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Analysis of Samples Treated by Resistance Test Method Exposed to Accelerated Aging

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Abstract:

Global awareness that packaging has to be fully adequate and of high quality, is gradually increasing. That is why printing inks and substrates, which have no detrimental effect on packed products, should be considered a compulsory precondition for food and tobacco packaging. Printing inks that have been developed in the recent years, especially for food and tobacco packaging, have low-odour and low migration into the printing substrate during the drying process. Their migration into the printing substrate is within the acceptable limits and has no detrimental effect in terms of food safety. Another extremely important element of prints in high quality food and tobacco packaging is their stability, as they have to be resistant to liquids and chemicals, which are a part of packed product. The selection of an appropriate printing substrate is also extremely relevant, since the interaction of substrate with printing inks should have zero effect on the packed product and should not change the physical appearance of packaging. This paper presents the results of analysing the stability of laboratory samples printed with low-migration inks, observed immediately after the printing (unaged) and two treatments of accelerated aging. The accelerated aging of prints was conducted in order to simulate conditions in which food and tobacco packaging can be found due to the prolonged indoors storage. The stability of prints was analysed based on optical characteristics by observing the prints' relative reflectance curves.

Keywords:

Accelerated aging, Low migration inks, Packaging, Resistance, Stability

1 Introduction

Apart from providing excellent physical protection for its content, contemporary packaging currently in use also has to have high quality multi-colour prints with no detrimental effect on the packaged product. A very important element that

has to be considered when printing food and tobacco packaging is the printing ink's possibility to migrate through the printing surface and get in touch (even contaminate) the content of the packaging. In order to avoid that, the industry has developed printing inks with low migration into the printing substrate. These printing inks contain components that ensure reduced migration of printing inks, that

is, migration within the accepted limits of tolerance (Sun Chemical Corporation, 2011). Printing inks with low migration into the printing substrate were developed in accordance with the regulations: Regulation EC No. 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and Commission Regulation (EC) No 2023/2006 of 22 December 2006 on good manufacturing practice for materials and articles intended to come into contact with food (** 2014a).

Since papers and boards are porous heterogeneous materials substances with low molecular weight can easily migrate through them. The migration can occur due to various factors: prolonging contact time, increasing temperature, the level of chemical substances in the packaging but also by expanding contact surface and having aggressive food ingredients as the packaging content. Substances in printing inks can migrate into the printing substrate by penetration, contact, evaporation or condensation. Migrated substances may cause physical or chemical changes in foodstuffs, visibly detected as changes in food colour or food odour causing the loss of product's attraction. (Leach, 2008; Castle, 2000). The most dangerous effect of the migration of the printing inks is the contamination of the packaging content, which may seriously harm health and food safety, that is, the well-being of the consumer.

Migrated substances originate mainly from offset printing inks, which contain between 25% and 50% of mineral oils. Different phthalates in adhesives can also migrate into the food packaging and have detrimental effect on consumer health. The cause for intensified ink migration may also be inadequate storage conditions for paper or unadjusted temperature and / or humidity inside the printing houses, either during the transportation or during the printing process (Thompson, 2004; ** 2015).

The stability of prints is another extremely important reproduction quality element, especially in the packaging industry. Excellent packaging can be described as outstanding only if the surface of prints represents well a graphic product. Each product is assessed and judged based on its most important descriptive factor – graphic reproduction quality (Eldred, 2001).

The aim of this research was to analyse the graphic reproduction quality of prints made by low migration inks in respect to their resistance. The analysis of resistance or stability was observed in unaged prints and in prints after two different treatments of accelerated aging (dry-heat and xenon lamp). All observed prints were subsequently treated with four liquid agents to prove the prints' resistance to liquids and chemicals, which could be ingredients of the packaged product. Stability of all examined prints was further observed based on optical deterioration of prints reproduction quality after treatments with liquid agents compared against untreated prints.

