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LIGHT FASTNESS OF COLOUR OF NOT DYED AND DYED PAPER PULPS

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SYNOPSIS. The article reveals the results of the research conducted on colour light fastness of paper pulp. The research involved the use of bleached softwood and hardwood chemical pulps, bleached chemithermomechanical pulp – not dyed and dyed with blue cationic direct dye. The question of colour change is discussed.

KEY WORDS: softwood chemical pulp, hardwood chemical pulp, chemithermomechanical pulp, colour, dyeing, cationic direct dye

INTRODUCTION

The basic component of paper and cardboard is lignocellulosic pulp (usually 90-100% of the product weight), thus the proper selection of it has influence on majority of application properties and production costs of paper products.

Primer lignocellulosic pulp is the basic raw material in papermaking industry. These pulps are produced mainly from vegetable material, where wood is a dominant (89%), and non-wood materials make about 11%. Wood is therefore the elementary raw material used for the production of paper pulp and one may predict that this fact will not undergo considerable changes in a long time (Stanisławczyk and Stupińska 2000).

Fundamental factors that have influence on the usefulness of lignocellulosic pulps in production of paper products are, apart from the type of material, the method and conditions of pulp production (Gullichsen 2000, Lindholm and Kurdin 2000).

Production of paper pulp is concerned with wood processing – the material of compact fibrous construction – into pulp consisting of single fibers. This process is called pulping. The pulp obtained in this way form the primer lignocellulosic pulp. There are three methods of obtaining the lignocellulosic pulp: chemical, mechanical, and chemimechanical. They differ from one another *inter alia* with respect to the yield *per* wood: chemical pulps are obtained with 35-55% yield, mechanical – 91-99%, and chemimechanical with 65-99% (Wandelt 1996).

Due to the increase in wood prices and aiming at environmental protection, it is necessary to produce lignocellulosic pulp of possibly highest yield from wood and with appropriate optical and strength properties. Such pulps will more and more often replace the expensive low-yield chemical pulps. In case of pulps obtained with mechanical and combined methods, proper dyeing is particularly important, since the improvement of their brightness should be achieved without lignin removal – the component responsible for lignocellulosic pulp colour.

Colour is one of the most crucial parameters of paper products, frequently associated (though not always rightly) with appropriate quality features. Natural colours of paper and cardboards are the resultant of their components mixture: pulps, fillers, sizing agents, other process and functional chemical additives.

Natural colours of paper products do not always appeal to the observers' taste. Therefore, paper is dyed with various methods in order to achieve products of chromatic hues. Hue and dyeing intensity are adapted to demands of the recipients. Usually, the direct dyes are used for paper dyeing.

The initial wood material as well as pulping and bleaching methods exert influence upon the colour of lignocellulosic pulp. The colour of wood depends on a tree species, climate, and soil conditions in which the tree was growing, the age of the plant and its humidity, as well as on other factors. Sapwood trees has uniform, light tint in its whole section – ISO brightness from 60 to 67%. Pine chips have ISO brightness rating from 38 to 45%. Slight colour aberrations appear between lighter early wood and darker late wood. Young heartwood trees have homogeneous tint and – not earlier than reaching a certain age – the heartwood gains darker tinge in comparison with light sapwood. ISO brightness of dark tree species is below 20%.

Directly after being chopped down, the tree wood is quite bright and gets darker under the influence of light and oxygen, only after some time, especially in the first weeks of storing. Oxidation of non-cellulose components is the cause of this darkening. Such phenomenon is particularly observed for hardwood. Brightness of softwood stored for one year in the form of chips pile might be decreased by 2-4%, and in case of hardwood – even up to 20% (Olszewski 1972).

Paper lignocellulosic pulp, obtained from wood by means of different methods, are tinted to lesser or larger extent. The colour of unbleached chemical pulp ranges from yellowish to brownish and depends on the factors connected with chemical composition and wood properties, applied chemicals as well as on pulping conditions and further pulp handling (washing, sorting, drying). In order to brighten the colour, lignocellulosic pulp undergoes bleaching processes. The level of the resultant brightness is dependent on delignification degree of the pulp. This indirectly affects its susceptibility to dyeing and colour reversion under influence of light and other external factors (Alén 2000).

In alkaline methods of wood delignification, we obtain brown chemical pulp, characterized by ISO brightness of approximately 25% lower than the brightness of the initial material. This proves that during the process there are reactions that lead to formation of new chromophors, which strongly absorb visible light (Holah and Heitner 1992).

