STUDY ON THE PROPERTIES OF DYED WITH REACTIVE DYES OFFSET PRINTING PAPER

ИЗСЛЕДВАНЕ НА СВОЙСТВАТА НА ОБАГРЕНА С РЕАКТИВНИ БАГРИЛА ОФСЕТОВА ХАРТИЯ ЗА ПЕЧАТ

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Abstract: *The amount of paper dyed is increasing each of the last few years, mainly because the increasing consumption of corrugated board papers. Paper is colored by dyes of different chemical nature – inorganic pigments; synthetic organic pigments; basic, acid, direct dyes and others. The reactive dyes are capable of forming covalent dye-polymers bonds, for instance, with the hydroxyl groups of cellulose. In this experiment are being used two laboratory synthesized reactive dyes, derivatives of chlorotriazine and one of them contains a stabilizer fragment. Dyes are used in the composition of offset printing paper with a fiber content of bleached softwood and hardwood pulp in a ratio of 1:1. The paper is sized with alkyl ketene dimer and as filler is used natural calcium carbonate. The strength and hydrophobic properties are being examined. The optical properties are also been examined before and after accelerated thermal ageing of the resulting paper samples and it is being found out that the examined dyes can be of an interest for an industrial production.*

Keywords: OFFSET PAPER, CHLOROTRIAZINE DYES, REACTIVE DYES, OPTICAL PROPERTIES, STRENGTH PROPERTIES, ACCELERATED THERMAL AGEING

1. Introduction

Dyes are widely used in many industries such as textile, paper, plastic, cosmetic and food manufacturing for coloring of their products. Economic and environmental aspects made the world`s paper production change to colored products manufactured from pulp with high content of recovered paper as well as mechanical pulp grades. The amount of paper dyed is increasing each of the last few years, mainly because the increasing consumption of corrugated board papers. According to Smithers Pira, the paper and board demand in the region of Central and East Europe, is expected to increase with about 2 million tons during 2014 to 2019 and not a small part of it is colored paper [1].

The paper manufacturing process is a complex technology considered of the following stages: preparation and refining of fiber semi-finished product, paper stock preparation, forming of a paper sheet material in the five main sections of the paper machine – head box, wire section, press section, drying section and the tambours with the produced paper. Paper is colored by dyes of different chemical nature – inorganic pigments; synthetic organic pigments; basic, acid, direct dyes and others [2,3]. The most commonly used method for dyeing of the paper is by adding the dye solution into the paper suspension before the paper web is formed. The advantage of this method is adsorption of dye molecules on the entire surface of cellulose fibers and the end result is entirely dyed paper.

The reactive dyes are widely used for dyeing of textile. By reactive dyes the following fibers can be dyed successfully: cotton, rayon, flax and other cellulosic fibers; polyamide and wool fibers; silk and acetate fibers but they have only limited use in paper. They have been tested in the late 1800s [4]. The first reactive dye is synthesized by IG Farben in 1932, but it first appeared commercially in 1956, after their invention in1954 by Rattee & Stepheness at the Imperial Chemical Industry (ICI), Dyestuffs Divion site in Bleckley, Manchetor, UK [5,6]. The reactive dyes are capable of forming covalent dye-polymers bonds, for instance, with the hydroxyl groups of cellulose [4]. In the last few years some experiments are carried out for dyeing of paper.

The purpose of the present study was to investigate the suitability of dyeing of offset printing paper with two laboratory synthesized reactive dyes and their effect over the main paper properties.

2. Materials and methods

The investigations are being carried out with laboratory obtained paper samples (70g/m^2) from bleached hardwood and softwood pulp in proportion 1:1, with beating degree 42°SR (Schopper Riegler). The paper samples are being sized with Alkyl Ketene Dimer (AKD) – 2% from o.d.f., filled with natural calcium carbonate ($CaCO_3$) – 20% from o.d.f. and as a retention additive (RA) is used modified poly acryl amide with cationic charge in consumption 0,05% from o.d.f. The two examined dyes are laboratory synthesized red reactive dyes, derivatives of chlorotriazine, one of which contains a stabilizer fragment (Fig.1):

