



## ANALYSIS OF EFFECT PIGMENTS PRINTED ON SYTHETIC PAPER USING FTIR SPECTROSCOPY

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### **Abstract:**

*In the present paper effect pigments based on mica were investigated. Transparent mica pigments acquire their color effect through interference. The investigation was focused on FTIR analysis and also on the flop index of pigments. The flop is optical property of effect pigments. Two types of pigments, and a fiber synthetic paper as a printing substrate were used. Effect pigments were overprinted on CMYK backgrounds in offset technique. On the bases of FTIR analysis it was established that overprinted pigments gave different absorbencies in comparison to solid offset prints. The most obvious differences were seen at black offset background. Further, the analysis of flop index of both pigments showed the highest values when printed at black background also.*

### **Keywords:**

*Effect pigments, mica, fiber synthetic paper, FTIR analysis, flop index.*

## **1 INTRODUCTION**

Various visual effect created by effect pigments can be found in various products and end-user applications. They are used for different purposes, and one of them are also packaging materials. Effect pigments can be classified into different groups, and one of them are the pearlescent pigments based on platelets of natural or synthetic mica coated with thin layers of  $\text{TiO}_2$  or  $\text{Fe}_2\text{O}_3$ . Mica pigments acquire their color effect through interference [1-2].

For evaluation of effect pigments exists a lot of non-destructive and destructive methods. In this research we were focused on colorimetric and FTIR analysis of pigments. Due to its chemical constitution and physical properties, every single pigment particle behaves like an interference filter. It separates incident light into a reflected portion of one color and a portion of transmitted light with a complimentary color. The important interference property connected to this is the color change at different angles of view [3]. Infrared (IR) spectroscopy is useful in the elucidation and identification of molecular structure and in applications of quantitative analyses. IR radiation is usually defined as that electromagnetic radiation whose frequency is between  $2800$  and  $10 \text{ cm}^{-1}$  ( $0.78$  and  $1000 \text{ }\mu\text{m}$ ) [4]. FTIR (Fourier Transform Infrared) Spectroscopy, or simply FTIR Analysis, is a non-destructive analysis technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic. The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule. During FTIR analysis, a spot on the specimen is subjected to a modulated IR beam. The specimen's transmittance and reflectance of the infrared rays at different frequencies is translated into an IR absorption plot consisting of reverse peaks [5-6].

In the present paper two different mica based pigments in combination with solid offset inks have been studied in detail by means of FT-IR absorbance and flop index.



## 2 EXPERIMENTAL

In the research, two types of effect pigments (Pigment 1: *Iriodin*<sup>®</sup> 119 Polar White and Pigment 2: *Iriodin*<sup>®</sup> 325 Solar Gold) and a fiber synthetic paper (*Pretext*) as a printing substrate were used. The natural mica is the basis for both pigments. Pigments were overprinted on 24 hours dried CMYK backgrounds in offset technique (printed KBA Performa74). In Table 1 properties of effect pigments are presented.

*Table 1: Properties of effect pigments.*

| Properties    | Pigment 1                                 | Pigment 2  |
|---------------|---|--|
| Physical form | Dry, free-flowing powder                  | Dry, free-flowing powder   |
| Composition   | Mica, TiO <sub>2</sub> , SnO <sub>2</sub> | Mica+SiO <sub>2</sub> , TiO <sub>2</sub> , Fe <sub>2</sub> O <sub>3</sub> , SnO <sub>2</sub> |
| Color         | Silverwhite                               | Gold   |
| Particle size | 5-25 µm                                   | 5-25 µm  |
| pH Value      | 8-11                                      | 5-10   |

CMYK offset prints and also overprinted effect pigments on them were determined with ATR-FTIR technique on a FTIR spectrometer PerkinElmer SpectrumGX. The setting were as follows: range 4000-500 cm<sup>-1</sup>, 32 scans, resolution 4.00 cm<sup>-1</sup>. The effect pigments were measured also by X-Rite MA68II multi-angle spectrophotometer at D50 illumination. On the basis of those measurements the flop index were evaluated.

## 3 RESULTS

### 3.1 Optical properties of synthetic paper

In the first part of the investigation, the printing substrate was analyzed. In Table 2, the optical properties of fiber synthetic paper are presented.

