Optical Properties of Printed Recycled Paper Exposed to Ageing

V. Džimbeg-Malčić, V. Mikac Dadić and Z. Bolanča
Faculty of Graphic Arts, Zagreb, Croatia

Abstract

Recently attention has been paid to recycled paper and demand for its use has increased because its use plays a vital role in the preservation of our natural environment. In this paper optical characteristics of the recycled substrates, printed by conventional offset technique, exposed to the natural and accelerated ageing has been examined. The both types of examinations show changes in the reflectance measurements and in the chosen colorimetric values. These results are discussed and compared to the same type of our measurements made on fine art and offset surfaces.

1. Introduction

The recycled fibers become greater and more important source of raw materials in paper production. Some of the reasons for that are: forest preservation, saving energy and water, less air and water pollution and more reasonable price of secondary raw materials.

The recycling process includes detachment of ink from fibers, removal of detached ink from pulp, water clarification for reuse and disposal of removed ink and stickies. Stickies are agglomerations of resinous materials from the paper being recycled, such as plastic coating and adhesives. Chemical, mechanical and thermal forces are utilized to detach ink from fibers (1).

Flotation system consists of an aqueous phase, two solid phases to be separate from each other, and a source of air bubbles. Flotation is effective when one phase is hydrophobic and susceptible to attachment to the air bubbles, while the second phase is hydrophilic. In the flotation cell the air bubbles rise through the paper slurry and selectively attach to ink particles. The air bubbles carry ink particles to the surface where they are caught into froth and are removed.

The efficiency of deinking flotation process depends among other things on kind of printing technique and kind of printing ink and substrate (2). In general, each technique, starting from the conventional ones (offset, gravure, relief, flexoprinting and screen printing) to the digital ones (on the principle of electrophotography, ion deposition, electrostatic, magnetographic and electrographic) sets different tasks on inks and toner respectively, in order to satisfy the given principles of the process (3). The inks for conventional offset printing, letterpress and flexographic printing and rotogravure printing consist of the vehicles, colorants (pigments or dyes) and additives. The vehicles are either as the carrier (e.g. solvents- mineral oil, toluene, ethanol, isopropanol, ethyl acetate, benzine) or as the binder (e. g, resins- hydrocarbon resin, alky resin, phenol modified colophony resin, acryl resins, maleic resins).

Unlike the conventional printing inks, toners in digital printing on the principle of electrophotography contains synthetic binders based on polyester or copolymers of styrene with acrylates, methacrylates and butadiene, charge control agens (quaternaly ammonium salts, sulphonates, zinc complex), colorant (pigment or dye) and other technical additives (4).

In this article the influence of natural ageing on some of optical characteristics of printed recycled samples exposed to electromagnetic radiation (visible and near UV) and of accelerated ageing (elevated temperature and relative humidity) have been examined.

The quality of paper and its ingredients determine how resistant it is to ageing. Generally speaking, groundwood-containing paper grades, i.e. paper made from mechanical pulp, have a shorter life span as they contain lignin, which makes the paper turn yellow after prolonged exposure to sunlight or to artifical sources of UV and visible electromagnetic radiation (5,6). If the product is intended to last a really long time, groundwood-free paper is to be recommended, i. e. paper made from chemical pulp. These days paper can be almost 100% recycled, and to minimize the paper industry´s impact on the environment it is essential that the fibers are recycled to the greatest extent possible. Since the cellulose fibers are processed and circulated several times, they wear out. The physical strength of a piece of paper is directly linked to the length of the individual paper fibers. With each recycling, the fibers become progressively shorter and therefore weaker. This is why it is not possible to completely close the paper ecocycle, as new or virgin fibers will always be necessary in the paper industry. The quality and strength of different recycled papers can vary greatly according to the type and percentage of recycled fibers used.

