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# Effects of color mixing components on offset ink and printing process

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**ABSTRACT**

In printing, the most important element is to obtain the correct substrate and ink combination. Transparent white and opaque white are used for the lightening of printing inks, but they are also an important component for the mixing of inks. The primary objective of this study was to assess the result of using transparent and opaque white in mineral oil-based offset printing inks on the rheological and printability properties of these inks as well as the ideal mixing ratios in terms of print quality. Transparent and opaque white were added into the standard offset magenta ink variable ratios. Differences in ink viscosity, tack, and flow (rheological) values affect such parameters as adhesion, transferability, and printing stability in these inks. Prints were made on matt-coated papers of the same grammage with these inks, and contact angle, solid ink density, color strength, and print gloss values of these ink films were measured. Color differences ($\Delta E^*_{ab}$) of inks in comparison to the standard ink were calculated and the effects of transparent and opaque white on the rheological and printability properties of the ink were presented. Finally, the ideal mixture ratios of transparent and opaque white into the ink were determined in terms of print quality and recommendations were presented.

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Color; ink; lightening; mixing; offset; opaque; printability; transparent

## Introduction

The greatest proportion of the process of printing occurs in the transfer of ink onto the substrate surface. The visible character and condition of printed materials relies strongly on how well the ink has bonded to a board or paper's surface, and, in particular, on the ink's fixing and drying process [1].

In essence, ink is a dispersion system consisting of pigment, binder, and solvent. It is based on a structure allowing the pigment to dissolve or disperse within varnish. However, inks have different chemical contents depending on the areas of usage (Table 1) [2].

Inks gain rheological and printability properties thanks to the chemicals and additives they contain. When the content of the ink changes, thus, these properties are affected. The ink should not dry on the container, rollers, and mold surface. It should be able to disperse homogeneously in the rollers and hold on to them in the form of a thin film, and from there, it should be transferred to substrates at the same thinness level and should dry in a short time [2]. Such rheological features of the ink as viscosity, tack, and flow are of great importance so that it can properly hold on to the printing material and it can have resistance against physical and chemical factors following printing; in other words, its visual features are not deformed. The ink having the right rheological features is transferred from the ink tank of the printing machine to the printing plate and substrates properly [3], while inks having varying rheological structures lead to printing problems. Thus, color mixing components should not change such rheological properties of the ink as viscosity, tack, and flow [4]. Also, achieving the same printing features (density, color, and print gloss) with these inks as the base color inks is another significant target.

The ink is increased generally by its transparent structure consisting of resin. In terms of the structure of the mixture, what differentiates transparent white from classical ink is the lack of coloring pigments. Apart from that, all other components such as varnish and drying agents display similar properties with a classical mineral oil-based ink.

Pantone catalogue displays the proportional compositions of the standard ink colors to be used in printing. Both transparent white and opaque white can be used for obtaining new colors with Pantone colors and for bleaching processes. Transparent white is an ink which has no pigment, but simply the other two elements of an ink, vehicle and dryer/modifiers. This ink is mixed with other inks in order to lessen the pigment load of the ink in order to either make the ink lighter or to make the ink more transparent. Differently from transparent white, opaque white contains white pigment granules. Another area of usage of opaque white is obtaining spot colors other than Pantone. This ink can be used in mixing, but generally serves the purpose of lightening the ink with which it is mixed. It is used in creating tints of colors and pastels. Opaque whites are mostly used to cover backgrounds, but they are also added to spot inks to achieve a covering effect [4].

The main objective of this study is to assess the effects of color mixing components on ink rheology and printing quality parameters in offset inks and to present the ideal addition ratios in terms of printing stability.

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Table 1. Chemical composition of the inks.

| Ink contents | Mineral oil-based inks |
|---|---|
| Pigment | Organic and inorganic pigment |
| Binding agent | Phenolic and hydrocarbon resins |
| Solvent | Mineral and herbal oils (soybean oil, linseed oil, etc.) |
| Additive | Drying agents, wax, filling materials |

## Materials and Methods

In the present study, transparent white and opaque white were added into standard process magenta ink (DIN ISO 2846-1) at varying ratios and test inks were obtained (Table 2). The ratio of magenta color-pigment standard ink was kept stable at 50% in all mixtures.

In order to determine the printing performances of the prepared inks, offset prints were made on matt-coated papers whose features are shown in Table 3.

The rheology of the ink, which affects printability, is determined by the chemicals and additives, which it contains as well as their amounts.

