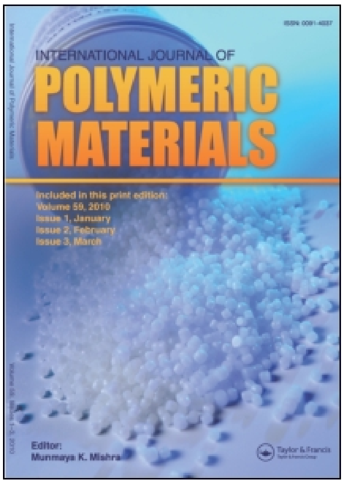

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Effects of Filler Content and Coating on the Water and Oil-Based Ink Interactions with a Paper Surface

Cem Aydemir[a]; Arif Karademir[b]; Sami İmamoğlu[c]
[a] Department of Printing, Faculty of Technical Education, Marmara University, Goztepe, Istanbul, Turkey [b] Department of Forest Product Engineering, Faculty of Forestry, Kahramanmaras Sutcuimam University, Kahramanmaras, Turkey [c] Department of Forest Product Engineering, Faculty of Forestry, Artvin Coruh University, Artvin, Turkey

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Cem Aydemir,[1] Arif Karademir,[2] and Sami İmamoğlu[3]

[1]Department of Printing, Faculty of Technical Education, Marmara University, Goztepe, Istanbul, Turkey
[2]Department of Forest Product Engineering, Faculty of Forestry, Kahramanmaras Sutcuimam University, Kahramanmaras, Turkey
[3]Department of Forest Product Engineering, Faculty of Forestry, Artvin Coruh University, Artvin, Turkey

The effects of filler and coating on the behaviors of water and oil-based ink on the paper surface were investigated. Fillers reduced the air permeability and surface energy hence increased the liquids uptake. The coating was more effective than the internal addition of fillers for the improvement of water and ink absorption. Sizing interfered with the fillers, but had negligible effects on the movements of oil-based ink on papers. The quality of coating in terms of printing performance was dependent on the improvement of surface smoothness, microcapillary formation and the absorption properties of fillers in the coating layer.

Keywords coating, IGT test, paper filler, paper roughness, print density, sessile drop, sizing

INTRODUCTION

Most paper and boards carry some part of printed images on them in different intensity, while some papers are specifically produced for printing, and thus

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Address correspondence to Cem Aydemir, Department of Printing Education, Faculty of Technical Education, Marmara University, Goztepe 34722, Istanbul, Turkey. E-mail: cemaydemir@marmara.edu.tr

undergo many operations such as calendaring, coating, and surface sizing as well as filler loading during production. Therefore, in addition to the many properties of paper products, the way they behave in printing and finishing operations is extremely important too. Paper surface properties such as smoothness, surface energy, and porosity as well as sizing degree greatly affect the interactions between liquids and papers. Fiber properties such as coarseness, beating, filler loading, pressing [1], calendaring and coating are some of the main factors that mostly affect the surface roughness and porosity of paper products. Diameters of pores and uniform distribution in paper structure are also important for ink absorption [2]. Paper sizing is defined as the addition of some hydrophobic chemicals to the paper during manufacturing (internal sizing) or after the sheet formation (surface sizing). The sizing performance is significantly affected by the presence of fillers in the stock, higher beating, pH, and the bleaching degree of pulps [3].