Acidity is one of the greatest enemies of paper. Over time it will weaken the paper fibers causing brown discoloration and brittleness. Until recently, a great deal of acidity was often present within paper at the point of manufacture. Fortunately more and more paper manufacturers are converting to alkaline processes, providing paper against the forces of deterioration.

2. Experimental

2.1 Examined samples

The printing machine MAN Roland has been used for printing. The test form contained wedges of tonal values from 0-100% coverage in the steps of 10%. Additional conditions in printing were following: the solid area must be completely covered by ink, the screen path with 90% screen value must not be close and the field with 10% screen value must be correctly printed. The composition for the ink used in this investigation is presented in Table I.

Table I Composition for the used ink

Component of ink			Ratio of components (%)
Colorant		Pigment	15.0
Vehicles	Binders	Alkyd resin	10.0
		Modified colophony resin	28.5
	Cariers	Mineral oil	28.5
		Vegetable oil	5.0
		Aditives	13.0

The used printing substrate was recycled paper, grammage of 100g/m^2. In all measurements, the standard methods were use.

2.2 Methods of measurements

All paper contains a small amount of moisture, and is highly sensitive to changes in temperature and humidity in the surrounding air. So, in a specially prepared chamber the increased temperature in the presence of a reasonable level of relative humidity (RH) is responsible for accelerated ageing. Ageing of printed samples is done at the 80^{o}C temperature and 65% RH in the period of 21 days.

Natural ageing was performed by two light sources: electric lamp that emits visible part of electromagnetic radiation and electric lamp that emits visible and near UV. Examined samples were exposed to radiation in time interval of 2 hours for UV irradiated samples and 5 days for visible irradiated samples.

Following exposure to the various light sources, samples were kept in the closed steel cabinet in the paper testing room maintained at 23^{o}C and 60% relative humidity. The temperature of the samples reached the value about 37^{o}C and the samples exposed to visible radiation about 28^{o}C.

Spectrophotometric measurements have been performed using X-Rite Spectrophotometer, Digital Swatchbook. Reflectance has been measured in the interval of the wavelengths from 390 nm to 700 nm for every 10nm, for all samples exposed to accelerated and natural ageing. The standard illuminant was D65, 10^o observer. The measurements, performed by X-Rite spectrophotometer, were supported by ColorShop 2.0 software and the results were calculated by Data Analysis and Technical Graphics Origin 6.0 Professional.

Colorimetry was used as a quantitative, objective measure of colour appearance. Reflectance throughout the visible range were recorded (TAPPI 442), and CIE colour space (CIE xyY) utilizing the x and y chromaticity coordinates, plus the luminance value Y and CIELAB values were generated from these. Symbols L*, a*, b* are used to designate measured values of three attributes of surface-colour appearance: L* represents lightness, increasing from zero for black to 100 for a perfect white; a* represents redness when positive, greenness when negative, and zero for grey; b* represents yellowness when positive, blueness when negative and zero for grey (TAPPI 524).

3. Results and discussion

3.1. Spectrophotometric results

The spectrophotometric measurements on recycled papers by three types of above mentioned ageing processes are performed. Recycled paper printed by cyan and magenta with three values of colours coverage, 20%, 40% and 100%, are chosen in accelerated and natural (UV and visible irradiated) ageing.

The results for accelerated aged samples in Fig.1., Fig.2. and Fig.3. are presented. Spectral data for recycled paper (substrate, no-printed paper), in the interval of the wavelength from 390nm to 700nm, are given in Fig. 1.