The colour of lignocellulosic pulp after sulphate pulping is also influenced by metal ions diffusion, caused by the contact of the pulp with metal elements of the equipment. This additionally exerts impact on the colour of paper pulp as a result of complex bonds of chromophor heavy metal ions with thiolignin, formed as a result of pulping. Also the production water used for pulp washing contains some amounts of dissolved metal salts which affect the pulp colour. Some ions, such as Fe^{3+}, are present already in wood material.

To improve aesthetical value of lignocellulosic pulp and achieve high and enduring brightness, the pulp is exposed to bleaching. In this process, lignin is nearly completely removed from the pulp. Therefore, the bleaching is actually a further delignification, initiated during wood pulping. During bleaching other coloured substances in pulp are discoloured as well. Bleaching of high-yield pulp does not aim at lignin removal. In this case only the coloured substances become discoloured. The colour of paper pulps undergoes disadvantageous changes while being used, especially when exposed to light.

MATERIAL AND METHODS

Due to increasing importance of bleached chemithermomechanical pulps in production of graphic paper, there have been tests concerning the influence of this kind of lignocellulosic pulp on optical properties, that is: colour, brightness, and endurance of these factors upon usage. Comparison has been made between colour of softwood and hardwood chemical pulps as well as the bleached CTMP. Furthermore, there has been research on susceptibility of these pulps to dyeing, by the example, of blue cationic direct dye. In tested undyed and dyed pulps their light fastness has been determined.

Experimental materials

– paper pulp in form of dried sheets delivered by domestic producers; their properties are depicted in Table 1,

– blue cationic direct dye.

Cationic direct dye was applied, since this type of dyes are known to completely retain on paper fibers.

Research methodology

Pulp beating was carried out on the laboratory scale in the Valley's beater to freeness of 30°SR, according to standard PN-ISO 5264-1:1999: "Pulps. Laboratory beating. Part 1. Valley beater method". The CTMP freeness was 30oSR. Suspension of 2.5% was made from recycled pulp and water.

The dyes were added to a 2.5% pulp suspension at temperature of 20°C, with pH approx. 7.5. The contact time of dyeing substances with the pulp amounted to 10 minutes. The chemical additives were not added on purpose. The amount of the substantive dye was 0.5 and 5% based on bone dry pulp (b.d. pulp). Paper sheets

Table 1. Properties of pulps

Properties	Type of pulp		
	bleached softwood chemical pulp A1	bleached hardwood chemical pulp A2	bleached chemi-thermomechanical pulp A3
Apparent density [g/cm^3]	0.65	0.61	0.41
Specific volume [cm^3/g]	1.54	1.64	2.44
ISO Brightness [%]	88.2	89.08	68.57
Colour difference ΔE^* with reference to white standard	4.0	6.6	8.4

of approx. 80 g/m^2 were made in laboratory conditions using the Rapid-Köthen apparatus, according to standard PN-EN ISO 5259-2:2001: "Pulps. Preparation of laboratory sheets for physical testing. Part 2. Rapid Köthen method". Residual dye content in the white water was determined calorimetrically with the Perkin Elmer Lambda 40 apparatus in relation to the model solution and it was determined how large amount of the used dye was not absorbed by the pulp.

Before testing, the samples were conditioned, according to standard PN-EN 20187: 2000 "Paper, board and pulp – Standard atmosphere for conditioning and testing and procedure for monitoring the atmosphere and conditioning of samples".

Colour parameters were determined with the SpectroEye apparatus produced by the GretagMacbeth Company (lighting illuminant D65, observer 10°), according to the following standards: TAPPI T 524 om-94: "Color of paper and paperboard (d/0° geometry)" and ISO 2470:1999: "Paper and board. Measurement of diffuse blue reflectance factor (ISO brightness)".

Light resistance was checked exposing samples on the Xenotest apparatus, according to standard PN-ISO 105-B02: 2006: "Textiles. Test for colour fastness. Part B02: Colour fastness to artificial light: Xenon arc fading lamp test". Due to the significant differences in the resistance to light between tested samples, colour change was tested after a five-hour-exposure (resistance to light in ISO scale – approx. 3).

