

The Influence of Pulp on the Colour of Dyed Papers

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Abstract

The dyeability of bleached chemical pulps, bleached chemithermomechanical pulp and deinked pulp with anionic and cationic direct dyes was investigated. It was found that direct dyes may be used for mechanical and recycled pulps to reduce the cost of the paper manufacturing process by the application of cheaper semi-finished fibrous products. However, the colours attained differ from the colour of dyed chemical pulp. To obtain the required colour, we needed larger amounts of dye, but in this way the savings obtained by using cheaper pulp grades may be wasted.

Key words: bleached cellulose pulp, bleached chemithermomechanical pulp, deinked pulp, colour, direct dyes.

reducing the amount of wood required for the same volume of paper.

Observers do not always like the natural colour of paper products, which is why paper is dyed using different methods to obtain products with chromatic hues ranging from bright pastel to dark saturated hues. The hue and intensity are adjusted to the requirements of customers.

On an industrial scale, papers are usually coloured by adding a colouring agent to the paper stock at the preparation stage. Almost 95% of all dyed paper is prepared in this way [1, 2]. For this purpose direct (anionic and cationic) as well as acidic and basic dyes are used. The process of dyeing in the stuff is the most efficient because the dye penetrates all the fibres of the paper. When selecting the dye, closer attention should be paid to its tendency for white water colouring resulting in difficulties when switching over to the production of paper with a different colour, as well as making waste water management more problematic. Growing ecological concerns prevent the usage of substances which may cause a risk for the environment, specifically dyes, as well as interim and final products of their biodegradation.

The dyeing mechanism of papermaking cellulose fibres is complicated and has not been entirely explored yet. Apart from various forces retaining dyes on fibres, an important role is played by the physicochemical properties of dyes and dyed fibres, as well how they behave in water.

During the dyeing process, dyes interact physicochemically with fibres. Forces binding a dye with a fibre can be of intermolecular or ionic nature resulting from

electrostatic charges. A dye may also be precipitated on the fibre surface [3, 4].

Dye binding with intermolecular forces takes place as a result of co-operation between “ π ” electrons of the dye with electrons of the cellulose hydroxyl group. Anionic direct dyes work according to the same rule. Van der Waals forces, hydrogen bonds, and the aggregation ability of dyes within the amorphous regions of fibers are the most important types of direct dyes-cellulose interactions. Suitable affinity of dyes to cellulose fibers is usually ensured by increasing the size of dye particles, maintaining – at the same time – a flat and linear structure of the particles.

To obtain high affinity, it is important that the dye molecule is stretched and lain in the same surface as several chemical groups, making it easier for the dye molecule to be solved in water.

Ionic strengths arise between the negative centre of cellulose fibres and cationic products, such as cationic direct dyes. The dyes can also be precipitated on fibres as deposits formed as a result of the reaction with the acid, aluminium sulfate or fixing agent.

Research works on pulp dyeing

The specialist literature contains articles on results of dyeing bleached chemical pulps with direct dyes. However, it is difficult to find descriptions of the influence of high-yield (with a high content of lignin) and recycled pulps on dyeing results with the use of these dyes, despite the fact that it is said that direct dyes are useful in the necessary dyeing of papers containing mechanical, semi-chemical and recycled pulp grades. The application

■ Pulp dyeing

The growing demand for dyed paper has forced the development of new technologies for the production of these grades. Paper colour not only improves the aesthetic aspect of the product, but also in a practical way i.e. better segregation of files, a reduced sight tiring contrast between paper whiteness and black print as well as attention attraction.

Printing and writing paper is made from bleached grades of chemical soft- or hardwood pulp as well as bleached mechanical and recycled pulp. The quantity of these pulps and their brightness have an impact on the final optical properties of the paper produced. When only bleached pulps are used, manufacturing costs go up along with the paper price. The environmentally friendly approach involves the application of larger amounts of high yield pulps and paper recovered in the manufacture of these products, thereby

Table 1. Fibrous composition and chromacity of the model paper pulps: ^{a)} CIE Whiteness below 40, e.g. lower limit for white paper pulps and papers.