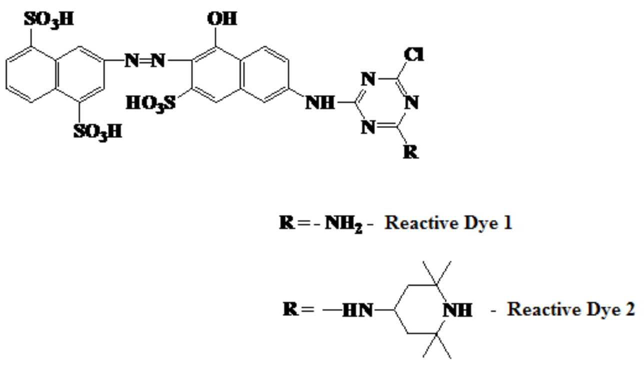


Fig.1 *Chemical characteristic of reactive dyes*

The consumption of Reactive Dye 1 (RD1) and Reactive Dye 2 (RD2) in the paper is 0,2%, 0,4%, 0,6% from o.d.f. For straightening out the interactions, the Dewatering time of paper furnishes were determined for 700ml, s. by Schopper Riegler method. The white waters are also being studied:

- Turbidity – NTU nephelometric acc. ISO 7020 (Turb 350 IR)
- Conductivity - µS acc. ISO 7888 (conductometer EC215)

The obtained paper samples are being examined for its strength properties - the Tensile Index (TI), Nm/g acc. ISO 1924-2:2008, hydrophobic properties – water absorptiveness Cobb$_{60}$, g/m^2 acc. ISO 535:2014 and optical properties – color coordinates L*, a* and b* before and after accelerated thermal ageing (105°C , 12h, 24h, 36h) by Frank – PTI spectrophotometer / D65_10.

3. Experimental results and discussions

- *Influence of the quantity and type of the reactive dyes, on the properties of the white waters*

The accelerated dewatering and increased retention as a result of flocculants effect usually means purer waters in paper mill as well. In the process of adding of the reactive dyes into the paper suspensions a covalent chemical bond - dyes-cellulose is obtaining. This is the reason of capturing part of the hydroxyl groups from the cellulose fibers, so they are not capable of forming bonds with the water. Therefore, the cellulose fibers are not so hydrated and it is easier for the water to pass through the formed cellulose web. Reactive dye 2 (RD 2) at 0,2% consumption gives best results for the dewatering ability (Fig.2). With increasing the dyes consumption the dewatering ability is decreasing, most probably because the saturation of the paper suspension with negative charge.

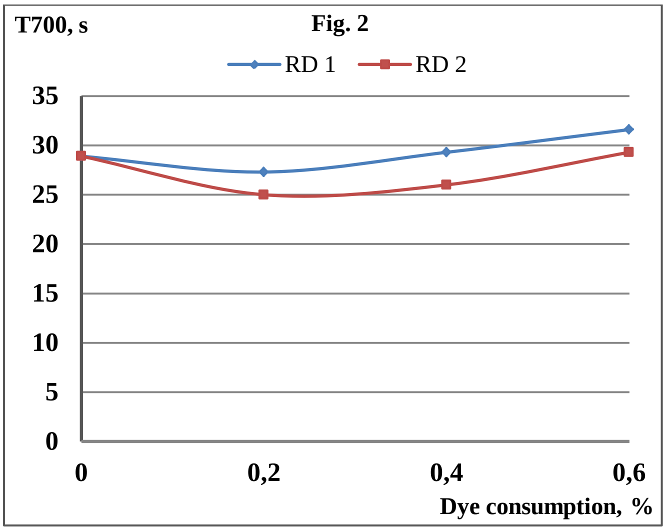


Fig.2 *Dewatering time (T_{700},s) of the paper suspensions at different Reactive Dyes (RD)consumption*

Regarding the turbidity of the white waters, the results are not so definitive, as well as it is for the dewatering ability and the conductivity. The both reactive dyes gives clarified white waters, but again best effect is seen in presence of RD 2 at 0,2% consumption (Fig.3). With increasing the dye quantity the turbidity is being aggravated and it is getting worse at RD 2 at 0,6% consumption, but still stays closely to the levels of the result for the paper without reactive dye. Probably with increasing the dye consumption the retention of the fines onto the fiber web is less, so that they occurs more in the white waters.

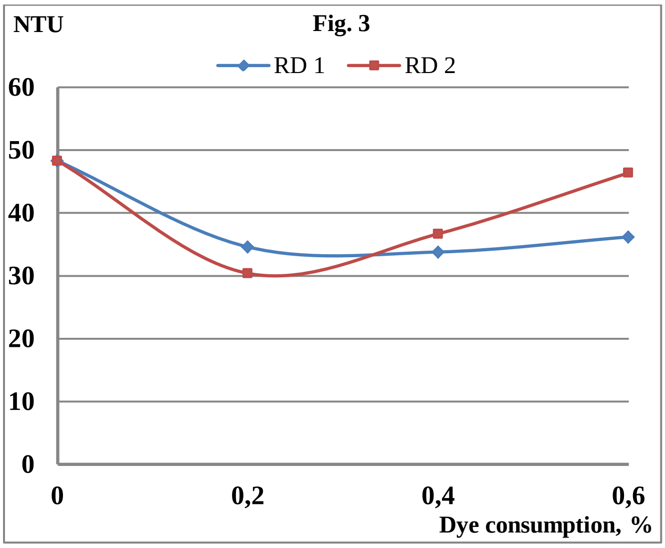


Fig.3 *Turbidity (NTU) of the paper suspensions at different Reactive Dyes (RD) consumption*