2 Materials and methods

Food and tobacco paper packaging is mainly printed using the offset printing technique (Kipphan, 2001). Tested samples in the research presented in this paper, were printed with the printability test device Prüfbau, which allows for the simulation of offset printing, using magenta ink based on triglycerides (manufacturer Sun Chemical), which belongs to the group of low migration inks for offset printing (Sun Chemical Corporation, 2011). The migration levels of these vegetable oil based inks were below the global migration limit of 60mg per 1 kg of food (60ppm) (** 2014b). Magenta ink was used because of its pigment has very low resistance (Bates, et al. 2009). The ink was applied by the pipette on the distribution rollers in the amount of 0.2 cm³ and after 15 rotations it was transferred from the distribution rollers to the rubber plate. Printing was performed at a speed of 3 ms⁻¹ and the pressure of 150 Ncm⁻². The printing ink was printed on three different printing substrates: on coated cardboard (manufacturer Sappi), coated paper (manufacturer Sappi) and recycled paper (manufacturer UPM).

After the printing process, one part of the laboratory prints was left unaged, one part of prints was exposed to accelerated ageing with xenon lamp (60°C Black Standard Temperature) for 72 hours and the remaining part underwent accelerated aging process by elevating temperature to 60°C also for 72 hours, according to the INGEDE Method 11p. According to INGEDE Method 11p, the applied exposure time of accelerated aging

Table 1. Characteristics of printing substrates

	Grammage (g/m ²) ISO 536	Surface roughness (μm) ISO 8791-4 (top side)	ISO Brightness (%) ISO 2470 (R 457+ UV) (top side)	Whiteness (%) ISO 2470 (top side)
Coated cardboard	270,0 +/- 5%	2,0 +/- 0,6		101,5 +/- 2%
Coated paper	80 +/- 4%	1,2 +/- 0,4	93 +/- 2%	
Recycled paper	45	100,0 - 205,0 ml/min (ISO 8791-2)	58,0	

corresponds to the period of 3 to 6 months of natural aging (INGEDE, 2009). Treatment with elevated temperature was performed in the Universal Oven UNB 400 (manufacturer Memmert) and aging treatment with xenon lamp by Solar-box 1500e (manufacturer Cofomegra). In Solar-box 1500e the simulation of indoor conditions was achieved by using indoor filter, which admits infrared radiation and absorbs ultraviolet light. It is common knowledge in the printing industry that heat, moisture and light also have significant effect on the paper stability and the quality of graphic product (Bates et al., 2012; Plazonic et al., 2012; Strlic et al., 2005; *** 2012).

Stability of all observed prints was additionally analysed in respect to four liquid agents according to the standard ISO 2836-2004. International Standard ISO 2836:2004 in the field of printing industry defines methods of assessing the resistance of prints to liquid and solid agents, solvents, varnishes and acids.

Table 2. The details of resistance test methods

Substance	Surface receptor	Temperature (°C)	Duration of exposure	Contact conditions
Water (distilled)	Filter paper	23 +/- 2	24 h	1 kg/54 cm ²
Oil (sunflower)	Filter paper	23 +/- 2	24 h	1 kg/54 cm ²
Alkali (1% NaOH)	Filter paper	23 +/- 2	10 min	1 kg/54 cm ²
Alcohol (96% ethanol)	Test tube	23 +/- 2	5 min	

The influence of water, oil, alkali and alcohol on unaged laboratory prints and laboratory prints exposed to accelerated aging were assessed by observing optical characteristics of prints. The optical characteristics of prints were monitored in respect to the relative reflectance curves of the prints. Prints reflectance spectra measurements were processed using spectrophotometer SpectroEye (manufacturer X-Rite), in the interval of wavelengths from

In order to test the resistance of prints to water, oil and alkali, four filter papers were soaked into the liquid agents and drained until there were no agent drops dripping off filter paper. Two soaked filter papers were placed on the glass surface with the laboratory print placed on it. That same print was then covered with another two soaked filter papers and the second glass was placed on top of everything. As the last step, the entire construction was burdened with a weight of 1 kg for a prescribed times (Tab. 2). The method of testing resistance of prints to alcohol was performed in a test tube, which was half filled with alcohol.

After treatments with all liquids agents were performed, the laboratory prints were rinsed and dried in an oven (for 30 minutes) at a temperature of 40 °C. The details of resistance test methods are presented in Table 2 (ISO 2836, 2004).

