

Article

Comparative Analysis of Anthraquinone Reactive Dyes with Direct Dyes for Papermaking Applicability

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Abstract

Aiming to compare the applicability and the successfulness of reactive dye printing papers' coloration, two laboratory-synthesized anthraquinone reactive dyes are studied in comparison with two commercially available anionic and cationic direct dyes. Reactive dye 1 is monochlorotriazine and reactive dye 2 is bifunctional (contains two reactive groups—one is a monochlorotriazine atom and one an unsaturated allylic group). The synthesized reactive dyes are investigated through a paper slurry, white waters and paper sample properties comparative analysis. The drainage ability, flocculation volume and sedimentation index of paper slurries are determined. The turbidity, conductivity, pH and dye concentration in the white waters are also examined to ensure dye fixation. Through SEM, the paper structure is evaluated. The strength properties, colorimetric characteristics and stability at accelerated light aging of all 15 paper samples are investigated. The dewatering ability is enhanced, the white waters are clarified, the conductivity and pH level are stable and the dye concentration is on the same levels as for the direct dyes. The paper structure is uniform, the strength is slightly enhanced and color differences are indistinguishable compared to those of the direct dyes, when the ratio of the fixing agent to dye is appropriately optimized.

Keywords: reactive dye; anthraquinone; direct dye; papermaking; light aging; printing paper

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1. Introduction

According to the latest Cepi (Confederation of European Paper Industries) press release, the European pulp and paper industry showed signs of recovery in 2024, with production increasing by 5.2% and consumption rising by 7.5%. Packaging grades led this growth, expanding by 6.5% and now accounting for 63% of total production. Graphic paper saw a 5.2% increase, its first growth since 2010, suggesting a temporary stabilization in demand for printing and writing paper. Tissue paper demand also rebounded, growing by 5.8%. Despite these positive trends, production levels remain below pre-pandemic figures. The industry continues to face challenges such as a difficult economic environment and high regulatory costs. The use of paper for recycling rose by 4.1%, and exports grew by 7.2% by the end of September 2024, with notable increases in markets such as North America and Latin America. However, overall production is still 10–15% below 2021 levels. A sluggish European economy and rising regulatory costs continue to affect the industry's competitiveness. In response, the sector is placing a strong emphasis on sustainability and decarbonization, while calling for greater policy support from the EU to ensure a level playing field for European producers [1].

In this context, focusing new research in the field of paper production from primary cellulosic fiber raw materials would be of scientific and applied interest. At the same time, the capabilities for a potential increase in the aesthetic aspect of the final products from paper and cardboard are of importance, which makes the dyeing of paper an excellent opportunity to achieve an exclusive and meaningful appearance. Colored papers are less tiring on the eyes and more eye-catching, but apart from their aesthetic appeal, their production can result in increased effluent generation.

Dyeing of paper (90–95% of total dyed papers) is performed with the following dye groups: cationic and anionic direct dyes (DDs)—63%; basic dyes—30%; acid dyes—7%; colored pigments and sulfuric dyes. From this group, anionic and cationic direct dyes are the most important ones used for paper coloration. Anionic ones have a diverse nature and vary in lightfastness, while cationic ones have excellent attraction with cellulose fibers. Anionic DDs are widely used in tissue, printing and writing paper production. In mechanical fibers, paper furnishes and those containing anionic trash cationic DDs could face some issues. Both DDs have molecule adsorption on the entire cellulose fiber surface with no fixing additive needed at ambient temperature (20–25 °C) application [2,3].

As is known, each glucose unit in the cellulose possesses three hydroxyl groups, two secondary and one primary. With those groups, three types of color retention mechanisms for cellulose occur. The only type of dye that can form a covalent bond with the hydroxyl group of cellulose is the reactive dye (RD), while direct dyes rely upon both Van der Waals forces and hydrogen bonds between fiber and long planer dye molecules. In the case of sulfur, vat and azoic dyes, water-soluble precursors are applied to the fiber and then the water-insoluble dye molecules are generated inside the fiber and trapped inside the fiber pores [3,4].

Reactive dyes are modern synthetic dyes with a wide application in the textile industry for the dyeing of natural (wool, cotton, silk) [5].

The reason for the success of this class of dye is the wide shade gamut, which they give, brightness, good fastness properties, low cost, easy application, etc. The latest reactive dye investigations have only limited use in practical application in the papermaking process and single reports on laboratory experiments [6,7].

Investigations on cotton coloration [8–11], reactive dyes' abolition from wastes [12–14], fixation through chitosan treatment [15], cationization [16] or urea modification [15] and printing with reactive dyes on textile production [17,18] are highly spread.

Among the reactive dyes, azo dyes and anthraquinone dyes are two of the most important chromophores used. Anthraquinone dyes are very well known in the literature, being the second largest class of textile dyes after azo dyes. They are distinguished by their brilliance, excellent lightfastness and stability of the chromophore under both acid and alkaline conditions. However, a disadvantage of anthraquinone dyes is the relatively low molar absorption coefficient. Anthraquinone dyes are most commonly used for green, blue and violet hues. Some of the very important blue dyes are derivatives of the sodium salt of 1-amine-4-bromo-anthraquinone-2-sulfonic acid (bromamine acid). Recent investigations with anthraquinone reactive dyes are focusing on the following: performance and pathway characteristics on anaerobic biodegradation by resuscitated strain JF4 [19], a new method for enhancing the anaerobic degradation of anthraquinone dye with resuscitation-promoting factors [20], used as the target compound for an experimental investigation on the decolorization performance of natural manganese mineral [21], evaluating the influence of biochar preparation conditions [22] and others. Some of the newest and promising applications of dyed paper are in the field of analytical chemistry for paper-based sensors [23–25].

Two anthraquinone reactive dyes have been synthesized according to the procedure described before [26], where RD1 is a monochlorotriazine reactive dye and RD2 is a bifunctional reactive dye (contains two reactive groups—one is a monochlorotriazine atom and one an unsaturated allylic group).

Unlike all classes of dyes, reactive dyes covalently bond with the fiber structure and thus become an integral part of the substance. As for all reactive dyes, the synthesized anthraquinone reactive dyes contain the typical reactive dye structure with chromophore (blue in color), water-solubilizing groups ($-\text{SO}_3\text{H}$ groups), a bridging group ($-\text{NH}$ groups) and reactive groups (residue of monochlorotriazine or allylamine). The reactive groups are capable of reacting with the hydroxyl groups of the cellulose by substitution or addition reactions. In between the two functional groups, a bridge group connects but also insulates the chromogen from the reactive group to prevent the color generated by the chromogen from changing [2,4].

Aging is determined as the irreversible change that occurs slowly over time. In the case of paper, it results in the deterioration in complex properties that can render it unsuitable as an information carrier. Understanding paper aging requires the study of the aging of its main component—cellulose—and how certain additives and impurities with concentrations ranging from traces to substantial percentages can affect it [27–29]. Factors that have an effect on paper aging are numerous. High temperature, moisture, oxygen and acidity (low pH) are often investigated. Metal or other contaminants, poor initial paper quality, degraded insulating oil and others are also very important. These environmental characteristics and paper constituents could cause increased reaction rate degradation, promotion of hydrolysis of cellulose, oxidative breakdown, catalyzation of cellulose hydrolysis, acceleration of degradation reactions, faster onset of aging, contribution of acids and moisture and others.