For the pulps after light exposure, colour change ΔE^* in the CIELAB system has been examinated, according to standard PN-EN ISO 105-A05:2000: "Textiles. Tests for colour fastness. Part 05. Instrumental assessment of change in colour for determination of grey scale rating". Additionally, the visual colour change has been evaluated with reference to grey scale, according to standard PN-EN 20105-A02: 1996 "Textiles. Test for colour fastness. Part A02. Grey scale for assessing change in colour".

RESULTS

A1 and A2 pulps had more or less the same light reflection curves, and their colours were very similar. BCTMP was characterized by high absorption in the range of blue colours and light reflection coefficients in the range of yellow colours approaching slightly A1 and A2 pulps (Fig. 1).The colour of BCTMP was significantly moved towards yellow colours (Fig. 2 and Table 2).

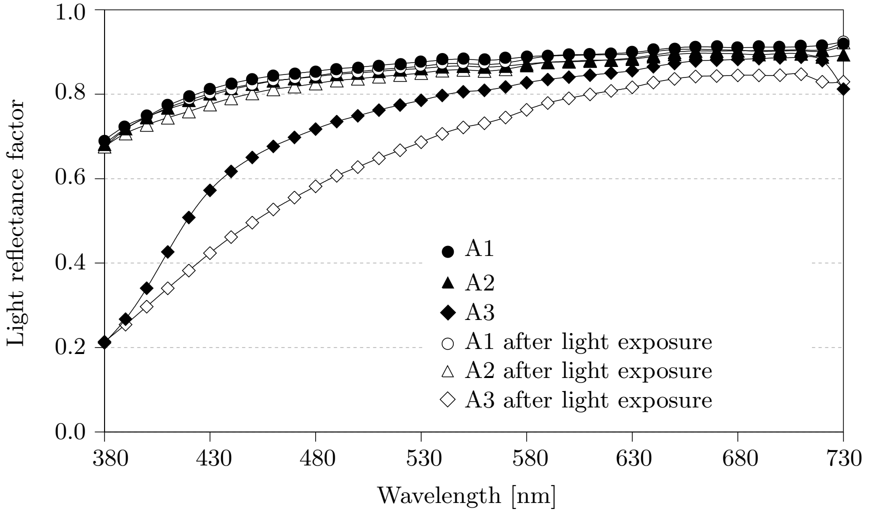

Fig. 1. Light reflectance curves of paper pulps before and after light exposure: A1 – bleached softwood pulp, A2 – bleached hardwood pulp, A3 – bleached chemithermomechanical pulp

Table 2. Colour difference ΔE^* of coloured pulps with reference to white standard

Pulp	Content of dye to pulp [%]	Colour difference ΔE^* with reference to white standard
Bleached softwood chemical pulp (A1)	0	4
	0.5	31.4
	5	57.8
Bleached hardwood chemical pulp (A2)	0	6.6
	0.5	29.8
	5	58.7
Bleached chemithermomechanical pulp (A3)	0	8.4
	0.5	28.0
	5	50.8

After the light exposure of sheets, the light reflectance decreased in all pulps (reflection curves were situated lower). The largest change was observed for light reflectance of pulp A3 (BCTMP) (Fig. 1). This resulted in change of paper pulp

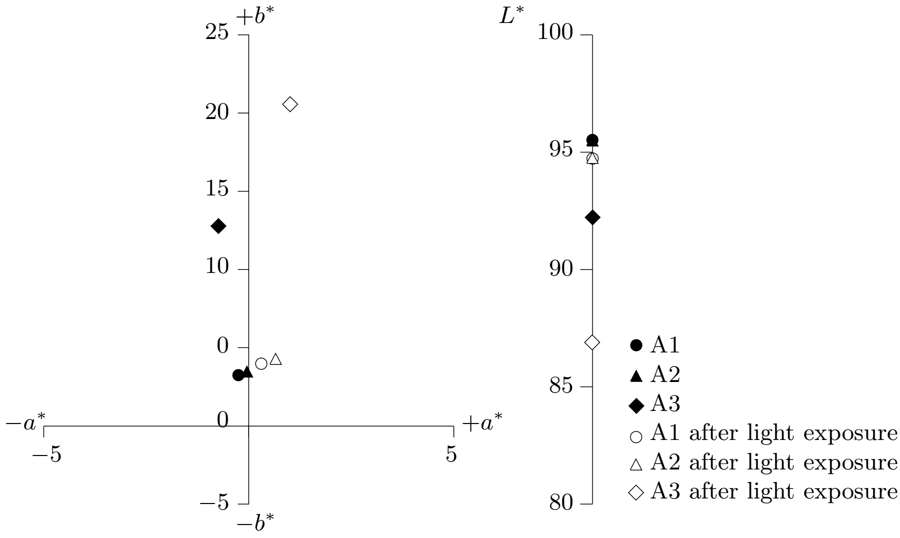

Fig. 2. Chromaticity coordinates of paper pulps before and after light exposure: A1 – bleached softwood pulp, A2 – bleached hardwood pulp, A3 – bleached chemithermomechanical pulp

