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Determination of wet fastness and colour resistance to repeated washings of reactive dyes depending on chromophore group

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The resistance of colour to repeated domestic washing is a critical performance requirement for cotton fabrics dyed with reactive dyes, particularly in terms of maintaining acceptable wet fastness and colour stability. Although the washing fastness of reactive dyed products is generally good, colour change remains an inevitable issue, particularly under repeated washing conditions. Within the scope of this study, this research aimed to determine how wet fastness values, and especially colour change after repeated washes, are influenced by the dye chromophore group, which is the primary colour-determining component of reactive dyes. The results demonstrated that monoazo, metal azo and anthraquinone-based dyes exhibited lower levels of colour change after repeated washes, whereas other dyes (phthalocyanine, copper formazan, bisazo and triphendioxazine) showed more pronounced colour changes. Regarding the effect of washing frequency, the colour differences observed between 0-1-5-10-20 washes and between 20-30-40-50-60 washes were found to be statistically insignificant. These findings indicate that colour loss remains at acceptable levels up to the first 20 washes, while substantial colour loss occurs after approximately 30 washes, depending on the dye type.

Keywords: Chromophore, Colour, Dye, Fabric, Washing fastness

1 Introduction

As is well known, reactive dyes constitute the most important class of dyes used in the dyeing and printing of cellulose-based fibres and blends due to their advantages such as high wet fastness, a wide colour palette, and suitability for many dyeing methods[1]. The washing fastness of reactive dyes is generally very good due to the covalent bond between the fibre and the dye. However, hydrolysed dye that is not adequately removed (due to insufficient washing or the use of high-substantivity dyes), factors that degrade the chromophore (bleaching agents and detergents containing such agents), and factors that break the bond between dye and fibre (acid, alkali, temperature, etc.) may cause problems in washing fastness[2].

Consumers, retailers, and suppliers of garments and fabrics frequently complain of unacceptable discolouration and colour loss in 100% cotton fabrics or fabrics with a high cotton content, particularly in dark blue and black garments made from 100% cotton fibres[3]. It has long been known that washing causes colour loss or colour change in dyed textiles. This is due either to the physical removal of dye during washing or to the chemical degradation of the dye by components present in detergents[4].

Some researchers have suggested that careful dye selection is important to prevent fading of cellulose-based garments dyed with reactive dyes. Studies have emphasised the superiority of monochlorotriazine (MCT) dyes and attributed colour fading to light and/or thermo-oxidative hydrolysis. In metal complex dyes, it has long been known that the catalytic effect of metals in activating peroxide causes strength loss in cellulose fabrics. With the increasing use of oxidative bleaching agents in household laundry detergents, copper-complex azo reactive dyes have gradually disappeared from the market; another reason for their declining popularity is their low colour fastness to light and perspiration[5].

Additionally, oxidation of triazine and pyrimidine rings by peroxide can lead to significant dye losses, particularly in difluoro-monochloropyrimidine (DFP)-based dyes[6,7].

The world's best-selling reactive dye, CI Reactive Black 5, has been widely recognised as an economical option for dyeing cellulosic substrates in dark navy

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blue and black shades. However, the introduction of increasingly powerful household detergents has shown that this dye, along with many others, is unstable in the presence of modern active bleach-containing detergents[8]. Akerman *et al.*[8] investigated the design, synthesis, and evaluation of CI Reactive Black 5 analogues with improved resistance to oxidative bleach fading. According to their experimental results, ortho-position bonding of a halogen atom (chlorine or bromine) to the azo group has little effect on the oxidative bleach resistance of monohalogenated derivatives of CI Reactive Black 5. In contrast, the addition of chlorine or bromine at the ortho position of the hydrazo group exhibited a beneficial effect, indicating that dye degradation largely occurs in the vicinity of the hydrazo group.

Numerous studies have investigated the colour fastness behaviour of reactive-dyed cotton fabrics under various conditions, particularly with respect to washing durability and the effects of detergent components[9-10]. Although reactive dyes form covalent bonds with cellulose fibres and generally provide good initial wash fastness, repeated domestic laundering can still result in noticeable colour loss due to progressive dye degradation and the combined chemical and mechanical stresses of laundering[9-11]. In addition, several authors have highlighted that laundering parameters (including detergent formulation (notably oxidising bleach additives), wash temperature, and related washing conditions) can significantly influence colour retention[9,11,12]. Despite this established need for multi-cycle assessment, comparatively fewer studies explicitly address how the dye's molecular features (particularly the chromophore) govern colour fastness and hue change under repeated domestic laundering for reactive dyes on cotton, which motivates the focus of the present work.