A liquid droplet touching a paper surface tends to both penetrate into the paper structure and spread over the surface. The extent of penetration or spreading depends on both the properties of paper and liquids (ink) as well as environmental conditions, like temperature, humidity, and pressure. The inks can be classified in three main groups according to the carrier medium as solvent-based, oil-based, and water-based. Depending on the nature of the interaction between the ink and the paper, some distortion on the paper surface may be created to some extent. Lepoutre and Skowronski conducted research on the relationships between ink penetration and surface roughness and concluded that ink penetration into paper causes stress relaxation, swelling and debonding [4–6]. Such changes on paper surfaces are more prevalent in the case of water-based inks [7,8] since water naturally swells the cellulose fibers, expands them and weakens the fiber-fiber bonds. A physicochemical interaction between paper and printing ink greatly determines the spreading of wet ink, as well as setting and drying. Interactions are purely physical in nature when solvent-based inks are used, but it gets quite complicated and complex in the case of water-based inks [9]. Aydemir recently concluded his detailed work and stressed that the relationship between water and a cellulose-based substrate can not be fully understood if the microstructure of the cellulose-based materials and the three main mechanisms, namely evaporation, absorption and hygroexpansion, are not taken into account simultaneously [10]. Water in the inks itself interacts with all the ingredients of papers and leads to a distortion on papers. pH of water needs to be carefully controlled and kept over pH 9 too [9,11]. In spite of such problematic aspects, the use water-based inks is still highly encouraged instead of solvent-based inks due to environmental and the health concerns. Oil-based inks, compared to water-based, do not cause great detrimental distortion on paper surface and do not create a danger to health and the environment like solvent-base ones. There are three basic mechanisms that control the ink behavior on paper surfaces. These mechanisms, namely penetration, evaporation of fluid and swelling, were studied in detail by some researchers [2,10–14].

Printing inks basically consist of a carrier medium such as water, solvent or oil, and coloring ingredients, pigments, may be some kinds of binders too. During printing, the carrier medium tends to get inside the paper through capillaries and voids between fibers/fillers and also into the lumens of cellulosic fibers. Pigments, however, cannot so easily travel into the paper structure compared to the carrier, but rather stay on the surfaces. Pigment movements to the inner parts of the paper are improved by the help of paper porosity. The more porous the paper, the deeper the pigments move in. From the point of printing quality, pigments should stay actually on the paper surface and give a higher print density with a limited amount of ink. Papers absorbing inks as a whole with carrier and pigments directly increased the ink consumption and the operation cost while giving a poor density profile. Some evaporation from ink carrier also occurs [15, 16]. The time required for inks to settle, dry and harden are important as far as the economy is concerned.

This work is designed to investigate the effects of filler on the sizing and the print density properties of some papers that were uncoated, matte-coated and gloss-coated. The change of water drop volume was also monitored and recorded via a sessile droplet method. Behaviors of inks and waters on sheets tested are discussed in detail.

MATERIALS AND METHODS

In the first part of this work, a number of internally alkali-sized papers (% 0,3 alkyl ketene dimer (AKD)) (Raisifob, Ciba Chemical, Istanbul, Turkey) produced from bleached long fibers with the addition of 0, 5, 10, 20 and 30% precipitated calcium carbonate fillers (Hisarcal EX3, Hisar Madencilik, Konya, Turkey) (PCC) were tested to determine the ash content, surface roughness, air permeability and contact angle according to TAPPI T 211, ISO 5636-3:1992, T 555 and T 458 om-89, respectively. The surface energy of tested papers was calculated according to an equation developed by Fowkes (1964) [17], and derived by Owens and Wendt (1969) (Eq. (1)) [18].

$$1+\cos\theta = 2\sqrt{\gamma_s^d\left(\frac{\sqrt{\gamma_L^d}}{\gamma_{Lv}}\right)} + 2\sqrt{\gamma_s^h\left(\frac{\sqrt{\gamma_L^h}}{\gamma_{Lv}}\right)} \tag{1}$$

where,

θ = the contact angle
γ_s^d = the dispersion force component of the surface
γ_L^d = the dispersion force component of the liquid

Table 1: Some properties of offset ink used.

Parameters	Values
Boiling point	250°C
Flash point	>100 °C
Ignition point	200 °C
Vapor pressure (at 20°C)	<0.1 hPa
Density (at 20°C)	1.088 g/cm^3
Solvent content	Organic solvents < % 0,5 Water < % 0,5

γ_{Lv} = the surface energy of the liquid
γ_s^h = the hydrogen bond component of the surface
γ_L^h = the hydrogen bond component of the liquid.