In this study, viscosity measurement was performed via Physica MCR 50 Rheometer (Timber Ridge Drive Ashland, Virginia 23005, USA), tack values were measured via Inkometer device, and flow tests were carried out at the 1–10 and 60th minutes on a 45° glass plate with the aim of determining the rheological behaviors of standard magenta and other mixed inks.

Before printing, papers were conditioned for 24 hours at 23 ± 1°C and 50% ± 3% relative humidity in laboratory conditions. The ink transfer was carried out with standard ink using the IGT-C1 Offset Printability Tester (IGT, The Netherlands), under laboratory-controlled conditions. Test prints using the inks obtained were carried out at 350 Newton printing pressure and 0.3 m/s printing speed under optimal printing conditions in compliance with DIN ISO 12647-2:2013 standard. The standard conditions were preserved in the measurements following printing.

Solid ink density and colorimetric values of test inks were measured via Gretag Macbeth SpecktroEye Spectrophotometer (CIE standard illuminant D50, CIE standard observer 2°, 0°/45° instrument geometry, and white backing) and recorded.

Table 2. Ratios of transparent white and opaque white in ink mixtures.

| Mixture/ink | Unit | Ink1 (base) | Ink2 | Ink3 | Ink4 | Ink5 | Ink6 |
|---|---|---|---|---|---|---|---|
| Process magenta | (%) | 100 | 50 | 50 | 50 | 50 | 50 |
| Transparent white | (%) | 0 | 0 | 50 | 37.5 | 25 | 12.5 |
| Opaque white | (%) | 0 | 50 | 0 | 12.5 | 25 | 37.5 |

Table 3. Properties of the paper substrate used in experimental study.

| Properties | Unit | Test method | Matt coated |
|---|---|---|---|
| Basis weight | $g/m^2$ | ISO 536 | 115 |
| Gloss Lehmann | % | ISO 8254-2 | 48 |
| Brightness D65/10° | % | ISO 2470-2 | 100 |
| Whiteness CIE | % | ISO 11475 | 129 |
| Opacity ISO | % | ISO 2471 | 94.5 |
| Bulk | $cm^3/g$ | ISO 534:1995 | 0.87 |
| Gloss Hunter | % | ISO 8254-1 | 51 |
| Air permeability | µm/Pa · s | TAPPI T 460 | 0.0580 |
| Smoothness PPS 1 MPa | µm | ISO 8791-4 | 1.3 |

The study is based on CIE $L^*a^*b^*$ Cyan coordinates (accepted in ISO 12647-2:2013). A density value of 1.40 which is ideal $L^*a^*b^*$ is accepted from all inks test prints. The changes in the value of the density are measured in a time-dependent manner.

Print gloss values of ink films were measured at 60° geometry via BYK Gardner, Sheen Instrument, U.K., Glossmeter in accordance with ISO 2813:2014.

## Results and Discussion

Viscosity, tack, and flow properties of inks are of paramount importance so that the ink can be transferred, can disperse homogeneously in and hold on to the rollers, and dries on the substrates [5].

In the present study, the effects of compounds used in the preparation of mixed inks on ink rheology were tested and the results are given in Table 4.

It was detected in rheological characterization that opaque white liquefies ink while transparent white makes it more viscose and thick. The flow value of standard ink is lower than those of the inks mixed with transparent white and opaque white. As the amount of opaque white increased, flow value of the ink increased as well. The flow value closest to that of base ink was obtained in the mixture (Ink3) where the rate of transparent white was highest. In the rheological tests, it was observed that transparent white increased the tack value of the ink while opaque white reduced viscosity and tack values. According to the addition ratios of all components into the ink, the viscosity, flow, and tack values closest to those of the base ink were obtained with 50% transparent white.

In the process of offset print, the drying occurred with the absorption of the liquid phase in the ink film that was transferred to the print substrate by the porous print surface. In this mechanism, the paper surface absorbed the dissolvent in the ink film that formed the varnish and then resolved it from the resin and pigment. The dissolvent was resolved from the resin and pigment mixture due to its chemical structure and penetrated into the thin capillary ductules of the paper both horizontally and vertically (Fig. 1). Thus, the freed resin and pigment created a hard and firm layer on the surface. The surface of the ink film was displayed via SEM, which paved the way for a better observation of the pigmentation differences between the inks (Fig. 2).

