Nordic Pulp & Paper

RESEARCH JOURNAL

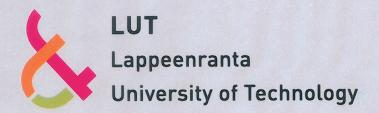
28 (1) 2013





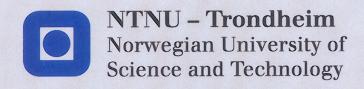








CHALMERS



Editorial board

Chairman Lars Wågberg, Royal Institute of Technology, Stockholm, Sweden
Peter Axegård, Innventia, Stockholm, Sweden
Per Engstrand, Mid Sweden University, Sundsvall, Sweden
Lars Järnström, Karlstad University, Karlstad, Sweden
Mikael E. Lindström, Royal Institute of Technology, Stockholm, Sweden
Philip Reme, Paper and Fibre Research Institute, Trondheim, Norway
Anna Sundberg, Åbo Akademi University, Åbo (Turku), Finland
Kaj Backfolk, Lappeenranta University of Technology, Finland
Hans Theliander, Chalmers University of Technology, Gothenburg, Sweden
Karin Walter, Eka Chemicals AB, Bohus, Sweden

Scientific Advisory Board

Lars Wågberg, Royal Institute of Technology, Stockholm, Sweden , chairman

Tamara Bush, Council for Scientific and Industrial Research, Congelia, South Africa

Jorge Colodette, Federal University of Vicosa, Vicosa Brazil

Patrick Gane, Omya Development Ag, Offringen, Switzerland and Aalto University, Espoo, Flnland

Gil Garnier, Australian Pulp and Paper Institute, Melbourne, Australia

Øivind Gregersen, Norwegian University of Science and Technology, Trondheim, Norway

Akira Isogai, Tokyo University, Tokyo, Japan

Janne Laine, Aalto University, Espoo, Finland

Mikael Lindström, Royal Institute of Technology, Stockholm, Sweden

Orlando Rojas, North Carolina State University, Raleigh, USA

Herbert Sixta, Aalto University, Espoo, Finland

Hans Theliander, Chalmers University of Technology, Gothenburg, Sweden

Stefan Willför, Åbo Akademi University, Turku (Åbo), Finland

Nordic Pulp & Paper

RESEARCH JOURNAL

Nordic Pulp and Paper Research Journal is the well-known scientific journal owned by Mid Sweden University

Nordic Pulp and Paper Research Journal publishes original manuscripts not published or scheduled for publication elsewhere in the fields of science and technology for wood constituents, pulp and paper, new fibre-based materials, energy and biorefinery

All manuscripts are peer-reviewed by well-known scientists according to common practice.

Editorial Staff

Editor-in-chief: Elisabet Brännvall Scientific editor: Per Stenius

Editorial Board

Lars Wågberg (Chairman), Peter Axegård, Per Engstrand, Lars Järnström, Kaj Backfolk, Mikael E Lindström, Philip Reme, Anna Sundberg, Hans Theliander, Karin Walter

Postal address, phone, fax, e-mail and Internet

NPPRJ, Mid Sweden University Holmgatan 10, SE-851 70 Sundsvall, Sweden Phone: +46 (0)771- 975 000 Fax: +46 (0)60-14 88 20 E-mail: info@npprj.se Internet: www.npprj.se

Published

Nordic Pulp and Paper Research Journal is published quarterly in March, June, September and December

Prices for Subscriptions

Prices for subscriptions (print+On line): In Sweden: SEK 3,600 + VAT (6%) For all other countries: SEK 3,900 (postage included)

Prices for subscriptions (print + On line including IP address): In Sweden: SEK 7,300 + VAT (6%) For all other countries: SEK 8,000

Owne

Mid Sweden University

Publisher: Per Engstrand. E-mail: per.engstrand@miun.se

Printed by service and maintenance office, Mid Sweden University, Sundsvall, Sweden

Nordic Pulp and Paper Research Journal under New Management

The ownership of NPPRJ was taken over by Mid-Sweden University, Sundsvall, Sweden on January 1, 2013. The journal is now run as a project with four Swedish, three Finnish and one Norwegian University as participants in the project and they all have members of the editorial board – please also visit our website or cover page of the journal for the complete list of board members and members of our scientific advisory board.

Apart from having the same scientific Editor and Editor in Chief the journal is now directly supported by scientists deeply engaged in research inspired by the present efforts to increase utilization of forests not only for construction and paper products but also as sources of environmentally sustainable raw materials that may replace materials now based on the use of fossil resources.

Since its start-up in 1986 NPPRJ has endeavoured to publish peer-reviewed articles in the field of pulp and paper science of direct relevance to the forest products industry and of the highest possible scientific quality. We are convinced that the change in ownership makes it possible for us to continue to do so, facing the dramatic changes in emphasis of research and development of commodities and advanced forest products that is presently taking place.

In conjunction with these changes we have undertaken a thorough overhaul of our website and its visibility in databases and search engines, so that the site now meets the demands of an up-to-date scientific journal. Thus, among other things, articles are now published on the web as soon as they have been finally approved for publication, all issues of NPPRJ since its start in 1986 are available for free for subscribers and for downloading at a moderate cost by anyone else, and the full text of all articles is searchable, which we believe is a rather unique feature.

We hope that you will find NPPRJ a scientifically interesting, technologically stimulating and generally important journal – and we look forward to your manuscripts that are essential for us and will help us to maintain and improve the scientific and technological status of the journal.