*Table 2: Optical properties of synthetic paper.*

| Properties     | ISO brightness | Gloss at 75° [%] | Opacity |
|----------------|----------------|------------------|---------|
| ISO brightness | 95             | 27               | 90      |

Synthetic papers are defined as a products composed of at least 20% synthetic substances. These papers have a well-developed surface capable of absorbing printing inks, a coefficient of maximum ink absorption of at least 50%, and the capability of fixing the printing inks, even those with low adhesiveness to the base paper Fiber synthetic paper contains natural fibers combined with synthetic fibers (PA, PES, PP, etc.) [7].



### 3.2 FTIR analysis

The applicability of FTIR spectroscopic method to the analysis of solid CMYK offset prints and also overprinted effect pigments on them was evaluated in the second part of this research. In Figures 1-4 the FTIR spectra are presented.

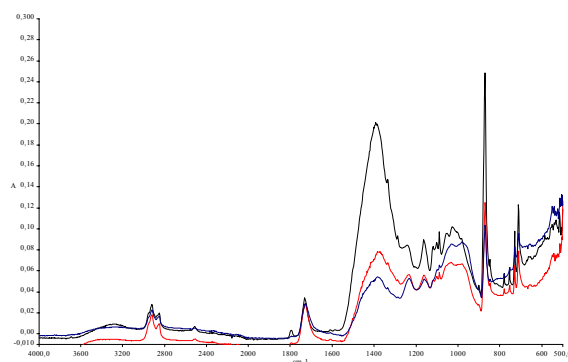


Figure 1: FTIR spectra of cyan ink and effect pigments (\_\_\_ cyan, \_\_\_ C+Pig.1, \_\_\_ C+Pig.2).

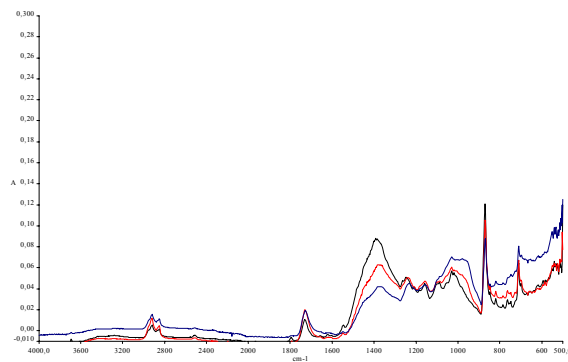


Figure 2: FTIR spectra of magenta ink and effect pigments (\_\_\_ M, \_\_\_ M+Pig.1, \_\_\_ M+Pig.2).

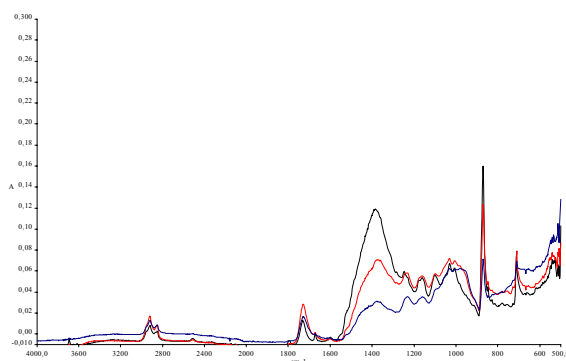


Figure 3: FTIR spectra of yellow ink and effect pigments (\_\_\_ Y, \_\_\_ Y+Pig.1, \_\_\_ Y+Pig.2).

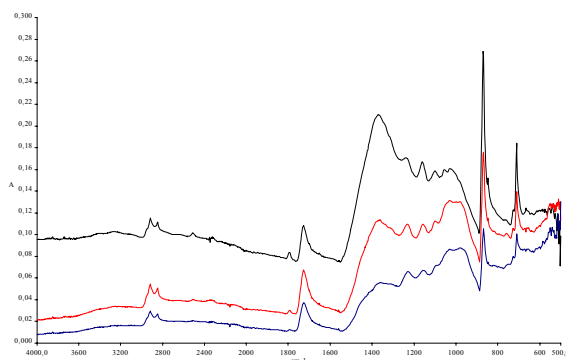


Figure 4: FTIR spectra of black ink and effect pigments (\_\_\_ K, \_\_\_ K+Pig.1, \_\_\_ K+Pig.2).