Today, users demand high wet fastness values. Although the washing fastness of reactive dyed products is generally good, colour change remains an inevitable issue, particularly under repeated washing conditions. Some special reactive dyes have been developed as a solution to this problem. However, their high cost creates difficulties under current economic conditions. Previous studies conducted by Atav et al. have investigated the effect of reactive dye chromophores on colour removal efficiency in wastewater[13-16] and on colour stripping from fabrics[17].

Within the scope of this study, this research aims to determine how wet fastness values, and particularly colour change under repeated washings, are affected by the dye chromophore group, which is the colour-determining component of reactive dyes. Additionally, the study seeks to identify chromophore groups with high resistance that can meet customer expectations without incurring additional costs. Since no studies in the literature have investigated wet fastness and colour resistance to repeated washing of reactive dyes in relation to chromophore groups, this study is considered original and is expected to contribute to the literature.

2 Materials and Methods

In this study, 100% single jersey knitted cotton fabric (weight: 150 g/m²), ready to be dyed (scoured and bleached), was used. Initially, fabrics were dyed with reactive dyes having different chromophore groups (azo and bisazo, metal complex azo, anthraquinone, phthalocyanine, triphendioxyazine, and formazan) according to the exhaust dyeing method. Dyeings were carried out following the temperature rise method (45 °C to 60 °C) (Fig. 1), using 0.8 g/L sequestering agent, salt (sodium chloride), alkali (soda ash and caustic soda), and dye (Table 1). Various properties of reactive dyes used in experiments are given in Table 2.

After dyeing, samples were subjected to cold rinsing (8 min at 40 °C) → neutralisation (0.25 g/L CH_3COOH, 10 min at 50 °C) → warm rinsing (10 min at 70 °C) → warm rinsing (10 min at 60 °C) → cold rinsing (5 min at 40 °C), respectively. Since the colour yield (K/S value) of the fabrics should be comparable to allow a meaningful evaluation of wet fastness and colour retention under repeated washings, the dyeing depth (% owf) was individually

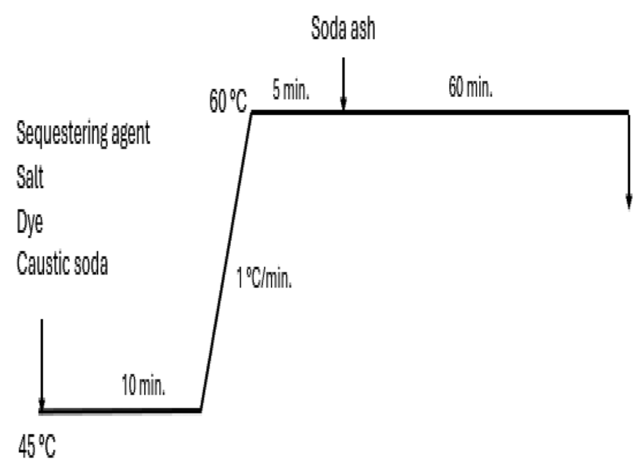

Fig. 1 — Dyeing graph used in experiments

Table 1 — Reactive dyeing recipes used in experiments

Dye	Salt (gL)	Soda ash (g/L)	Caustic Soda (45 °Bé) (mL/L)	Dyeing Depth (%)	Colour Yield (K/S)
Remazol Bril. Red 3BS	45	18	-	0.95	1.28
Remazol Black B	25	14	-	0.35	1.17
Remazol Red 3B	65	5	1.85	3	1.22
Remazol Br. Blue R Special	40	17	-	0.85	1.32
Remazol Bril. Blue BB	60	5	1.8	1.9	1.16
Remazol Turquoise Blue G	60	5	1.8	1.8	1.38
Levafix Royal Blue EF-R	45	18	-	1.1	1.34

Table 2 — Reactive dyes used in experiments[9,12]

