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Eco-friendly method for paper dyeing with reactive dyes

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Abstract: *Eco-friendly method for paper dyeing with reactive dyes.* The authors pre-evaluated possible application of kayacelon dyes (synthesized in the Institute of Polymer and Dye Technology, Technical University of Lodz) in paper dyeing combined with a polyelectrolyte - polycondensate of hexamethylene -1.6 diamine and guanidine. In the light of the research results presented here, the dye and retention agent dyeing method, which is to be patented, turned out to be very effective. The dye was practically entirely saturated on the pulp fibrous components, fines had good retention parameters contributing in this way to high purity of white water. It is particularly important in the environment friendly production of dyed papers in tightly closed water loops.

Keywords: paper dyeing, kayacelon dyes, dye retention

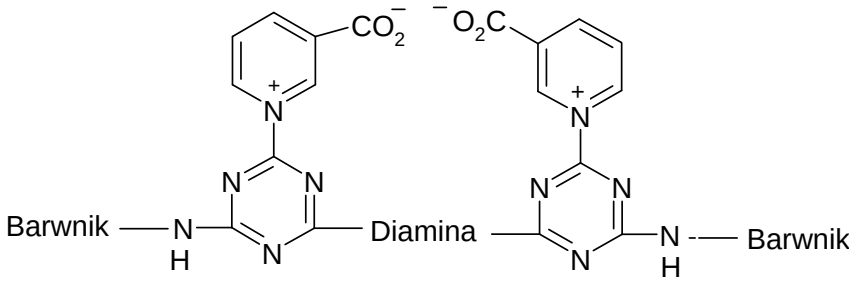
INTRODUCTION

Environmental and economic aspects made the world's paper production change to coloured products manufactured from pulp with high content of recovered paper as well as mechanical pulp grades. The production of white papers demands significantly more raw materials per a finished product, apart from that more wastewater is produced. A colour catches the eye. Coloured paper products are used as advertising materials, newsprint, packaging as well as towels, serviettes, toilet rolls, etc. Aside from an aesthetic aspect, their advantages include also health aspects as the colour does not make the eyes feel tired. Recently coloured papers started to replace gray grades. Additionally, almost all paper grades are dyed to change their hue.

The paper manufacture is a complex technological process consisted of the following stages: preparation and refining of fibrous semi-finished products, stock preparation, paper web consolidation in the sections of paper machines (forming, pressing and drying) as well as paper finishing.

The most commonly used method for dyeing paper products is dyeing in the stuff in which a dye is added to the pulp suspension before paper web formation on the paper machine. In this method the dye is applied in the room temperature of 20 - 25 ºC, within 0.5 - 3 min, usually without any auxiliaries. The advantage of this method is adsorption of dye molecules on the entire surface of cellulose fibres. After paper web drying, an entirely dyed paper product is obtained.

When working on the research project aimed at finding eco-friendly cellulose fibres useful for dyeing in neutral medium of reactive dyes, the authors turned their attention to Kayacelon React with a following structure:



Barwnik – Dye

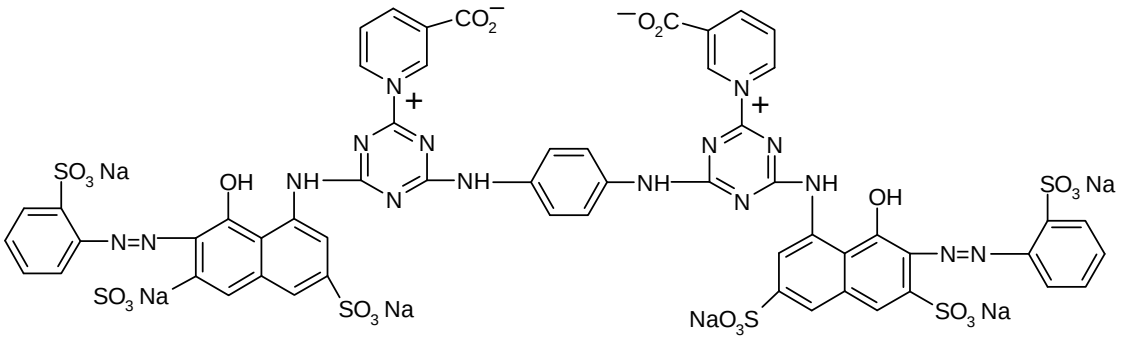
Diamina – Diamine

The dyes of this type are able to react with cotton fibres in neutral medium in temperature of 100-130ºC, that is in the temperature of paper web drying.