Ink films where transparent white and opaque white were intensely used were preferred along with the reference ink so that the surface analyses could be distinctive. SEM images of the surface characterization of ink films were also taken by utilizing Jeol JSM-5910 LV, operated at 20 kV, respectively (Fig. 1).

When surface topography of offset-printed ink films was examined via SEM, it was detected that the pigmentation on the surface of the standard process magenta color ink film was highly smooth and homogeneous (Ink1). It was also determined that the homogeneity and smoothness closest to this surface film were obtained with the ink film containing 50% transparent white (Ink3). Addition of an excessive amount of opaque white into the ink resulted in sporadic white pigment clusters and negatively affected homogeneity

**Table 4.** Rheological properties of printing inks.

| Properties/inks | Ink1 | Ink2 | Ink3 | Ink4 | Ink5 | Ink6 |
|---|---|---|---|---|---|---|
| Ink tack (g-m)$^{c}$ ASTM D 4361 | 6.8 | 5.5 | 6.8 | 6.5 | 6.2 | 6 |
| Viscosity(Pa.s./25°C/25 s-1/CP50) ASTM D4040-81 | 38.7 | 26.6 | 37.7 | 36.6 | 34.4 | 32.2 |
| Flow (cm) 1 min | 4.1 | 6.9 | 5.5 | 6 | 6.2 | 7 |
| Flow (cm) 10 min | 9.1 | 15.6 | 11.8 | 12.3 | 14 | 16.1 |
| Flow (cm) 60 min | 18.5 | 21 (30 min) | 19.4 | 21 (55 min) | 21 (38 min) | 21 (30 min) |

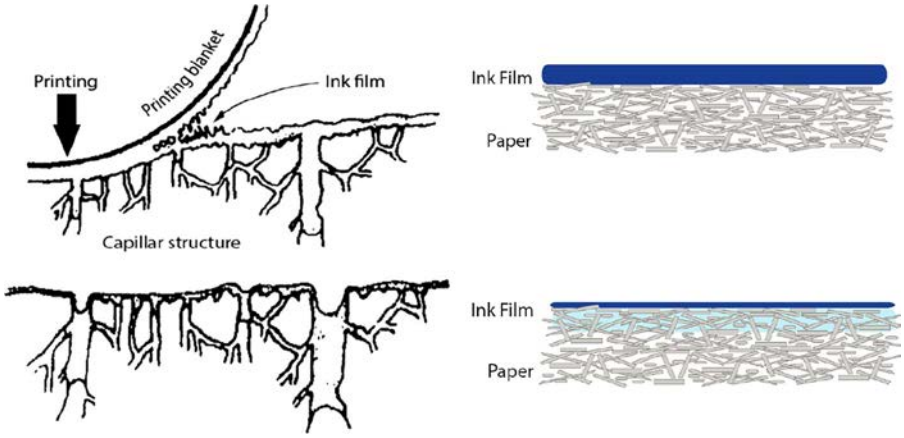



**Figure 1.** Absorption mechanism of offset printing inks [2].

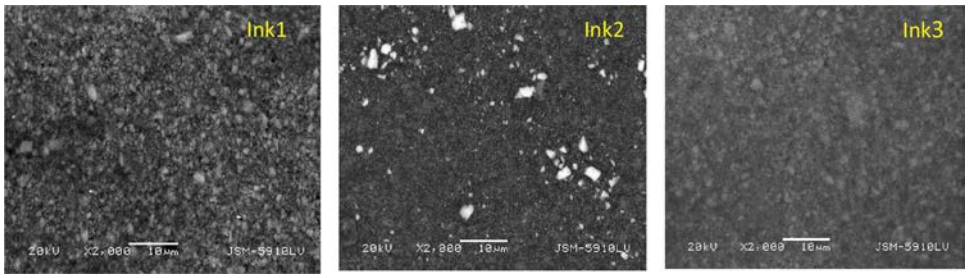



**Figure 2.** Surface SEM images of test ink films.

(Ink2). This is a possible outcome of the existence of pigments in the structure of opaque white, which affects the quality of solid printing in an adverse manner.

Surface energy has a sensitivity to the surface chemistry, as well as to the existence and morphology of adsorbed materials. The adsorption of chemicals on a surface lowers its surface free energy (wettability). Surfaces that possess high surface energies will show a greater tendency in their capacity to adsorb atmospheric materials (e.g., particles of dust or moisture), which decreases wettability [6]. The primary data in wettability studies are generally the measurement of contact angles. This points to the degree of wetting that occurs in the interaction of a fluid and a solid. Larger contact angles (>90°) demonstrate low wettability, whereas smaller contact angles (<90°) demonstrate high wettability [7].

