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New Eco-friendly Method for Paper Dyeing

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Abstract
For economical and environmental reasons, the paper industry has shifted the production of paper products towards dyed products made from pulp grades with a high content of recovered paper. The basic method for dyeing paper products is pulp colouring with direct and basic dyes. Disadvantages of this method include coloured white water and so-called „bleeding" processes when using those products. „Bleeding" processes are undesired when using tissue products. A new eco-friendly method for dyeing pulp with adducts of reactive dyes and selected cationic aliphatic polyamine compouds was developed. A reactive dye is added to refined pulp and then a cationic polyamine compound. The dyeing substance is adsorbed on the entire surface of refined cellulose based semi finished products in a water medium with a pH near to neutral. After web consolidation, an uniform dye penetrated paper product is obtained, with high colour life and strength. Reactive dyes contain 3'-carboxypyridine-1,3,5-triazine systems that react with cellulose in a medium near to neutral and at a temperature similar to web drying. As polyamine compounds, polycondensates of guanidine with hexamethylene-1.6-diamine and octamethylene-1,8-diamine were used. As was proved by a test done on coloured paper, these compounds are characterised by bactericidal and fungicidal properties, which are advised for tissue paper. The polyamine compounds mentioned cause the quantitative adsorption of dyes on cellulose based pulp, increasing the retention of cellulose fibre fines, and the white water is practically colourless. In principle, this dyeing method does not change the strength, optical, structural and dimensional properties of selected paper products.

Key words: *paper dyeing, reactive dyes, retention agents, biocidal properties , pulp dyeing, reative dye derivatives, 3'-carboxypyridinetriazine.*

Introduction

Economic and environmental aspects have made the world's paper industry concentrate on the manufacture of dyed products made from pulp grades with a high content of recovered paper [1]. The production of white papers demands significantly more raw materials per final product. Apart from that more effluents are generated.

Colour catches the eye. Aside from aesthetic aspects, colour does not make the eyes feel tired. Coloured paper products are used in print advertising as newsprint, packaging and other commonly used products.

Paper manufacture is a complex technological process consisting of the following stages: the preparation and refining of fibrous, semi-finished products, stock preparation, paper web consolidation (forming, pressing and drying), and paper finishing [1 - 4].

In the production process, three methods for paper dyeing are used [5 - 8]:
- dyeing in stuff,
- application of a dyeing substance to the surface of the paper web on a calender,
- coating - adding a colouring substance to pigment and adhesive paste which is used to coat the paper web (coating machine).

The method most commonly used for paper dyeing is dyeing in stuff (90 - 95% of total production). The dye is applied at room temperature of 20 - 25 °C for 0.5 - 3 min. An advantage of this method is the adsorption of dye molecules on the entire surface of cellulose fibres. After paper web drying, an entirely dye penetrated paper product is obtained.

The following groups of dyes are used for dyeing in stuff [7 - 9]:
- direct: anionic and cationic (63%),
- acidic (7%),
- basic (30%),
- coloured pigments,
- sulphuric.

Anionic and cationic direct dyes are the most important group of dyes used for paper colouration with this method. Between an anionic direct dye containing anionic sulpho groups and negatively ionised cellulose fibre, a barrier of electrostatic repulsion is formed preventing the dye from exhaustion from the bath. A disadvantage of this group of dyes is often coloured white water and the so-called bleeding effect appearing when using paper products. Coloured white water also makes environmental and technological problems.

The high affinity of the cationic direct dyes to papermaking pulp is connected with the positive charge of molecules. The colour obtained is intensive, however not vivid enough. There are also problems with the solubility of dyes in an aqueous medium.

Basic dyes are used for the coloration of paper grades containing a large amount of lignin. In most cases the colour obtained has low light fastness.

Reactive dyes are not used for dyeing papermaking pulp. In the process, cyanuric and vinyl sulphonyle dyes do not form covalent bonds with the cellulose. Optimal parameters for reactions with the hydroxyl groups of cellulose are t = 70 - 80 °C & pH 10 - 12 [9, 10].

On the basis of literature [11,12] and own research projects [13,14] aimed at finding reactive dyes which are environmentally friendly and useful for dyeing cellulosic fibres in a neutral medium, the authors turned their attention to reactive dye derivatives of 3'carboxypyridinetriazine (Kayacelon React, Nippon Kayaku, Japan). Dyes of this type are able to react with the hydroxyl groups of cellulose in a neutral medium at a temperature of 100 - 130 °C, that is at that of paper web drying (***Figure 1***, see page 122). The process of dyeing paper products with dyes containing two 3'carboxypyridinetriazine groups is closely connected with the production technology of those products. The method of determining of the bonding coefficient has been fully discussed in earlier publications [12, 13].