Dye	C.I. Generic Name	Chromophore Group	Reactive Group	Molecular formula	Mol. Wt (g/mol)	Number of sulfo groups
Remazol Bril. Red 3BS	Reactive Red 239	Monoazo	VS	$C_{31}H_{19}ClN_7Na_5O_{19}S_6$	1136.3	6
Remazol Black B	Reactive Black 5	Bisazo	VS/VS	$C_{26}H_{21}N_5Na_4O_{19}S_6$	991.78	6
Remazol Red 3B	Reactive Red 23	Metal azo	VS	$C_{18}H_{13}N_2Na_3O_{14}S_4$	678.53	4
Remazol Br. Blue R Special	Reactive Blue 19	Anthraquinone	VS	$C_{22}H_{16}N_2Na_2O_{11}S_3$	626.5	3
Remazol Bril. Blue BB	Reactive Blue 220	Copper formazan	VS	$C_{22}H_{16}CuN_4Na_4O_{15}S_4$	733.10	3
Remazol Turquoise Blue G	Reactive Blue 21	Phthalocyanine	VS	$C_{40}H_{25}CuN_9O_{14}S_5$	1079.6	5
Levafix Royal Blue EF-R	Reactive Blue 224	Triphendioxazine	VS/VS	$C_{26}H_{24}Cl_2K_1N_4Na_1O_{20}S_6$	1037.87	2

adjusted for each reactive dye. This adjustment accounts for differences in the inherent reactivity and substantivity of the chromophores, which affect the degree of fixation onto the cellulose fibres. By standardising the resulting K/S values across all dyes, the influence of chromophore type on fastness properties could be assessed independently of initial colour intensity, ensuring a fair and chemically sound comparison. The results are given in Table 1.

Washing (at 40 °C according to the A1M programme)[18], rubbing[19], perspiration (acidic and alkaline)[20], and water[21] fastness tests were then carried out according to ISO standards. In addition, the dyed fabrics were subjected to repeated domestic laundering according to ISO 6330:2021[22], using a standard 4N programme at 40 °C with normal spin speed and tumble drying. The fabrics were washed for up to 60 cycles, and after each selected cycle (1, 5, 10, 20, 30, 40, 50, and 60 washes), the colour yield (K/S) values were measured to assess the changes in fabric colour and identify chromophores exhibiting high colour fastness.

All experimental results were statistically analysed using Minitab 19 software. A two-way analysis of variance (ANOVA) was performed to evaluate the effects of dye type and number of washing cycles on the measured responses. The assumptions of ANOVA, including normality and homogeneity of variance, were checked before analysis. To further identify specific differences among groups, Tukey's honestly significant difference (HSD) post hoc test was applied. The mean and standard deviation variability. Interaction plots were also generated to visualise the combined effect of dye type and washing cycles on colour yield. The statistical significance level was set at $p < 0.05$.

Table 3 — Analysis of variance results on colour yield values after repeated washes depending on the dye chromophore

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Dye	6	1,0916	0,18193	10,05	0,000
Washing Cycle	8	1,1010	0,13763	7,61	0,000
Error	48	0,8686	0,01810		
Total	62	3,0611			

2.1 Determination of colour yield values

To determine the colour yield after dyeing, %R (reflectance) values of the fabric samples were measured using a spectral photometer (D 65/10°) in the spectral region of 400-700 nm and maximum absorption (minimum reflectance) wavelength. Then colour yield (K/S) values were calculated according to the Kubelka/Munk formula as follows[23];

$$K/S = (1 - R)2 / 2R$$

R: Reflectance value at maximum absorption wavelength
K: Absorption coefficient
S: Scattering coefficient

3 Results and Discussion

In the study, reactive dyes with seven different chromophore groups were used, and the colour changes over 60 repeated washing cycles were examined. The results of the analysis of variance (ANOVA) on colour yield (K/S) values are presented in Table 3.

When Table 3 is examined, it is evident that the effect of both dye type and number of washing cycles on colour yield is statistically significant ($p < 0.05$). Tukey's post hoc analyses were also performed to identify the source of the differences, and the results are presented in Tables 4 and 5.

When Tables 4 is analysed, it is observed that the dyes can be divided into two distinct groups based on their behaviour under repeated washing. Monoazo, metal azo, and anthraquinone-based dyes belong to Group A and exhibit smaller colour changes, whereas phthalocyanine, copper formazan, bisazo, and triphendioxazine dyes form Group C and show greater colour loss. According to the Tukey post hoc analysis (Table 4), Reactive Red 239, Reactive Red 23, and Reactive Blue 19 display statistically similar colour yield values after repeated washing, indicating high colour retention, while Reactive Blue 21, Reactive Blue 220, Reactive Black 5, and Reactive Blue 224 exhibit significantly lower K/S values, demonstrating higher colour loss. This grouping clearly highlights the effect of different chromophores on washing fastness and provides a practical distinction among dyes based on their colour retention properties.