colour (Fig. 2). In the research conditions, colour change was visible only to an experienced observer ($\Delta E^* < 2.1$), whereas the colour of BCTMP changed considerably into yellow ($\Delta E^* > 11.6$; Table 2).

Reflectance curves of dyed pulp are depicted in Figures 3, 4, and 5. Maxima of light reflectance in blue range (wavelength of 430 nm) and minima of light reflectance in yellow range (wavelength of 610 nm) are situated lower on the dyed pulp A1 and A2 curves than on the dyed BCTMP curves. This indicates higher colour saturation of the dyed chemical pulp than that of the dyed BCTMP.

Analysing *Lab* diagrams (Fig. 6) and colour change ΔE^* with reference to white standard (Table 3), it has been stated that the colours of dyed softwood chemical pulp (A1) are slightly more intense (more distant from the achromatic point of *0,0* coordinates) than the colour of dyed hardwood chemical pulp (A2). This phenomenon is probably related to bigger volumen of the hardwood sheet than the softwood one – and thus more light undergoes dispersed reflection in pores of fiber-matt made of hardwood pulp than of the other one. Colour change ΔE^* between these two pulps was a little lower than 4. So it could be seen only by an experienced observer.

In comparison with chemical pulp, the intensity of dyed BCTMP (A3) was far lower. BCTMP has yellowish colour itself and it additively adds to the dye colour, changing its hue. Dyeing this pulp with blue dye – with only little amount of it – led to shifting the colour to achromatic colour (white – chromaticity coordinates a^* and b^* approached *0,0 values*). Only by adding more dye, blue colours were obtained, but less intensive than for dyed chemical pulps. Such behaviour of BCTMP can be explained by light refractive index of lignin – higher than light refractive index of cellulose. That is why less light – that should activate the dye – reaches particles of the dye in case of BCTMP samples.

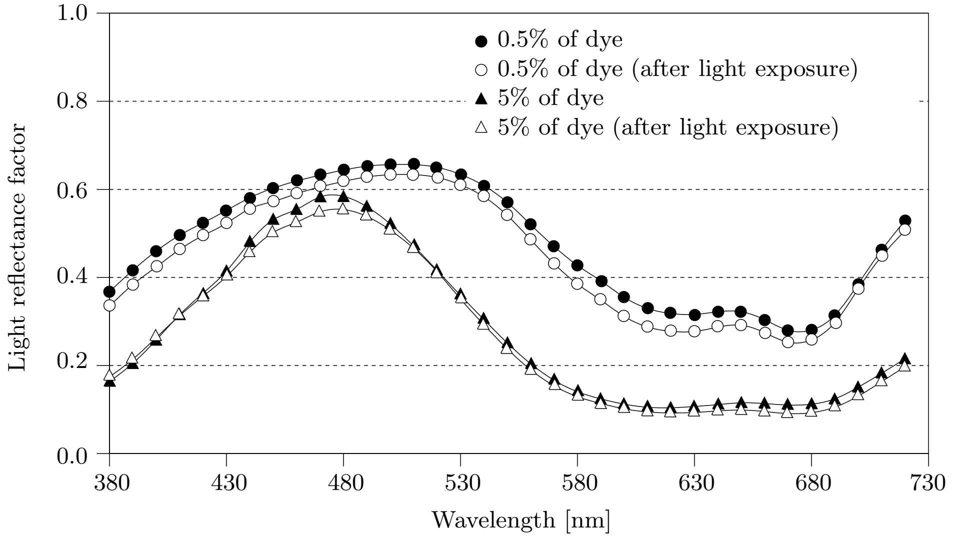

Fig. 3. Light reflectance curves of paper pulp A1 (bleached softwood pulp) before and after light exposure); level of blue cationic direct dye: 0.5% and 5% based on b.d. pulp