Young was the first to properly investigate the interaction between fluids and solids in 1805. A state of equilibrium is achieved when the solid, liquid, and gas phases mutually interact, as shown in Fig. 3. The interaction between the outer limits of each of the three phases determines the droplet's shape and form as well as its wetting behavior with regard to the surface of the solid [8]. When the surface area of a liquid (the adhesive) is smaller than the surface energy of the solid, it will wet the solid (the adherend). For contact angles that are larger than 0, Young's equation provides the force equilibrium or balance at the solid–liquid boundary (Eq. (1)) [6].

**Young from the interfacial tensions** [8].

$$\gamma_{lv}\cos\theta = \gamma_{sv} - \gamma_{sl} \tag{1}$$

where

$\gamma_{lv}$ = liquid–vapor interaction
$\gamma_{sv}$ = solid–vapor interaction

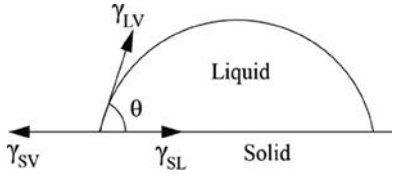



**Figure 3.** Contact angle <90° [2].

$\gamma_{sl}$ = solid–liquid interaction

where $\theta$ represents the contact angle, and $\gamma_{lv}$, $\gamma_{sv}$, and $\gamma_{sl}$ represent the surface free energies of the liquid–vapor, solid–vapor, and solid–liquid boundaries. As the contact angle decreases, the tendency for the fluid to wet the solid increases, until the stage is reached at which full wetting has occurred (contact angle $\theta = 0$, $\cos\theta = 1$). For complete and full wetting to be present, the surface tension of the liquid has to be smaller than or equivalent to the critical surface tension found in the substrate ($\gamma_{sv} - \gamma_{sl}$). A poor and incomplete degree of wettability can be the result of larger contact angles (Fig. 3) [6].

The wettability of the ink film is one of the most important features for the acceptance of inks of other colors in printing and the drying process as well as the initiation of procedures after printing, including, but not limited to, finishing and folding as well as the final binding. In this study, the wettability was determined as the contact angle with the sessile water droplet method (Fig. 4). The characteristics of printed ink film surfaces were determined with volume change and contact angle (TAPPI T 458). Distilled water was employed as the wetting liquid in order to determine and measure the functions 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 "free" energy was calculated according to ASTM D5946 standard test method [10] depending on the water contact angle.

Surface energy of ink film containing 50% transparent white (Ink3) is closer to that of standard ink film (Ink1) when compared to the ink film containing 50% opaque white (Ink2) (Fig. 5). When SEM images of the base ink film which had the highest level of surface energy (Ink1) were examined, it was determined that it had the smoothest and most homogeneous surface structure and as the surface energy of other printed ink films reduced, surface roughness and heterogeneity increased. When the print made with the ink containing opaque white was examined, it was observed that white pigment pieces decreased surface smoothness efficiently (Fig. 2).

The observed density of the ink film was a significant parameter [11]. Ink density changes outside the tolerances negatively affect the CIE $L^*a^*b^*$ color space values. Ink density value which refers to the ability of the printed ink film to absorb the light and affects print quality differs depending on the components of the ink. Differences in the amounts of pigments, binding agents, solvents, and additives that the ink contains result in changes in the density value of cyan ink

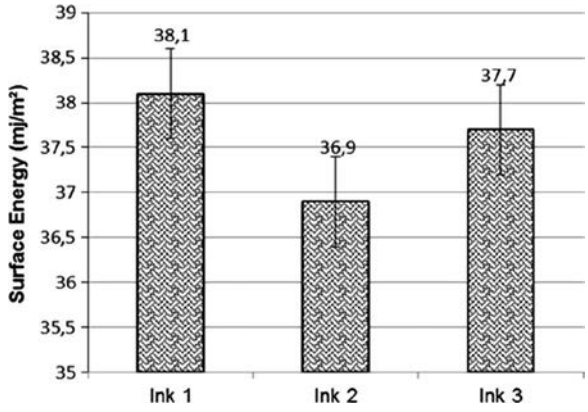



**Figure 5.** The surface energy of ink films.

[1]. In this study, the effects of transparent white and opaque white on the density value of the ink film were measured (ISO 12647-2:2013) periodically for 96 hours depending on the time as of the moment of printing.