After analysing stability in the prints exposed to accelerated aging by elevated temperature, no significant reflectance difference could be detected in the entire measured wavelength range in the prints made on coated paper (Fig. 2b). On the other hand, prints made on coated cardboard and recycled paper showed changes in reflectance values after being treated with oil: $\Delta R=0,1$ in red part and $\Delta R=0,08$ in blue part (Fig. 2a); $\Delta R=0,05$ in red

400 nm to 700 nm for every 10 nm. Spectrophotometric results are presented as an average value of ten measurements of the laboratory prints and were statistically processed in Origin Lab 8.0.

3 Results and discussion

Figures 1a-c present experimental results of unaged laboratory prints and figures 2a-c and 3a-c present experimental results for laboratory prints exposed to accelerated aging in respect to untreated prints and prints treated with all four liquid agents.

Unaged prints on coated cardboard showed changes in the red part of reflectance spectrum (650-700 nm) when treated by oil ($\Delta R=0,09$) ($\Delta R=R_{\text{before_treatment}} - R_{\text{after_treatment}}$) (Fig. 1a). The similar trend was observed in unaged prints made on recycled paper ($\Delta R=0,06$) (Fig. 1c). It could be seen in the Figure 1b that unaged prints made on coated paper did not show reflectance differences in the red and green parts of the reflectance spectrum. All unaged prints showed optical degradation in the blue part of the spectrum (380-400 nm) after being treated with oil (Fig. 1a-c).

part and $\Delta R=0,06$ in blue part of the reflectance spectrum (Fig. 2c).

The measured reflection spectra of prints exposed to accelerated aging by xenon lamp after being treated by four liquids showed that prints made on coated cardboard and coated paper had most significant reflectance changes after being exposed to the alkali substance (Fig 3a-b). The changes were visible especially in the middle part of the spectrum (400-560 nm), where magenta ink absorbed wavelengths of the incident light, with ΔR going until -0,56. Prints made on coated cardboard and aged by xenon lamp, showed same changes like unaged prints and prints aged by elevated temperature in a red part of the spectrum after the analysis of oil resistance had been performed ($\Delta R=0,13$) (Fig 3a). Likewise, all tested prints that underwent aging process by being exposed to xenon lamp had degradation in the blue part of spectrum after being treated with oil from $\Delta R=0,1$ to $\Delta R=0,05$ (Fig. 3a-c). The stability of prints made on recycled paper which were aged by being exposed to xenon lamp presents the best results with only small degradation in the red part of spectrum after being treated with alkali substance, $\Delta R=0,07$ (Fig. 3c).

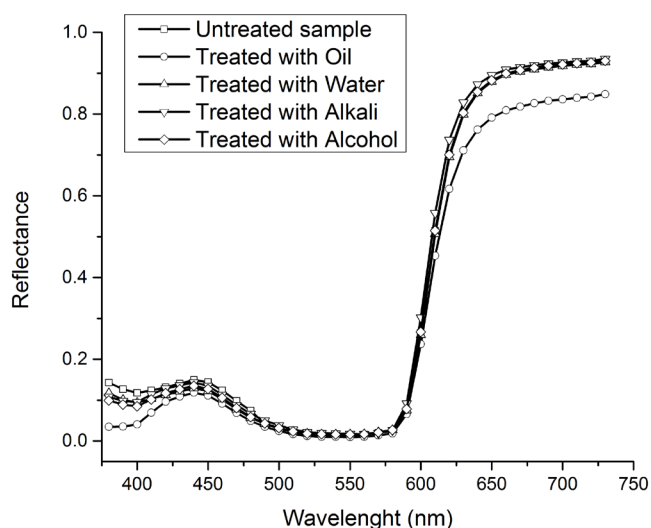


Figure 1a. Reflectance spectra of untreated and treated samples by resistance test method applied on coated cardboard

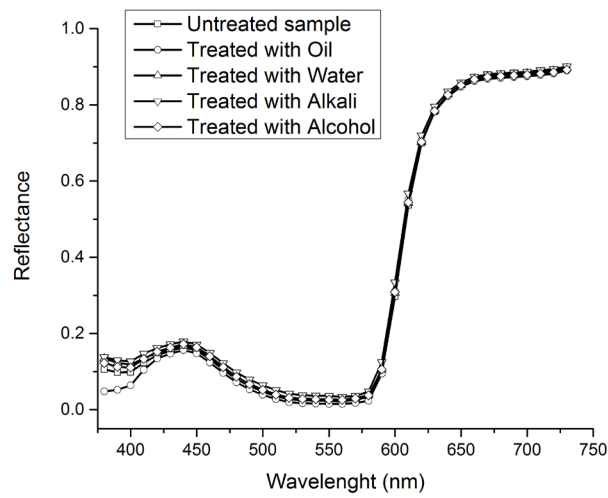


Figure 1b. Reflectance spectra of untreated and treated samples by resistance test method applied on coated paper