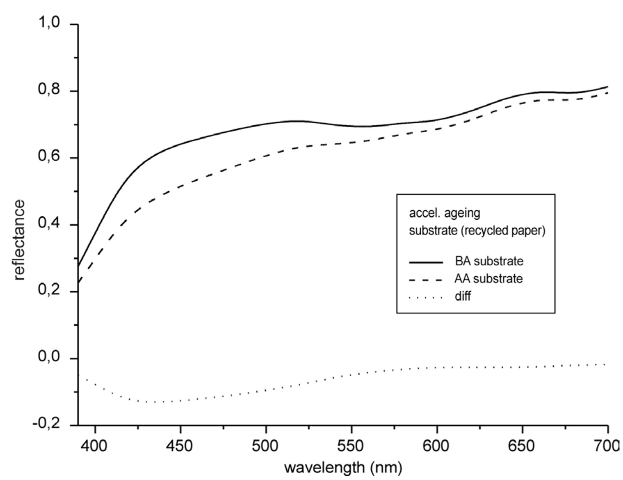

Fig.1. The reflectance of the recycled paper; before ageing (BA); after ageing (AA); and the difference of the reflectance (diff); accelerated ageing

The reflectance curves are presented with the line _BA, before ageing, the line _AA, after ageing and the line _diff, difference of the reflectance of both of them. The values of the reflectance for substrate are about 0,7 for the shorter wavelengths with increasing to the value of about 0,8 for longer wavelengths, for no-ageing samples. After ageing, the reflectance decreases all along the wavelength interval, with more significant change in the shorter wavelength range, presented with the minimum of the _diff line. The highest decreasing of the reflection measured after accelerated ageing is about 0,12 (or 12%) as is presented in the _diff curve in Fig.1.

The decreasing of the reflectance in the blue wavelength range causes the yellowness colour appearance of the sample, what is the empirical knowledge of many of us. Such appearances and their understanding we would discuss later. It can be point that the low values of the reflectance for the shortest wavelengths are depended on the sensitivity limit of the used device, and because of that they are not the points of interest.

The reflectance curves of the printed samples, exposed to accelerated ageing, are presented in the following figures. Fig.2. to Fig.3. show the changes during the accelerated ageing of the recycled samples printed by cyan and magenta. The reflection ranges of those samples are in blue and green wavelength intervals for cyan samples and in blue and red intervals for magenta.

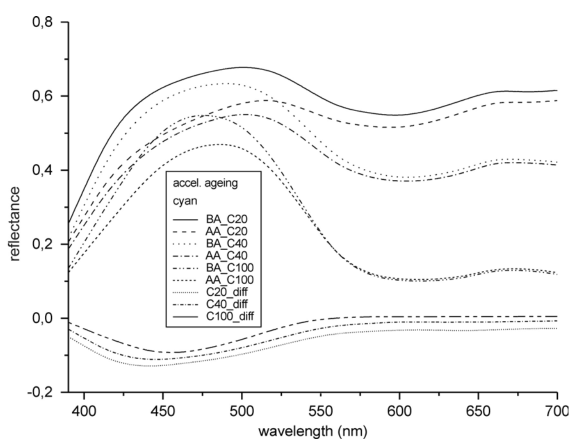

Fig.2. The reflectance of the recycled paper printed by cyan; before ageing (_BA), after ageing (_AA), and the differences of the reflectance (_diff), for chosen tonal values; accelerated ageing

For both printed inks and all coverage chosen, the decreasing of the reflectance after ageing is observed; the _diff lines on both pictures. The decreasing of the reflection appears in the ranges of the own reflection of the particular printed sample. The values of the differences are higher at the lower colour coverage. The intervals of the significant changes of the reflectance are in blue wavelength interval (from 400 to 500nm) and considerable lower changes are in red interval (from 570 to 700nm); for both inks (cyan and magenta). The maximal values of the differences of the reflectance are about 0,12 (or 12%) near the 425nm wavelength range for the 20% tonal values. The numerical values of the differences of the reflectance will be presented in Table II., for all aged samples.