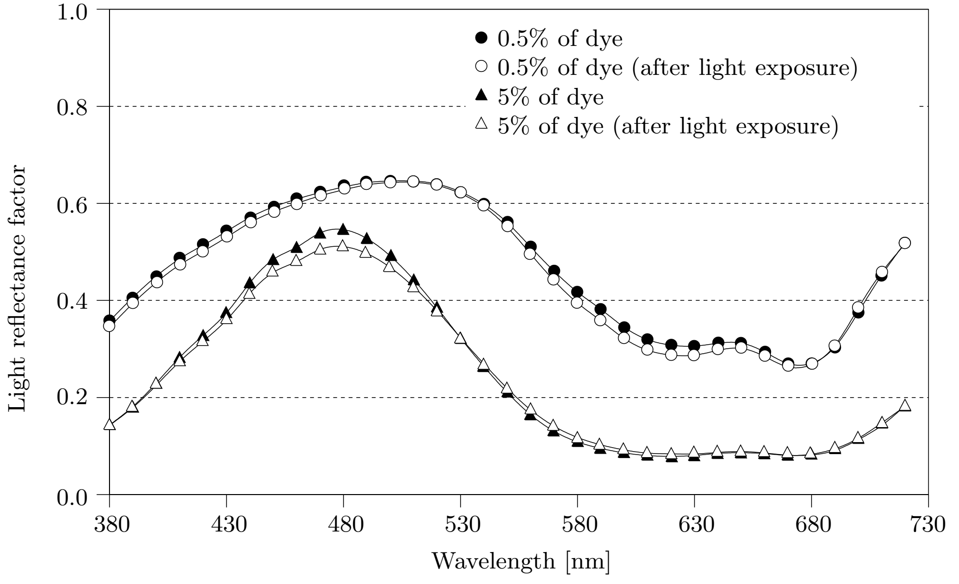

Fig. 4. Light reflectance curves of paper pulp A2 (bleached hardwood pulp) before and after light exposure); level of blue cationic direct dye: 0.5% and 5% based on b.d. pulp

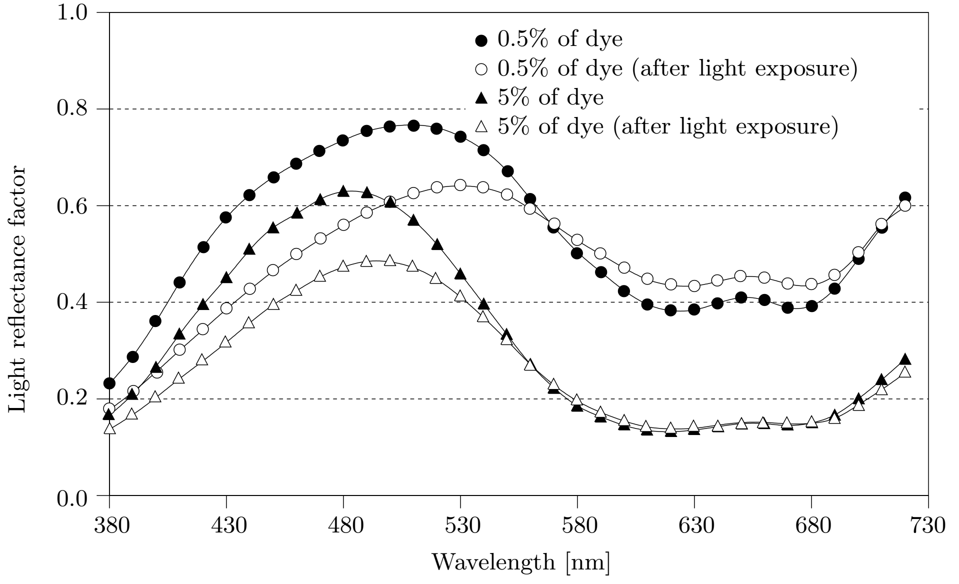

Fig. 5. Light reflectance curves of paper pulp A3 (bleached chemithermomechanical pulp) before and after light exposure; level of blue cationic direct dye: 0.5% and 5% based on b.d. pulp

Table 3. Colour change ΔE^* of pulps before and after light exposure

Pulp and dye level, percentage of b.d. pulp	Colour change		
	ΔE^*	GS_C grey-scale values	qualitative change of colour
Bleached softwood chemical pulp (A1)			
0	2.0	4	Y
0.5%	0.6	4	W
5%	0.9	4	W
Bleached hardwood chemical pulp (A2)			
0	1.5	4	Y
0.5%	1.4	4	W
5%	1.3	4	W
Bleached chemithermomechanical pulp (A3)			
0	13.7	1	Y
0.5%	18.8	1	G
5%	13.4	1	G

ΔE^* – CIELAB colour difference; GSC – grey-scale values; Y – more yellow, G – more green, W – less intense.