Pulp No.	A1	A2	A3	A4
Fibrous composition	bleached sulphate softpulp	bleached sulphate hardpulp	bleached chemithermo-mechanical pulp (CTMP)	deinked pulp (DIP)
Properties:				
ISO Brightness, %	88.2	89.08	68.57	68.83
CIE Whiteness	78.0	76.7	(22.32) ^a	45.97
CIE Tint	-1.42	-0.51	-4.62	-2.34
Chromacity coordinates:				
L*	96.0	95.37	91.70	87.81
a*	+ 0.22	- 0.24	- 0.70	+0.12
b*	+2.69	+2.44	+13.34	+5.3
Colour difference ΔE^* with reference to white standard	4.8	5.2	15.7	13.3

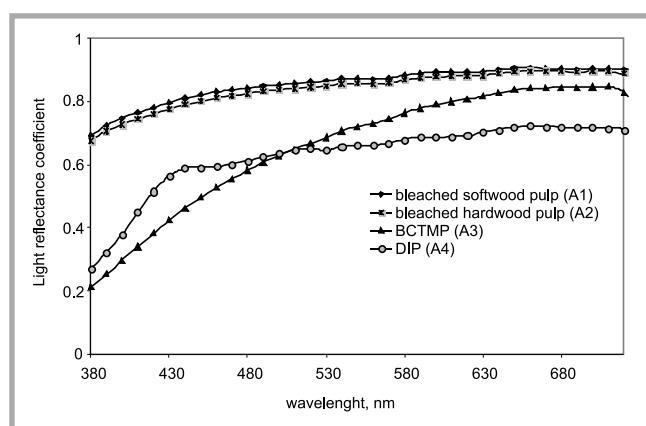


Figure 1. Light reflectance curves of pulps A1 – A4.

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

Colour parameters were determined with SpectroEye apparatus produced by the company GretagMachbeth (lighting illuminant D65, observer 10°), according to the following Standards: PN -EN ISO 105-J01:2002 "Textiles. Tests for colour-fastness. Part J01: General principles for measurement of surface colour", ISO 2470:1999 "Paper and board - Measurement of diffuse blue reflectance factor (ISO brightness)", PN-ISO 11475: 2002 "Paper and board. CIE whiteness, D65/10° degrees (outdoor daylight)".

The influence of pulp grade on the colour of paper products containing direct dyes

The following model pulps were used in the research: bleached sulphate softwood (A1), bleached sulphate hardwood (A2), bleached chemithermomechanical (A3) and deinked pulp (DIP) (A4). The colour characteristics of the pulps is shown in Table 1 and Figures 1 & 2.

Pulps A1 and A2 had more or less the same light reflectance curves, and their colours were very similar. BCTMP pulp was characterised by high absorption in the range of blue colours, and light reflectance coefficients in the range of yellow colours, slightly approaching those of pulps A1 and A2. The colour of BCTMP had significantly moved towards the colour yellow.

of these pulp grades reduces costs owing to the use of cheaper semi-products.

Chemical pulp is obtained from the chemical cooking of wood. The yield of this pulp with reference to wood is about 50%. Chemothermomechanical pulp (CTMP) is mechanical pulp produced by treating wood chips with chemicals and steam before mechanical defibration. This pulp is produced at a yield of > 85%. Deinked pulp (DIP) is waste paper from which printing ink has been removed.

The aim of the research focused on examining the impact of pulp grades on dyeing with the direct dyes.

Methodology of the experimental tests

During the experiments, the following materials were used:

- fibrous pulps: bleached softwood and hardwood sulfate pulps, bleached chemithermomechanical pulp (BCTMP) and deinked pulp (DIP),
- anionic direct dyes: Pergasol Blau 2R fl., Pergasol Rot 2B fl. and Pergasol Gelb 6G fl. (CIBA Specialty Chemicals Inc.),

- cationic direct dyes: Pergasol Turquoise F fl., Pergasol Rot F – 2B fl. and Pergasol Gelb F-6GZ fl. (CIBA Specialty Chemicals Inc.).