Aiming to determine the applicability and the successfulness of reactive dye printing papers' coloration, two laboratory-synthesized anthraquinone reactive dyes are studied in comparison with two commercially available and widely used anionic and cationic direct dyes. For achieving the goal with paper slurries, their white waters and resulting paper sample are studied for cellulose fixation and dyed paper properties determination, such as the structure, strength and aging stability at accelerated light exposure.

2. Materials and Methods

2.1. Materials

The dyes were synthesized in accordance with a procedure described before [26] by condensation of 1-amine-4-bromo-anthraquinone-2-sulfonic acid (bromamine acid) with 1,3-phenylenediamine-4-sulfonic acid and a consequent reaction of the anthraquinone acid dye obtained with a corresponding derivative of cyanuric chloride (2-amino-4,6-dichloro-1,3,5-triazine or 2-allylamino-4,6-dichloro-1,3,5-triazine) schematically represented in Figure 1. The dyes obtained correspond to those described before.

2.2. Methods

The obtained reactive dyes were evaluated for papermaking applicability. The softwood cellulose, delivered by Svenska Cellulosa Aktiebolaget (SCA), Sundsvall, Sweden, is bleached sulfate kraft pulp from pine and spruce wood trees, while the hardwood cellulose was delivered from Svilosa AD, Svishtov, Bulgaria, under the registered trademark SVILO-CELL. It is also bleached kraft pulp from beech trees. Direct dyes Pergasol Türk F-2GN (dye DD1) and Pergasol Türk R (dye DD2) are Solenis® products of Solenis International LLC, Wilmington, DE, USA. For the reactive dyes' fixation, a cationic fixing polymer (Fix) on the basis of epichlorhydrin–dimethylamine copolymer—Kemira® Levogen E 1063 LQ

(Kemira Oyj, Helsinki, Finland)—was used. To be hydrophobic, the laboratory-obtained paper samples were sized with alkyl ketene dimer (AKD)—Kemira® Fennosize KD 157YC (Kemira Oyj, Helsinki, Finland). A retention additive (Ret) was used as a modified cationic polyacrylamide with a molecular weight of 11.106 g/mol and a charge density of +1.05 from Ciba Specialty Chemicals-Ciba® Percol®Co (Basel, Switzerland).

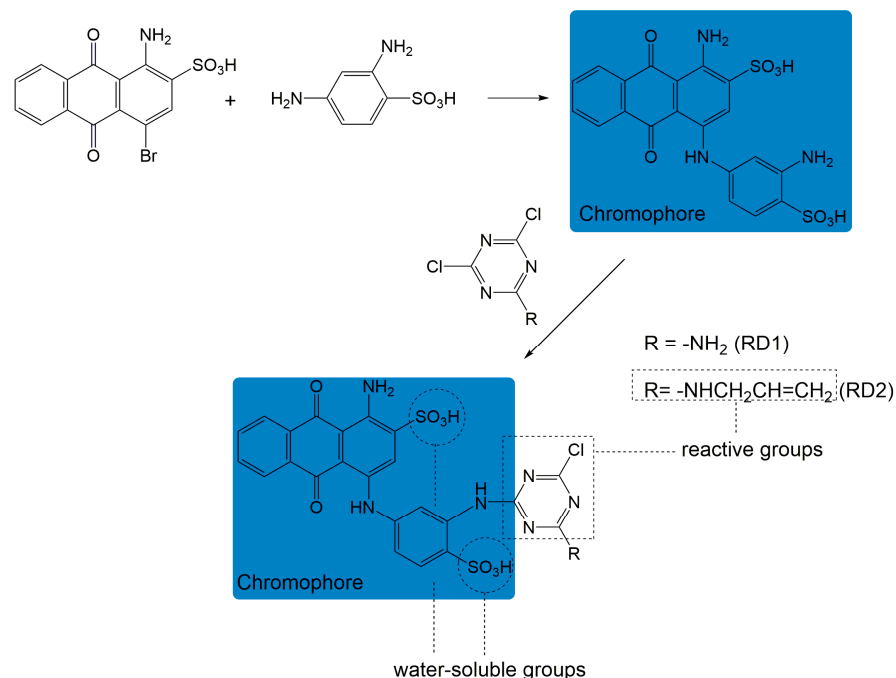


Figure 1. Synthesis of the reactive dyes RD1 and RD2.

Using a laboratory Jokro refining mill apparatus (Frank-PTI GmbH, Birkenau, Germany), consisting of six refining units, the raw kraft celluloscs were refined in accordance with ISO 5264-3:1979 [30]. The suspension concentration in each unit was 6% (16 g oven-dry fibers (o.d.f.) in 267 mL water). Bleached soft and hardwood celluloscs were separately refined to 20 °SR and 32 °SR (Schopper Riegler Value (ISO 5267-1/AC:2004) [31]), respectively. The resulting two paper suspensions, with a concentration of 2%, were prepared and mixed in a ratio of 1:1. The total cellulose slurry refining degree was 25 °SR.

For obtaining paper sheet samples with different compositions, a paper sheet forming machine, Rapid-Kothen (Birkenau, Germany), was used for the papermaking simulation process, acc. to ISO 5269-2:2005 [32]. All paper samples were prepared with a basic weight of 70 g/m², at a drying temperature of 96 °C and with a duration of 7 min.

As the experimental design was comparing direct and reactive dyes in wood-free printing and packaging paper production, the following wet-end chemical additives were added sequentially: dye fixing additive (Fix)—1% of o.d.f., two direct and two reactive dyes, additive for paper hydrophobicity—1% of o.d.f. and retention additive (Ret)—0.05% of o.d.f. Two commercial types of direct dyes have been used—a cationic direct dye 1 (CDD1) and anionic (ADD2) charge—and two laboratory-synthesized anthraquinone reactive dyes (RD1 and RD2) with a consumption of 0.2%; 0.4%; 0.6% of o.d.f. The reaction time between the additives was in the range of 2–3 min.

After preparation, each pulp mixture was examined for its dewatering ability on the Schopper Riegler apparatus, flocculation volume and sedimentation index.

After placing 1000 mL paper furnish with a concentration of 0.2% in a measuring vessel with a diameter of 150 mm, the necessary amount of retention additive was added, stirred for 10 s at slow speed (30 rpm) and was allowed to precipitate at rest. After 15 min, the

front of the sedimentation expressed in flocculation volume FV, mL in the measuring vessel, was determined and the sedimentation index SI , % was calculated, following Equation (1).

$$SI = \frac{(V_o - V_n)}{V_o} \times 100, \quad (1)$$

where V_o —the flocculation volume without dye (Cellul+Fix+AKD+Ret); V_n —flocculation volume for a corresponding amount of dye (Cellul+Fix+Dye+AKD+Ret).

The dewatering ability measuring conditions were the same as for the determination of the beating degree (described above), but the central vertical out-pipe was closed. The slurry concentration was 0.2% (2 g o.d.f. in 1000 mL water). In the current experiment, the dewatering time was taken by measuring the time (in seconds) to obtain 700 mL of filtrate.

The resulting white waters were evaluated for the dyes' concentration, turbidity in NTU (at TB1 Portable Turbidimeter (VELP Scientifica, Usmate, Italy) according to ISO 7027-1:2016 [33]), conductivity in μS (HI-2315 Bench-Top Conductivity Meter (Hanna Instruments, Nieuwegein, The Netherlands), according to ISO 7888:1985 [34]), pH with an HI-8314N pH meter (Hanna Instruments, Nieuwegein, The Netherlands) and temperature.

For determining the white waters' dye concentration, the absorbance of the dyes in the white waters and in the three standardized dye solutions were examined by using a UV/visible scanning spectrophotometer, UV 3300 PC of BIOBASE Co., Ltd., Jinan, Shandong, China, and the concentrations were given in percent.