Measuring the electric conductivity gives an indication of the total concentration of electrolyte in the liquid phase. As it is shown on Fig.4, in the white waters from paper suspensions dyed with RD 2 there are more electrolytes and the conductivity is higher than that at RD 1. For this parameter the increasing of the dyes consumption do not gave effect over the conductivity. This effect probably is due to the bigger charge density of RD 2.

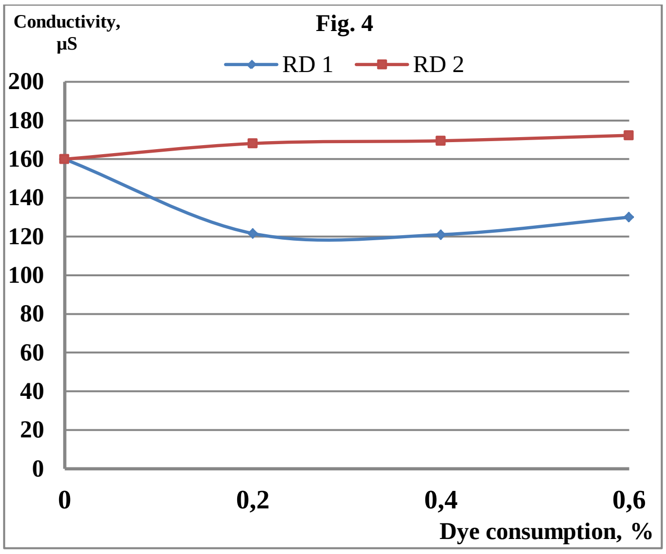


Fig.4 *Conductivity of the paper suspensions at different Reactive Dyes (RD) consumption*

- *Influence of the quantity and type of the reactive dyes, on the properties of the papers*

Tensile Index, N.m/g

This parameter depends primarily on the amount and strength of the bonding forces between the fibers in the finished paper sheet. As it is shown on Fig.5, with adding of reactive dyes, at consumption of 0,2% and 0,4%, the reactive dye causes a decrease for the tensile index of the paper samples. When adding 0,6% of RD the result is - increasing of the tensile index. Probably, with the small consumption of the reactive dyes the hydrogen bonds between the fibers are less, but after 0,5% dye, the bonding forces in the paper are also with the participation of the hydroxyl groups from the dye molecule.

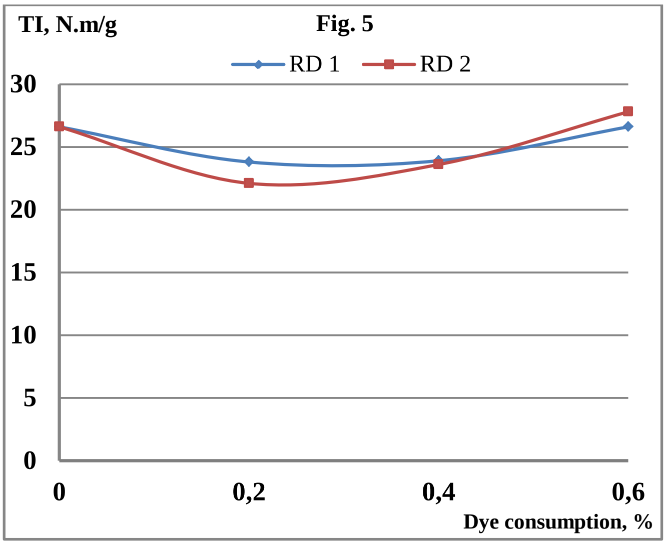


Fig. 5 *Tensile Index (TI) of the paper samples at different Reactive Dyes (RD) consumption*

Water absorptiveness Cobb$_{60}$, g/m^2

On Fig.6 are shown the water absorptiveness Cobb 60, g/m^2 of the obtained paper samples. With increasing the RD consumption, the water absorptiveness decreases, because of the presence of covalent bonds and the less free hydroxyl groups, which can react with the water.