Pulp beating was carried out on laboratory scale in a Valley's beater to a freeness of 30 °SR, according to Standard PN-ISO 5264-1:1999. The BCTMP freeness was 30 °SR. A suspension of 2.5% was made from recycled pulp and water.

The dyes were added to a 2.5 % pulp suspension at a temperature of 20 °C, with a pH of approx 7.5. The contact time of dyeing substances with the pulp amounted to 10 minutes. Auxiliary agents were not added for this purpose. The amount of the direct dye was 0.5, 2.5, 5 and 10%, expressed in absolutely dry pulp. Paper sheets of approx. 80 g/m² were made in laboratory conditions with Rapid – Köthen apparatus, according to Standard PN-EN ISO 5259-2:2001. Residual dye content in the white water was determined by colorimetric measurements taken on a Perkin Elmer Lambda 40 spectrophotometer in relation to the model solution, and the amount of dye used which was not absorbed by the pulp was also estimated.

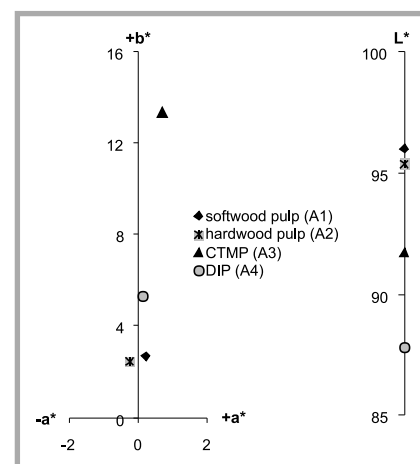


Figure 2. Chromacity coordinates of uncolored paper pulps A1 – A4.

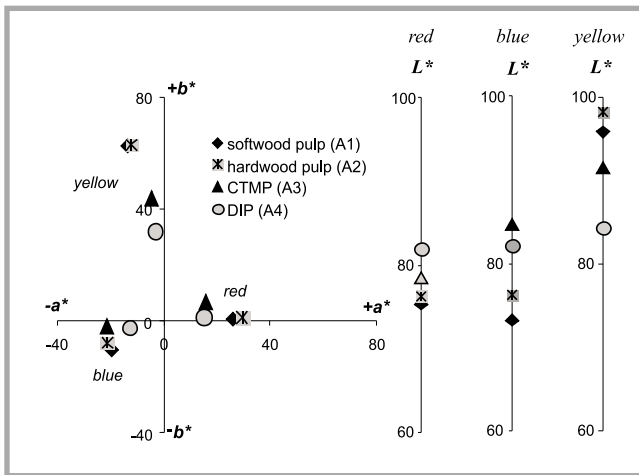


Figure 3. Chromacity coordinates of paper pulps A1 – A4 dyed with the use of cationic direct dyes; with a dye concentration of 0.5% on the weight of the dry pulp.

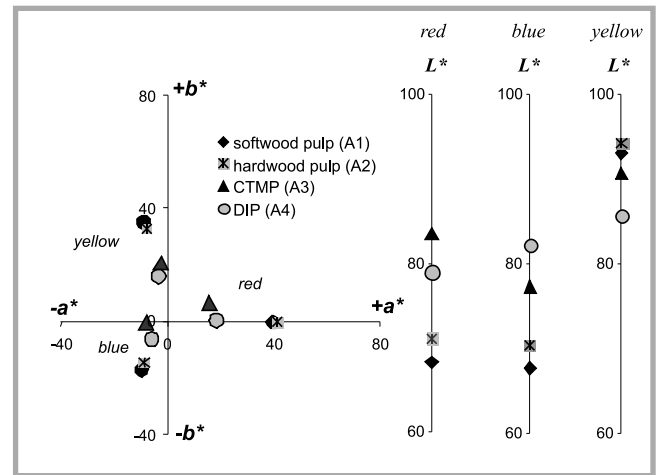


Figure 4. Chromacity coordinates of paper pulps A1 – A4 dyed with the use of anionic direct dyes; with a dye concentration of 0.5% on the weight of the dry pulp.

DIP had low brightness and low light reflectance coefficients in the entire range of colours, which shows that the residues of printing inks had not entirely been removed and had left the pulp grey hued. The characteristic peak with a wavelength of 440 nm shows that the fluorescent whitening agent was not entirely removed from this pulp either.