Before measurements, the examined paper samples were conditioned at 50% RH and 23 ± 2 °C for 72 h.

The SEM micrographs of paper sample surfaces were taken with a scanning electron microscope (JSM6060 LV, Jeol Ltd., Tokyo, Japan). The instrument operated at 10 kV and at the magnification of $200\times$ and $500\times$.

The tensile strength of the paper samples was determined as the tensile index, Nm/g on a Zwick/Roell tensile testing machine (ZwickRoell GmbH & Co., Ulm, Germany), according to ISO 1924-2:2008 [35]. A minimum of ten probes for each sample were tested. The cross-speed head was 20 mm/min. Paper stripes of 18 cm in length and 1.5 cm in width were used and the distance between the clamps was 10 cm.

The artificial light aging was examined, by light exposure with 765 ± 75 W/m² intensity and 290–800 nm wavelength, according to ISO 5630-7:2014 [36]. The test duration was 48 h. On each 6 h, the color coordinates L^* , a^* and b^* in the CIE Lab color space were measured at D65₁₀, by a Konica Minolta Spectrophotometer CM-3630 from Frank—PTI (Birkenau, Germany), according to ISO/CIE 11664-4:2019 [37]. The CIE $L^*a^*b^*$ color space diagram, with the relationship of the three colors axes, is well known, where L^* —indicates lightness/darkness; a^* —the degree of redness/greenness of paper; b^* —the degree of yellowness/blueness of paper [3]. For each sample, ten measurements were made at different locations on the surface. From the measured L^* , a^* and b^* values of the color reflection, the CIEDE2000 (1:1:1) color differences (ΔE^*_{00}) for each of the fifteen paper samples were calculated using Equation (2) [38,39]. The color coordinates of the paper samples measured prior to light exposure were used as the reference.

$$\Delta E^*_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \left(\frac{\Delta C'}{k_C S_C}\right) \left(\frac{\Delta H'}{k_H S_H}\right)}, \quad (2)$$

One-way ANOVA with a confidence level of 95% ($p < 0.05$) statistical analysis was carried out using Microsoft® Excel 2016 with ToolPak data analysis.

3. Results

3.1. Dyes' Influence on Paper Slurries' Characteristics

The synthesized anthraquinone dyes RD1 and RD2 objected and presented in Figure 1 were characterized with absorption spectra and compared to the two direct dyes (cationic DD1 and anionic DD2). Records were taken in water with a concentration of 2×10^{-4} g/mL and the resulting spectra are presented in Figure 2. As can be seen from the chart, the investigated reactive dyes absorb in the range of 450–750 nm with $\lambda_{\max} = 592$ nm, while the direct dyes are in the range of 500–750 nm with $\lambda_{\max}$ at 610 nm. In the group comparative analysis, the dyes' absorbance differs between 450 and 580 nm wavelengths continuing with almost overlapping between 550 and 750 nm.

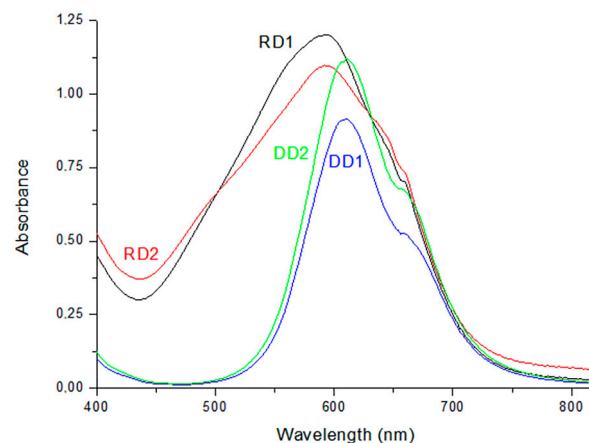


Figure 2. Absorption spectra of the investigated dyes in water.

The key slurry parameters characterizing the resulting furnish behavior were the flocculation and sedimentation dynamics, given in Tables 1 and 2. Both of them were used as a prerequisite for “wet-end” chemicals' retention and the paper properties' functional optimization. Additionally, these parameters directly indicated on the fiber and fines' drainage rate, as well as resulting in white water cleanliness. The average dye concentration, dewatering ability, conductivity, turbidity and pH of the resulting white waters are also presented in Tables 1 and 2. The data for the used direct dyes are given in Table 1, while the data for the synthesized reactive dyes are given in Table 2.

Table 1. Characteristics of paper slurries and white water properties of undyed and dyed with cationic and anionic direct dyes paper furnishes.

Paper Slurries and White Water Properties	Paper Slurry with Added Direct Dyes								
	Without Dye			Cationic DD1			Anionic DD2		
	Only Pulp	Pulp+AKD+Ret	Pulp+Fix+AKD+Ret	0.2%	0.4%	0.6%	0.2%	0.4%	0.6%
FV, mL	430	430	443	420	453	415	425	430	443
SI, %	-	-	-	5.19	2.25	4.04	4.06	2.93	0
T ₇₀₀ , s	17.35	13.25	17.55	12.02	11.82	11.83	14.73	12.25	12.55
Dye concentration, %	-	-	-	1.535×10^{-6}	1.416×10^{-6}	1.469×10^{-6}	2.578×10^{-6}	1.683×10^{-6}	1.388×10^{-6}
Turbidity, NTU	10.03	8.38	15.31	5.81	5.32	4.64	9.41	10.12	11.67
Conductivity, μ S	123.3	123.2	129.1	124.5	125.5	125.5	123.7	124.3	130.7
pH	7.49	7.47	7.49	6.85	6.83	6.96	7.12	6.94	7.01

In the detailed analysis, it is seen that the properties of the paper furnish without dyes, compared to those of only cellulose (OC), stay constant (FV, mL; Conductivity, μ S; pH) or are being improved (T₇₀₀, s; Turbidity, NTU), which confirms the hydrophobicity chemical additive (AKD) and retention additive (Ret) optimal dosage and expediency. All the investigated parameters in CDD1 are at their optimal levels and with an enhanced effect, compared to those without dye.

Table 2. Characteristics of paper slurries and white water properties of undyed and dyed with synthesized reactive dyes paper furnishes.

Paper Slurries and White Water Properties	Paper Slurry with Added Reactive Dyes								
	Without Dye			RD1			RD2		
	Only Pulp	Pulp+AKD+Ret	Pulp+Fix+AKD+Ret	0.2%	0.4%	0.6%	0.2%	0.4%	0.6%
FV, mL	430	430	443	430	445	450	430	490	460
SI, %	-	-	-	2.93	0.45	1.58	2.93	10.61	3.84
T ₇₀₀ , s	17.35	13.25	17.55	13.85	11.36	11.35	13.52	11.85	11.15
Dye concentration, %	-	-	-	1.653×10^{-6}	1.733×10^{-6}	2.347×10^{-6}	1.845×10^{-6}	1.824×10^{-6}	1.806×10^{-6}
Turbidity, NTU	10.03	8.38	15.31	10.46	7.89	5.88	12.51	8.03	7.39
Conductivity, μ S	123.3	123.2	129.1	129.7	133.2	136.2	131.5	132.5	134.1
pH	7.49	7.47	7.49	7.11	7.15	7.15	7.2	7.18	7.12

The overall results for the cellulose furnish behavior and its dewatered white water properties of the undyed and dyed with DD paper slurries, as shown in Table 1, are similar to those for the RDs, as shown in Table 2. The average flocculation volume (FV, mL) for the CDD1 is 429.3 mL, while for the ADD2, it is slightly higher—432.6 mL—confirming the repulsive effect with the negatively charged cellulose fibers. An additional effect is observed regarding the dewatering (T_{700} , s), as it decreases. Cellulose flocks were bigger, forming a fiber mash with a larger dewatering space. Moreover, the conductivity and turbidity increased, characterizing richer fines and “wet-end” chemical additive white waters.