March 2013

Elisabet Brännvall Editor-in-chief Per Stenius Scientific editor

Per Engstrand Publisher Lars Wågberg Chairman, Editorial Board

8th International Paper and Coating Chemistry Symposium, 2012

6 Topo-chemical modification of fibres by grafting of carboxymethyl cellulose in pilot scale

Mikael Ankerfors, Elisabeth Duker and Tom Lindström

- 15 Effect of a new cationic-polymer/CMC bilayer-treatment on paper wettability
 Besma Ben Fadhel, Jean-Pierre Joly, Evelyne Mauret and Yves Chapleur
- 22 Silica pigment produced from silicate mining side-streams for ink-jet paper coating application

Eija Kenttä, Taina Lamminmäki, Hille Rautkoski, Sebastian Teir, John Bacher, John Kettle and Juha Sarlin

28 Gloss, hydrophobicity and surface texture of papers with organic nanoparticle coatings

Pieter Samyn, Jürgen Van Erps, Hugo Thienpont, Gustaaf Schoukens, Dirk Stanssens, Leo Vonck, Henk Van den Abbeele

Mechanical pulping

42 Sample pretreatment for oxalate analysis and the effect of peroxide bleaching parameters on oxalate formation

Matti Häärä, Jonas Konn, Anna Sundberg, and Stefan Willför

51 Brightness reduction of mechanical pulp in the wet end of a paper machine: The effect of pH, pulp washing and shear rate

Pekka Varhimo, Jonas Konn, Marcus Lillandt and Jouni Paltakari

59 Brightness reduction of calcium carbonate and calcium sulfate fillers in the wet end of a paper machine

Pekka Varhimo, Jonas Konn, Marcus Lillandt and Jouni Paltakari

68 Filler clay induced discolouration of bleached mechanical pulp

Hanne Narvestad, Øyvind W. Gregersen and Kjell-Arve Kure

Paper chemistry

82 The concept of stickies exposure for paper recycling processes

Patrick Huber, Thierry Delagoutte, and Sylvie Ossard

Paper and ink interactions

94 A physical model for liquid movement into a porous substrate under the action of a pressure pulse

Li Yang

Printing

- 101 Accelerated and natural ageing of offset prints covered with different varnishes

 Branka Lajić, Igor Majnarić, and Ivana Bolanča Mirković
- 111 Stability of ink-jet prints under influence of light
 Barbara Blaznik, Klementina Možina and Sabina Bračko

Paper physics

119 Flow modelling in a low consistency disc refiner

Grzegorz Kondora and Dariusz Asendrych

131 Non-destructive high resolution measurements of spatial filler content distribution in paper

Håkan Hägglund, Ole Norberg, and Per Edström

137 Web-wide imaging of paper: Analyzing the potential of on-line light transmittance measurement in quality control and diagnostics of paper

Jukka-Pekka Raunio, Ville Tirronen, Ilkka Lehtoranta, Risto Ritala

Paper technology

146 Testing an activity-based costing model with a virtual paper mill

Heikki Korpunen and Jouni Paltakari

Accelerated and natural ageing of offset prints covered with different varnishes

Branka Lajić, Igor Majnarić, and Ivana Bolanča Mirković

KEYWORDS: Ageing, Offset, Water-based dispersion varnish, UV varnish, Colour difference, Gamut

SUMMARY: The aim of this work was to determine the dependence of the colour fading of offset prints on the ageing process, relative to prints overprinted with water-based dispersion varnish and UV-cured varnish. Natural ageing (outdoor conditions and the exposure to sunlight filtered by glass windows) and accelerated ageing (moist heat and light xenon arc lamp) treatments were carried out. In order to determine colour fading, colour difference, 2D gamut values and characteristic cross sections L20, L50 and L80, as well as 3D gamut values were used.

The yellow colour showed the largest colour difference when offset prints were exposed to accelerated ageing by means of exposure to xenon light. Magenta followed yellow. No significant stability was achieved by varnishing the yellow print with water-based dispersion varnish and UV-cured varnish. This was also the case with magenta. An increase of the gamut occurred after one week's exposure of prints coated with water-based dispersion varnish to moist heat ageing. In contrast, on exposure of prints coated with UV-cured varnish, a decrease of gamut appeared. On further exposure of prints covered with either kind of varnish a decrease of gamut was evident. Indoor exposure of varnished prints to sunlight through a glass window had a minor influence on the gamut volume change in comparison with the exposure of prints to outdoor conditions.

ADDRESSES OF THE AUTHORS:

Branka Lajić (branka.lajic@grf.hr), Igor Majnarić (igor.majnaric@grf.hr), Ivana Bolanča Mirković (ivana.bolanca@grf.hr) University of Zagreb, Faculty of Graphic Arts, Getaldićeva 2, 10000 Zagreb, Croatia,

Corresponding author: Ivana Bolanča Mirković

Varnishing is used to heighten a glossy or matt finish and to protect the surface of a printed product from wear, scratches and fingerprints. When deciding whether a coating should be used, it is important to consider the application, required durability and life span of prints (Thomson 2004).

Throughout their life cycle, prints overprinted with varnish can be exposed to physical phenomena. Weathering and light exposure are important causes of damage to printed substrate, inks and other organic materials. Damages include the loss of gloss, colour fading, yellowing, loss of tensile strength (Havlinova et al 2002; Bolanca et al. 2004; Dobric et al. 2009; Belanyi et al. 2003; Debeljak, Gregor-Svetec 2010; Vesely et al. 2010; Dzik et al. 2010; Karlovits, Gregor-Svetec 2011, Kačerova et al. 2010; Stepankova et al. 2010; 2011).

Light fastness implies resistance to the action of daylight without direct influence of weather (Debeljak, Gregor-Svetec 2010). Weather resistance is the resistance

to the simultaneous action of radiation and atmospheric properties such as humidity, ozone, waste gases (Geisenberger et al. 2003; Vesely, Dzik 2009).