Hue and saturation depend on the dye type, which is why only the influence of various pulp types on colour parameters was compared; however, these colours were not compared to each other. It was concluded that with a small addition of a dye, the shade of softwood pulp (A1) is more intensive than the shade of hardwood pulp (A2), which is possibly was connected with the higher volume of softwood pulp; as a result less light underwent dispersed reflection in the pores of fibrous layers (Figures 3 and 4). With a large addition of the dye, the difference was almost indiscernible (Table 2).

The shade depth of pulp A3 (bleached CTMP) was much lower than in case of chemical pulps. The dyeing of this pulp type in particular, with small amounts of the blue dyes, made the colour shift towards achromatic colours (white) (Figures 3 and 4). Blue colours were obtained when a larger amount of the dye was added, but they were less intensive than the shades of chemical pulps (Table 2). Such behaviour is connected with a higher index of light refraction for pulp, which is why in these samples less light (which was supposed to activate the dye) reaches the dye molecules. Besides this, the bleached CTMP itself is of a yellow-

ish colour which adds to the colour of the dye, changing its hue. According to subjective estimations, the most attractive shades of this pulp were achieved with yellow dyes.

Dyeing recycled pulp (deinked pulp A4) did not bring good results due to the fact that residual amounts of printing ink caused a graying effect. In daylight the colour was also effected by the fluorescent whitening agent which remained in the pulp and made the pulp sheets

(coloured with small doses of yellow dyes) greenish as a result of mixing its colour with the dye colour. Besides this, horny secondary fibres could not attach molecules of the dyes as easily as in the case of primary fibres.

Colour saturation

Colour saturation of dyed pulps can be expressed based on figures obtained from the Kubelka – Munk formula. The formula is based on the relation between absorption coefficients K and scattering

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

Type of direct dye	Colour of dye	Pulp No.	Dye concentration % (on the weight of dry pulp)			
			0.5	2.5	5	10
anionic	red	A1	52.0	62.3	66.1	68.9
		A2	49.8	62.0	65.6	69.0
		A3	23.6	37.5	44.1	49.0
		A4	28.0	39.1	44.7	49.3
	blue	A1	38.0	51.4	58.7	62.6
		A2	34.2	52.0	59.1	63.9
		A3	19.5	28.0	30.7	39.0
		A4	24.0	36.6	43.0	47.0
	yellow	A1	34.1	52.2	61.7	66.9
		A2	38.3	57.0	61.4	68.2
		A3	22.7	28.3	32.6	35.2
		A4	21.6	29.0	33.5	38.0
cationic	red	A1	35.0	58.1	64.4	70.0
		A2	36.9	58.9	64.5	70.4
		A3	24.9	42.5	49.5	53.8
		A4	26.0	43.7	50.9	58.0
	blue	A1	30.8	51.6	57.1	62.8
		A2	32.8	53.1	59.7	63.7
		A3	17.6	35.2	39.3	46.4
		A4	22.2	43.1	50.1	57.6
	yellow	A1	64.1	81.4	84.8	89.5
		A2	64.1	92.5	86.2	89.9
		A3	44.9	69.2	76.2	85.9
		A4	36.0	64.8	73.0	74.7

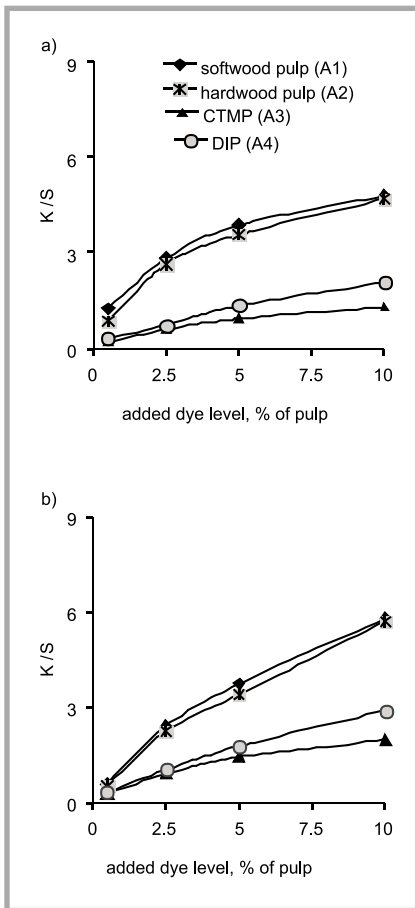


Figure 5. *K/S* values of paper pulps coloured with: a) anionic red direct dye, b) cationic red direct dye.