For the RDs’ overall characterization, a clear trend is observed with the RDs’ increased consumption—the dewatering ability was enhanced, the white waters were clarified, the conductivity and pH level were stable and the dye concentration was at the same levels as for the DDs. From the perspective of papermaking, the results confirm the applicability of the investigated reactive dyes for wood-free printing papers. The average flocculation volume increases when adding RD2, with 18.4 mL growth to 460 mL, compared to the 441.6 mL for RD1. Interestingly, with the increased FV, no hampering of dewatering is observed. On the contrary, the DR2 cellulose and other chemical additives formed evenly distributed flocks with larger volume, but the turbidity of the resulting white water is clarified. Despite the slightly increased conductivity of the white water, the pH values are closer to those of the undyed paper slurries and higher than those measured for CDD1. RD2 fixation is confirmed by the decreasing white water dye concentration with increased dye consumption, showing values between $1.845 \times 10^{-6}\%$ and $1.806 \times 10^{-6}\%$. On average, these values are lower than those for RD1 and ADD2, but still higher than those for CDD1.

3.2. Dyes’ Influence on Paper Samples’ Characteristics

Natural fiber properties, suitable for the papermaking process, depend on a very wide range of characteristics, such as natural wood origin type, refining conditions and resulting fiber length, diameter, geometry and pore structure [40–42]. Therefore, each paper slurry with its “wet-end” chemical additives is giving a specifically modified paper sheet. Having an overall observation of the paper structure could provide valuable answers with expected fluctuations on additives’ applicability. The surfaces and the color of the laboratory-obtained undyed and dyed paper samples are continuous and homogeneous, proven not only from the visual identification (see Figure 3A), but from the SEM analyses, as shown in Figure 3B,C. The SEM image result of the undyed paper sample (see Figure 3B) additionally shows that the used bleached kraft softwood cellulose is from spruce wood, as the typical cell structure is well visible (outlined in the left rectangular) and the bleached kraft hardwood cellulose is from beech wood (outlined in the right rectangular). The SEM image (Figure 3C) clearly visualized that the resulting reactive dyed paper samples’ structure does not differ from the undyed one, as shown in Figure 3B, as fibrils of the fiber surface, as well as the fines settling in the pores of the fiber interstices, forming an interlaced

network. The resulting SEM images confirm that the RDs used do not negatively affect the formation and uniformity, in terms of the structural properties. There is no predominant fiber direction, as in the used sheet forming equipment, the paper formation onto the web is without motion, i.e., there is no machine or cross-direction of the sample.

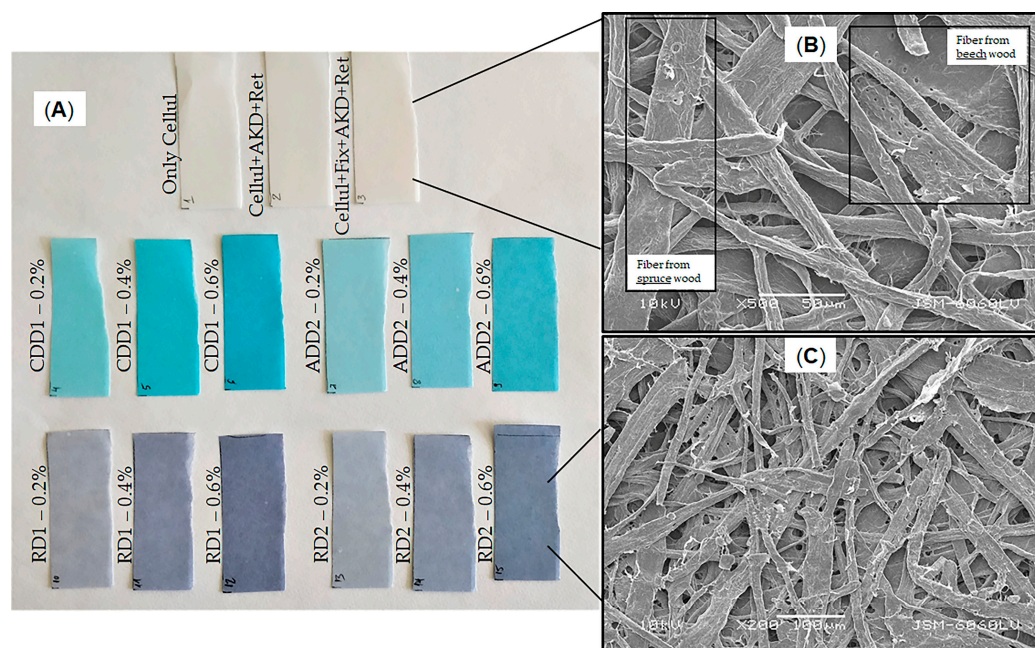


Figure 3. Visualization of obtained colored papers (A) and SEM images of (B) undyed paper sample; (C) dyed with 0.6% RD2 paper sample.

The effect of the investigated two direct and two reactive dyes on the paper samples' strength properties was determined using two methods with four parameters—the tensile and TEA indexes (Figure 4) and elongation and tear index (Figure 5).

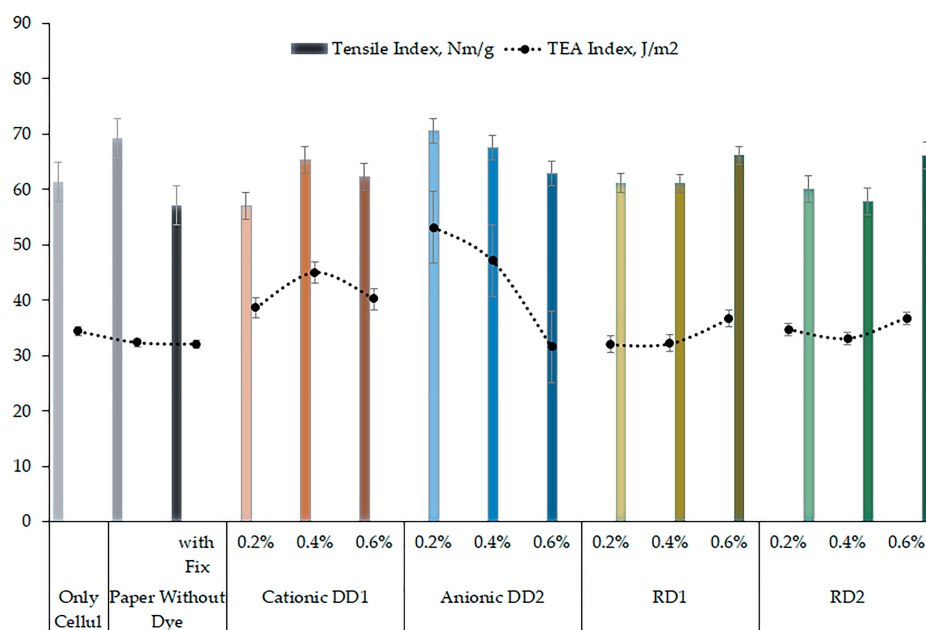


Figure 4. Tensile index and TEA index of undyed and dyed paper samples.

