Sensitivity Analysis Of Vynyl Sulphone And Bis-Monochlorotriazine Reactive Groups Of Reactive Dyes

Sanjida Sultana
Primeasia University, Dhaka, Bangladesh
Dr. Ummul Khair Fatema
Bangladesh University of Textiles, Dhaka Bangladesh
Md. Aminul Islam
Huntsman Pte Ltd, Singapore

doi: 10.19044/esj.2016.v12n18p337 URL:http://dx.doi.org/10.19044/esj.2016.v12n18p337

Abstract

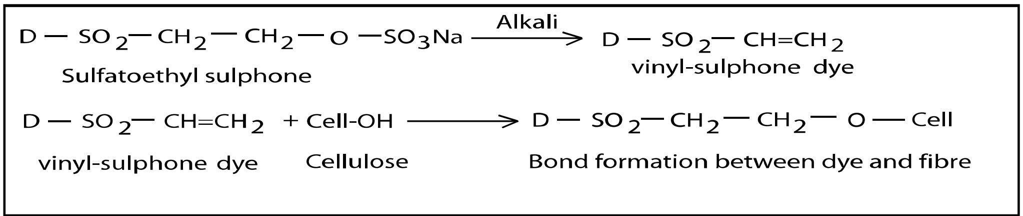
Reactive dyes contain different types of reactive groups which have different levels of sensitivity. Reactive dyeing is carried out by exhaust method on cotton knit fabric. A trichromatic combination is chosen containing vinylsulphone and bis-monochlorotriazine reactive groups. Dyeing of fabric is carried out with standard condition and variation of the conditions (electrolyte concentration, pH, exhaustion time, fixation time and M:L). Colorimetric data (DE*) is produced by comparing the difference between standard shade and the resulting shades by using spectrophotometer. Between the investigated reactive groups of reactive dye bis-monochlorotriazine shows lower sensitivity in other terms higher robustness than vinyl sulphone.

Keywords: Sensitivity, Reactive dye, Vinylsulphone, Bis-monochlorotriazine, Exhaust dyeing

Introduction

Colour of textile is one of the most important quality parameter required by the customer. But it is very difficult to achieve according to standards even with the support of modern colorimetric system and computer colour matching due to the complexity of the dyeing processes. Among all dyes reactive dyes are mostly used for dyeing cotton substrate. Reactive dyes contain different types of reactive groups which are important for dyeing because they are sensitive to different variables of dye-bath to different extent. The sensitivity causes color difference due to any change of variables (like pH, electrolyte concentration, temperature, time, M:L, etc.). This sensitivity is reciprocal of robustness (correctness) where robustness is defined as the dispensing error that would produce a color difference of one unit between the correct recipe and incorrect recipe (McDonald, 1997). It follows that highly sensitive recipes are not very robust and hampers right first time to be produced. Should dyeing errors occur, the less sensitive the recipe to such errors, the more chance there is that the resultant shade will be successful (Monsoor, 2012). The goal of this work is to help the exhaust dyer to select the right recipe for higher production with lower sensitivity and higher robustness. The exhaustion and fixation of reactive dyes depends on sensitivity of reactive groups and are determined by number of factors. The most important factors are: the pH of dye bath, the temperature of dyeing, concentration of electrolyte, the time of dyeing and the material to liquor ratio. Among the investigated reactive groups vinyl sulphone is mono-fuctional and bis-MCT is bi-functional. The general structure of vinyl sulphone reactive dye is as follows:

The reactive group that has had the greatest impact on the market is the 2-sulfooxyethylsulfonyl group (Klaus, 2003). Treatment with alkali in this case causes the elimination of sulfuric acid to form a vinylsulfonyl moiety that reacts with cotton to give a dye-fiber bond. This has an elimination-addition sequence.



Reaction 1: Covalent bond formation between vinyl sulphone reactive dye and cellulosic fibre, where D= Chromophore.