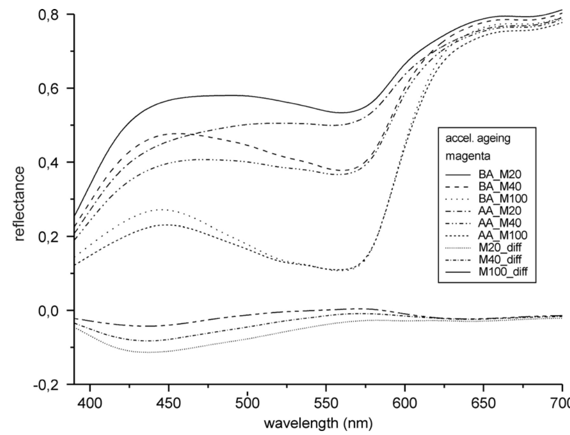

Fig.3. The reflectance of the recycled paper printed by magenta; before ageing (_BA), after ageing (_AA), and the differences of the reflectance (_diff), for chosen tonal values; accelerated ageing

The changes of the reflectance of the naturally aged samples, exposed to the source of the partially contended UV near radiation, are represented in Fig.4. and Fig.5., for both printed inks (cyan and magenta).

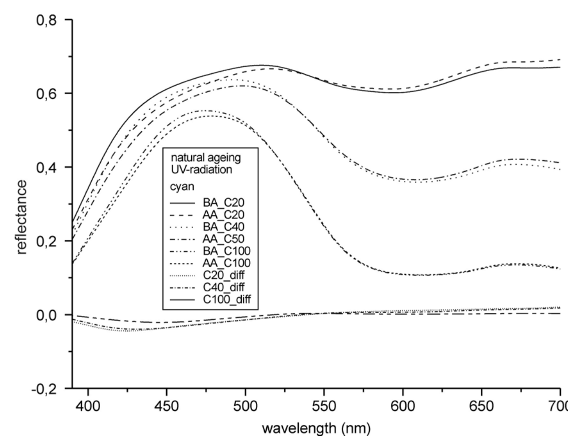

Fig.4. The reflectance of the recycled paper printed by cyan; before ageing _BA), after ageing (_AA), and the differences of the reflectance (_diff), for chosen tonal values; UV radiation

The changes of the reflectance show the significant lower values by this type of ageing. The wavelength interval (from 400 to 500nm) and the type of the changes (decreasing of the reflection) remain the same in the short wavelength interval. We make a special point of it for such behaviour. But, in the range of the longer wavelengths, the reflectance has the increasing tendency after ageing period; for both inks (Fig.4. and Fig.5.). The increase of the reflectance is especially expressed by cyan printed samples (Fig.4.), just in the interval of the own absorption. The both types of the changes (increasing or decreasing of the reflectance), by UV irradiated samples, are higher at lower tonal values (40%, 20%).

The changes of the reflection, for the samples exposed to the source of the controlled spectrum of visible radiation are presented in Fig.6. and Fig.7..

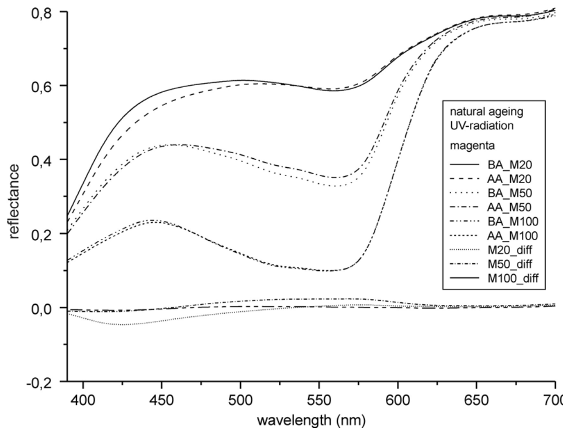

Fig.5. The reflectance of the recycled paper printed by magenta; before ageing _BA), after ageing (_AA), and the differences of the reflectance (_diff), for chosen tonal values; UV radiation