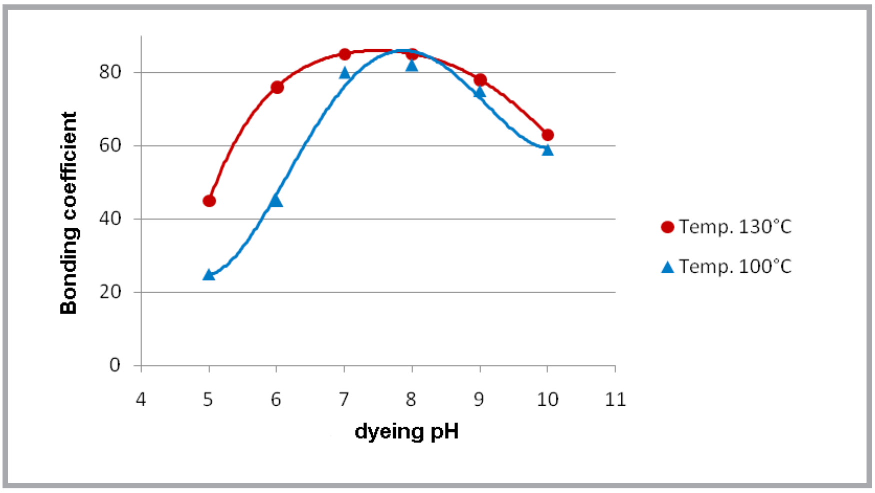


***Figure 1.** Effect of pH and temperature on the bonding coefficient of dye with cellulose.*

***Table 1.** Spectrophotometric properties of dyes.*

Dye symbol	Spectrophotometric properties		Colour
	λ_{max}, nm	ε_{max}, dm³/(mol·cm)	
B-1	389.9	39,500	yellow
B-2	405.0	37,200	yellow
B-3	507.8	38,700	red
B-4	511.4	38,100	blue red
B-5	588.1	37,900	dark blue
B-6	625.0	47,300	green

Experimental

Dye synthesis

A group of compatible 3'-carboxypyridinetriazine reactive dyes was selected for testing and then synthesised.

The synthesis of the dyes is based on the condensation of di(monochloro)triazine dyes [15] with nicotinic acid in an aqueous medium at a pH of 6.3 - 6.7 and temperature in the range of 85 - 90 °C for 3 - 6 h using a 50% surplus of nicotinic acid at a mole ratio to the dye [13]. All reactions were monitored by paper chromatography. (Whatman 3, eluent pyridine: 25% ammonium: 1% brine 1:1:8 by vol.). The dyes were extracted from the reaction medium by salting out with sodium chloride. The sodium chloride content in the dyes, dried at a temperature of 60 °C, was 25 - 60%. Spectrophotometric properties of the dyes are listed in ***Table 1***.

Pulp dyeing with reactive dyes

A new method for pulp coloration with adducts of reactive and cationic dyes of selected polyamine compounds was developed [16]. Kraft bleached hardwood pulp (SaBI) was refined to a freeness of 25 °SR in a laboratory Valley beater according to Standard PN-EN ISO 5264-1:1999. To the refined pulp, with a consistency of 0.3% of the absolutely dry mass at a temperature of 20 - 25 °C, a solution (20 g/dm³) of reactive dye was added in the amount of 1% of dry dye in relation to absolutely dry pulp and then a solution (20g/dm³) of polycondensate of hexamethyleno-1,6-diamine with guanidine in an amount ranging from 0.8% to 4% in relation to absolutely dry pulp, the pulp pH ranging from 6.5 to 7.0. The contact time between the dye and pulp solution ranged from 30 to 120 seconds from the moment of forming a test sheet of 75 g/m² on Rapid-Koethen (England) apparatus (acc. to Standard PN-EN 5259-