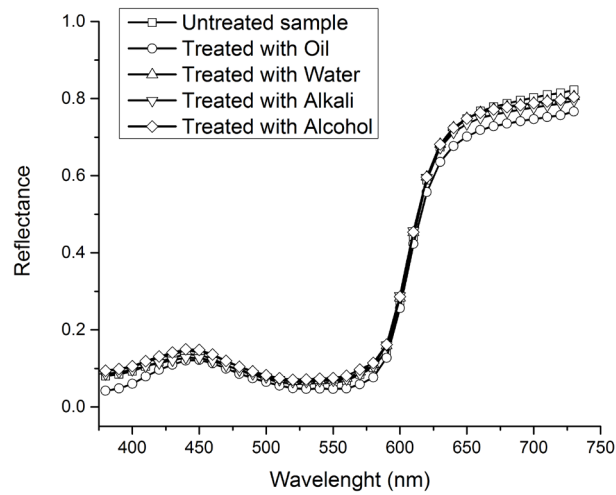


Figure 1c. Reflectance spectra of untreated and treated samples by resistance test method applied on recycled paper

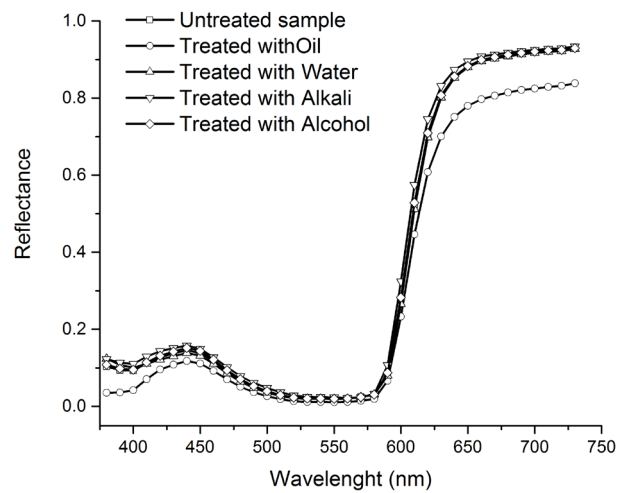


Figure 2a. Reflectance spectra of untreated and treated samples by resistance test method, after aged with elevated temperature, applied on coated cardboard

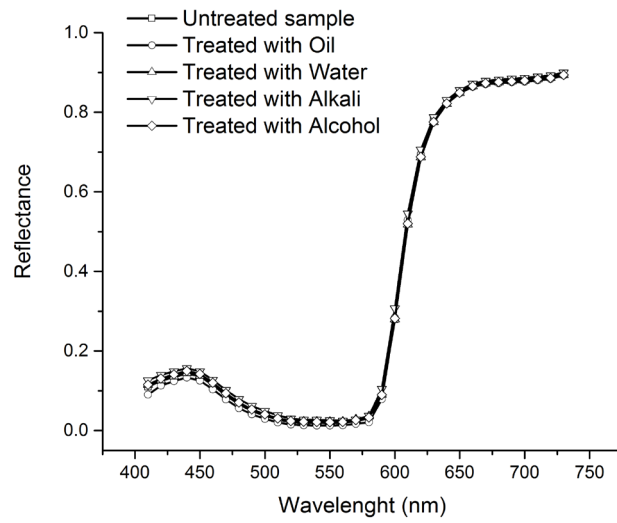


Figure 2b. Reflectance spectra of untreated and treated samples by resistance test method, after aged with elevated temperature, applied on coated paper