In the study, it was observed that transparent white increased the density value of ink film as of the moment of printing. The increase in the amount of transparent white added into standard ink is directly proportional to the increase in the ink density value. As for opaque white, it decreased ink density in the course of time.

In cases where transparent white and opaque white were added into standard ink at equal amounts, a significant change was not observed in the density of the printed ink in time. The time-dependent density changes remain within ±0.10 tolerances which is specified in ISO 12647-2 (Fig. 6).

One of the most significant qualities of all print products is gloss [12]. When an ink appears glossy, sufficient ink vehicle has filmed on the surface of the paper to provide a covering layer for pigment particles in the ink. When an ink appears dull, sufficient vehicle has been drained from the surface so that the irregularities of the individual pigment particles and paper surface are not covered with a vehicle film thick enough to create gloss [13].

The highest print gloss values were obtained with the addition of transparent white into standard ink alone and at the rate of 50% as for opaque white; it decreased print gloss at the rate of addition (Fig. 7). Opaque whites are based on titanium dioxide, which achieves a very high opacity; however, they have a higher density compared to the colored pigments contained in offset inks. The particles are larger and harder



**Figure 4.** Sessile water droplet images.

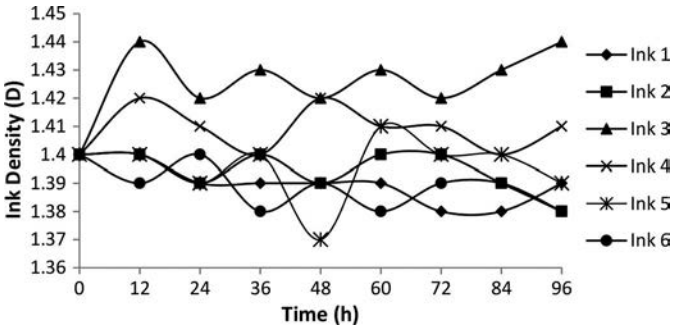



**Figure 6.** Changes in cyan ink film density on matt-coated paper.

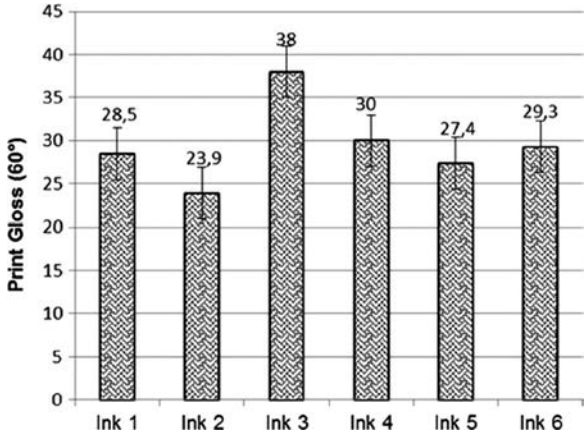



**Figure 7.** Print gloss values of inks on matt-coated papers.

[14]. The failure of the inks mixed with opaque white to reach a satisfactory print gloss level is attributed to the titanium dioxide concentration that opaque white contains.

Colorimetric coordinates allow a color to be placed in a colorimetric space. By these means, the characterization of an object's color as it is apprehended and perceived by a hypothetical observer looking at it in standard lighting conditions can be demonstrated mathematically. By placing diverse samples within this area, colorimetric differences can be effectively calculated [15,16].

The CIE delineated a color space known as CIE $L^*a^*b^*$ in 1976. This is still widely deployed in the measurement of color. According to the CIE $L^*a^*b^*$ color space, the interval between the measurement coordinates is calculated within three-dimensional color space. By using the Euclidean distance measure, the distance ($\Delta E$) between those two points which represent the colors in the color space can be assessed [17,18].

Primarily, color $L^*a^*b^*$ (CIELAB space) value measurements were carried out for base ink (Ink 1) and printed mixed ink films via spectrophotometer with the aim of detecting the color differences ($\Delta E^*_{ab}$) of the test inks from to the base (reference) ink. The color differences given in Table 5 were calculated according to the following equation specified in the $L^*a^*b^*$ color space CIE in 1976 (Eq. (2)):

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

[19].

where $\Delta L^*$, $\Delta a^*$, and $\Delta b^*$ are differences in $L^*$, $a^*$, and $b^*$ values between specimen color and target color.