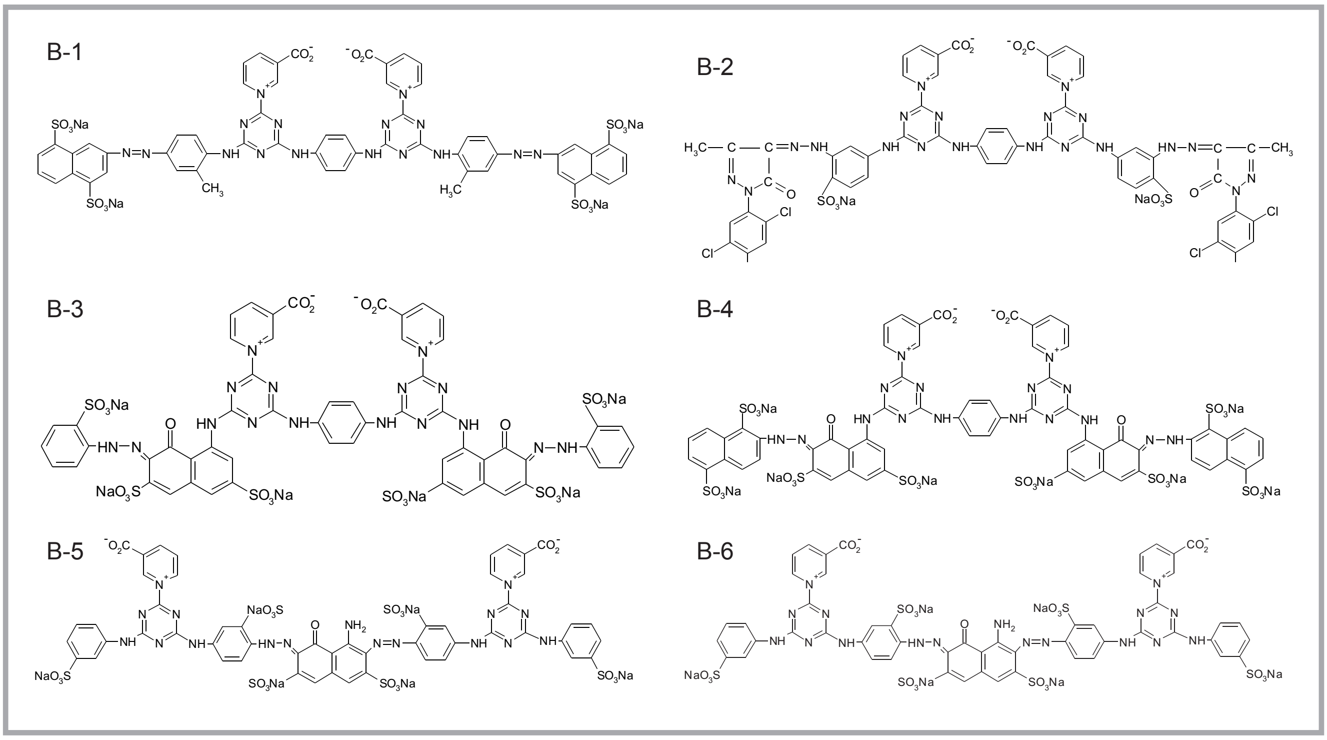


***Figure 2.** Structures of dyes used in the work.*

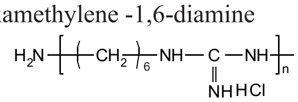
2:2001). The test sheet was dried in a dryer at a temperature of 130 °C [17].

The following pulp grades were dyed: hardwood, softwood, eucalyptus, deinked recycled pulp of different freeness values, SR value ranging from 11 to 65 ºSR (Schopper-Riegler).

Synthesis of poliamine retention compounds

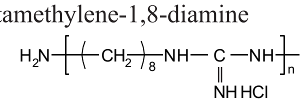
As retention compounds, guanidine copolymers were used with:

- hexamethylene -1,6-diamine



n ≈ 15

- octamethylene-1,8-diamine



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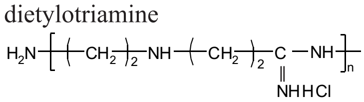
- dietylotriamine