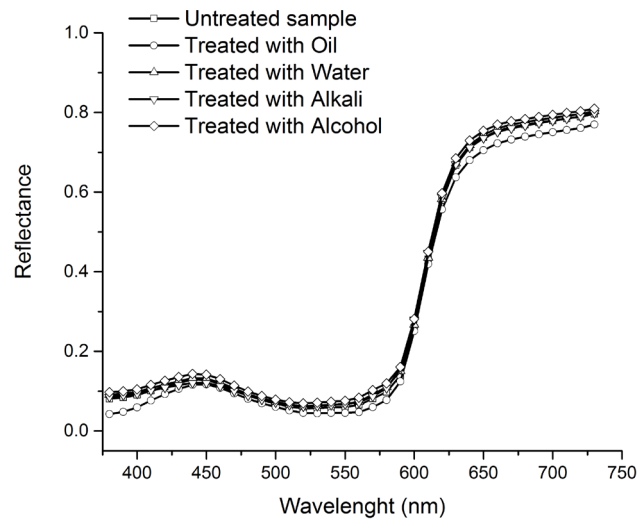


Figure 2c. Reflectance spectra of untreated and treated samples by resistance test method, after aged with elevated temperature, applied on recycled paper

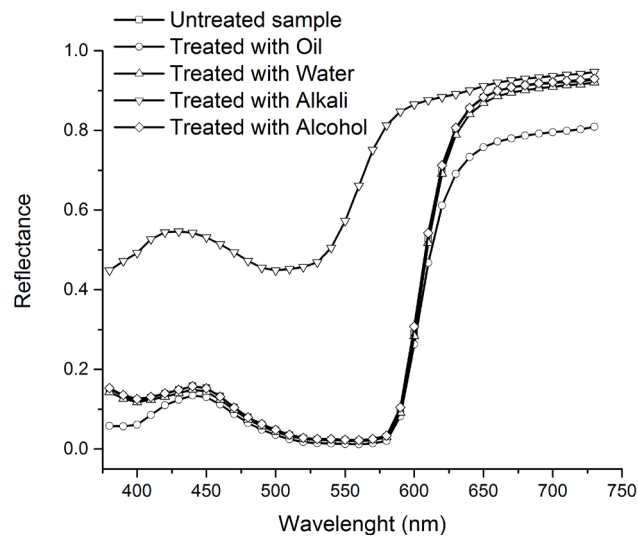


Figure 3a. Reflectance spectra of untreated and treated samples by resistance test method, after aged by xenon lamp applied on coated cardboard

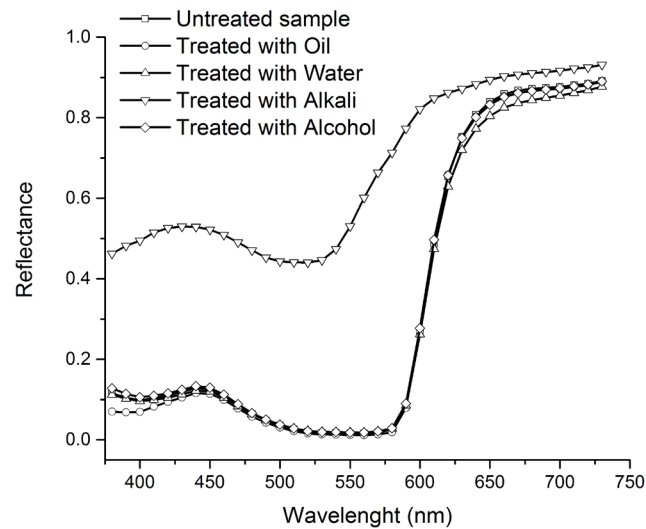


Figure 3b. Reflectance spectra of untreated and treated samples by resistance test method, after aged by xenon lamp applied on coated paper

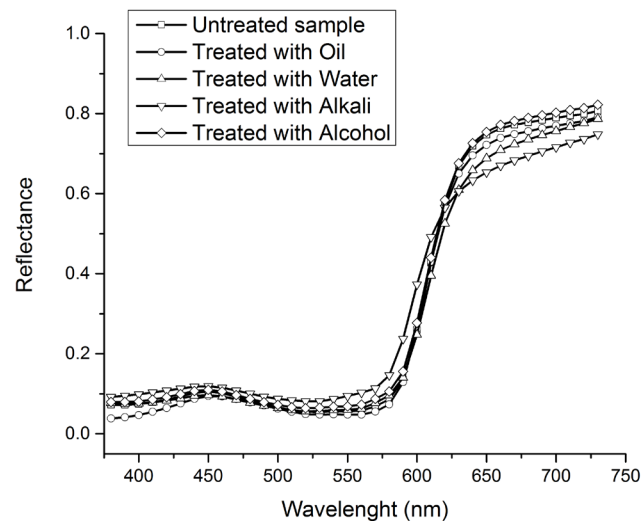


Figure 3c. Reflectance spectra of untreated and treated samples by resistance test method, after aged by xenon lamp applied on recycled paper

4 Conclusion

The paper presents the process of testing and obtained results after the application of resistance test method on unaged prints and aged samples printed with low migration inks.