Some researchers use natural exposure testing, while others use the accelerated ageing with xenon arc and the QUV weathering tester. Natural exposure testing is realistic, easy to perform and inexpensive, but the results vary from year to year and from site to site and it takes several years to obtain the results. Xenon arc lamps provide the best available match to sunlight (Baumann, Hofmann 2004).

Accelerated weathering instruments use three factors to test materials: light, temperature and water exposure. Each factor will affect materials differently when activated alone, but together, they often work synergistically (Grossman 2006).

Spectral sensitivity varies from material to material and for less durable ones, such as some pigments and dyes, longer-wave UV and even visible light can cause damage (Malešić et al. 2005). The effects of light exposure are accelerated when temperature is increased.

When paper is exposed to sunlight filtered by glass windows, the spectrum of visible light contains wavelengths higher than 340 nm, which can have a less destructive influence on some materials. Malešić and coauthors proved that the extensive oxidative degradation of cellulose occurs during exposure to light with >340 nm (Malešić et al. 2005).

For the investigations presented in this work both natural ageing treatment (outdoor conditions), and indoor conditions (exposure to sunlight filtered by glass windows and exposure to accelerated ageing, i.e. moist heat and light xenon arc lamp), were used. The aim of this paper was to determine how the colour fading of offset prints depend on the ageing processes, relative to prints overprinted with water-based dispersion varnish and UV-cured varnish

Materials and Methods

A six colour offset printing machine (KBA Rapida 105/6+1) was used for the preparation of prints. In this way were obtained CMYK prints without varnish, prints obtained by combination of CMYK with water-based dispersion varnish and CMYK prints with primer and UV-cured varnish.

The printing form contained the following printing elements: standard ISO illustration, CMYK RGB step-like wedges ranging from 10% to 100% screen value, patches for dimensional stability determination, passer control, wedges for greyness determination, standard FOGRA PMS wedge and the wedge with 1535 patches for making the ICC profile and 3 D gamuts.

The form was exposed on a Luscher CTP CPose 160

Table 1. Properties of the board

Property	Standard	Value
Grammage (g/m²)	ISO 536	400
Caliper (µm)	ISO 534	545
Stiffness (mNm)	ISO 2493	MD 28,10; CD 12,50
Smoothness (ml/min)	DIN 53017	50
Brightness (%)	ISO 11475	83
Gloss (%)	ISO 8254	35

Cardboard (Bona GD₂ Mayr Melnhof, Gernsbach GmbH) was used as the printing substrate. The board properties are presented in *Table 1*.

Conventional offset printing inks (SHF SunChemical) were used in printing. Prints were varnished with water-based dispersion varnish G 9/378 P-60, SunChemical. This varnish has a pH value between 7.0 and 9.5 and relative density of 1.04 g/m² at 20°C. It contains volatile organic compounds with concentrations of 2.359% EC and 2.302 % CH. The water-based dispersion varnish was applied on the printing sheet using an anilox roller.

In addition, the UV-cured varnish 14-CH-144 SunChemical was used. This varnish has medium viscosity and weak odour. It does not contain benzophenone and it is suitable for printing on food packaging. When applying the UV varnish on prints with the offset inks, a primer was used in order to avoid possible problems with ink drying and undesirable gloss decrease (the drawback effect). After this treatment the UV varnish was applied.

Light fastness was analysed by exposing the prints to the Xenotest in order to conduct the light fastness analysis (Solarbox 1500 E, Co. Fo. Me. Gra.). The samples were exposed to xenon arc light at temperature 35°C and 65% relative humidity (HRN ISO 12040 2004). The temperature of the black standard was 50°C and xenochrome 320 nm filter was used. The samples were 100% covered with ink. Non-varnished and varnished samples were exposed to Xenotest for 6, 12, 24, 48, 72, 98, 148 and 244 hours.

The second sample series was exposed to moist heating ageing at 80°C and 65% relative humidity in a Kätermann chamber without the influence of radiation (ISO 5630-3 1996). In the third sample series the prints were exposed to outdoor conditions during winter months (ASTM 3424-11 2011). The fourth series of samples was subjected to indoor exposure to sunlight through a glass window (ASTM 3424-11 2011).

The unexposed and the exposed samples were evaluated by spectrophotometric measurements.

The spectrophotometer X Rite DTP 41 and the application ColorShop X were used for calculating output results such as: L*a*b*, c*, H*, x, y, Y, greyness, spectral reflection in the visible part of the spectrum and the screen values of inking. All values were measured six times and average values were used for further analysis. The colour difference ΔE_{2000}^* was calculated using the following equations (Luo et al. 2001; Johnson, Green, 2001).

$$\Delta E_{2000}^{\star} = \sqrt{\left(\frac{\Delta L^{\star}}{S_{L}k_{L}}\right)^{2} + \left(\frac{\Delta C^{\star}}{S_{C}k_{C}}\right)^{2} + \left(\frac{\Delta H^{\star}}{S_{H}k_{H}}\right) + R_{f}\left(\frac{\Delta C^{\star}}{S_{C}k_{C}}\right)\left(\frac{\Delta H^{\star}}{S_{H}k_{H}}\right)}$$
[1]

where ΔE^* is the colour difference, ΔL^* is the light difference, ΔC^* is the chroma difference, ΔH^* is the hue difference and k_L , k_C , k_H are parametric weighting factors