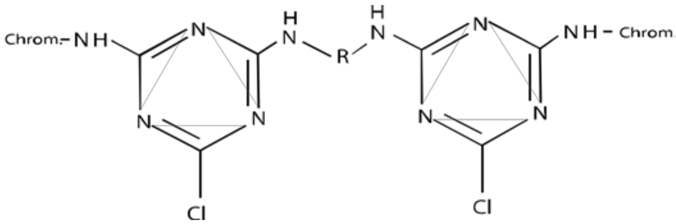
$$\text{Crom.} - SO_2\text{-}CH_2\text{-}CH_2\text{-}X + \text{Alkali} \rightarrow \text{Crom.} - SO_2\text{-}CH{=}CH_2 + HX$$

Where, $X = OSO_3H$, Cl

Reaction 2: Vinyl sulphone dye formation from 2-chloroethylsulfonyl derivatives.

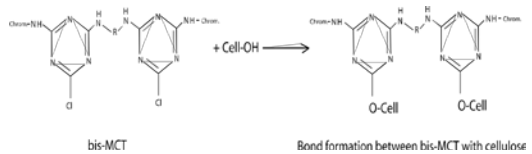
Reactive vinyl sulphones are also prepared from 2-chloroethylsulfonyl derivatives, which lead to the desired intermediates by elimination of hydrogen chloride (Klaus, 2003):

Numerous derivatives of ethylsulfonyl and vinylsulfonyl groups have been prepared in recent years, though none have approached the economic importance of the sulfate esters. These dyes have medium reactivity and lower substantivity (Clariant, 2002). Exhaust dyeing temperatures between 40°C and 60°C may be chosen, depending on pH (John, 1995). These dyes are applicable by a wide variety of batch wise and continuous processes (John, 1995). In case of bis-MCT reactive group, two monochlorotriazine units are connected by a suitable bridge (Clariant, 2002)..



Structure 2: General structure of bis-monochlorotriazine Reactive Dye (Klaus, 2003).

The synthetic approach to these compounds makes it possible to combine two different chromophores in a single system, opening the way to certain color shades that are not easily accessible via a single chromophore (Klaus, 2003). Procion HEXL dyes were designed to have substantially increased substantivity, exhaustion and fixation values compared with corresponding products carrying only one chlorotriazinyl group. The triazinyl group readily lends itself to substantivity enhancement and this property, together with an application temperature of 80°C, was used to facilitate good exhaustion and outstanding leveling properties. This approach led to improved colour utilization and in turn to less colour in the effluent (Renfrew, 1999). Reactivity of bis-MCT dye is low and the substantivity is high (Clariant, 2002). The additional technical features offer improvements in robustness and reproducibility.



Reaction 3: Reaction involved in bond formation between bis-MCT reactive dye and Cellulose.

Experiment:
Materials & Method

100% Cotton scoured and bleached single jersey knit fabric of 180 GSM was used. Lab grade chemicals of Glauber's salt ($Na_2SO_4.10H_2O$) of 95% purity, Soda ash (Na_2CO_3) of 98% purity, Acetic acid (CH_3COOH) of 98% purity were purchased from Merck LTd, Germany. Lab grade chemicals of Eriopon R (Sodium salt of a modified polyacrylic acid) which is a soaping agent was purchased from Huntsman Pte, Ltd. Singapore.

Table 1: Investigated reactive groups of reactive dye

Functionality	Reactive Group	Reactive dye	Brand name	Manufacturer
Mono-functional	vinyl sulphone	Remazol Yellow RR	Remazol	Dystar
		Remazol Briliant Red F3B		
		Remazol Blue BB		
Homo bi-functional	bis-monochloro-triazine	Procion Yellow HEXL	Procion	Dystar
		Procion Crimson HEXL		
		Procion Sapphire HEXL		

Dyeing method:

Exhaust dyeing method was used for dyeing cotton fabric. 0.3% shade was dyed for light shade and 2.1% shade was dyed for dark shade.