n ≈ 15

Polyhexamethylene guanidine (PHMG) was obtained through a polycondensation reaction of guanidine with hexamethylene-1,6-diamine [18, 19]. As literature data show, depending on the process parameters i.e. the temperature, pressure, stoichiometry of substrates and reaction time, a product of linear or branched structure and adequate polymerisation degree is obtained [18,19]. PHMG was obtained using a 5% surplus of guanidine hydrochloride at a mole ratio to hexamethylene-1,6-diamine. Substrates were heated at 120 - 130 °C for 4 - 5 h, then heated up to 170 - 180 °C for 2 h and kept at such a temperature for 8 - 10 h (hardening of reaction mixture). Raw PHMG was purified by dissolving in water (a 50% solution) acidified with hydrochloric acid to a pH of 5.0 ± 0.1, and then precipitation of polymer from the solution was performed using caustic soda (alkaline pH on yellow indicator). A 50% solution of polymer in water acidified with hydrochloric acid to pH 6.0 ± 0.1 was produced. Polyoctamethylene guanidine (POMG) was obtained as a result of heating octamethylene-1,8-diamine with guanidine hydrochloride at 180 - 200 °C for 7 hours. An aqueous solution of polymer of 40% and pH 6.0 ± 0.1 was made. Additionally condensation of dietylotriamine with guanidine hydrochloride (PDETAG) at 160 - 170 °C for 10 h was carried out. A 50% solution of polymer in water corrected with hydrochloric acid to pH 6.0 ± 0.1 was made. Mass spectrometry MALDI TOF (Shimadzu, Japan) showed that the average molecular weight of polycondensate PHMG obtained was 2150 g/mole, for POMG – 2470 g/mole and for PDETAG – 1950 g/mole, which means approximately 15 moles in a chain.

Polyhexamethylene guanidine (PHMG) has biocidal and disinfecting properties [20 - 23]. Owing to its broad spectrum effect against pathogenic microorganisms (bacteria, virus, fungus, unicellular algae), it is used in:

- disinfectants in medicine,
- agents for drinking water conditioning,
- flocculants and agents capturing metal ions,
- components of cosmetics,
- biocides in paper technologies,
- air sterilisers and odour adsorbers.

The tests proved that polyoctamethyleneguanidine (POMG) also has biocidal properties. Limited biocidal properties are also shown by PDETAG.

Determination of the amount of retention compound

The amount of polyamine compound added to cellulose based pulp, required for entire dye retention and partial retention of fines, was determined experimentally by measurement of the electrokinetic potential of white water (Mütek PCD 02, Germany). The electrokinetic potential depends on the structure of the dye molecule and its concentration in a solution as well as on the grade of the cellulose based pulp and freeness value. The relationship between the electrokinetic potential of white water and PHMG is presented in ***Figure 3***. The dye amount added dye was 1% in relations to absolutely dry cellulose pulp.

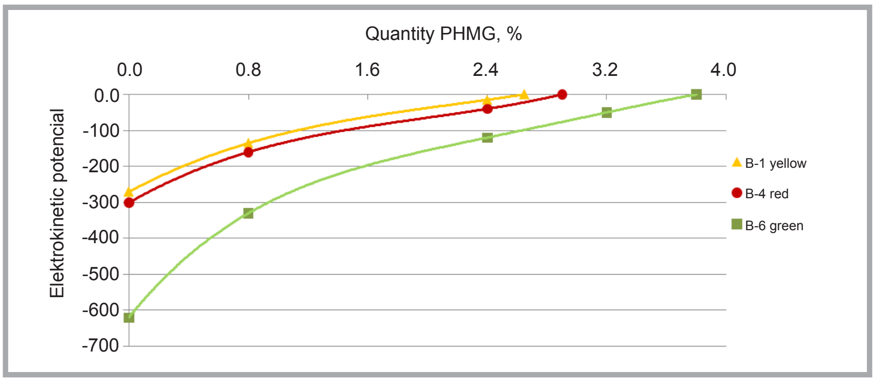


Figure 3. *Relationship between the electrokinetic potential of white water and PHMG, with a dye amount of 1% in relation to cellulose pulp.*

After adding the retention agent, dyes in the form of "dyeing systems" (adducts) are wholly deposited on the cellulosic fibres. The average molecular weight of adducts obtained by precipitation with a polyamine compound and determined with a MALDI TOF mass spectrometer (Shimadzu, Japan) was 6000 - 6500 g/mole. Additionally the content of fines in white water is significantly reduced (by 60 - 70%), and the fines left easily sediment.

Basic properties of dyed papers

After paper web drying at a temperature of 100 - 130 °C, dyed paper has high wet fastness („it does not bleed"). The dyes are permanently bonded with paper. From the paper sheets coloured with dyes of the Kayacelon React type, from 3% to 8% of the dye (spectrophotometric measurement, Spectrophotometer Jasco, Germany) were extracted by pyridine azeotrope (85% pyridine water solution) at a temperature of 80 °C. From the test sheets coloured with direct dyes of similar chemical structure and retention in fibres, from 27% to 30% of the dyes were extracted. In both cases, PHMG was used as a retention agent for paper coloration. The results show that covalent bonds are formed between the dye of the Kayacelon React type and hydroxyl groups of the cellulose pulp.