Other parameters are defined as follows:

$$S_{L} = 1 + \frac{0.015(\overline{L'} - 50)^{2}}{\sqrt{20 + (\overline{L'} - 50)^{2}}}$$
 [2]

$$S_{c} = 1 + 0.045\overline{C'}$$
 [3]

$$S_{H} = 1 + 0.015\overline{C}T$$
 [4]

$$T = 1 - 0.17 \cos(h' - 30^{\circ}) + 0.24 \cos(2h') + 0.32 \cos(3h' + 6^{\circ}) - 0.20 \cos(4h' - 63^{\circ})$$
 [5]

$$R_{\rm c} = 2\sqrt{\frac{\overline{C'}^7}{\overline{C'}^7 + 25^7}}$$
 [6]

$$R_{\tau} = -\sin(2\Delta\theta)R_{c} \tag{7}$$

$$\Delta\theta = 30 \exp\left\{-\left[\left(h' - 275^{\circ}\right)/25\right]^{2}\right\}$$
 [8]

The presented pattern includes the following modifications: a hue rotation term to deal with the problematic blue region, compensation for neutral colours (the primed values in the L*, C*, h differences), a compensation for lightness, a compensation for chroma and a compensation for hue.

The X-Rite DTP 41 device is suitable for measuring a large number of patches (in this case the test chart with 1535 colour patches). The measurements were used to create the ICC profiles using the program MonacoProfiler Platinum v 4.8. From the generated ICC profiles space the colour gamut was formed and gamut volumes were detected in the program Gamut Works v.1.0.

Spectrophotometric measurements were used to create a 2D gamut in the CIELAB a* b* colour diagrams. Three characteristic cross-sections of 2D gamut for lightness L20, L50 and L80 were done.

Results and Discussion

The colour difference ΔE^* is important for graphic reproduction because two tones can be compared with it and information about the reproduction quality can be obtained, i.e. the deviation of the reproduction from the original. Indirectly, this value presents the aberration of the three stimulus values that correspond to the perception of colour in the human eye. In these investigations ΔE^* represents the change in colour between the unexposed prints and their post-exposure, faded conditions. Fig 1 shows the time dependence of the colour differences of offset prints during accelerated ageing with light treatment in Solarbox for offset prints without the varnish, prints overprinted with water-based dispersion varnish and prints treated with primer and UV-cured varnish.

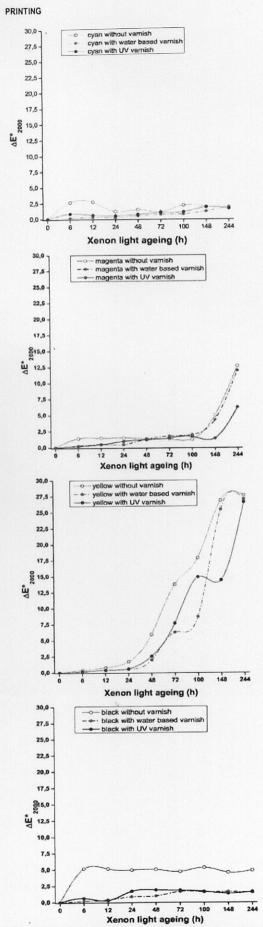


Fig 1. Dependence of colour difference on the time of exposure to the xenon arc light

The yellow colour showed the largest colour difference of the offset prints. During the first 12 h of exposing prints to light there were no significant changes in ΔE^* , but after that an abrupt increase of values followed. Print varnishing offered only insignificant protection. During the exposure in the period from 24 to 100 h a smaller ΔE^* occurred on prints with water-based dispersion varnish. On further increase of the exposure time UV-cure varnish provided better protection.

The sequence of changes in the color difference for magenta was similar. Smaller values in ΔE^* changes appeared on the prints exposed to light up to 94 h. After that a quick increase in the value ΔE^* appeared. In this range the water-based dispersion varnish gave almost no protection of the print from light exposure, as opposed to the UV-cured varnish, by which a reduction of the colour difference by about 50% could be achieved.

The changes in ΔE^* with the time of light exposure of non-varnished black and cyan prints differed from the previously described ones.

For black and cyan, maximum values of ΔE^* appeared after the first 6 h of print exposure.

Cyan was the most light-resistant printing ink during the described experimental conditions. This result originates from the resistivity of the phthalocyanine pigment in cyan to fading. Cyan prints with water-based varnishes showed smaller ΔE^* values than the ones with UV-cured varnish.

By covering the black offset print with water-based varnish, for 6, 24 and 48 h exposure to light only, an advantage in light protection could be achieved relative to the UV-cured varnish.

Since the differences in lightness (ΔL^*), chroma (ΔC^*) and hue (ΔH^*) are important variables in the expression for colour difference, their specific characteristics were monitored within the investigated system.

Fig 2 shows the dependence on time during accelerated ageing with xenon arc light of the lightness differences of offset prints without varnish, offset prints overprinted with water- based dispersion varnish and offset prints with primer and UV-cured varnish.

The cyan print with the water-based dispersion varnish achieved a negative value of ΔL^* after 24 h exposure to light. If ΔL^* is negative, the prints exposed to xenon arc light are darker than those not exposed. If ΔL^* is positive, an exposed print is lighter than a non-exposed print.

The lightness differences of magenta prints covered with water-based dispersion varnish were negative during the whole exposure period to xenon arc light, as opposed to the non-varnished sample and the print covered with UV-cured varnish. The non-varnished print and the print overprinted with water-based dispersion varnish achieved very large negative values at maximum exposure to xenon arc light.

The ΔL* curves for yellow print overprinted with the water-based varnish and the UV-cured varnish did not differ unambiguously from each another.