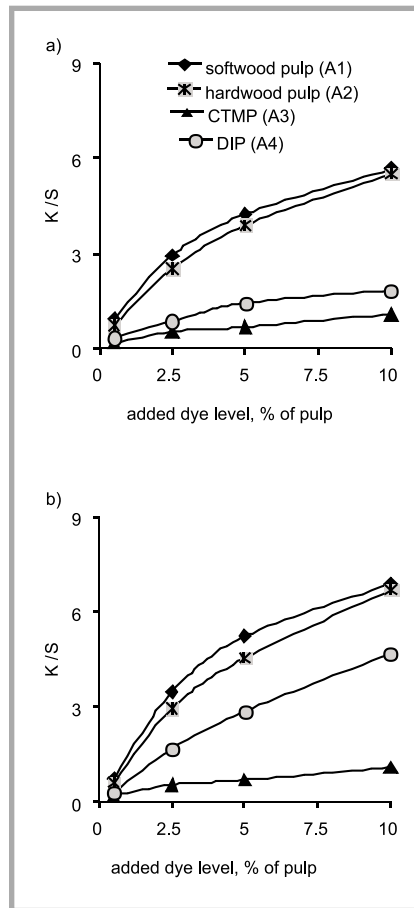


Figure 6. *K/S* values of paper pulps coloured with: a) anionic blue direct dye, b) cationic blue direct dye.

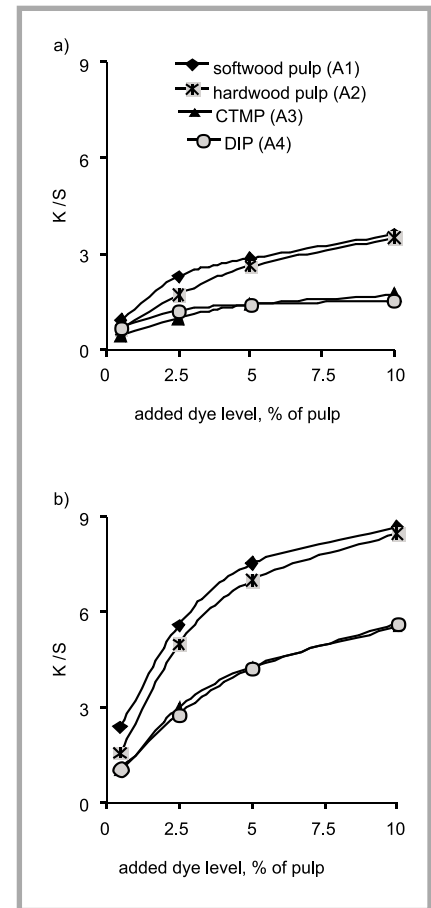


Figure 7. *K/S* values of paper pulps coloured with: a) anionic yellow direct dye, b) cationic yellow direct dye.

coefficient *S*, with coefficient *R* of light reflectance on a certain non-transparent object.

Colour saturation can be expressed as the relation of absorption coefficient *K* to scattering coefficient *S*. The higher the value of this relation, the better the colour saturation is. Absorption coefficient *K* depends on the type and amount of the dye in the fibre, whereas coefficient *S*

depends on the fibre surface and the pulp sheet structure. Figures 5-7 show the relation *K/S*, depending on the dose of the dye used and the pulp type.