In the second part of this study, three different papers, uncoated, matte-coated and gloss-coated, were analyzed. The base sheets were made from bleached virgin printing grade pulps with ash content of % 18,2. The brightness of papers were in a similar range while other properties especially roughness and air permeability values varied considerably (Table 1). Papers were tested to determine the following properties: brightness, gloss, surface roughness, air permeability and ash content in accordance to T 452 om-02, T 480 om-09, ISO 8791–4, T 555 and TAPPI T 211, respectively.

Sessile drop methods were employed and the changes in both the drop volume and the contact angle were recorded in a time span up to 6 min. Printing applications at 35 mm width were conducted on sheets with an offset ink from Michael Huber Resista Cyan series (DIN ISO 2846-1). The properties of ink are given in Table 1. The IGT printing device was operated at 0,3 m/s speed and 350 N pressures according to ISO 12647-2 standard in a controlled atmosphere where samples were also kept for at least 24 h at 23 ± 1°C and %50 ± 3% relative humidity before the printing. Print density measurements on printed papers were done with a Gretag Macbeth SpectraEye device adjusted at D50 illumination, 2° monitoring and 0/45 black area. Changes in print lightness were also recorded. Measurements were repeated in a period of 48 h with close intervals.

RESULTS AND DISCUSSION

Effect of Filler Loading on Surface Energy

It was clearly noted that the increasing amount of fillers in paper structure were significantly reducing the contact angle, air permeability and surface roughness. The surface energy was noted to be increased parallel to ash content (Figure 1). Results basically showed that the fillers remarkably

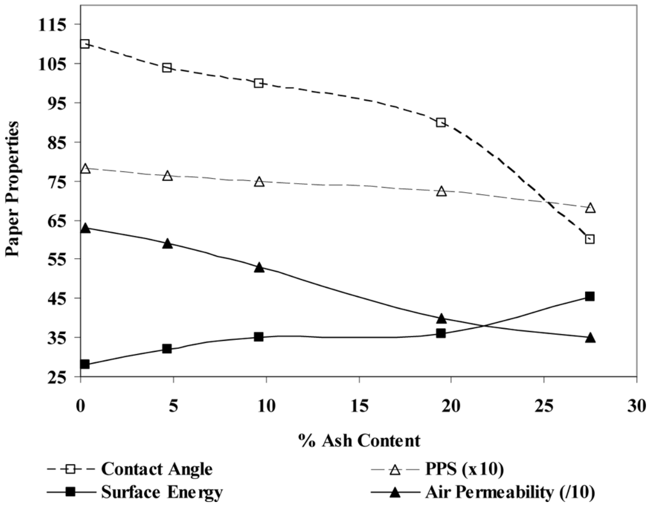

Figure 1: Fillers reducing air permeability and surface energy of papers.

interfered with the sizing chemical as reported elsewhere [19, 20]. It is explained by the increase in the total surface area in the paper structure as a result of filler addition, which requires a greater amount of sizing agent. Filler addition closed the gaps and capillaries in the paper structure, hence reduced the porosity of papers. A paper with lower porosity, in fact, should show greater resistance against water penetration as reported in literature [13, 14]. The oil absorption properties of fillers (26 ml/100 g given by the producer) related to their surface area and particle morphology should be taken into account here. The filler addition gave more compact paper structures with higher air resistance and smoother surface as well as increasing the liquid absorption capacity of the paper due to both its remarkably higher surface area and absorbent properties.

Effects of Coating on Water and Ink Behaviors on the Paper

In this part of the study, three different papers were tested to reveal the interactions with water- and oil-based ink. Results were discussed in respect to the printing quality of papers.

Paper Surface Properties

Some properties of papers used in this part of the experiment are given in Table 2 below. The whiteness and thickness value of samples were in a similar range while others were greatly different.

Table 2: Some properties of papers used.