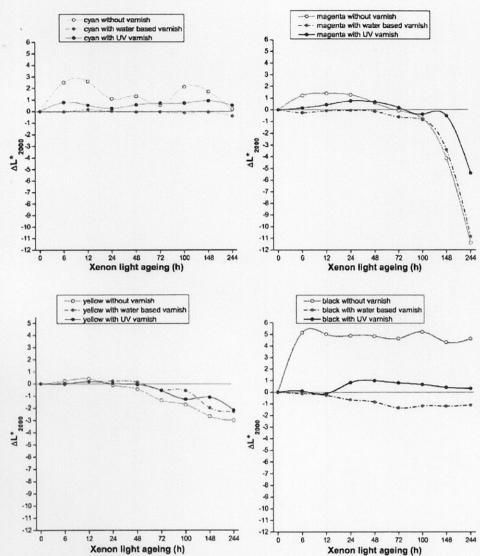


Fig 2. The dependence of lightness difference on the exposure time to the xenon arc light.

The ΔL^* values of black prints were characterized by large differences between non-varnished and varnished prints through the whole exposure area of prints.

Fig 3 shows the dependence on time of the chroma differences for offset prints without varnish, offset prints overprinted with water-based dispersion varnish and offset prints with primer and UV-cured varnish during accelerated ageing with xenon arc light.

The smallest change of ΔC^* was obtained for cyan, following by magenta. Greater stability of magenta prints was achieved by overprinting with UV-covered varnish than by using water-based dispersion varnish.

The yellow colour showed the largest chroma difference on offset prints. A somewhat better stability of yellow prints could be achieved by using UV-cured varnish.

Depending on the time of exposure, the ΔC^* of the black ink was negative. If ΔC^* is negative the prints exposed to xenon arc light are less saturated than the non-exposed ones.

Fig 4 shows dependence on time of the hue differences of offset prints without varnish, offset prints overprinted with water-based dispersion varnish and offset prints with primer and UV-cured varnish during accelerated ageing with xenon arc light.

The ΔH^* indicates the magnitude of the hue change. The dependence of ΔH^* on exposure time during xenon light ageing for cyan prints overprinted with water-based varnish and UV-cured varnish is somewhat stronger relative to the non-varnished prints. The values of ΔH^* for the two varnishes did not differ much.

The changes with time of ΔH^* of magenta prints were to a certain degree similar to those for cyan because in this case too, negative values were linked to shorter times of exposure, i.e., ΔH^* increased and became positive by increasing the exposure time. After 244 hours exposure the values of ΔH^* were similar for all observed samples.

For the non-varnished and varnished yellow prints the lowest ΔH^* values occurred when exposing the samples to xenon arc light for the first 100 hours. During further exposure ΔH^* increased and after 244 hours it obtained positive values.

The values of ΔH^* for carbon prints were characterized by greater differences between non-varnished and varnished prints relative to other CMY inks. Black prints overprinted with UV-cured varnish had the lowest ΔH^* values and those without varnish had the highest.

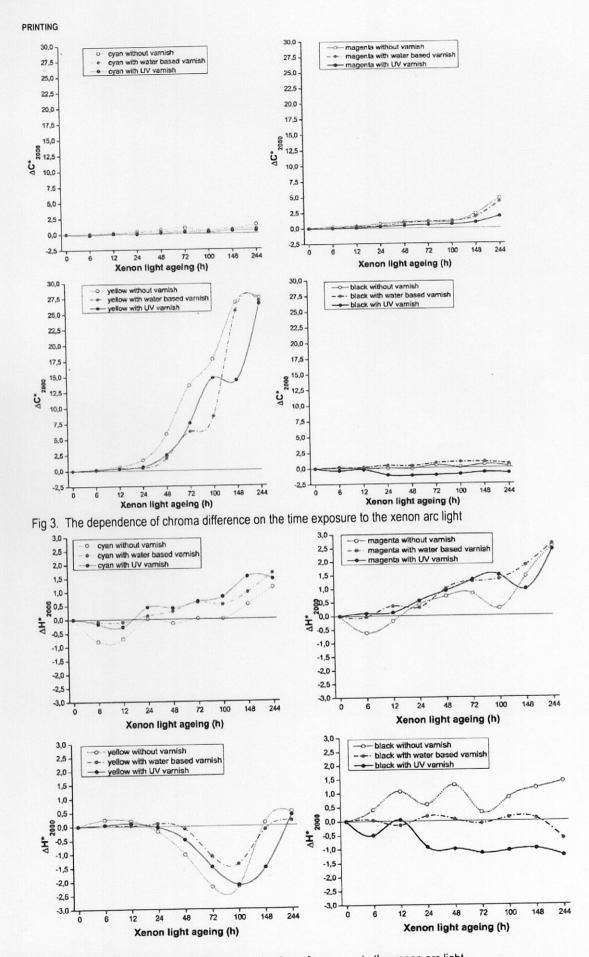


Fig 4. The dependence of hue difference on the time of exposure to the xenon arc light

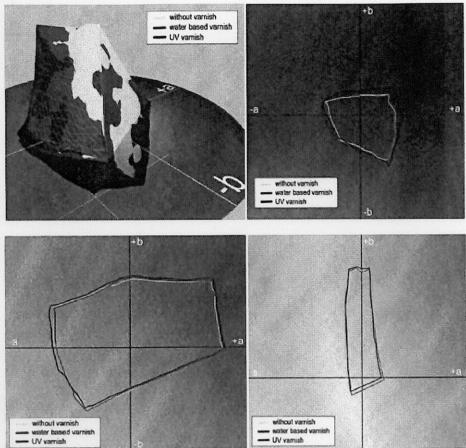


Fig 5. Gamut of prints without varnish and covered with different varnishes a) 3D; b) 2D, L= 20; c) 2D, L=50; d) 2D, L = 80.