The following could be concluded after the results' analysis:

- prints' stability in all samples printed on cardboard demonstrate significant optical deterioration in the red part of spectrum and minor

deterioration in the blue part after being treated with oil

- aging by exposure to the xenon lamp caused major changes in prints made on coated cardboard and coated paper after the analysis of alkali resistance was performed; in other words, it resulted in extremely poor print quality

- changes in the reflectance spectrum of prints made on recycled paper after the ageing process by exposure to xenon lamp were minor after the treatment with alkali substance and insignificant after the treatment with another substance.

- it could be concluded from the reflectance measurements that the effects of resistance of prints to liquid agents after the process of aging by exposure to elevated temperature and without aging, were very similar.

- unaged samples and samples aged with elevated temperature that were printed on coated paper provided best stability of prints, that is, their print quality was still optimal and a healthy human eye could not see the difference in coloration.

Packaging printed with low migration inks on cardboard and coated paper with the sun exposure through the window and in the presence of alkali compounds suffered negative effects on the quality of printed product. That may lead to printed information on the products being lost or even to the contamination of packaged goods and surrounding area.

5 References

- Bates, I., Miletić, M., Zjakić, I., 2009. Research on the Mechanical and Chemical Resistance of Print, DAAAM International Scientific Book 2009. Vienna, Austria. pp. 561-572
- Bates, I., Džimbeg-Malčić, V., Itrić, K., 2012. Optical deterioration of samples printed with basic Pantone inks. *Acta graphica, Journal for Printing Science and Graphic Communications*. 23, 3-4, pp. 79-90
- Castle, L., 2000. Exposure estimates used in risk assessment. Measuring migration to food is important – Why and How?. 2nd International Symposium on Food Packaging: Ensuring the Safety and Quality of Foods, Austria, Vienna
- Eldred, N. R., 2001. What the Printer Should Know about Ink. Pittsburgh: GATF
- International Association of the Deinking Industry (INGEDE), 2009. Assessment of Print Product Recyclability- Deinkability Test, Method 11p. Bietigheim- Bissingen, Germany.
- International Standard ISO 2836, 2004. *Graphic Technology- Prints and printing inks- Assessments of resistance to various agents*. Geneva, Switzerland
- Kipphan, H., 2001. *HandBook of Print Media*. Berlin: Springer
- Leach, R., 2008. *The Printing Ink Manual*, 5th ed. Heidelberg: Springer-Verlag
- Plazonic, I., Barbaric-Mikocevic, Z., Džimbeg-Malcic, V., 2009. Office papers stability during accelerated ageing, DAAAM International Scientific Book 2009. Vienna, Austria. pp. 333-340
- Strlic, M., Kolar, J., 2005. *Ageing and stabilisation of paper*. Ljubljana: National and University Library
- Sun Chemical Corporation, 2011. *Low Migration Best Practice Guide*. SL3 6PJ: UK
- Thompson, B., 2004. *Printing materials: science and technology*. 2nd ed., London: Pira
- *** (2012) "A Consumer Guide to Traditional and Digital Print Stability", available at: <https://imagepermanenceinstitute.org/>, [accessed: 23th June 2012] .
- *** (2014a) Zakon o materijalima i predmetima koji dolaze u neposredan dodir s hranom available at: <http://www.zakon.hr/z/569/Zakon-o-materijalima-i-predmetima-koji-dolaze-u-neposredan-dodir-s-hranom>, [accessed: 26th February 2014],
- *** (2014b) Sun chemical website, available at: <http://www.sunchemical.com/product/sunpak/>, [accessed: 7th December 2014],
- *** (2015) Koni Grob, "The missing ink" available at: <http://www.packaging-gateway.com/features/featurethe-missing-ink/>, [accessed: 3th March 2015],