Properties	Units	Substrate (paper) Types Gloss-coated paper (wood-free)	 Matte-coated paper (wood-free)	 Uncoated white paper
Thickness	μm	105	107	107
Whiteness	%	83,55	84,50	84,02
Gloss (Hunter 75)	%	79,2	29,9	6,0
Surface roughness (PPS method)	μm	0,82	1,36	5,42
Surface roughness (Bendtsen)	ml/min	1,60	13,20	195,10
Air permeance (Bendtsen)	μm/Pa s	0,97	0,112	5,610
ASH (Total)	%	38,2	38,9	18,2

Uncoated white papers showed the roughest surface and porous structure compared to coated ones as measured by both Parker Print Surface (PPS) and Bendtsen methods (Table 2). Gloss coating is achieved by passing matte-coated paper between hot cylinders, which makes coated layers shiny, giving improved smoothness and air resistance. Ash tests revealed the amount of internally added filler in uncoated paper and total fillers in coated samples. The irregularities over coated layer seems to get greatly eliminated and capillaries and voids in paper structures were believed to be filled and even out as a result of hot pressing in gloss-coated paper.

ATR spectrums taken from three papers are seen in Figure 2. Peaks in the spectrums were interpreted according to reference table (Table 3) [21,22]. Clear peaks indicating the presence of fillers ($CaCO_3$) are visible in the spectrums. Gloss-coated papers seem to have some more peaks which was actually believed to be the effects of hot supercalendering.

Drop Volume and Contact Angle

Volume changes of distilled water droplets sitting on the surface of test samples over time provided excellent information on the water absorbency properties of tested sheets. Figure 3 clearly revealed that despite the rougher surface and porous structure of the uncoated sheet, the water droplet stayed on the surface with little change in volume over some time. The amount of fillers on the surface of the uncoated sheets was expected to be normally lower than that of coated ones. This would decrease the water absorption degree of uncoated paper compared to that of coated ones if other properties are not taken into account. Nevertheless, noting the huge differences between both air permeability and surface roughness of uncoated and coated papers (Table 2), the uncoated paper should have showed greater water absorbency

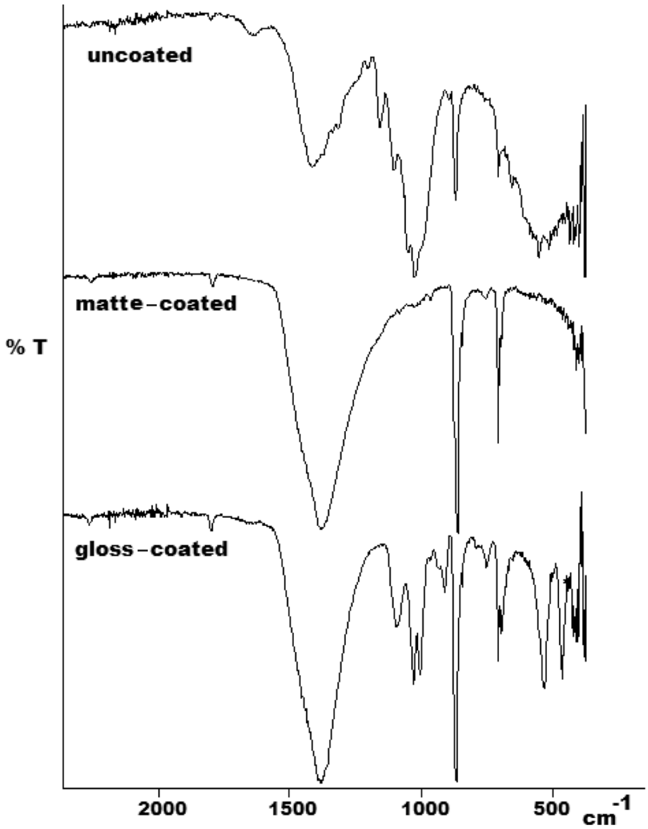

Figure 2: ATR peaks taken from cellulose papers.

and faster changes of the drop volume in a certain time span. However it is not the case here which obviously illustrates the stronger sizing effects on the interactions between water and cellulosic material.

Differences between gloss- and matte-coated samples should be evaluated according to their surface roughness and air permeability values (Table 2) since they had no sizing agent. Having similar amounts of fillers on their

Table 3: Some ATR peaks taken from surfaces of papers (21,22).