Table 2. Volumes of gamut V CIE L*a*b* CCU

Vwithout varnish	Vwater-based dispersion varnish	V _{UV-cured} varnish		
765.607	803.687	810.364		

3D gamut and 2D gamut cross sections of three characteristic areas for print without varnish, print with water-based dispersion varnish and print covered with UV-cured varnish are presented in Fig 5.

The gamut was increased by print varnishing, which resulted in the greater quality of prints ($\Delta V_{water-based}$ dispersion varnish - without varnish=38.080 gamut units, $\Delta V_{UV-varnish}$ - without varnishing yielded somewhat better values than the water-based dispersion varnish ($V_{UV-varnish}$ - water-based varnish=6.677gamut units).

Analysis of the characteristic cross-sections of gamut showed that the changes due to varnishing in the lighter areas (L=20) along all coordinates were larger than those for the darker and medium tones. Print varnishing influenced the reproduction somewhat more in the area from yellow to red. In the area L=50 there were smaller changes on all coordinates. Changes and a better reproduction were more visible in the area of green for prints varnished with UV-cured varnish. The influence of varnishing on the reproduction of darker tones was noticed in the violet area.

Fig 6 demonstrates the relative gamut volume changes of prints without the varnish and the varnished prints as a function of exposure to moist heat ageing at 80°C and 65% relative humidity, without the influence of radiation.

The gamut of the print coated with water-based dispersion varnish increased after a one-week exposure to moist heat ageing (ΔV one-week-aged – non aged =88.877 unit).

The gamut volume of print overprinted with UV-cured varnish exposed under the same conditions decreased by 53.743 units. By further exposure, the gamut volumes of both the print covered with water-based dispersion varnish and the one overprinted with UV-cured varnish decreased.

This result could be explained by different mechanisms of drying of these two kinds of varnishes. The water-based dispersion varnish systems dry by physical processes. They contain about 55% of water. Dispersion varnishes dry for the most part by water absorption (70%). The amount of drying that occurs by the evaporation of water is relatively small and usually overestimated (30%). Film formation in dispersion varnishes is largely complete even when 20-30% of the water is still present in the varnish.

UV varnish is cured by a photo-initiated free-radical polymerization mechanism. Highly cross-linked polymer networks are produced by photo-initiated polymerization of multifunctional monomers and oligomers. UV-cured varnishes are usually made of acrylate-based resins, which undergo radical-type polymerization upon UV exposure in the presence of a photoinitiator. This chain reaction is strongly inhibited by atmospheric oxygen, which scavenges very efficiency both the initiating and the polymer radicals. Chemical components used in UV curing react very rapidly upon exposure to high intensity UV light.

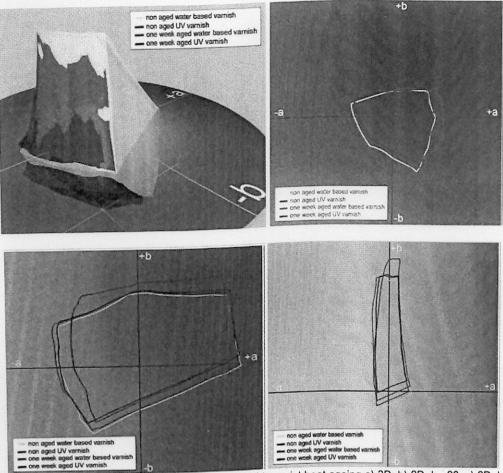


Fig 6. Gamut of prints covered with different varnishes and exposed to moist heat ageing a) 3D; b) 2D, L= 20; c) 2D, L=50; d) 2D, L = 80. Prints exposed to moist heat ageing for one week.

It could be concluded that in the first week of exposing the varnished prints to moist heat ageing, the process of print drying continued on the print covered with water-based dispersion varnish, which resulted in the gamut increase. The print with UV-cured varnish dried much quicker and during the exposure to moist heat ageing even in the first week, the gamut volume decreased with the exposure time.

In the characteristic cross sections of gamut bodies of the varnished prints certain deviations in tones with regard to the print ageing process were observed. The greatest changes were seen in the whole area (except the yellow one of the cross-section at lightness L = 20) between one week aged print covered with water-based dispersion and the aged print covered with UV varnish, but also between on non-aged prints with both varnishes (Fig 6b). An increase was also noticed in one very narrow purple area. At L=20 there was no considerable change between the non-aged and the aged print covered with UV-cured varnish. However, in the yellow area, all noticed prints had small values of inking intensity.

At L=50 a decrease of colour intensity appeared in the one-week-aged print covered with water-based dispersion varnish, from magenta over purple and blue area to a greater part of the green area (Fig 6c). In contrast, in the

smaller part of the green area greater values were noticed in the one-week-aged print covered with UV-cured varnish than in the one-week-aged print covered with water-based dispersion varnish.

In the lowest gamut cross section (L=80) the changes in the direction of the coordinate b were characteristic. In the one-week-aged print covered with water-based dispersion varnish a deviation in the positive direction of the axis in b+ area appeared, while all other prints had equal values (6d). In the direction b- i.e. blue-violet area the greatest change was observed for non aged print covered with water based varnish, and in sequence toward smaller values there were: non aged print covered with UV varnish, one week aged print covered with water based dispersion varnish and one week aged print covered with UV varnish.

At higher gamut cross section L=20 the differences between one week ageing and three-week aged prints were not significant for any of the observed prints (Fig 7b). Smaller changes were noticed in three-week-aged print covered with water-based dispersion varnish in the whole area except the yellow one, and in the narrow part of purple, than in one week aged print covered with water based dispersion varnish.