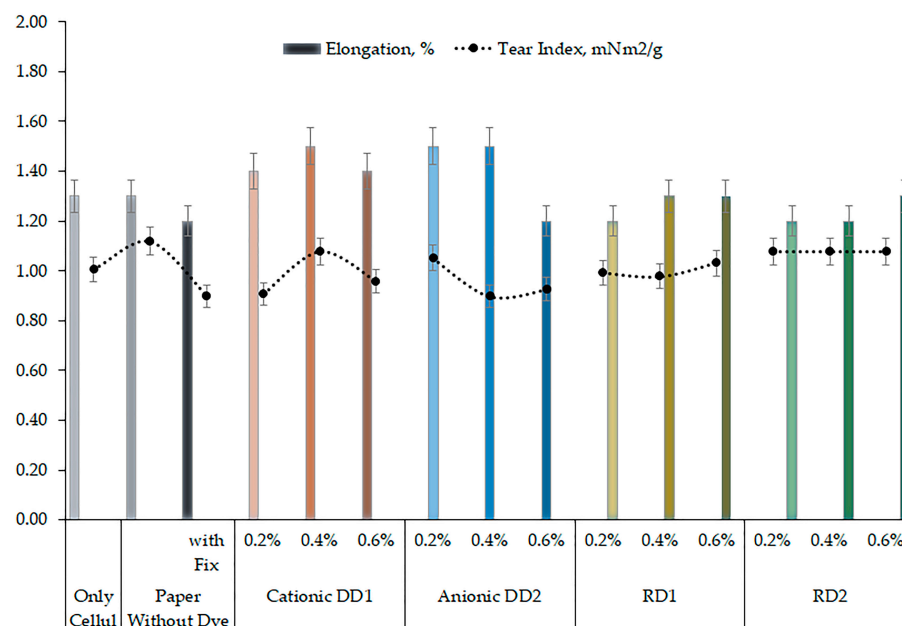


Figure 5. Elongation and tear index of undyed and dyed paper samples.

When comparing the strength properties of the resulting dyed paper samples shown in Figures 4 and 5, at first glance, the higher results obtained for both the cationic and anionic DD used are visible, while the synthesized RDs' results are at the located reference samples' levels. An enhancement in the tensile and TEA indexes was observed at the maximum RD2 consumption of 0.6% o.d.f.

Regarding the dyes' consumption variations, the overall results analysis shows that the CDD1 sufficient consumption is 0.4% of o.d.f., while when using the anionic one, even less—0.2% of o.d.f.—is required, as a drop in the strength properties is observed when adding more than 0.4% dye from the o.d.f. As for the investigated synthesized RD2 analysis, a 0.6% of o.d.f. is needed to improve the strength properties of the resulting paper samples, compared to the sample without RD (paper without dye with fixing additive).

The examined paper samples' elongation results obtained (see Figure 5) with both DDs possess a more flexible paper structure. The investigated RDs do not affect negatively the paper elongation (the values are in the range of 1.2% to 1.3%) but improve the tear resistance, as the results are at the levels of the reference paper samples and higher, respectively. The tear strength values for the two batches of reactive dyed papers are very close to each other, with values ranging from 0.978 mNm²/g to 1.078 mNm²/g. The standard deviations were also low (from ± 0.005 to ± 0.007 , respectively), indicating dye consistency in the dyeing process.

Traditionally, most accelerated aging experiments have excluded the effect of light. In the present study, the established accelerated light aged undyed and dyed paper sample updates about the light aspects on the measured color coordinates L^* , a^* and b^* and the calculated color difference ΔE^*_{00} are presented. The results in the following three tables and Figure 6 are being discussed.

When analyzing the L^* , a^* and b^* color coordinates data presented in Table 3 and the calculated total color change (ΔE^*_{00}) results shown in Figure 6, a specific trend in the aging process of the undyed and dyed paper samples can be inferred. Our experimental findings highlight that light exposure affects the undyed paper samples predominantly in the first 18 h of the 48 h exposure period, causing the color to become yellowish. In contrast, for the dyed paper samples, 24 h of the 48 h exposure period are required to observe a noticeable color change. The effect of the color change is mostly at the b^* and a^* color coordinate, with

a higher difference in the OC samples, followed by the “Cellul+AKD+Ret” samples and “Cellul+Fix+AKD+Ret”. The sizing agent increases the b^* coordinate values, resulting in whiter paper, which is very often difficult to see with the human eye. The overall decrease in the lightness (L^* coordinate) is between 0 and 0.9, with no change for the OC sample and a higher light drop in the “Cellul+Fix+AKD+Ret” paper sample. Regarding the a^* and b^* coordinates, an increase is observed of about 0.65 and 1.96, respectively, meaning the paper hue is becoming reddish and yellowish. The b^* coordinate in the “Cellul+Fix+AKD+Ret” paper sample is characterized by an increase of only 0.33, most likely affected by the presence of the cationic dye-fixing agent, which is added prior to the addition of the dye. Due to its cationic character, it affects the system by neutralizing the anionicity inherent in cellulose fibers [3] and shows the paper aging, producing both a duller shade and a predominant drop in the light parameter.

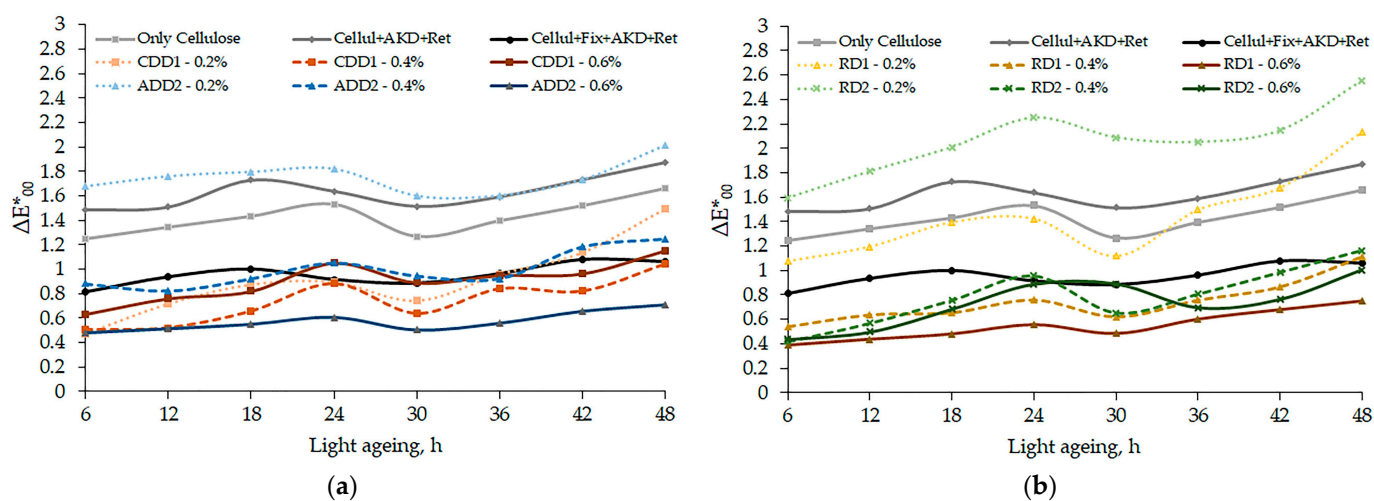


Figure 6. Total color change (ΔE^*_{00}) in paper samples with the light exposure time: (a) undyed and dyed with DDs; (b) undyed and dyed with RDs.