Table 2: Recipe of dyeing of cotton fabric with VS reactive dye (Light shade)

Dyes/Chemicals	Sample 1 (Standard)	Sample 2	Sample3	Sample 4	Sample5	Sample 6	Sample7	Sample8	Sample9	Sample 10	Sample 11
Remazol YellowRR	0.1% owf	0.1 % owf	0.1% owf	0.1 % owf	0.1% owf	0.1 % owf	0.1% owf	0.1% owf	0.1% owf	0.1 % owf	0.1 % owf
Remazol Brilliant Red F3B	0.1% owf	0.1 % owf	0.1% owf	0.1 % owf	0.1% owf	0.1 % owf	0.1% owf	0.1% owf	0.1% owf	0.1 % owf	0.1 % owf

Remazol Blue BB	0.1% owf	0.1 % owf	0.1% owf	0.1 % owf	0.1% owf	0.1 % owf	0.1% owf	0.1% owf	0.1% owf	0.1 % owf	0.1 % owf
Glauber's Salt	20 g/lit	16 g/lit	24 g/lit	20 g/lit	20 g/lit	20 g/lit	20 g/lit	20 g/lit	20 g/lit	20 g/lit	20 g/lit
Soda ash	12 g/lit	12 g/lit	12 g/lit	9.6 g/lit	14.4g /lt	12 g/lit	12 g/lit	12 g/lit	12 g/lit	12 g/lit	12 g/lit
M:L	1:8	1:8	1:8	1:8	1:8	1:8	1:8	1:8	1:8	1:6	1:10
pH	10.1-10.5										
Exhaustion time	30 min	30 min	30 min	30 min	30 min	15 min	45 min	30 min	30 min	30 min	30 min
Fixation time	60 min	60 min	60 min	60 min	60 min	60 min	60 min	40 min	80 min	60 min	60 min
Temperature	60°C	60°C	60°C	60°C	60°C	60°C	60°C	60°C	60°C	60°C	60°C

Table 3: Recipe of dyeing of cotton fabric with VS reactive dye (Dark shade)

Dyes/Chemicals	Sample 1 (Standard)	Sample 2	Sample3	Sample 4	Sample5	Sample 6	Sample7	Sample8	Sample9	Sample 10	Sample 11
Remazol YellowRR	0.7% owf	0.7 % wf	0.7% owf	0.7 % owf	0.7% owf	0.7 % owf	0.7% owf	0.7% owf	0.7% owf	0.7 % owf	0.7 % owf
Remazol Brilliant Red F3B	0.7% owf	0.7 % owf	0.7% owf	0.7 % owf	0.7% owf	0.7 % owf	0.7% owf	0.7% owf	0.7% owf	0.7 % owf	0.7 % owf
Remazol Blue BB	0.7% owf	0.7 % owf	0.7% owf	0.7 % owf	0.7% owf	0.7 % owf	0.7% owf	0.7% owf	0.7% owf	0.7 % owf	0.7 % owf
Glauber's Salt	50 g/lit	40 g/lit	60 g/lit	50 g/lit	50 g/lit	50 g/lit	50 g/lit	50 g/lit	50 g/lit	50 g/lit	50 g/lit
Soda ash	16 g/lit	16 g/lit	16 g/lit	12.8 g/lit	19.2g /lt	16 g/lit	16 g/lit	16 g/lit	16 g/lit	16 g/lit	16 g/lit
M:L	1:8	1:8	1:8	1:8	1:8	1:8	1:8	1:8	1:8	1:6	1:10
pH	10.6-11										
Exhaustion time	30 min	30 min	30 min	30 min	30 min	15 min	45 min	30 min	30 min	30 min	30 min
Fixation time	60 min	60 min	60 min	60 min	60 min	60 min	60 min	40 min	80 min	60 min	60 min
Temperature	60°C	60°C	60°C	60°C	60°C	60°C	60°C	60°C	60°C	60°C	60°C

Table 4: Recipe of dyeing of cotton fabric with bis-MCT reactive dye (Light shade)