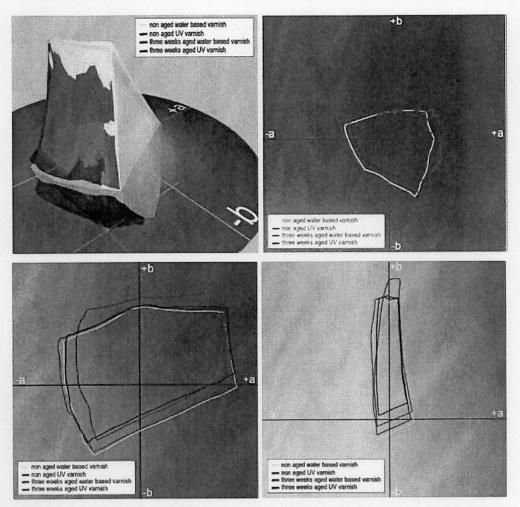


Fig 7. Gamut of prints covered with different varnishes and exposed to moist heat ageing a) 3D; b) 2D, L= 20; c) 2D, L=50; d) 2D, L = 80. Prints exposed to moist heat ageing for three weeks.

Table 3. Volumes of gamut V CIE L*a*b* CCU. Prints exposed to moist heat ageing

Sample	V non-aged print	Vone-week-aged print	Vthree-week-aged print	
Water-based dispersion varnish	803.687	892.564	857.301	
UV-cured varnish	810.364	756.621	721.485	

Table 4. Volumes of gamut V CIE L*a*b* CCU. Prints exposed to outdoor condition

Sample	V non aged	V one week	V _{three} weeks	ΔV=V _{one week aged} −V _{non aged}	ΔV=V _{three weeks} aged—V _{non aged}	ΔV=V _{one week aged} − V _{three weeks aged}
Water-based varnish	803.687	849.627	831.011	45.940	27.324	18.616
UV-cured varnish	810.364	805.125	768.185	-5,239	-42.179	36.940

After three weeks of ageing, at L=50, only small deviations could be noticed in comparison to the prints aged for one week (Fig 7c). Deviations, such as a greater intensity in the purple area, were noticed in three-weekaged print covered with water-based dispersion varnish in comparison to the one-week-aged print covered with the same varnish. In addition, there were increases in the green and green-blue areas for non-aged print covered with UV varnish, compared to other samples.

At L=80 a somewhat greater saturation in green i.e. in the yellow – green area (Fig 7d) was observed in non-aged print covered with UV varnish, except that three weeks aged prints covered with water based dispersion varnish and with UV varnish in violet – blue area gave a small shift in the b+ coordinate.

In *Table 4* the gamut volume of the varnished non-aged prints and the prints exposed to outdoor conditions during the winter time is presented.

After the first exposure to outdoor conditions the gamut volume of prints overprinted with water-based dispersion varnish was increased by 45.940 units, while the volume of prints covered with UV-cured varnish decreased by 5.239 gamut units. By further exposure, the decrease of the gamut volume appeared for prints varnished with both varnishes. After the third week of exposure to outdoor conditions, the volume decreased for print with UV cured varnish by 36.940 units, while in the case of the print covered with water-based dispersion varnish it decreased only by 18.616 units at the described conditions of the experiment.

Table 5. Volumes of gamut V CIE L*a*b* CCU. Indoor prints exposed to the sunlight through the glass window

Sample	V non aged	V one week	V _{three} weeks	ΔV=V _{one week aged} -V _{non aged}	ΔV=V _{three} weeks aged−V _{non} aged	ΔV=V _{one week} aged− V _{three} weeks aged
Water-based varnish	803.687	837.520	826.256	33.833	22.569	11.264
UV-cured varnish	810.364	807.247	796.628	-3.117	-13.736	10.736

After the first week of indoor print exposure to the sunlight through the glass window, the gamut volume of prints covered with water-based dispersion varnish increased (ΔV=V_{one-week-aged} - V_{non-aged}=33.833 units). For the same period of exposure, the gamut volume of the prints overprinted with UV cured varnish decreased by 3.117 units. By further exposure the trend of decreasing print gamut was established on both kinds of prints. Somewhat greater stability to exposure was present on prints covered with UV cured varnish.

When comparing the results, it was observed that the exposure of the varnished samples to the sunlight through the glass window influenced the gamut to a smaller extent than the exposure to outdoor conditions (ΔV_{water}

based varnish, outdoor = $V_{one-week-aged}$ print $V_{three-week-aged}$ print = 18.696 gamut units, $\Delta V_{water-based}$ varnish, indoor = $V_{one-week-aged}$ print $V_{three-week-aged}$ print = 11.264 gamut units, $\Delta V_{UV \text{ varnish}}$, outdoor = $V_{one-week-aged-print}$ - $V_{three-week-print-aged}$ = 36.940 gamut units, $\Delta V_{UV \text{ varnish}}$, outdoor = $V_{one-week-aged}$ - $V_{three-week-aged}$ - $V_{three-week-aged}$ = 10.619 gamut units).

The spectrum of sunlight was weighted toward the visible and infrared. However, it was a small fraction of UV light that was responsible for most of the damage to the varnish, the colorants and the polymers. The most destructive is the UVC (100-290nm). Indoors, where the sunlight is filtered by glass windows, the spectrum of visible light contains wavelengths higher than 340 nm (Klemann 2003). This was the reason of the decreased gamut of prints exposed to the sunlight through the glass window relative to the exposed to outdoor conditions.

Literature

ASTM 3424-11 (2011): Standard Practice for Evaluating the Relative Light-fastness and Weatherability of Printed Matter

Baumann, E. and Hofmann R., (2004): The equivalence of light sources in light stability testing, Proceedings/ NIP20, International Conference on Digital Printing Technologies, pp. 699-704

Belanyi, F., Havlinova, B., Brezova, V., Čeppan, M., Novotna, M. and Jakubikova, Z. (2003): The stability of offset inks on paper upon ageing, WPP, pp. 462–467.