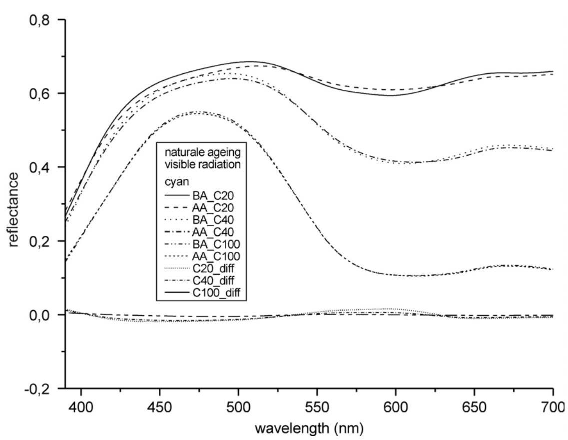

Fig.6. The reflectance of the recycled paper printed by cyan; before ageing (_BA), after ageing (_AA), and the differences of the reflectance (_diff), for chosen tonal values; visible radiation

These changes show the similar values of the differences of the reflectance differences those UV irradiated. The _diff lines for 40% and 20% tonal values, by cyan and magenta printed samples, change the sign at twice. The sign has negative values for the shorter wavelength, positive for the middle of the spectrum and again negative for the longer wavelengths.

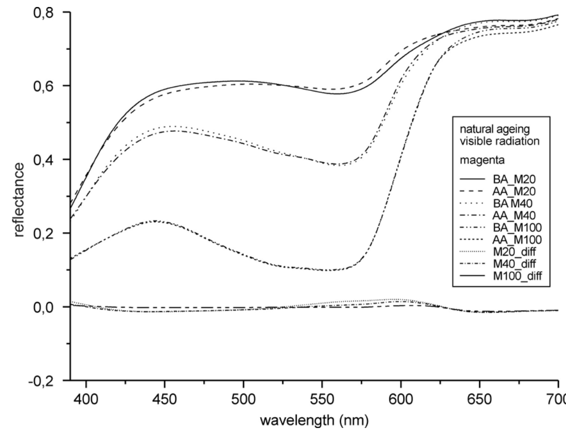

Fig.7 The reflectance of the recycled paper printed by magenta; before ageing (_BA), after ageing (_AA), and the differences of the reflectance (_diff), for chosen tonal values; visible radiation

One must point out, that the increasing of the reflectance in the absorption interval is not observed on offset and fine art glossy samples for the same types of ageing. Comparing the two types of ageing, (accelerated and natural), one can maintain: 1) all aged samples show the changes in the shorter wavelength interval and 2) the changes in the longer wavelength interval by natural aged samples are only observed. As is known, the accelerated ageing includes the knowledge of the temperature and relative humidity as the completely determined parameters of that change; external radiation is not present. By natural ageing, along with the temperature and relative humidity values, the external radiation is additionally parameter to be included and controlled during the ageing process. It should be affirmed; the temperature and the relative humidity cause the changes in the shorter wavelength interval, which is common interval for both types of ageing. The changes in the longer wavelength interval are caused by the applied radiation. Table II. shows the numerical values of the differences of the reflectance for all types of the ageing, for both inks and for maximal, 100%, and minimal, 20%, tonal values used in this presentation.

Table II. The differences of reflectance of recycled paper in shorter and longer wavelength's intervals

		ΔR%(shorter λ)		ΔR%(shorter λ)	
Type of ageing	Sample	100% ton.val.	20% ton. val.	100% ton.val.	20% ton. val.
Accelerated	Substrate		-12		-3
	Printed by cyan	-9	-12	0	-2
	Printed by magenta	-4	-12	-2	-2
UV	Printed by cyan	-1	-4	0	+1
	Printed by magenta	~-1	-4	0	0
visible	Printed by cyan	0	-2	0, 0	+2, -1
	Printed by magenta	0	-1	0, -1	+2, -1

* negative values denote the decreasing of the reflectance after ageing and positive the increasing of it

Completely repeatedly range of the changes in the shorter wavelengths interval, 400-500nm, presented in figures (1. -7.) is observed. The samples exposed to the visible radiation (natural ageing) show two opposite ranges of the changes; negative and positive values of the differences of the reflectance in the same table, Table II.