Dyes/Chemicals	Sample 1 (Standard)	Sample2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10	Sample 11
Procion Yellow HEXL	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf
Procion Crimson HEXL	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf
Procion Sapphire HEXL	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf	0.1% owf
Glauber's Salt	20 g/lit	16 g/lit	24 g/lit	20 g/lit	20 g/lit	20 g/lit	20 g/lit	20 g/lit	20 g/lit	20 g/lit	20 g/lit
Soda ash	12 g/lit	12 g/lit	12 g/lit	9.6 g/lit	14.4g /lit	12 g/lit	12 g/lit	12 g/lit	12 g/lit	12 g/lit	12 g/lit
M:L	1:8	1:8	1:8	1:8	1:8	1:8	1:8	1:8	1:8	1:6	1:10
pH	10.1-10.5										
Exhaustion time	30 min	30 min	30 min	30 min	30 min	15 min	45 min	30 min	30 min	30 min	30 min
Fixation time	60 min	60 min	60 min	60 min	60 min	60 min	60 min	40 min	80 min	60 min	60 min
Temperature	80°C	80°C	80°C	80°C	80°C	80°C	80°C	80°C	80°C	80°C	80°C

Table 5: Recipe of dyeing of cotton fabric with bis-MCT reactive dye (Dark shade)

Dyes/Chemicals	Sample 1 (Standard)	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10	Sample 11
Procion Yellow HEXL	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf
Procion Crimson HEXL	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf
Procion Sapphire HEXL	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf	0.7% owf
Glauber's Salt	50 g/lit	40 g/lit	60 g/lit	50 g/lit	50 g/lit	50 g/lit	50 g/lit	50 g/lit	50 g/lit	50 g/lit	50 g/lit
Soda ash	16 g/lit	16 g/lit	16 g/lit	12.8g /lit	19.2g /lit	16 g/lit	16 g/lit	16 g/lit	16 g/lit	16 g/lit	16 g/lit
M:L	1:8	1:8	1:8	1:8	1:8	1:8	1:8	1:8	1:8	1:6	1:10
pH	10.6-11										
Exhaustion time	30 min	30 min	30 min	30 min	30 min	15 min	45 min	30 min	30 min	30 min	30 min
Fixation time	60 min	60 min	60 min	60 min	60 min	60 min	60 min	40 min	80 min	60 min	60 min
Temperature	80°C	80°C	80°C	80°C	80°C	80°C	80°C	80°C	80°C	80°C	80°C

Working Procedure:

- 1% stock solution of each dye has been prepared carefully.
- Additional water has been calculated and taken in dyeing pots.
- Accurate amount of dye solution one by one has been pipette in every pot.
- Pre-treated fabrics loaded in those pots.
- Dyeing pots are loaded into the dyeing machine by setting exhaustion temperature for listed time.
- Addition of soda ash after maintaining required exhaustion time and checking pH of dyeing solution has been done and recorded.
- Then dyeing continued at mentioned temperature for required time.

After-treatment:

- The dyed samples were rinsed in cold water for 5 minutes.
- The labdip neutralized in 1gm/lit acetic acid at 40°C for 10 minutes.
- The labdip treated in 1gm/lit soaping agent (Eriopon R) at 90°C for 10 minutes.
- The labdip rinsed in hot water at 80°C for 10 minutes.
- The labdip was cold rinsed for 5 minutes.

Results & Discussion

For measuring color difference Datacolor 600^{TM} Spectrophotometer (made in: USA) have been used which is a reflectance spectrophotometer. For convenience of result discussion a grading system for sensitivity has been introduced.

Table 6: Grading system

DE* value	Sensitivity
0-0.5	Low
>0.5-1	Medium
>1	High

Table 7: Color difference (DE*) of VS and BIS-MCT reactive dye (Light shade)

Criteria	DE* of VS	Sensitivity of VS	DE* of Bis-MCT	Sensitivity of Bis-MCT
Low Salt	0.58	Medium	0.69	Medium
More Salt	1.22	High	0.29	Low
Low Alkali	0.74	Medium	0.3	Low
High Alkali	1.29	High	0.5	Low
Low Exhaustion Time	0.67	Medium	0.16	Low
High Exhaustion Time	0.73	Medium	0.35	Low
Low Fixation Time	0.52	Medium	0.64	Medium
High Fixation Time	1.08	High	0.99	Medium
Low M:L	1.02	High	0.21	Low
High M:L	0.32	Low	0.26	Low

From table no. 7 it can be said that VS reactive group shows higher sensitivity to electrolyte concentration variation, higher sensitivity to pH variation, medium sensitivity to exhaustion time variation, higher sensitivity to fixation time variation and higher sensitivity to M:L variation. It can also be said that Bis-MCT reactive group shows medium sensitivity to electrolyte concentration variation, low sensitivity to pH variation, low sensitivity to exhaustion time variation, medium sensitivity to fixation time variation and low sensitivity to M:L variation.