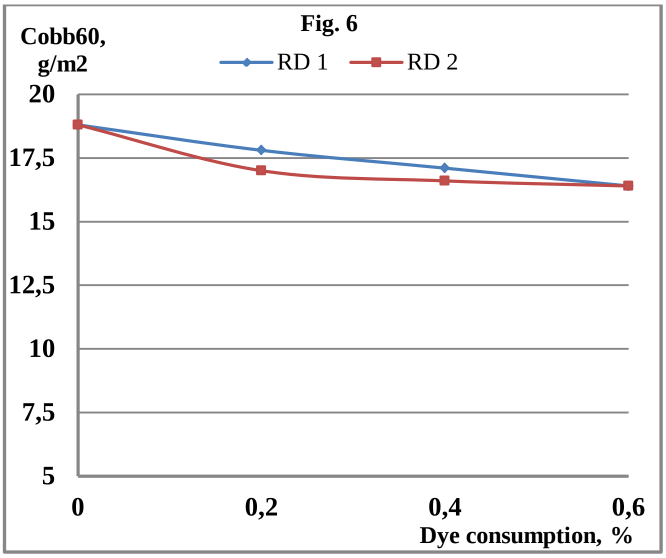


Fig. 6 *Water absorptiveness (Cobb$_{60}$) of the paper samples at different Reactive Dyes (RD) consumption*

Color coordinates L, a* and b* before and after accelerated thermal ageing*

The color coordinate - L*, which expresses the lightness, brightness and the brilliance of the paper, decreases with adding of both reactive dyes (Fig.7). The color parameters variation with time is comparatively low, being most sensitive during the first 24 hours. The differences between both dyes are small. At 0,2% consumption of the RD, the lightness of the paper samples is nearly the same and it stays stable after 36h accelerated thermal ageing. With increasing the dyes consumption and the duration of the thermal ageing, the color of the paper samples is slightly getting lighter.

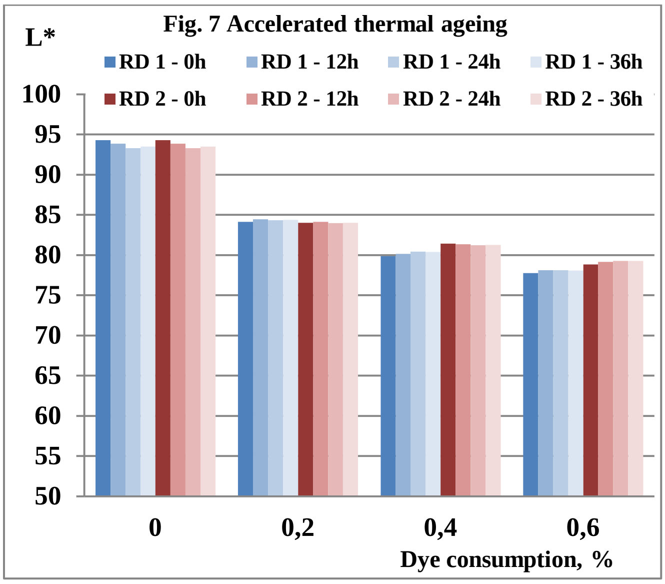
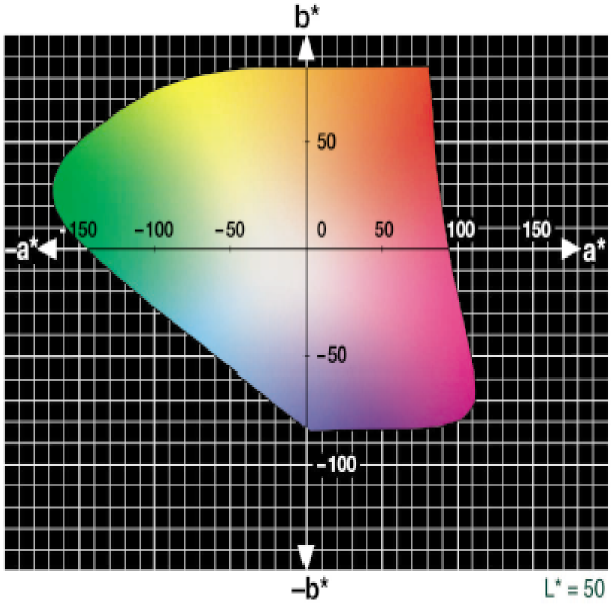


Fig. 7 *Color coordinate L* of the paper samples at different Reactive Dyes (RD) consumption, before and after accelerated thermal ageing*

With both reactive dyes are obtained paper samples with stable and uniform coloring. If the a* parameter, in the color system CIE L*a*b*, is positive the color is red and if the b* parameter is also positive the color is yellow (Pic.1) [7].