The colour loss and change observed during washing are known to depend on a variety of factors, including dyeing depth, the type of chromophore, the reactive group, molecular weight, and the number of solubilising sulfo groups present in the dye. In this study, these factors were systematically considered to understand their potential contribution to washing fastness.

Chromophores are the parts in a molecule that absorb light at certain wavelengths and are responsible for the colour of a compound. Conjugated compounds are inherently linked to the chromophore concept as delocalization of electrons through conjugation determines absorption wavelength. The colour observed for a compound is directly affected by the type or degree of conjugation[24]. On the other hand, aggregation phenomena, which vary between chromophore types, can reduce effective light absorption and lead to lower apparent colour strength despite similar levels of dye fixation. Consequently, reactive dyes with different chromophore groups require different dye concentrations to achieve comparable K/S values, even under identical dyeing conditions. The variations observed in this study therefore reflect fundamental differences in the optical and structural properties of the chromophores rather than differences in dye-fibre bonding efficiency alone. This interpretation is further supported by the fact that all dyes used in this study are vinyl sulfone-based reactive dyes and thus share a common fixation mechanism on cellulose fibres. In all cases, dye fixation occurs via a nucleophilic addition reaction between the vinyl sulfone group of the dye and the hydroxyl groups of cellulose under alkaline conditions, leading to the formation of stable covalent bonds[25].

Table 4 — Tukey analysis results for the effect of dye type

Dye	N	Mean	Grouping		
Reactive Red 239 (Monoazo)	9	1,28156	A		
Reactive Red 23 (Metal azo)	9	1,26044	A	B	
Reactive Blue 19 (Anthraquinone)	9	1,26040	A	B	
Reactive Blue 21 (Phthalocyanine)	9	1,08031		B	C
Reactive Blue 220 (Copper formazan)	9	1,03264			C
Reactive Black 5 (Bisazo)	9	0,97357			C
Reactive Blue 224 (Triphendioxazine)	9	0,96152			C

Table 5 — Tukey analysis results for the effect of number of washes

Washing Cycle	N	Mean	Grouping			
1	7	1,31783	A			
5	7	1,26180	A	B		
0	7	1,25561	A	B		
10	7	1,18920	A	B	C	
20	7	1,10339	A	B	C	D
30	7	1,05451		B	C	D
40	7	1,00923			C	D
50	7	0,97189			C	D
60	7	0,92997				D

The amount of dye required to achieve comparable colour depth varied significantly across chromophore types. For the dyes used here, the following approximate concentrations were required:

- Remazol Black B (Bisazo) - 0.35%,
- Remazol Brilliant Blue R Special (Anthraquinone), Remazol Brilliant Red 3BS (Monoazo), and Levafix Royal Blue EF-R (Triphendioxazine) – approx. 1%,
- Remazol Brilliant Blue BB (Copper formazan) and Remazol Turquoise Blue G (Phthalocyanine) – approx. 2%, - Remazol Red 3B (Metal azo) - 3%.

Notably, dyes exhibiting the lowest colour loss upon washing were not consistently associated with the smallest or largest required dye quantity. For instance, the K/S value achieved with 0.35% Remazol Black B (Bisazo) was comparable to that obtained with 3% Remazol Red 3B (Metal azo). This indicates that repeated washing does not simply reflect the concentration of dye used to achieve the target depth of shade.

The influence of the reactive group type was also considered, as washing fastness can be affected by hydrolysis of the dye-fibre bond. All dyes employed in this study contained the VS reactive group, with bisazo and triphendioxazine dyes being bifunctional. Based on bonding considerations, bifunctional dyes might be expected to exhibit higher washing fastness. However, this was not observed. Monoazo, metal azo, and anthraquinone-based dyes (Group A) displayed the smallest colour changes, suggesting that the reactive group type alone does not account for the observed differences in washing performance.

Similarly, molecular weight was evaluated as a potential determinant of washing fastness. Higher molecular weight is generally associated with greater fibre affinity and reduced dye leaching. In this study, molecular weights were approximately 1000-1100 for monoazo, bisazo, phthalocyanine, and triphendioxazine dyes, and 600-700 for metal azo, anthraquinone, and copper formazan dyes. The three dyes exhibiting the lowest colour loss belonged to different molecular weight ranges, indicating that molecular weight is not the primary factor governing washing behaviour.

The number of solubilising sulfo groups was also considered, as higher numbers may enhance water solubility and potentially increase dye loss during washing. In the present dataset, monoazo and bisazo dyes contained six sulfo groups; phthalocyanine five; metal azo four; anthraquinone and copper formazan three; and triphendioxazine two. Again, the dyes with minimal colour change belonged to different sulfo group categories, demonstrating that this parameter alone does not explain the differences observed.