Table 8: Color difference of VS and BIS-MCT reactive groups of reactive dye (Dark shade).

Criteria	VS	Sensitivity of VS	Bis-MCT	Sensitivity of Bis-MCT
Low Salt	0.58	Medium	1.02	High
More Salt	0.76	Medium	1.24	High
Low Alkali	0.36	Low	0.49	Low
High Alkali	0.46	Low	1.06	High
Low Exhaustion Time	0.03	Low	0.81	High
High Exhaustion Time	0.34	Low	1.04	High
Low Fixation Time	1.3	High	0.35	Low
High Fixation Time	0.34	Low	0.53	Medium
Low M:L	0.49	Low	0.74	Medium
High M:L	0.39	Low	0.63	Medium

From table no. 8 it can be said that VS reactive group shows medium sensitivity to electrolyte concentration variation, low sensitivity to pH variation, low sensitivity to exhaustion time variation, higher sensitivity to fixation time variation and low sensitivity to M:L variation. It can also be said that Bis-MCT reactive group shows high sensitivity to electrolyte concentration variation, high sensitivity to pH variation, high sensitivity to exhaustion time variation, medium sensitivity to fixation time variation and medium sensitivity to M:L variation.

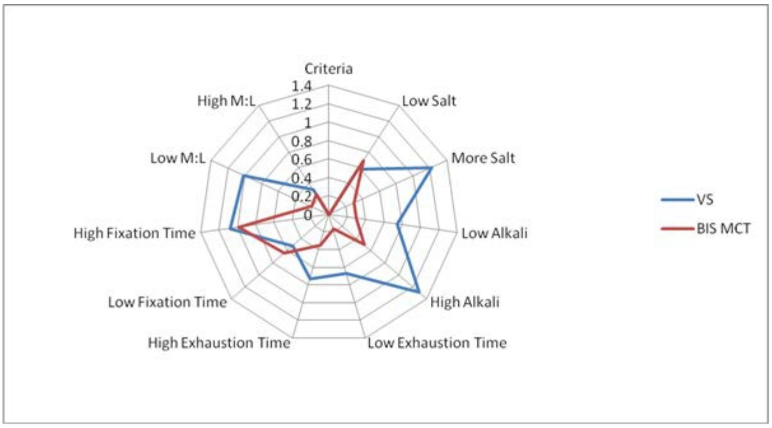


Fig 1: Comparative sensitivity of VS and Bis-MCT reactive groups of reactive dye (Light shade).

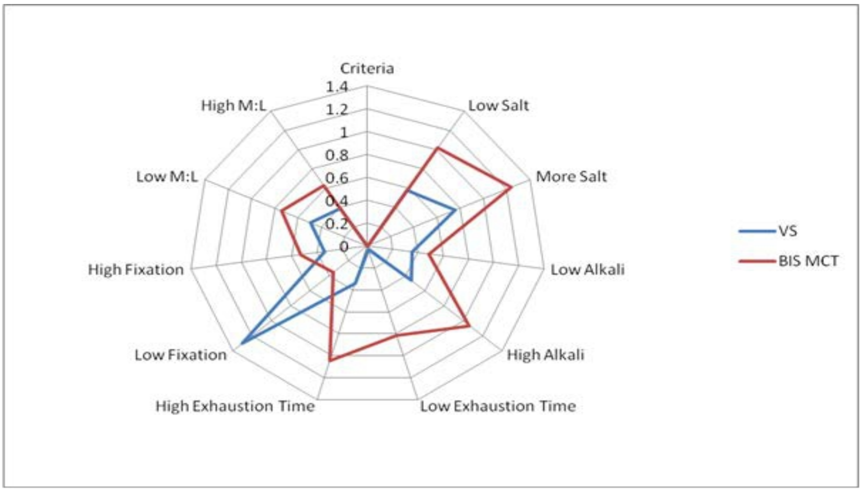


Fig 2: Comparative sensitivity of VS and Bis-MCT reactive groups of reactive dye (Dark shade).