Wave number (cm^{-1})	Assignment
1795	Peaks from $CaCO_3$
1385	Peaks from $CaCO_3$
1155	Antisym. bridge C–OR–Stretching (cellulose)
1110	Anhydroglucose ring (cellulose)
1030	C–OR stretching (cellulose)
872	Peaks indicating $CaCO_3$
712	Peaks indicating $CaCO_3$

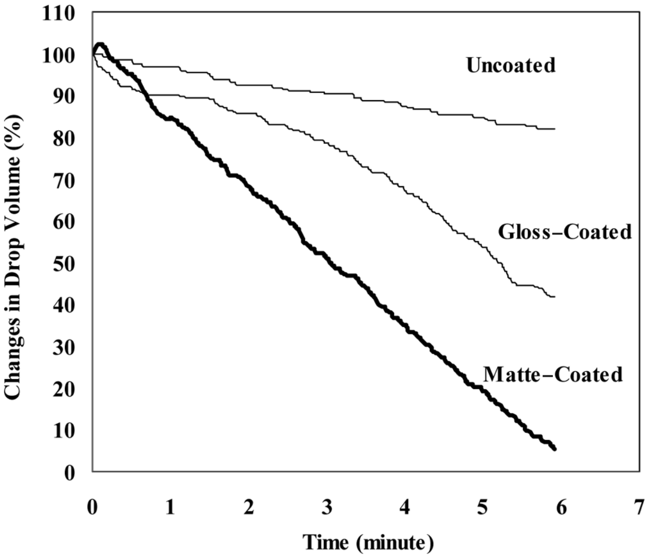

Figure 3: Water droplets stayed longer on an uncoated paper surface.

surfaces as coating layers, gloss-coated samples have the smoothest surface and the highest air resistance values, which were believed to be the governing factors regulating the changes in both drop volume and contact angle (Figures 3 and 4). The sheet with little permeability (capillarity), which is

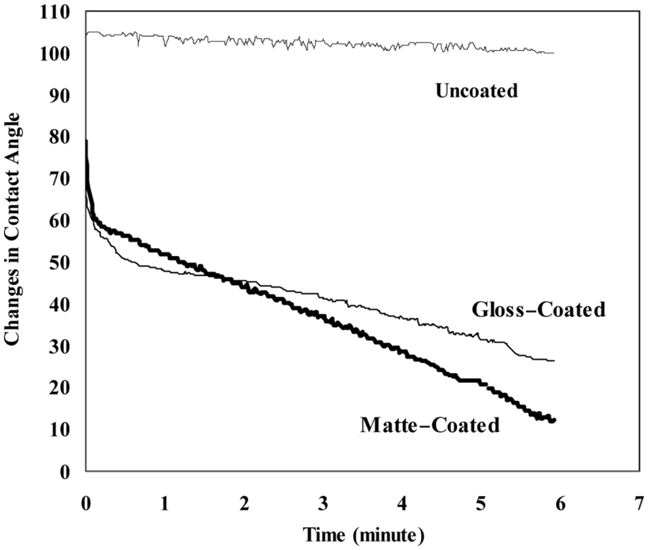

Figure 4: Changes in the contact angle between water drops and paper surfaces over time.

the gloss-coated one here, simply showed greater resistance against the penetrating water droplet.

A sudden drop in the contact angle values for both matte- and gloss-coated papers in the beginning of the test actually indicates the rapid wetting of samples by water, whereas the changes in contact angle on the surface of uncoated samples was negligible (Figure 4). It again indicates a good sizing degree of uncoated paper.

Print Density and Lightness

Since oil-based printing ink was used, the sizing effect of uncoated paper was not so visible here. The ink movements in the sheets were believed to be governed by the dominantly physical nature of the samples. Figure 5 shows that the inks as a whole were actually absorbed by both uncoated and matte-coated sheets. Having porous structures, uncoated and matte-coated papers seemed to have taken ink components as solvent and pigments in deeper, leaving less coloring pigment over the surface and thus giving lower print density values (Figure 5). Results simply say that most of the pigments would stay over the surface of gloss-coated papers. Gloss-coated samples required less inks compared to other samples due to their improved surface smoothness and lowest air permeability values, which only allows the ink carrier (oil) to penetrate the inner part of the materials while keeping the pigments on the surface.