Taken together, these observations suggest that the chromophore structure itself is the primary determinant of washing colour loss and colour change. Different chromophore types are known to influence not only the spectral properties but also the chemical stability of the dye under washing conditions (pH, detergents, temperature) and the strength of dye-fibre interactions. As reported in the literature, the washing fastness of reactive dyes is strongly influenced by the chromophore type. Anthraquinone- and copper formazan-based dyes are generally characterised by high washing fastness, along with excellent light and bleaching fastness, and stability under acidic and alkaline conditions. Monoazo dyes, in contrast, can display more variable wet fastness depending on their specific chemical structure, while bisazo dyes tend to provide darker shades but with somewhat inconsistent performance in laundering. Phthalocyanine dyes, despite their high light fastness and ability to provide bright turquoise and green shades, typically show limited resistance to washing. Triphenodioxazine dyes are often sensitive to acidic and alkaline environments[2,26]. The findings of the present study are therefore consistent with these reported tendencies, indicating that chromophore type is a primary determinant of colour retention under repeated domestic laundering. While other factors such as reactive group type, molecular weight, or the number of solubilising groups may contribute, they appear to play a secondary role in the observed colour changes.

Regarding the effect of the number of washing cycles, the colour differences between 0, 1, 5, 10, and 20 cycles are statistically insignificant, indicating that all dyes generally remain resistant up to 20 washes. Conversely, 30, 40, 50, and 60 cycles exhibit significant colour loss, with Tukey grouping (Table 5) confirming that repeated washing begins to affect colour retention from the 30th wash onwards, thus highlighting the threshold at which the stability of dye chromophores under repeated laundering becomes compromised.

These results are clearly illustrated in the "Interaction Plot for Colour Yield" (Fig. 2) and the "Main Effects Plot for K/S" (Fig. 3).

Washing, water, acidic perspiration, and alkaline perspiration fastness tests were performed on all

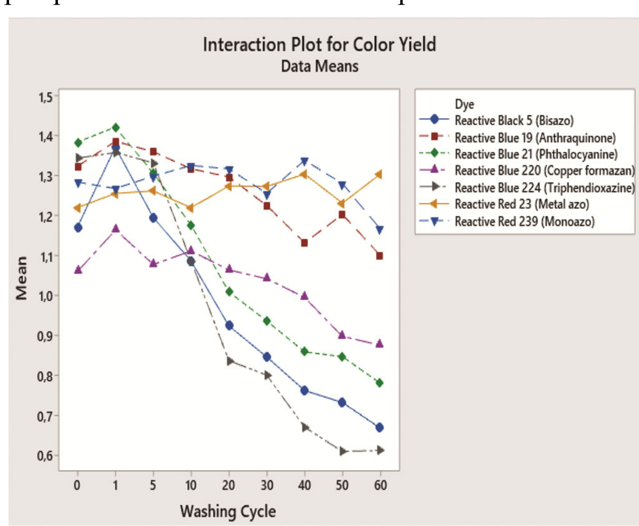

Fig. 2 — Interaction plot for colour yield

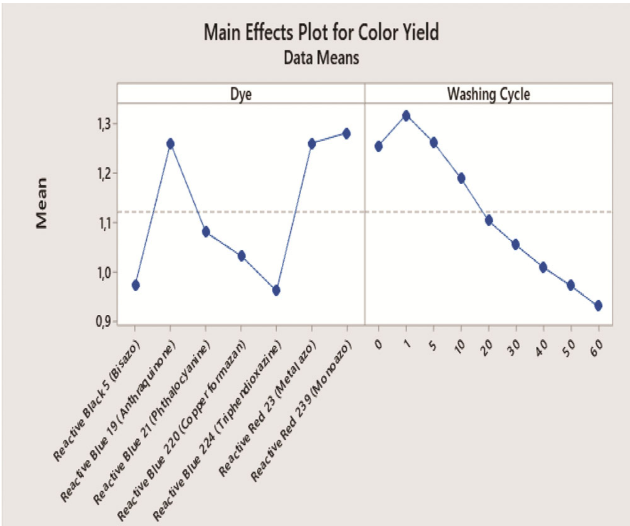

Fig. 3 — Main effects plot for colour yield

samples, and the results are presented in Tables 6, 7, 8, and 9, respectively.