The aim of this study was to use the reactive dyes, derivatives of 3`-carboxypirydyno-1,3,5-triazine in paper dyeing.

EXPERIMENTAL

For the testing purpose, a group of compatible 3`-carboxypirydyno-1,3,5-triazine reactive dyes was selected. Their synthesis was carried out in the Institute of Polymer and Dye Technology, Technical University of Lodz. The dyes are presented below(based on C.I.Reactive Red 221):



C.I.Reactive Red 221

In the first stage of the test, paper samples were dyed with the reactive dye (Kayacelon React) and coagulant (polycondensate of hexamethylene - 1.6 diamine and guanidine).

The second stage pre-evaluated an impact of the coagulant on purity of white water (defined by the fine content through measurement of absorbance of white water).

Dyeing of papermaking pulp with the reactive dye (Kayacelon React type) and the coagulant (polycondensate of hexamethylene - 1.6 diamine and guanidine)

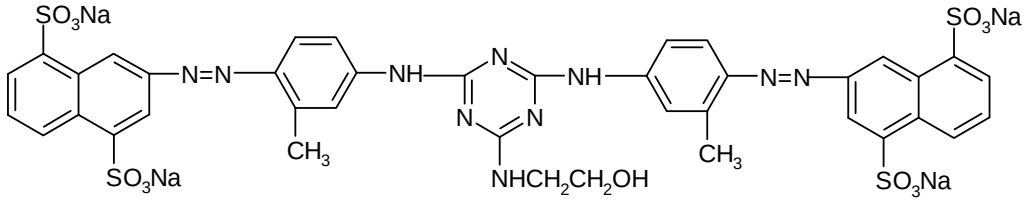
In temperature of 20 – 25 ºC, solution of 20 g/dm^3 of reactive dye containing 1% of dry dye in relation to absolutely dry papermaking pulp was added to papermaking pulp refined to 25 ^{0}SR value and consistency of 0,3% (absolutely dry) and then the solution (20g/dm^3) of polycondensate of hexamethyleno - 1.6-diamine and guanidine, in the amount of

1% calculated into polymer in relation to absolutely dry papermaking pulp; pH of papermaking pulp was 6.5-7.0.

Adducts formed of the reactive dyes and the polyamide were adsorbed on the surface of fibres of refined pulp within 30 seconds. Retention of the dyes on the cellulose fibres (defined by measurements of absorbance) exceeded 90%. The remaining small amount of the dye was totally adsorbed on rapidly sedimenting molecules of the fines in the white water, and finally white water was completely colorless. The paper sheet for tests, formed on the wire of the Rapid – Koethen apparatus, was dried in temperature of 130ºC. During paper web drying in temperature exceeding 100ºC covalent bonds are formed between reactive dyes and cellulose. The degree of bonding was determined by measurement of absorbance of solution from cooking paper sample in azeotropic mixture of pyridine and water (65% of pyridine) during 10 min in correlation with model curves. The determined degree of bonding between the paper and the dye was 96.7%.

Dyeing results obtained with use of this method were characterized by vivid hue, high intensity of colour and very good resistance to wet conditions.

For comparison, the tests regarding dyeing papermaking pulp with adducts of direct dye C.I. Direct Yellow 86 were performed.



C.I. Direct Yellow 86

It is a typical dye used commonly now for paper dyeing in combination with a coagulant being a product of polycondensation of hexamethyleno of 1.6 diamine and guanidine.
Also in this case, the adduct was completely retained on cellulose pulp, however degree of bonding between the dye and paper was 73.6%.

Effect of the amount of polyamide compound added to papermaking pulp on the amount of the fines in white water

In the tests, bleached kraft hardwood pulp (SaBl) of different refining degrees was used. 1% of C.I. Reactive Red 221 was added to 0.3 % suspension of pulp beaten in the Valley laboratory beater to a few ºSR, and then 1 or 2% of condensate of hexametyleno of 1.6 diamine and guanidine in relation to dry papermaking pulp. From pulp prepared in this way, the small sheets of paper of 75 g/m^2 were formed on the Rapid – Koethen apparatus (acc. to PN-EN 5259-2:2001). The fine content in white water was determined by measurement of absorbance of white water.
The pulp beating degree was described in terms of a Shopper Riegler (^{0}SR) numer. Measured absorbance values of white water for C.I.Reactive Red 221 are listed in Table 1.