Bolanca, Z., Milkovic, M. and Bolanca I., (2004): The permanence of conventional and digital offset prints, AIC 2004, Colour and prints, Interim meeting of the international colour association, Proceedings, Porto Allegro, 2004 pp.163-166

Debeljak, M. and Gregor-Svetec, D. (2010): Optical and colour stability of aged specialty papers and ultraviolet cured ink jet prints, J. Imaging Sci. Technol. 54(6), 60402-1-60402-9(9)

Conclusions

The determination of the stability of offset prints coated with water-based dispersion varnish and UV-cured varnish by application of moist heat and xenon light techniques of accelerated ageing as well as outdoor and indoor exposure to sunlight trough a glass window leads to the following conclusions:

The pigment type in offset ink has a great influence on colour stability. The yellow colour shows the largest colour difference on offset prints when they are exposed to accelerated ageing by xenon light technique. Magenta follows with a slightly smaller colour difference. These colours contain azo pigments which are not resistant to fading. No significant stability was achieved by varnishing the yellow print with water-based dispersion varnish and UV-cured varnish, unlikely in the case of the covered magenta print. After a print coated with waterbased dispersion varnish had been exposed to the moist heat for a week, an increase of print gamut appears, and after exposure of the print coated with UV-cured varnish a decrease is evident. The results are explained by the physical drying processes of water-based dispersion varnish in relation to the photoinitiated free radical polymerization drying mechanism of UV varnish. With further exposure of prints covered with one and another varnish kind, decrease of gamuts appears.

Similar trends of gamut changes appear by exposure of varnished prints to outdoor conditions in the winter. Longer exposure time of prints covered with UV cured varnish will have greater influence on the gamut of prints. In contrast to the exposure to outdoor conditions, indoor exposure of the varnished prints to sunlight through a glass window influences the gamut volume change to a smaller extent. Such changes are explained by filtering the sunlight by means of glass windows.

Dobrić, E, Bolanca Mirkovic I. and Bolanca, Z., (2009): Durability of Ink jet prints, Journal of Physics: Conference Series 231 012009, pp. 1-10

Dzik, P., Vesely, M., and Štepankova, E., (2010): Comparative study on the light-fastness of traditional and modern inkjet photographic output media, Proceedings/14th international conference on printing, design and graphic communications, Blaž Baromić 2010, Senj, pp. 88-97

Geisenberger, J., Saitmacher K., Macholdt H., T. and Menzel H., (2003): Stability of inkjet to gas fading-new developments, Proceedings/ NIP19, International Conference on Digital Printing Technologies, pp. 394-395

Grossman, D., M., (2006): The right choice: UV-fluorescent testing or xenon arc testing? http://www.pcimag.com./articles/cover_story_Accessed: 19.3.2011.

Havlinova, B., Babiakova, D., Brezova, V., Durovič, M., Novotna, M. and Belanyi. F. (2002): The stability of offset inks on paper upon ageing, Dyes Pigm. 54(2), pp. 173-188

HRN ISO 12040 (2004): Graphic technology- Prints and printing inks. Assessment of light fastness using filtered xenon arc light.

ISO 5630-3 (1996): Paper and board-Accelerated ageing-Part 3: Moist heat treatment at 80°C i 65% relative humidity.

Johnson, T. and Green, P., (2001): The CIE 2000 colour difference formula and its performance with graphic data set, Proceedings of IARIGAI 28th Research Conference, Montreal 2001, section 4.5

Kačerova, S., Vesely, M. and Dzik, P. (2010): Inkjet printouts long-term ageing, Proceedings / 5th International Symposium on Graphic Engineering and Design, Grid '10, Novi Sad, 2010, pp. 53–58.

Karlovits, M., and Gregor–Svetec D., (2011): Comparation of durability brtween UV inkjet and conventional offset prints exposed to accelerated ageing, Journal of Graphic Engineering and Design, 2(2), pp. 10-15

Klemann, B., M., (2003): Correlations between Xenon Arc accelerated weathering tests and outdoor weathering, Proceedings/ 19th International Conference on Digital Printing Technologies, pp. 406-410

Luo, M., R., Cui, G. and Rigg, B., (2001): The development of the CIE 2000 color difference formula: CIEDE 2000, Colour Res. Appl. 26(5), 340-350

Malešić, J., Kolar, J., Strlić, J., Kočar, D., Fromageot D., Lemaire J. and Haillant, O., (2005): Photo-induced degradation of cellulose, Polim. Degrad. Stabil. 89(1), 64-69

Stepankova, E,. Dzik, P., and Vesely, M.(2010): Gamut volume as a tool for print life time estimation, Proceedings/ 5th international symposium, GRID 2010, Novi Sad, pp.73-75

Štepankova, E., Vesely, M., and Dzik, M., (2011): Varnishes for Inkjet print protection, Proceedings/X Seminar in Graphic Arts, Pardubice, pp.136-141

Technical information (2003): Information on ACRYLAT® water-based dispersion varnish, Huber Group

Thomson, B., (2004): Printing materials: science and technology, Pira International, Leatherhend

Vesely, M. and Dzik, P., (2009): Gas and light fading study of inkjet prints on selected inkjet papers, Proceedings / 13th international conference on printing, design and graphic communications, Blaž Baromić 2009, Split, 2010, pp. 159-164.

Vesely, M., Dzik, P. and Kačerova, S. (2010): Optical density vs. gamut volumes for image light-fastness evaluation – an experimental study, Proceedings / 14th international conference on printing, design and graphic communications, Blaž Baromić, Senj, pp. 27-35

Manuscript received August 8, 2012 Accepted January 11, 2013