When Tables 6-9 are analysed, it is evident that the water, acidic, and alkaline perspiration fastness values of Reactive Red 239 (Monoazo) dye are lower than those of the other samples. In contrast, the washing and water fastness values of Reactive Blue 21 (phthalocyanine) dye are lower than the others. These results are consistent with the literature. It is well established that phthalocyanine-based reactive dyes exhibit limited washing fastness. However, the fastness values of azo dyes can vary depending on the chemical form of the dye[2]. Conversely, anthraquinone-based reactive dyes demonstrate chromophore stability in acidic and alkaline environments[26], and therefore, these dyes exhibit high bleaching fastness and very good washing fastness[2].

Table 6 —Washing fastness values of dyed samples

Reactive Red 239	Reactive Red 23	Reactive Blue 224	Reactive Black 5	Reactive Blue 21	Reactive Blue 19	Reactive Blue 220
4/5	4/5	4/5	4/5	4/5	4/5	4/5
4/5	4/5	4/5	4/5	4	4/5	4/5
4/5	4/5	4/5	4/5	4	4/5	4/5
4/5	4/5	4/5	4/5	3/4	4/5	4/5
4	4	4	4/5	2/3	4/5	4/5
4/5	4/5	4/5	4/5	4	4/5	4/5

Table 7 — Water fastness values of dyed samples

Reactive Red 239	Reactive Red 23	Reactive Blue 224	Reactive Black 5	Reactive Blue 21	Reactive Blue 19	Reactive Blue 220
4	4/5	4/5	4/5	4	4/5	4/5
4	4/5	4/5	4/5	4	4/5	4/5
4	4/5	4/5	4/5	4/5	4/5	4/5
3	4	4	4/5	3	4/5	4/5
2/3	4	4	4/5	3/4	4/5	4/5
4	4/5	4/5	4/5	4	4/5	4/5

Table 8 — Acidic perspiration fastness values of dyed samples

Reactive Red 239	Reactive Red 23	Reactive Blue 224	Reactive Black 5	Reactive Blue 21	Reactive Blue 19	Reactive Blue 220
4	4/5	4/5	4/5	4	4/5	4/5
4	4/5	4/5	4/5	4	4/5	4/5
4/5	4/5	4/5	4/5	4/5	4/5	4/5
3	4	4/5	4/5	4/5	4/5	4/5
2/3	4	4/5	4/5	4/5	4/5	4/5
4/5	4/5	4/5	4/5	4/5	4/5	4/5

Table 9 — Alkali perspiration fastness values of dyed samples

Reactive Red 239	Reactive Red 23	Reactive Blue 224	Reactive Black 5	Reactive Blue 21	Reactive Blue 19	Reactive Blue 220
4	4/5	4/5	4/5	4	4/5	4/5
4	4/5	4/5	4/5	4	4/5	4/5
4	4/5	4/5	4/5	4/5	4/5	4/5
4	4/5	4/5	4/5	4	4/5	4/5
2/3	4	4/5	4/5	4/5	4/5	4/5
4/5	4/5	4/5	4/5	4/5	4/5	4/5

4 Conclusion

This study investigated the influence of reactive dye chromophore groups on wet fastness and colour resistance to repeated domestic washing of cotton fabrics. The results clearly demonstrate that the chromophore structure plays a significant role in colour durability under multiple washing cycles. Among the dyes examined, monoazo, metal-complex azo, and anthraquinone-based reactive dyes exhibited superior resistance to colour change during repeated washing, indicating higher chromophore stability and stronger resistance to detergent- and washing-induced degradation. In contrast, phthalocyanine, copper formazan, bisazo, and triphendioxazine-based dyes showed more pronounced colour loss, particularly after extended washing cycles.

Statistical analysis revealed that colour differences between 0, 1, 5, 10, and 20 washing cycles were not significant, suggesting that most reactive dyes maintain acceptable colour stability up to 20 washes. However, beyond approximately 30 washing cycles, significant colour loss was observed, depending on the chromophore type. This finding highlights that repeated laundering, rather than single washing events, is the dominant factor influencing long-term colour durability.

Although the present study provides a comparative evaluation of different chromophore groups, it should be noted that definitive generalisations require the inclusion of a larger number of dyes representing each chromophore class. Nevertheless, the findings clearly indicate that careful selection of reactive dyes based on chromophore structure can significantly improve colour retention in cotton textiles without the need for higher-cost specialty dyes. Therefore, this study offers practical guidance for dye selection aimed at meeting consumer expectations for colour durability under repeated domestic washing conditions.

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