Bactericidal and fungicidal properties of dyed papers

Tests on bactericidal and fungicidal properties of dyed papers with reactive dyes in

Table 2. Antibacterial activity of papers tested.

Compounds contained in paper	Zone of inhibition, mm		
	Staphylococcus epidermidis	*Staphylococcus aureus*	*Escherichia coli*
Pure pulp 35 °SR	Growth under the test sheet		
PHMG 0.8%	2		No growth under the test sheet
PHMG 2.4%	3	4	
POMG 0.8%	1	2	
POMG 2.4%	2		
PDETAG 2.4%	1	3	Growth under the test sheet
PHMG 0.8% + red 1.0%	2	3	No growth under the test sheet
PHMG 2.4% + red 1%	4	5	
POMG 0.8% + red 1.0%	2	3	
POMG 2.4% + red 1%	4	5	
PDETAG 2.4% + red 1%	1	3	Growth under test sheet

Table 3. Fungicidal activity of papers tested

Compounds contained in paper	Zone of inhibition, mm	
	Candida albicans	*Aspergillus niger*
Pure pulp 35° SR	Increase under the sample	
PHMG 0.8%	No growth under the test sheet	
PHMG 2.4%	No growth under the test sheet	
POMG 0.8%	No growth under the test sheet	1
POMG 2.4%	No growth under the test sheet	2
PDETAG 2.4%	Growth under the test sheet	
PHMG 0.8% + red 1.0%	1	2
PHMG 2.4% + red 1%	1	3
POMG 0.8% + red	2	4
POMG 2.4% + red 1%	3	6
PDETAG 2.4% + red 1.0%	Growth under the test sheet	

the presence of cationic polyamine compounds were carried out using the method presented in standard [24]. 3 types of bacteria were used in the tests: *Staphylococcus epidermidis* ATCC 12228, *Staphylococcus aureus* ATCC 6538, and *Escherichia coli* ATCC 10536. Antibacterial activity of test papers coloured with red B-4 is presented in ***Table 2***. The paper was made from pulp of 35 °SR.

Fungicidal properties of the dyed papers were determined against *Candida albicans* yeast (ATCC 10231) and *Aspergillus niger* mould (ATCC 16404). Strains came from the American Collection of Pure Culture. Fungicidal activity of selected papers dyed with red B-4 is presented in ***Table 3***. The paper was made from pulp of 35 °SR.

Table 4. Light fastness of dyeings.

Dye symbol	Light fastness of dyeings
B-1	4
B-2	3
B-3	3-4
B-4	3-4
B-5	3-4
B-6	4

Light fastness of dyeing

Light fastness was one of the product properties chosen. Tests of colour fastness were carried out on a Xenotest 150S (USA) in accordance with Standard PN-ISO 105B-02: 2002.

The tests were carried out for 1% dyeing of paper made from pulp of 35^0 SR in the presence of retention agent PHMG with a concentration of 2.4% in relation to absolutely dry pulp. The results are listed in ***Table 4***.

Breaking strength tests of test sheets

Tests of the breaking strength of test sheets made of pulp refined to a freeness of 35 °SR and coloured with reactive dyes of 1% in relation to absolutely dry pulp with the addition of PHMG were carried out. The breaking strength is the minimal force needed for breaking a strip of paper, expressed in Newtons (N). Measurements were made on Instron (USA) apparatus according to Standard PN-EN ISO 1924-2: 2009. The breaking strength of paper dyed with reactive dyes with the addition of PHMG is presented in ***Figure 4***.

The test sheets were exposed to thermal ageing in a laboratory dryer at a temperature of 120 °C for 50 h according to Standard PN-EN ISO 5630-4:1986, and then they were tested for breaking strength. The results are listed in ***Figure 5***.