Table 1. White water absorbance

	Pulp beating degree	**Amount of addend polyamide compound** [% in relation to a.d. pulp]	**White water absorbance value**
1	11 ºSR	1	0.0970
2	11 ºSR	2	0.0679

3	25 ºSR	1	0.0933
4	25 ºSR	2	0.0582
5	37 ºSR	1	0.0779
6	37 ºSR	2	0.0557
7	65 ºSR	1	0.0569
8	65 ºSR	2	0.0288

I should be noted that small amount of adducts that penetrated to white water during paper forming on the wire of the Rapid – Koethen apparatus did not colour white water as it was entirely adsorbed on molecules of the fines that could be found in white water.

CONCLUSIONS

Presented here, the new method for paper dyeing in the manufacturing process with the adducts of the reactive dyes and the cationic polyamide compounds playing a role of a coagulant is tightly integrated with the paper production on the paper machine. Paper dyeing in the stuff is carried out in the water medium with pH close to natural in room temperature. In such conditions, the dyes are completely retained on the cellulose fibres. Some of the fines get through the wire. Their amount decreases along with the increased amount of added polyamide compound. The increase from 1% to 2% of added polycondensate of hexamethyleno - 1.6-diamine and guanine reduces the amount of the fines getting through the wire of the apparatus for forming paper sheets by 50% on the average. The fines from beaten pulp are adsorbed by the coagulant and then they are adsorbed along with the coagulant on the fibres in paper. During paper drying in temperatures exceeding 100ºC additional covalent bonding between the reactive dyes and the complex of 3`-carboxypyridino-1,3,5-triazine of hydroxyl groups of cellulose. Treatment of dyed papers with a buffer pyridine-water showed that it is permanently bonded with paper over 92% compared with 73.6% of the typical direct dye. It can be assumed therefore that at least 20% of the reactive dye is bonded by the covalent bonds with paper. The remaining amount of the dye may be bonded with paper by either covalent or ion bonds. Dyeing results achieved with this method are intensive with vivid hue and they are characterized by very high resistance to wet conditions. It is connected with the fact of forming ion bonds between sulfone monomolecules of the reactive dye and the cationic groups of a polymer. Owing to presence of large number of sulfone groups in the molecule, the reactive dyes are not aggregated in the water based solutions. The adducts formed are adsorbed on the surface of beaten cellulose fibres. In consequence, very intensive dyeing results are obtained.

When concluding it has to be stressed that, in the light of preliminary test results, the paper dyeing method “in the stuff” with the reactive dyes of Kayacelon React type, adsorbed on the fibres and the fines of papermaking pulp with polyelectrolyte in a form of polycondensate of hexamethyleno - 1.6 diamine and guanidine, seems to be an effective process both economically and environmentally. Polycondensate of hexamethyleno-1.6-diamine and guanidine is highly effective retention aid both for the koyacelon dye and for the pulp fines. As e result we have obtained not only complete saturation of the dye of fibrous constituents of papermaking pulp but also high retention of the fines, owing to this fact white water appearing in the process of the web consolidation on the paper machine practically does not contain any dye and it has significantly reduced suspension content. This fact is very important for present eco-friendly paper production from wood based pulp in conditions of tightly closed loops of production water.

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Streszczenie: *Proekologiczna metoda barwienia papieru barwnikami reaktywnymi.* Dokonano wstępnej oceny możliwości zastosowania w procesie barwienia papieru barwnika kayacelonowego (zsyntezowanego w Instytucie Technologii Polimerów i Barwników Politechniki Łódzkiej) w połączeniu z polielektrolitem będącym polikondensatem heksametyleno-1,6-diaminy z guanidyną. W świetle wyników badań zaprezentowanych w tej pracy, zgłoszony do opatentowania sposób barwienia papieru zaproponowanym układem barwnik – środek retencyjny okazał się wysoce efektywny. Stwierdzono praktycznie całkowite wysycenie barwnika na składnikach włóknistych masy papierniczej, co w powiązaniu z dobrą retencją frakcji drobnej, zapewnia wysoką czystość wód podsitowych. Jest to szczególnie istotnym dla proekologicznej produkcji drzewnych papierów barwnych w warunkach silnie zamkniętych obiegów wodnych.

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