Table 3. Color coordinates of undyed cellulose and paper samples before and during 48 h of accelerated light aging.

Light Aging, Hours	Only Cellulose			Cellul+AKD+Ret			Cellul+Fix+AKD+Ret		
	L^*	a^*	b^*	L^*	a^*	b^*	L^*	a^*	b^*
0	92.95	−0.82	5.82	92.3	−0.83	6.24	91.66	−0.53	10.28
6	93.23	−0.28	7.03	92.67	−0.22	7.76	91.00	−0.01	10.35
12	93.11	−0.23	7.13	92.57	−0.19	7.77	90.91	0.07	10.42
18	93.03	−0.22	7.27	92.47	−0.18	8.13	90.80	0.07	10.65
24	93.03	−0.26	7.48	92.47	−0.21	8.02	90.87	0.04	10.42
30	93.18	−0.24	7.01	92.58	−0.19	7.78	90.91	0.03	10.25
36	93.01	−0.20	7.18	92.46	−0.16	7.88	90.85	0.08	10.19
42	92.93	−0.21	7.40	92.39	−0.14	8.09	90.72	0.14	10.45
48	92.95	−0.23	7.65	92.37	−0.14	8.32	90.76	0.12	10.61

Lower ΔE^*_{00} values, perceptible only upon close observation (ranging from 0.8 to 1.1), were calculated for the “Cellul+Fix+AKD+Ret” paper sample, while the ΔE^*_{00} results for the OC and “Cellul+AKD+Ret” paper samples fall within the ranges of 1.2–1.6 and 1.5–1.9, respectively.

The light aging (or lightfastness) characteristics of the paper samples that were dyed differ depending on whether direct or reactive dyes were used. A detailed comparison of their color behavior under light exposure is given in Tables 4 and 5 and Figure 6.

Table 4. Color coordinates of dyed with anionic and cationic direct dyes paper samples before and during 48 h of accelerated light aging.

Light Ag-ing, Hours	CDD1-0.2%			CDD1-0.4%			CDD1-0.6%			ADD2-0.2%			ADD2-0.4%			ADD2-0.6%		
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	81.44	−20.33	−9.32	76.86	−25.18	−15.01	73.55	−27.43	−18.95	82.73	−17.05	−8.05	79.93	−19.3	−12.29	75.02	−23.53	−14.54
6	81.60	−20.31	−8.65	76.97	−24.64	−14.15	73.72	−26.81	−17.75	82.92	−16.01	−5.72	80.36	−18.92	−10.95	74.87	−22.80	−13.85
12	81.69	−19.96	−8.27	76.92	−24.60	−14.12	73.78	−26.68	−17.52	82.94	−15.87	−5.63	80.31	−18.97	−11.03	74.89	−22.78	−13.77
18	81.72	−19.80	−8.04	76.98	−24.48	−13.89	73.80	−26.64	−17.41	82.92	−15.85	−5.58	80.33	−18.90	−10.87	74.86	−22.71	−13.74
24	81.75	−19.75	−8.02	77.07	−24.30	−13.51	73.83	−26.48	−16.97	82.96	−15.87	−5.54	80.37	−18.87	−10.67	74.84	−22.71	−13.61
30	81.75	−19.91	−8.25	77.05	−24.49	−13.94	73.79	−26.58	−17.27	82.98	−15.94	−5.86	80.41	−18.80	−10.86	74.81	−22.83	−13.80
36	81.79	−19.73	−7.93	77.14	−24.30	−13.61	73.83	−26.50	−17.17	82.98	−15.89	−5.87	80.37	−18.84	−10.88	74.83	−22.71	−13.73
42	81.84	−19.58	−7.68	77.14	−24.29	−13.65	73.84	−26.54	−17.14	82.96	−15.81	−5.69	80.37	−18.67	−10.45	74.81	−22.67	−13.53
48	82.01	−19.05	−7.25	77.22	−24.05	−13.29	74.00	−26.32	−16.84	82.91	−15.78	−5.27	80.25	−18.75	−10.32	74.79	−22.71	−13.41

Table 5. Color coordinates of dyed with reactive dyes paper samples before and during 48 h of accelerated light aging.

Light Ag-ing, Hours	RD1-0.2%			RD1-0.4%			RD1-0.6%			RD2-0.2%			RD2-0.4%			RD2-0.6%		
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	76.59	−2.59	−6.32	69.56	−1.57	−11.35	65.27	−0.84	−13.55	76.34	−2.94	−7.22	71.28	−2.52	−10.74	65.82	−1.96	−13.45
6	77.30	−2.21	−5.22	69.63	−1.16	−11.01	65.22	−0.54	−13.33	77.49	−2.71	−5.46	71.20	−2.33	−10.19	65.94	−1.80	−12.81
12	77.36	−2.17	−5.09	69.60	−1.10	−10.89	65.25	−0.51	−13.26	77.53	−2.61	−5.18	71.21	−2.26	−9.99	65.90	−1.75	−12.73
18	77.38	−2.10	−4.84	69.63	−1.09	−10.87	65.28	−0.51	−13.11	77.57	−2.55	−4.93	71.29	−2.19	−9.73	66.02	−1.73	−12.45
24	77.38	−2.07	−4.82	69.67	−1.06	−10.66	65.28	−0.49	−12.96	77.69	−2.42	−4.68	71.35	−2.10	−9.48	66.07	−1.63	−12.18
30	77.28	−2.15	−5.19	69.63	−1.09	−11.01	65.14	−0.50	−13.17	77.61	−2.44	−4.87	71.21	−2.15	−9.96	66.02	−1.62	−12.17
36	77.43	−2.04	−4.75	69.62	−1.01	−10.82	65.15	−0.43	−13.02	77.55	−2.43	−4.90	71.25	−2.12	−9.71	65.98	−1.66	−12.47
42	77.48	−1.96	−4.56	69.76	−1.02	−10.51	65.23	−0.40	−12.87	77.57	−2.41	−4.78	71.27	−1.98	−9.55	65.97	−1.62	−12.38
48	77.63	−1.86	−4.02	69.79	−0.95	−10.11	65.24	−0.38	−12.74	77.68	−2.24	−4.32	71.40	−1.97	−9.29	66.12	−1.53	−12.07

At the initial stage, prior to any significant accelerated light aging, the lightness values for the DDs range from 81.44 for the CDD1 to 82.73 for the ADD2 at the lowest dye concentration of 0.2%. When the concentration increases to 0.6%, the lightness decreases to 73.55 for the CDD1 and 75.02 for the ADD2. As shown in Table 4, the data for the two studied DDs reveal a consistent trend: after 48 h of accelerated light aging, there is a noticeable lightening of the paper samples, with no color reversion. At all three dye concentrations, the brightness increases, while the values along both the red-green and yellow-blue color axes decrease.

In Figure 6a, a general observation is that the ΔE^*_{00} curves from 6 to 48 h of light aging fall into two main groups. The curve for the paper sample without dyes—“Cellul+Fix+AKD+Ret”—as well as those for CDD1 and ADD2 (with the exception of ADD2 at 0.2% consumption of o.d.f.) are compactly grouped within the ΔE^*_{00} interval of 0.5–1.0. The only sample with a total color change ΔE^*_{00} below the perceptibility threshold for the human eye (<0.5) is the ADD2—0.6% paper. The color changes in the papers dyed with CDD1 and with ADD2—0.4% fall within the range perceptible only upon very close observation. At the lowest ADD2 dosage of 0.2%, the ΔE^*_{00} values exceed 1.0, corresponding to a level of color change clearly perceptible through observation. The curve for this sample lies higher than those of the OC and “Cellul+AKD+Ret” paper samples. Color variations over time under light exposure are more pronounced in the examined DD paper samples, particularly in the CDD1 samples across all three consumption levels. The variations are also present in the ADD2 samples, but with reduced fluctuation.