Discussion

A new method for paper dyeing in the making process with adducts of reactive dyes containing two 3’- carboxypyridinetriazine groups and a cationic polyamine compound was developed. Dyeing was carried out in an aqueous medium with pH close to neutral. First the dye is added to the pulp, followed by the retention agent. In such conditions, a complete retention of adducts formed on cellulosic fibres occurs with partial retention of the pulp fine content. When using 2.4% of polyhexamethyleneguanidyne, the content of fines getting through the screen of the test sheet former decreases by 60-70% on average. During paper drying at a temperature of over 100 °C, the covalent bonding of dyes with pulp occurs. The dyeings obtained are resistent to wet factors. Only a small amount of the dye can be extracted with pyridine azeotrope at boiling point. After paper web consolidation, an evenly dyed paper product of vivid and intensive colour is obtained. The white water almost does not contain the dye and has a lower content of easily sedimenting fines, which is very important for today’s ecologic paper production with its tightly closed circulation of white water.

As retention compounds, guanidyne polycondensates with hexametylene-1,6-diamine (PHMG), octamethylene-1,8-diamine (POMG) and diethylenetriamine at a molecular weight of over 2 000 g/mole were used. PHMG and POMG have bactericidal and fungicidal properties. According to the literature [20, 21], PHMG is harmless for people. As the tests showed, PHMG or POMG added to the paper makes it biocidal. Paper containing PHMG or POMG can be used in products of personal hygiene. Adding PHMG or POMG to paper in ther form of adducts with dyes slightly increased the inhibition zones of bacteria and fungi, which is probably caused by the increased concentration of microbiocidal agents on the pulp surface. Adducts deposit on the surface of the fibres. PHMG or POMG added to the paper slightly impact structural,

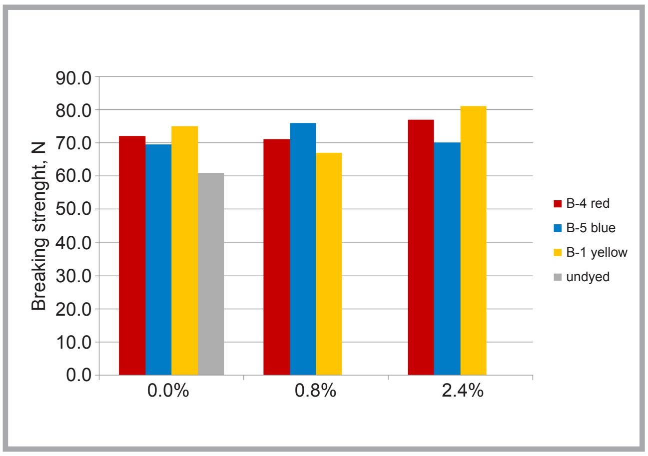


Figure 4. *Breaking strength of paper dyed with reactive dyes (1%) with the addition of PHMG in %.*

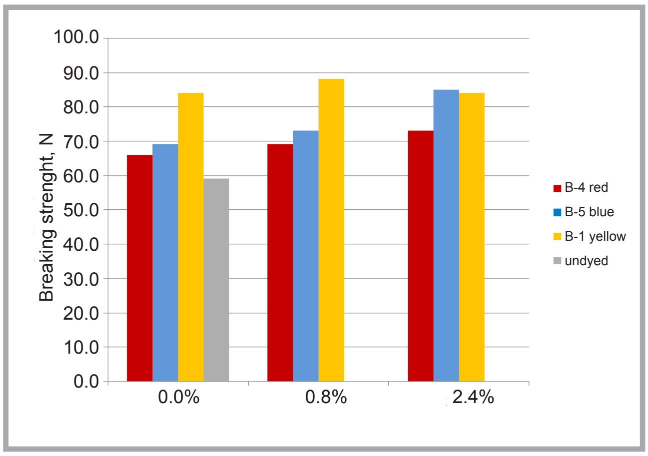


Figure 5. *Breaking strength of paper dyed with reactive dyes with the addition of PHMG in % and exposed to the ageing process at a temperature of 120 °C for 50 h.*

dimensional and strength properties of the test sheets formed before and after ageing [25]. The light fastness values are also comparable with the colour fastness of currently used dyes.

Summary and conclusions

1. The method of dyeing paper pulp with adducts of reactive dyes and cationic compound polyamine was adjusted to the papermaking process.
2. In this method, complete retention of the adducts (average molecule weight of 6000 - 6500 g/mol) occurred on the surface of cellulosic fibres.
3. The papers dyed were characterised by high vividness and intensity of colour and very good wet fastness.
4. The papers dyed with adducts of reactive dye derivatives of 3'-carboxypyridinetriazine with PHMG and POMG acquired bactericidal and fungicidal properties.
5. The method of dyeing paper pulps developed reduces the content of fines in white water.

Acknowledgment

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