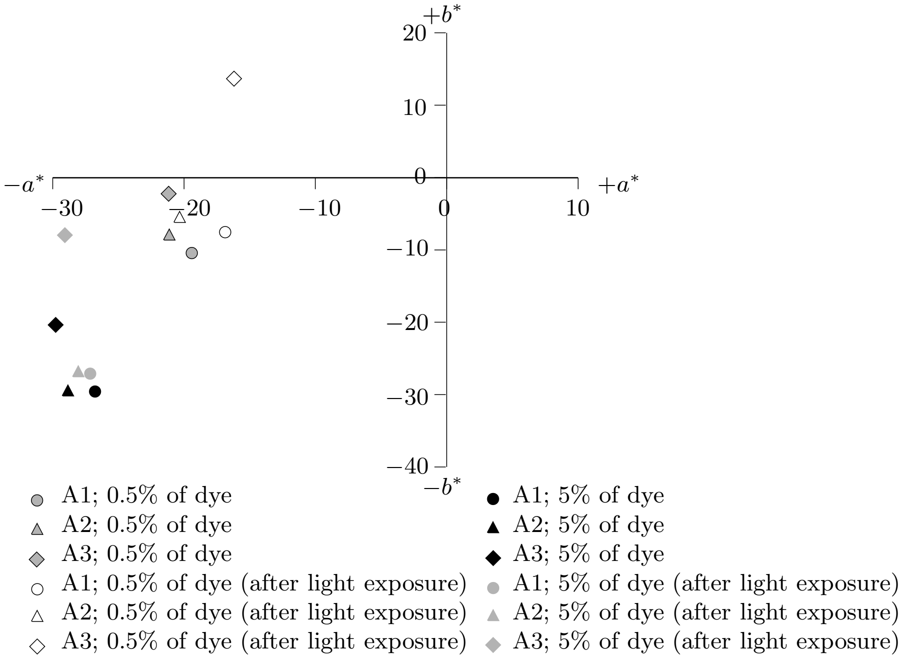

Fig. 6. Chromaticity coordinates of paper pulps before and after light exposure: A1 – bleached softwood pulp, A2 – bleached hardwood pulp, A3 – bleached chemithermomechanical pulp; level of blue cationic direct dye: 0.5% and 5% based on b.d. pulp

Addition of dyes has influence on photostability of dyed pulps. Differently from the undyed pulps, in case of the dyed lignocellulosic pulps, light fastness of colour was clearly dependent on the type of paper pulp and the amount of the added dye (Fig. 6 and Table 3). However, it was not only the light fastness that influenced the colour change, but also the alteration in lignocellulosic pulp colour. The least fading was observed in the dyed chemical pulp (A1 and A2), whereas the greatest vanishing in samples of BCTMP (A3). In case of the latter, not only the dye colour was vanishing, but also the pulp itself changed its colour into yellowish. That was connected with the modification of chromophore groups in the lignin.

Because of greater quality change of colour in case of dyed BCTMP, one can propound that the dye particles penetrate inside the fibers of BCTMP to lower extent than the fibers of chemical pulp. More light reaches the surface of lignocellulosic fibers than their interiors. The dye particles located on the surface are much more vulnerable to light radiation energy and react to the ambient conditions more easily (mainly to oxygen), changing construction and ability to absorb visible radiation. This in turn results in vanishing or change of the colour. At the same time, some coloured (yellowish-brown) chromophore groups are formed in the lignin, under the influence of light. This leads to increase of light reflectance in the yellow range, as well as decrease of it in the blue range, which causes the colour change of the tested products.

CONCLUSIONS

Study on light fastness of pulps containing BCTMP has demonstrated their high tendency to yellowing under the influence of sunlight. This may limit the usage of high-yield lignocellulosic pulps for high-quality papers, since these papers are expected to exhibit good colour stability. However, susceptibility to colour changes is not crucial for paperback editions, newspapers, packaging, and other publications of short life.

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