For the laboratory-synthesized RDs (Table 5), the lightness ranges from 76.59 (RD1 at 0.2%) to 76.34 (RD2 at 0.2%), and drops further to 65.27 (RD1 at 0.6%) and 65.82 (RD2 at 0.6%). From the analysis of the data on the color coordinate changes in the aged paper samples dyed with laboratory-synthesized RDs, several key trends were identified. At the initial stage (0 h, before the onset of light radiation), a consistent change in the color coordinates is observed with the increasing dye concentration, ranging from 0.2% to 0.6% of the o.d.f. For samples dyed with blue RD2, the color shifts towards a lighter green hue along the a^* axis (from −2.94 to −1.96) and a deeper blue along the b^* axis (from −7.22 to −13.45). Similar trends are observed in the samples dyed with blue RD1, though with slight variations: the a^* values range from −2.59 at 0.2% to −0.84 at 0.6%, and the b^* values change from −6.32 to −13.55.

The difference in lightness (L^*) between 0 and 48 h for samples dyed with DDs ranges from 0.18 to 0.58 (in absolute terms), while for RDs, the range is from 0.03 to 1.34. Although this might initially suggest poorer lightfastness in reactive dyes, a deeper analysis reveals that lower dye concentrations (0.2% RD) result in reduced stability. This is also confirmed by the results for the calculated RDs' color differences ΔE^*_{00} , presented in Figure 6b.

Similar to the results for the color change in the DD samples during 48 h of light aging, those for the reactive dyes are also grouped into two ranges: below 0.8 and above 1.1 ΔE^*_{00} . The paper samples dyed with 0.6% o.d.f. of RD1 and RD2 show total color change values below 0.5 ΔE^*_{00} , indicating barely noticeable variation or “not perceptible by the human eye,” followed by the samples dyed with 0.4% of the same dyes. Their characteristic curves lie below the curve of the paper sample containing Fix but no dye, which itself shows minimal fluctuations in the range of 0.8–0.9 ΔE^*_{00} . A color difference “perceptible through close observation” ($\Delta E^*_{00} > 1.0$) is observed in the two blank samples and the two dyed paper samples: the OC sample and the paper without the fixing additive, as well as the samples dyed with the lowest reactive dye consumption (0.2% o.d.f.). This is likely due to an imbalanced ratio between the dye and the fixing agent. In these experiments, the fixing agent was used at a constant 1% dosage of o.d.f., while the dye consumptions varied from 0.2% to 0.6% of o.d.f.

This explanation is further supported by the similarity in lightfastness between samples containing only the fixing agent (without dye) and those with 0.2% dye. In both cases, similar degrees of darkening were observed (see Table 3). However, in the samples dyed with 0.4% and 0.6% RD, this effect was significantly reduced or entirely absent, suggesting that appropriate balancing of the dye and the fixing agent is critical for optimal lightfastness.

These findings support the conclusion that the proportions between the reactive dye and the epichlorohydrin–dimethylamine copolymer-based fixing agent should be carefully controlled. In cases where the proportionality is maintained, samples RD1 and RD2 at 0.6% consumption, the lightfastness values fall within a narrow and favorable range of 0.03 to 0.3, respectively.

4. Discussion

Paper furnish characteristics play a significant role in determining the efficiency of the chemical additives added and quality of the sheet formation. Depending on the type of dye, its retention is generally caused by a chemical bonding with the cellulose fiber. This bonding might be affected by various factors including the cellulose type, its beating degree, the presence or absence of fillers and additives, etc. [3,40]. It is well known that fixing agents are products with cationic charge, which gives dyes complete fixation when ambient conditions prevent this occurring naturally. It is very likely that the quaternary ammonium groups from the epichlorohydrin–dimethylamine copolymer in the Fix, together with their strong ionic interactions with the carboxylic groups of the bleached cellulose—formed during the pulping process from cellulose carbonyl groups—provide the necessary dye fixation. As these products are related to the dye, their point of addition is very much product-specific, i.e., added pre or post the dye [3]. As this additive additionally charges the investigated system, no advisability is given to be used without paper dyeing.

The results of the paper furnish behavior and resulting white waters by adding a fixing agent are foreseen, as its cationic charge balances the paper furnish but predominantly when a dye is also presented. When comparing the direct dyed paper furnish indicators, according to our research, a clear conclusion occurs—CDD1 at 0.4% of o.d.f. consumption could be recommended when dyeing paper suspensions of the examined bleached virgin kraft pulp blend combinations. Even though it is not commonly used for the dyeing of bleached kraft cellulose mixtures, if necessary—due to a technological or other reason—an

ADD2 could be used. Still, ADD consumption should be in the range of 0.2–0.3% of o.d.f., as a higher dosage harms the investigated parameters even though the dye retention is improved by the fixing agent used. This result is probably due to the resulting repulsion effect of the negatively charged components—cellulose fibers and dye. Disruption of the uniformly formed components agglomerates, also proven by the FV, conductivity and turbidity results. Therefore, the product applicability determines the increased DD2 retention and clear wastewater, which sets a positive result for dyes' applicability in papermaking. When dyeing with both RDs at 0.6% consumption and with the used chemical additives, its functional and processed effect over the paper properties is very likely to be optimal, as the paper slurries' characteristics are in accordance. From the research conducted, the following trend is observed: as the dye consumption increases, the concentration of the corresponding dye in the white water decreases. This decrease is more pronounced for DD2 than DD1. In contrast, with RD1, the opposite trend is observed—its concentration in white water increases as the dye consumption rises. This can be explained by the well-known fact that, at slightly alkaline pH and near-neutral pH, hydrolysis of chlorotriazine dyes occurs. This is due to the highly reactive nature of the chlorotriazine group, which can interact with hydroxyl anions from water [43]. This also applies to the chlorotriazine group of RD2. In our previous publications on the dyeing of cotton and paper with reactive dyes containing allyl groups, we demonstrated that the percentages of dye exhaustion and fixation were higher compared to those achieved with dyes containing only the chlorotriazine reactive group [44–47]. This provided indirect evidence that the allyl group formed a chemical bond with the material through a nucleophilic addition mechanism. Hydrolysis of the dyes does not occur because water does not participate under dyeing conditions (near-neutral or slightly alkaline pH). Based on this, it can be concluded that the presence of the allyl group in dye RD2 is responsible for the observed trend in dyes DD1 and DD2.

In the TEA index results, shown in Figure 4, clear fluctuations in the parameters are observed. As expected, and in line with the well-known dependence of direct hydrogen inter-fiber bonding [40,48], the strength properties—tensile index and TEA index—of the investigated paper samples are higher for those dyed with cationic and anionic DDs. As reactive dyes integrate into the paper structure, the results for the reactive dyed paper samples, including their tear index (shown in Figure 5), also show higher values compared to those dyed with DDs. Additionally, paper tear resistance primarily depends on the nature and initial strength of the fibers, and secondarily on the fiber–web structural characteristics. The obtained results confirm that the covalent bonds formed during dyeing influence the paper tear resistance.