It was found out that the color differences ($\Delta E^*_{ab}$) occurring in all inks prepared in this study when base ink (Ink1) was taken as reference remained within the tolerance values specified in DIN ISO 12647-2. However, the closest color was obtained in the ink mixtures (Ink3, Ink4) where transparent white was used in excessive amounts. It was also observed that the color difference from the base ink increased linearly as the amount of opaque white increased (Ink4, Ink5, and Ink6, respectively).

The CIE $L^*a^*b^*$ color space is presented as a spherical, three-dimensional model. Lightness is represented by the $L^*$ axis which ranges from White to Black. In the model, $L^* = 100$ defines absolute White, while $L^* = 0$ represents absolute Black. The red area is connected to the green by the $a^*$ axis, while the $b^*$ axis runs from yellow to blue. Achromatic colors can be found at the sphere's center. The further away from the center a color shade is situated, the more saturated and brilliant it can be said to be.

Measuring the $L^*a^*b^*$ coordinates using the spectrophotometer enables any shade of color to be defined within the boundaries of this system [20].

Within the present study, CIE*$b$ values of standard magenta color and test inks were measured via spectrophotometer and results are shown in Fig. 8.

When CIE*$b$ value measurements of inks were assessed, it was seen that transparent white caused the color of the base ink to tend to blue while opaque white caused it to tend to yellow. When compared to standard ink, the closest results were obtained with the inks into which transparent white was added. The more opaque white was added, the more different the color became from that of standard magenta. It was concluded that the closest color to the standard one was

**Table 5.** Inks color difference ($\Delta E^*_{ab}$).

| Test Inks | Ink1 | Ink2 | Ink3 | Ink4 | Ink5 | Ink6 |
|---|---|---|---|---|---|---|
| $\Delta E^*_{ab}$ value | Ref. Ink | 3.3 | 1.11 | 0.53 | 1.42 | 2.01 |

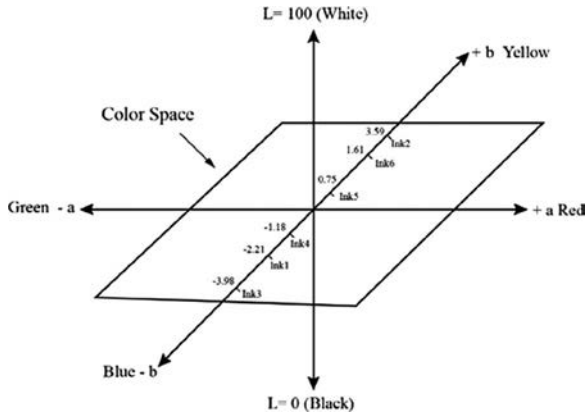



**Figure 8.** Display of CIE*$b$ values of mixed inks at Color Space.

obtained when transparent white was used intensely along with a small amount of opaque white (Ink4).

## Conclusion

Transparent white changed the rheological properties of process magenta ink to a lesser degree when compared to opaque white. Thus, if it is necessary to use both transparent white and opaque white within the ink system, in terms of rheological properties, the mixture containing a higher amount of transparent white should be preferred.

Since the use of opaque white in the ink alone increases the flow, it results in such problems as leaking through the rollers of the printing machine, misting (ink splatter), mottling, failure to strike a balance between water and ink, toning and lightening, dot gain, filling of halftone dot, sharpening, smearing, and strike through. Since it also reduces tack, it decreases the transfer of the ink, adhesion to the printing substrate, and resistance against external blows. In terms of rheological properties, the use of opaque white in print inks should be limited.

The examination on the surface topography (SEM) of solid printed ink films shows that opaque white should not be used within the ink system alone since it affects homogeneity in an adverse manner.

Surface energy value closest to that of the base ink was obtained with the ink containing transparent white. This is important in terms of the dispersion and smoothness of the ink film on the paper. Opaque white reduces the surface energy of the ink film and adversely affects print gloss and color, and thus, it should not be used alone.

In terms of the printability of the ink, CIE $L^*a^*b^*$, CIE $^*b$, and print gloss results closest to the reference color (process magenta) were obtained with the ink containing 50% process magenta, 37.5% transparent white, and 12.5% opaque white (Ink 4).

All results demonstrate that transparent white should be preferred in color mixing processes by considering the performance of the ink since it changes the printability and rheological properties of the ink to a lesser degree.

Since the type of the paper, surface structure, the color to be obtained, and working conditions of the printing machine affect ink rheology and printability, various working conditions should be considered in the use of color mixing components in inks.

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