From fig. 1 it is seen that in case of VS reactive group for Light shade salt sensitivity is high, alkali sensitivity is high, exhaustion time sensitivity is medium, fixation time sensitivity is high and M:L sensitivity is high. But for dark shade from fig. 2 salt sensitivity is medium, alkali sensitivity is low, exhaustion time sensitivity is low, fixation time sensitivity is high and M:L sensitivity is low. In all the parameters except fixation time variation vinyl sulphone dye shows improved performance with increasing shade % i.e, electrolyte sensitivity decreased from high to medium, pH sensitivity decreased from high to low, exhaustion time sensitivity goes from medium to low and M:L sensitivity decreased from high to low. But the fixation time sensitivity is unchanged which means that the vinyl sulphone dye is highly fixation time sensitive.

Vinyl sulphone dyes have moderate reactivity and lower substantivity (Clariant, 2002). The substantivity can be increased by increasing the pH upto 11 (Tanveer, 2012). When the shade% is high, the pH of the solution is also high. As a result the dye substantivity is increased with increasing pH and the sensitivity is decreased resulting better performance. Hence this dyestuff is suitable for dyeing medium to dark shades.

From fig. 1 it is seen that incase of BIS-MCT reactive group of reactive dye for light shade salt sensitivity is medium, alkali sensitivity is low, exhaustion time sensitivity is low, fixation time sensitivity is medium and M:L sensitivity is low. But for dark shade (fig. 2) salt sensitivity is high, alkali sensitivity is high, exhaustion time sensitivity is high, fixation time sensitivity is medium and M:L sensitivity is medium. In all the parameters except fixation time the performance have been decreased with increased shade% i.e, salt sensitivity increases from medium to high, pH sensitivity increases from low to high, exhaustion time sensitivity increases from low to high and M:L sensitivity goes from low to medium. But only fixation time sensitivity is in same order i.e, it is fixation time sensitive of medium order.

Reactivity of bis-MCT dye is low and the substantivity is high (Clariant, 2002). The bond energy of Cl (Chlorine) is 77kcal/gm which is moderate and less than F (fluorine) (Shenai, 2000). Hence dyeing temperature is higher to reduce color strike (instant pickup of dyestuffs at the fibre surface) to improve migration and levelness. pH is lower in light shade and higher in dark shade. So, at high temperature when pH is increased by increasing alkali dosage, alkaline hydrolysis occurs with the release of Chlorine (Cl) which results low yield of depth. For this reason the performance is decreased with increase of shade depth.

Conclusion

From results and discussion it is seen that VS reactive group shows high sensitivity incase of light shade and hence this dyestuff is suitable for dyeing medium to dark shades. Bis-MCT reactive group shows high sensitivity incase of dark shade and hence this reactive group is suitable for dyeing light shade.

References:

Roderick McDonald (Editor) (1997), Color Physics for Industry, SDC, Bradford. England, p. 292-372.

Mansoor Iqbal, Zeeshen Khatri, Aleem Ahmed, Javaid Mughal, Kamran Ahmed, (2012), “Prediction of low-sensitivity reactive dye recipe in exhaust dyeing influenced by material to liquor ratio and nature of salt”, Journal of Soudi Chemical Society, January, 16, 1, p.1-6.

John Shore (editor) (1995), Cellulosic Dyeing, Society of Dyers and Colorists, p.189-245.

Klaus Hunger (editor) (2003)**,** Industrial Dyes, Chemistry, Properties, Application, WILEY-VCH, p. 113-118.

Clariant (2002) Technical data sheet.

A Hunter M Renfrew (1999), Reactive Dyes for Textile Fibres, Society of Dyers and Colorists, p. 105-138.

Tanveer Hossain (2012), Exhaust dyeing with reactive dyes, academia.edu, p. 1-26.

Prof, V.A. Shenai (2000), Technology of Textile Processing, Chemistry of Dyes and principles of dyeing, Volume-II, p. 495-562.