3.2. Colorimetric results

We have chosen CIELAB colour space of presenting the colour appearance changes of the samples before and after ageing processes.

Fig.8. shows these changes for accelerated ageing, and Fig.9. for natural ageing, visible radiation. The changes of CIELAB values are significant higher for accelerated ageing compared with natural ones. In accelerated aged measurements the decreasing of lightness, L*, with associated changes of the colour appearance in a* and b* values is observed. For samples printed by cyan, the negative values of a* increase so that the greenness increase, and the negative values of b* decrease which mean the blueness decrease. These values, C20, C40 and C100, are presented on left sides of the Fig.8.. The right side of the same figure shows the changes for the samples printed by magenta, M20, M40 and M100. The positive values of a* decrease when redness decrease and the positive values of b* increase when blueness decrease.

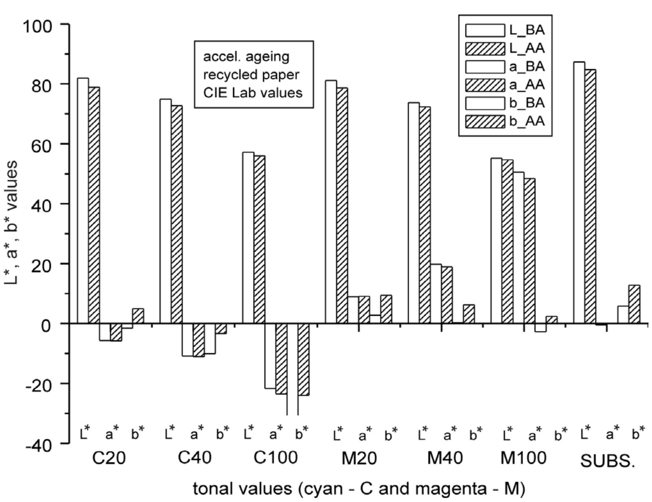

Fig.8. The colorimetric values, CIELAB, of cyan and magenta printed on recycled paper; accelerated ageing

Natural aged samples, Fig.9., show negligible small changes of the lightness and slightly higher changes of a and b for both printed inks.

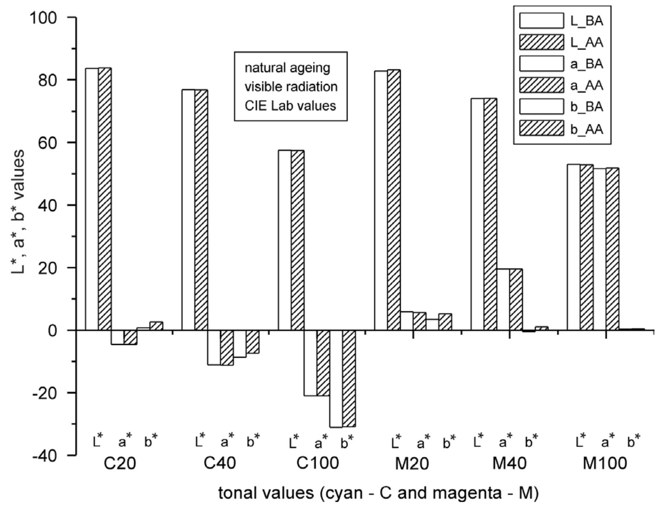

Fig.9. The colorimetric values, CIELAB, of cyan and magenta printed on recycled paper; natural ageing, visible radiation

4. Conclusion

Examination of the printed recycled surfaces exposed to the accelerated and natural ageing shows the changes in both types of the measurements; the reflectance and the colorimetric measurements.