Based on the strength results, we can summarize that both cationic and anionic DDs affect the inter-fiber connections by improving the tensile, TEA and elongation characteristics of the paper samples. In contrast, the synthesized RDs stabilize the web structure without additional fiber bonding, relying instead on covalent attraction, which enhances tear resistance. The consistency of the tear strength across the two batches of reactive-dyed papers demonstrates that the synthesized RD2 has a reliable and reproducible effect on the paper's tear resistance, with only minor variations between the different dye consumptions. These results are further confirmed by the SEM analysis shown in Figure 3, where the uniformity of the paper structure is clearly visualized. It is well known that when paper is exposed to light, it triggers the formation of free radicals, which initiate the photo-oxidation of cellulose. This process follows a mechanism similar to that of cellulose autoxidation. As a result, photo-oxidation lowers the degree of polymerization and weakens both the paper and the cellulose fibers. It also degrades the optical properties of the material, especially in lignin-containing paper and introduces carbonyl and carboxyl groups into the cellulose

structure. Additionally, light exposure can cause bleaching, likely due to the oxidation of chromophores formed during lignin degradation. In papers without lignin, bleaching may occur as carbonyl groups are further oxidized into carboxyls [49].

The issue of color instability in paper during aging is commonly referred to in the paper industry as “color or brightness reversion”. Pure cellulose does not absorb visible light (wavelengths above 400 nm) but strongly absorbs ultraviolet (UV) light below 200 nm. In the intermediate UV range, it exhibits a weak absorption peak around 260 nm, attributed to carbonyl groups (such as acetals or ketones), which are thought to initiate photochemical reactions. Hemicelluloses behave similarly to cellulose, whereas both natural and modified lignin absorb strongly across the UV and visible spectra. In mechanical pulps, color reversion is primarily caused by the photo-oxidation of lignin. This process is believed to involve free phenolic radicals, which lead to the formation of o-quinones, compounds largely responsible for the yellowing of aged paper [49–52].

No unexpected behavior was observed during the accelerated light aging of paper made from bleached cellulose dyed with DDs. These results are consistent with patterns well documented in the scientific literature [26–28,51,52], described as UV degradation of DD photo-oxidation as its structural stability is weakening with the accelerated light aging by breaking down into colorless components.

Dyeing with DDs relies on ionic bonds, hydrogen bonds or Van der Waals forces, while RDs form covalent chemical bonds and hydrogen bonds. One of our synthesized dyes is a monochlorotriazine dye, and its dyeing mechanism is well established worldwide. It is also known that at slightly alkaline pH, or pH values close to neutral, hydrolysis of chlorotriazine dyes occurs. This is because the chlorotriazine group is highly reactive and can react with hydroxyl anions from water [43]. The other synthesized dye, in addition to the monochlorotriazine group, also contains an allyl group. Our conclusions are based on previous investigations and publications involving the dyeing of cotton and paper with reactive dyes containing allyl groups. In those studies, we showed that the extraction and fixation percentages of these dyes were higher compared to those with dyes containing only the chlorotriazine reactive group. Hydrolysis of the dyes does not occur because the addition reaction of water to the double bond, under dyeing and papermaking conditions (near-neutral or slightly alkaline pH), does not take place. Therefore, we conclude that the improved fixation and photostability values of the samples with RD2 are likely due to the presence of this allyl group.

When dyeing with RDs, some unexpected reactions could cause color instability, as their reactive groups may catalyze the aging processes. Various studies provide evidence for the involvement of short-lived radical cations and radical anions, in addition to OH[•] adducts, in the photodegradation mechanism of triazine-based compounds [53]. Dye degradation is characterized by decolorization and a decrease in the total organic content, resulting from the mineralization of the dye solution. The kinetics of photolysis for triazine dyes strongly depend on the type of chromophore; azo-triazine dyes are more susceptible to photodegradation than anthraquinone-based dyes. Additionally, the shape and size of dye molecules play an important role in the photodegradation of triazine dyes [54].

Notably, for the laboratory-synthesized RDs, the green-red component (a*) is more pronounced in RD2-dyed samples, while the yellow-blue component (b*) shows similar values in both dye types. Lightness (L*) decreases as the dye concentration increases, indicating a darker and more saturated blue coloration. Overall, the results confirm successful paper dyeing with the examined anthraquinone RDs, characterized by reduced lightness and enhanced blue saturation with higher dye concentrations as the chlorine atom from the monochlorotriazine undergoes nucleophilic substitution with the hydroxyl

groups of cellulose under alkaline conditions and the allylic group participates in an addition reaction.

As expected, after accelerated light aging (conducted under standardized conditions), all dyed samples exhibit increased lightness (L^*), indicating fading, while the a^* and b^* values decrease. For the three-color coordinates, the changes are within different limits, but the overall change is in the range of 1–12%, with b^* being more light-sensitive, compared to the initial (0 h) values. Over the course of the next seven measurements, taken every 6 h up to 48 h, a reversible fluctuation in L^* from the color coordinates is observed, attributed to the presence of chromogen fragments from the reactive dye, preventing the coloring of the paper samples. In the dried paper samples, alongside the two key interactions—namely the ionic bond between the Fix and cellulose fibers, and the covalent bond between the RD and cellulose—a hydrogen bond is also formed. These complex inter-additive and inter-fiber interactions undoubtedly contribute to a reduction in the photo-oxidative effect, as evidenced by the lower ΔE^*_{00} values compared to the OC and “Cellul+AKD+Ret” paper samples, whose curves lie above those of the “Cellul+Fix+AKD+Ret” and dyed samples in Figure 6.

The results of the overall color change in the samples, dyed with the studied pairs of direct and reactive dyes, measured every 6 h over a 48 h light aging period, show fluctuations of a non-systematic character. During the 48 h aging process, samples dyed with RD exhibit gradual and reversible brightness changes. With increased consumption of RDs, these reversals in color values occur more frequently (2–4 times), but the overall trend remains—lightening of the paper samples after aging. The studied RDs demonstrate imperceptible by the human eye or perceptible through close observation decreases in their total color change ΔE^*_{00} under UV/visible light, very close to that of DDs, when the ratio of the fixing agent to dye is optimized.

5. Conclusions

With the synthesized RDs' increased consumption, the dewatering ability is enhanced, the white waters are clarified, the conductivity and pH level are stable and the dye concentration is on the same levels as for the DDs. SEM images confirm that the RDs used do not negatively affect the formation and uniformity, in terms of the structural properties. The RDs fully meet the common dyed paper requirements needed. The investigated RDs do not negatively affect paper elongation and improve tear resistance. Overall, the results confirm successful paper dyeing with the examined anthraquinone RDs, characterized by reduced lightness and enhanced blue saturation with higher dye concentrations. After accelerated light aging (conducted under standardized conditions), all dyed samples exhibit increased lightness (L^*), indicating fading, while the a^* and b^* values decrease. Notably, for the laboratory-synthesized RDs, the lightness (L^*) decreases as the dye concentration increases, indicating a darker and more saturated blue color, the green-red component (a^*) is more pronounced in the RD2-dyed samples, while the yellow-blue component (b^*) shows similar values in both dye types. The studied RDs become part of the paper fibers. The studied RDs demonstrate imperceptible by the human eye or perceptible through close observation decreases in their total color change ΔE^*_{00} under UV/visible light, very close to that of DDs, when the ratio of the fixing agent to dye is optimized, making them acceptable for long-term durability.

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Abbreviations

The following abbreviations are used in this manuscript:

RD	Reactive dye
DD	Direct dye
AKD	Alkyl ketene dimer
Fix	Fixing additive
Ret	Retention additive
CDD1	Cationic direct dye 1
ADD2	Anionic direct dye 2

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