From the Figure 1 it can be seen that the most obvious differences in absorption between solid cyan ink and effect pigments are in the region of  $1600\text{--}1000\text{ cm}^{-1}$ . The natural mica is the basis for both pigments, silver white Pigment 1 and gold Pigment 2. Pigment 2 is based on a special metal oxide coating offering a combination of high lustre and color intensity [8]. In the region from  $4000\text{ to }1600\text{ cm}^{-1}$  FTIR spectra of cyan offset ink and of overprinted Pigment 2 are the same, below  $1600\text{ cm}^{-1}$  the spectra begin to distinguish in intensity of absorption. Absorption of overprinted Pigment 1 is in the regions  $3600\text{--}1500\text{ cm}^{-1}$ ,  $1100\text{--}850\text{ cm}^{-1}$ , and  $820\text{--}500\text{ cm}^{-1}$  lower compared to overprinted Pigment 2 and solid cyan ink. Solid cyan ink showed the largest absorption at wavenumber of  $872\text{ cm}^{-1}$  ( $A=0.248$ ), followed by overprinted Pigment 1 ( $A=0.124$ ), and overprinted Pigment 2 ( $A=0.103$ ). The peak at  $872\text{ cm}^{-1}$  arises mainly from aliphatic and aromatic nitrogen-oxy compounds and possibly certain aromatic compounds, it could be due to  $\text{HPO}_4^{2-}$  or to inorganic compound, carbonate, possibly hydrated. In our case the peak at  $872\text{ cm}^{-1}$  corresponds probably to the C-O out of plane band of inorganic carbonate. FTIR spectra of magenta ink (Figure 2) have lower absorption compared to other inks. FTIR spectra of solid magenta ink and overprinted Pigment 1 are very similar, FTIR spectra of overprinted Pigment 2 is higher in whole region, except between  $1550\text{--}1100\text{ cm}^{-1}$  and around  $870\text{ cm}^{-1}$ . Pigment 2 overprinted on yellow ink (Figure 3) has also higher intensity of absorption in the region of  $4000\text{--}3000\text{ cm}^{-1}$ ,  $2800\text{--}1800\text{ cm}^{-1}$  and  $700\text{--}500\text{ cm}^{-1}$  than overprinted Pigment 1. The most obvious deviation in absorption is noticed in the region of  $1650\text{--}900\text{ cm}^{-1}$  for all three FTIR spectra curves. All three samples attained the largest absorption at  $872\text{ cm}^{-1}$  (yellow offset ink:  $A=0.159$ , Pigment 1:  $A=0.123$ , Pigment 2:  $A=0.071$ ). Black offset ink and overprinted pigments obtained the largest



absorbance compared to cyan, magenta and yellow inks. Also the differences in FTIR spectra between solid black ink and effect pigments were the most obvious in this case. The application of effect pigments on solid black ink contributes to decrease of absorption in all regions, especially at gold Pigment 2. Also in this case the highest absorbance was attained at  $872\text{ cm}^{-1}$  (black offset ink:  $A=0.268$ , Pigment 1:  $A=0.176$ , Pigment 2:  $A=0.105$ ). Printing ink is a complex mixture of ingredients that are combined in a specific formulation to meet desired characteristics of the printing application of the ink. Ingredients are pigments, resins, oils or carriers, and additives [9].

### 3.3 Flop index

The flop (also known as Travel or Two-Tone) is an optical property of effect pigments and is often simply called the metallic effect. This change in brightness can easily be determined visually, observing the test panel on face and after that at oblique angles. In reality, the flop is evaluated by inspection at different angles, in some cases also a change in color can be found (color-flop). The flop index is the measurement of the change in reflectance of a metallic color as it is rotated through the range of viewing angles. A flop index of 0 indicates a solid color, while a very high flop metallic basecoat color may have a flop index of 15-17. Flop index is mathematically defined by [10-12]:

$$F = 2.69 * \left( \frac{a}{b} \right) \quad (1)$$

with  $a = [L * (15^\circ) - L * (110^\circ)]^{1.11}$  and  $b = [L * (45^\circ)]^{0.86}$

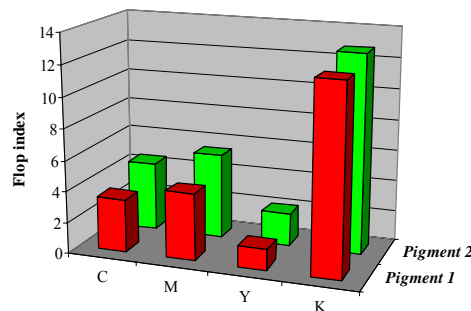


Figure 5: Flop index of effect pigments.

As can be seen from Figure 5, the flop index is higher at overprinted Pigment 2, and from all CMYK background colors, the highest flop index was obtained at black background (at Pigment 1  $F=12.07$  and at Pigment 2  $F=12.75$ ). This corresponds to superior appearance. Flop index at yellow background obtained the smallest values due to high lightness of yellow ink. Values were only  $F=1.34$  for Pigment 1 and  $F=2.08$  for Pigment 2.