For all types of the chosen inks the decreasing of the reflectance in the shorter wavelength interval, 400-500nm, has been observed. The similar interval by other types of surfaces (offset and fine art) has been showed in our previous article (7,8) in the same type of experiments. In all measurements with different types of surfaces the same printed ink was used. The decreasing interval for the offset and fine art printed surfaces was narrower (420-430nm) with higher values of ΔR. The surface characteristics, not printed inks can cause that phenomenon. It can be supposed, that this interval is some function of the temperature and of the relative humidity for all types of surfaces.

The significant changes for the longer wavelength intervals exist only by natural ageing. These changes are decreasing or increasing of the reflectance. The first type of changes (decreasing), we suppose, may be attributed to either the occurrence of the photochromism or the disintegration of the surfaces and the second one (increasing) may be caused by the fluorescence effect. To verify such hypothesis, optical measurements of the examined surfaces under the controlled temperature, relative humidity and the intensity of the incoming electromagnetic radiation in the more extensive intervals must be done.

The results of these investigations will contribute to better knowledge of the influence of kind of printing substrate on ageing mechanisms and some optical characteristic of prints. They do not have only theoretical value, but also the practical approach in usage of prints.

References

1. Göttsching, L Pakarinen H., (2000), *Recycled Fiber and Deinking,* FPEA & TAPPI Press, Helsinki
2. Dorris M. Sayegh N (1997) *The Rolle of Print Layer Thickness and Cohesiveness on Deinking of Toner-Printed Papers in Abubakar S*, (Ed) Anthology of Published Papers. TAPPI Pres, Atlanta
3. Thompson, B.(1998), *Printing Materials*, Science and Technology, PIRA Press, Surrey
4. Baur R, Macholdt H, T., (1995), *Organic Pigments for Digital Colour Printing*, Proceedings of 11th International Congress on Advances in Non Impact Printing Technologies, Carolina
5. S. B. Lee, J. Bogaard and R. L. Feller, *Darkening of Paper following exposure to visible and near- ultraviolet Radiation*, JAIC 1989, Vol.28, No.1, 1-18
6. Reyden van der, D. (1992), *Effects of aqueous light bleaching on the subsequent aging of paper*, Journal of the American Institute for Conservation (JAIC), 1992, Vol.31, No.1.pp. 289-331.
7. Mikac Dadic, V.; Dzimbeg-Malcic, V.; Petric Maretic, K. & Modric, D. (1998), *Optical Examination of Paperboard Surfaces Exposed to Ageing at Laboratory Conditions*, Proceedings of 15th International Scientific Conference on Graphic Arts, pp.176-186, Zagreb, 1998
8. Mikac Dadic, V.; Dzimbeg-Malcic, V. & Bolanca, Z. (2002), *Optical examination of printing surfaces exposed to electromagnetic radiation*, 13th DAAAM Intrnationl Symposium, Annals of DAAAM International 2002 & Proceedings, Vienna 2002, 257-258.

Biography

Vesna Džimbeg-Malčić obtained her Bachelors Degree in Physics from the University of Zagreb in 1981. and Masters Degree in Atomic Physics in 1989. from the University of Zagreb, Croatia. Since 1984. she has worked at Faculty of Graphics Arts. She belongs to Department of Physics of Faculty of Graphics Arts as a lecturer. She has carried out research in the area of printed paper optics.

Višnja Mikac Dadić obtained her Bachelors Degree in Physics from the University of Zagreb in 1968. and Masters Degree in Biophysics in 1973. from the University of Zagreb, Croatia. Since 1981. she has worked at Faculty of Graphics Arts. She belongs to Department of Physics of Faculty of Graphics Arts as a lecturer. Her current research interests include study of the printed surfaces examined by optical methods.

PhD Zdenka Bolanča is professor and head of the Department for Ecological Engineering at the Faculty of Graphic Arts, University of Zagreb. She is associate member of the Crotian Academy of Engineering. Professor has been the head of research Projects of the Croatian Ministry of Science and Technology.