Pic.1 *CIE L*a*b* color space, at L*=50*

The color coordinates a* and b*, expressed as the stability of the color, for RD 1 are shown on Fig. 8, those for RD 2 are shown on Fig. 9.

The paper dyed with the Dye 1 is of lesser color stability and higher differences in color shade compared to the dye 2. Paper samples dyed with RD 2 have more saturated red color, barely perceptible to the human eye, but its color shade is more stable and the difference before and after the thermal aging of the paper is smallest at consumption of the dye at 0.6%. The process of ageing of both dyes alters the color of the resulting paper in a different way. The color of the paper with RD 1 is amended to a greater extent to the yellow hues, while those with RD 2 less. When the dyeing is obtained with RD 1, with the increasing of the quantity of the dye and the duration of the aging, paper is yellowing more compared to RD 2, by which the color remains more in the red shades.

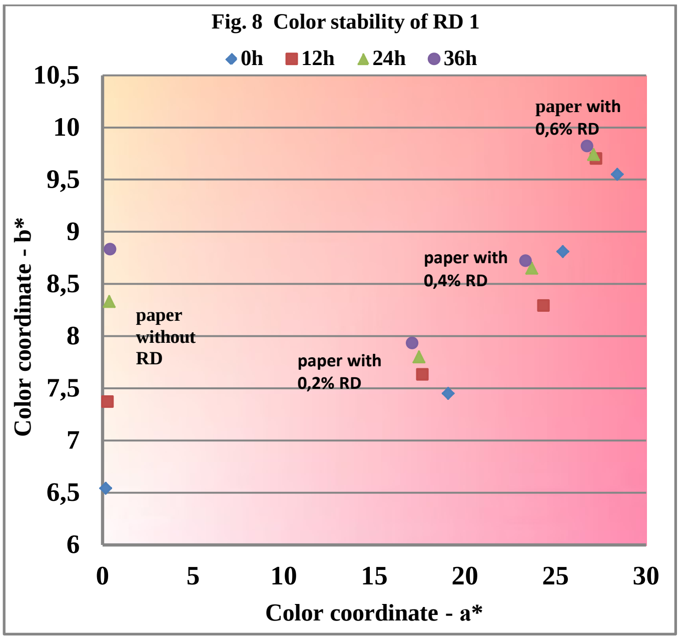


Fig. 8 *Color stability of RD 1 of the paper samples*

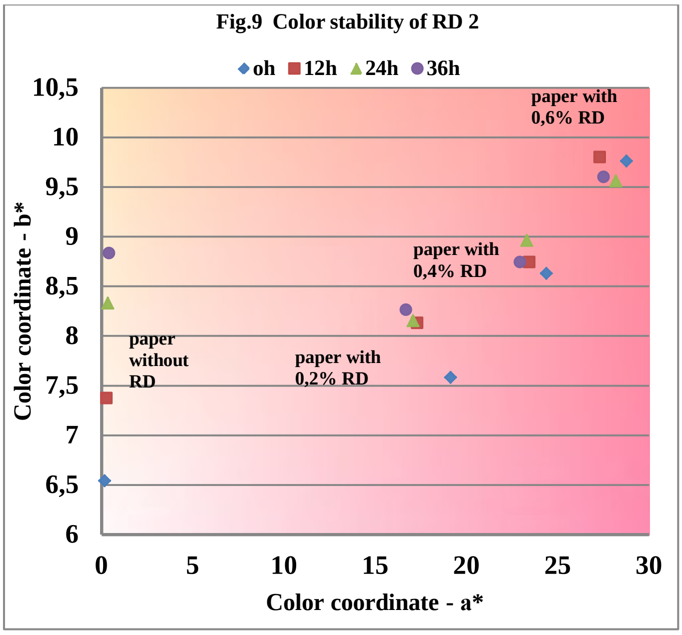


Fig. 9 *Color stability of RD 2 of the paper samples*

4. Conclusion

On the basis of the results of the studies carried out for dyeing wood free neutrally sized paper by two laboratory synthesized reactive dyes, using cationic polyacrylamide as retention additive and with a view of the complex influence on the processes and properties the following conclusions can be made:

- With both reactive dyes are obtained paper samples with stable and uniform coloring.
- Both reactive dyes, gave paper with close color shades, distinguished by stability under thermal aging.
- Most suitable in terms of dewatering ability and turbidity of the white waters, is reactive dye 2 at 0,2% consumption,
- Regarding all the properties of the obtained paper samples, best result are obtained with reactive dye 2 at consumption 0,4%.
- Both examined reactive dyes are suitable for dyeing of offset printing paper and may be of interest to industrial production.

5. Literature

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