To obtain equal colour saturation for/in the chemical pulps, a larger dose of direct dye would be needed for dyeing hardwood than that for softwood pulp. Bleached CTMP (model pulp A3) with a large lignin content had lower colour

saturation due to the higher light scattering coefficient. Therefore, dyeing this pulp type with direct dyes did not bring positive results. Only dyeing with the yellow cationic dye produced quite good colour intensity (Figure 7b); however, it worse than colour saturation of pulps A1 and A2. Recycled pulp dyeing (type A4) was better than in the case of bleached CTMP, but it was worse than that of chemical pulps and rather unattractive.

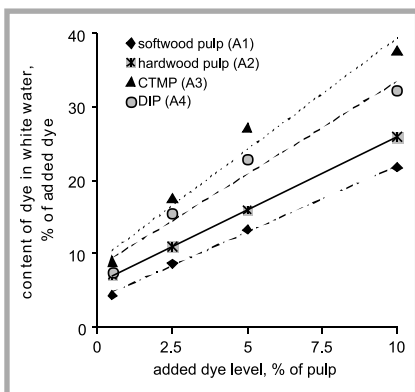


Figure 8. Influence of paper pulp type on the anionic red direct dye content in white water.

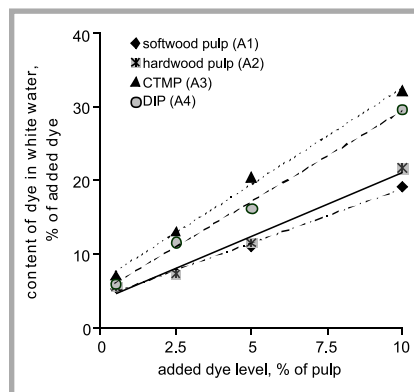


Figure 9. Influence of paper pulp type on the anionic blue direct dye content in white water.

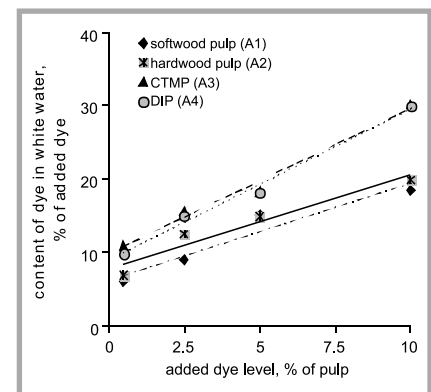


Figure 10. Influence of paper pulp type on the anionic yellow direct dye content in white water.

This was connected with light absorption by the residual amounts of printing ink present in this pulp.

Impact of pulp grade on white water colour

The cationic direct dyes showed a strong affinity for bleached chemical pulps. With the use of cationic dyes, high colour saturation of pulp was obtained, without any losses in white water (colouration was non-measurable). With the same amount of dyes added, colour saturation of model pulps A1 and A2 was lower in the case of anionic direct dyes, whereas colouration of the white water (Figures 8, 9 and 10) was clearly seen with the naked eye. The white water was strongly coloured with saturated colours, ie. with large dye dosage. Model pulp A3 (bleached CTMP) had a lower dyeability with anionic dye, whereas the white water was not coloured when the pulp was dyed with cationic dyes. Deinked pulp behaved in a similar way (pulp A4). When using anionic dyes, the white water quality can be improved by additional application of cationic fixatives.

Summary

Direct dyes may be used for mechanical and recycled pulps, thereby reducing paper production costs through application of cheaper fibrous semi-products. However, the colours obtained are different when compared with the colour of dyed chemical pulps. To obtain the required colour, a larger amount of dye should be used, which, on the other hand, may decrease savings obtained through the application of cheaper pulp grades.

References

1. Szwarcztajn E., *Przygotowanie masy papierniczej*, WNT Warszawa 1991.
2. Roberts, J.C., *Paper Chemistry*, Blackie Academic and Professional, London, Great Britain 1996.
3. Beck U., Müller F., Mummenhof P., *Färben und Aufhellen – Echtheits- und Ökologieaspekte im Neutralbereich*, *Wochenbl. Papierfabr.* 116, nr 15, pp. 529 - 534 (1983).
4. Arnold E., Martin G., *Einfluß der Faser- und Füllstoffe auf die Färbung mit Direktfarbstoffen*, *Wochenbl. Papierfabr.* 130, nr 9, pp. 459 - 462 (1997).

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