#### 4 CONCLUSION

In the present paper we have analysed two types of effect pigments in combination with process offset inks. With FTIR spectroscopy we investigated the influence of solid CMYK offset inks overprinted with effect pigment on intensity of absorbance. From FTIR spectra, it was found that black offset ink attained the largest absorption, while magenta offset ink the smallest. By applying effect pigments on the CMYK offset inks deviations in FTIR spectra between samples were noticed. The absorption was mainly decreased, especially in the case of black background. Moreover, the flop index was the highest at both pigments printed on black background due to the darkness of ink.

#### 5 REFERENCES

- [1] Maile, F.J.; Pfaff, G & Reynders, P.: EFFECT PIGMENTS – PAST, PRESENT AND FUTURE, *PROGRESS IN ORGANIC COATINGS*, VOL. 54 (2005), PP. 151-163.
- [2] MAGICAL MIXTURES [WEB PAGE]. AVAILABLE FROM: [HTTP://WWW.UA.ES/AREA/VISION\\_COLOR/DOCS/CRAMER/CRAMER3.PDF](http://www.ua.es/area/vision_color/docs/cramer/cramer3.pdf) ACCESSED: 2010-10-04
- [3] Pfaff, G.: *SPECIAL EFFECT PIGMENTS: TECHNICAL BASIS AND APPLICATIONS*, HANNOVER: VINCENTZ NETWORK, 2008, PP. 40-45, 78.
- [4] FTIR SPECTROSCOPY [WEB PAGE]. AVAILABLE FROM: [HTTP://WWW.SILICONFAREAST.COM/FTIR.HTM](http://www.siliconfareast.com/ftir.htm) ACCESSED: 2010-10-04
- [5] Townshend, A.: *ENCYCLOPEDIA OF ANALYTICAL SCIENCE*, LONDON: ACADEMIC PRESS, 1995, P. 2170.
- [6] FTIR ANALYSIS OF COATED PAPERS SPECTROSCOPY [WEB PAGE]. AVAILABLE FROM: [HTTP://COOL.CONSERVATION-US.ORG/COOLAIC/SG/BPG/ANNUAL/V08/BP08-01.HTML](http://cool.conservation-us.org/coolaic/sg/bpg/annual/v08/bp08-01.html) ACCESSED: 2010-10-04
- [7] Paszkowska, K. & Podsiadlo, H. INFLUENCE OF THE FIBRE COMPOSITION OF PAPER CONTAINING SYNTHETIC FIBERS ON PRINTING PROPERTIES, *PAPER TECHNOLOGY*, VOL. 46 (2005), NO. 1, P. 21.
- [8] MERCK [WEB PAGE]. AVAILABLE FROM: [HTTP://WWW.MERCK-CHEMICALS.COM/PIGMENTS](http://www.merck-chemicals.com/pigments) ACCESSED: 2010-10-04
- [9] WHAT IS INK? [WEB PAGE]. AVAILABLE FROM: [HTTP://WWW.ANKEETARTS.COM/RESOURCE\\_CENTRE/WHAT%20IS%20INK.PDF](http://www.ankeetarts.com/resource_centre/what%20is%20ink.pdf) ACCESSED: 2010-10-04
- [10] METALLIC EFFECT PIGMENTS [WEB PAGE]. AVAILABLE FROM: [HTTP://WWW.SILBERLINE.COM/UPLOADEDFILES/AUTOMOTIVE\\_COATINGS/EFFECT\\_PIGMENTS\\_FOR\\_AUTOMOTIVE\\_COATINGS/PLATINUM\\_SILVER/AUTO%20BROCHURE%20SILBERLINE\\_USA.PDF3](http://www.silberline.com/uploadedfiles/automotive_coatings/effect_pigments_for_automotive_coatings/platinum_silver/auto%20brochure%20silberline_usa.pdf3) ACCESSED: 2010-10-04
- [11] Karbasi, A., Mordian, S., Thamssebi, N. & , Ghodsi, P: ACHIEVEMENT OF OPTIMAL ALUMINUM FLAKE ORIENTATION BY THE USE OF SPECIAL CUBIC EXPERIMENTAL DESIGN, *PROGRESS IN ORGANIC COATINGS*, VOL. 57 (2006), PP. 175-182.
- [12] Wißling, P.: *METALLIC EFFECT PIGMENTS, FUNDAMENTALS AND APPLICATIONS*, HANNOVER: VINCENTZ NETWORK, 2008, PP. 26-28.



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