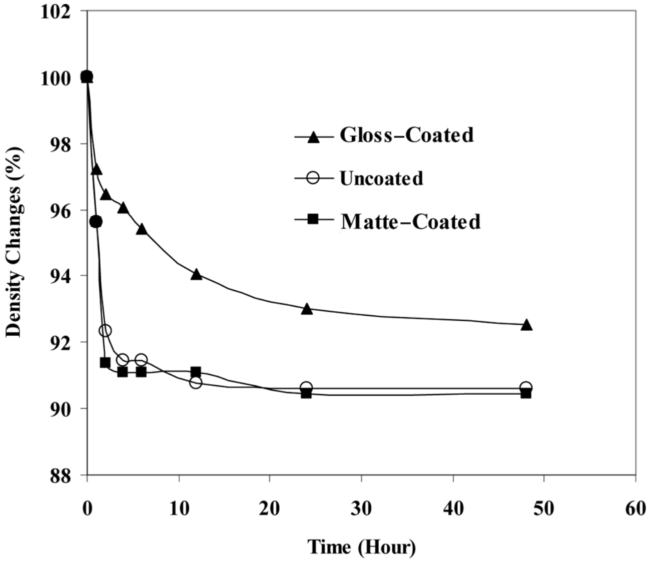

Figure 5: Changes in the print density over time.

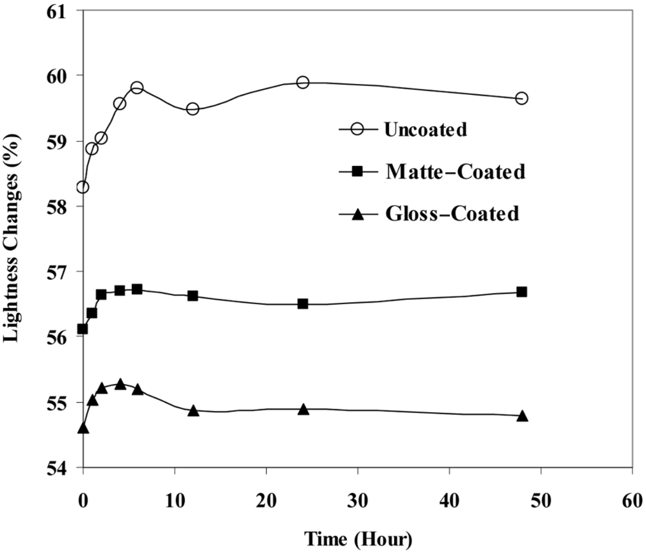

Figure 6: Changes in the print lightness over time.

Changes in the print lightness on tested sheets were also measured (Figure 6). It again shows that the uncoated paper took more ink into the inner parts and left lesser pigments on the surface and thus gave a higher lightness value (Figure 6). Results in Figure 6, in a sense, show the porosity and also pigment absorption capacity of tested samples. Gloss-coated papers gave the lowest print lightness at the beginning and the lowest lightness changes within 48 h. This means that gloss-coated paper is much better as far as print quality concerns compared to uncoated and matte-coated sheets.

CONCLUSION

Filler addition to the paper reduced the air permeability and improved the surface smoothness. But it also significantly reduced the surface energy too, making papers more absorbent. Porous materials normally would take more liquids in if no sizing effect is in force. Sized paper despite its rougher surface and higher air permeability showed greater resistance to water penetration compared to that of unsized papers with smoother surface and lower porosity. In this work, the sizing degree was found to be extremely important if water-based ink is to be used. In the case of oil-based ink, physical structures of sheets were seen to be more important than the sizing level. Gloss-coating gave the highest print density and the lowest density changes in time compared to other samples.

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