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Sensitivity Analysis of Vinylsulphone and Monochlorotriazine/Vinyl Sulphone Reactive Groups of Reactive Dyes in Dyeing.

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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 vinyl sulphone and mono-chlorotriazine / vinyl sulphone 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. Here sensitivity is quantitatively expressed as color difference. Between the investigated reactive groups of reactive dye VS reactive group is more sensitive than MCT/VS reactive group of reactive dye.*

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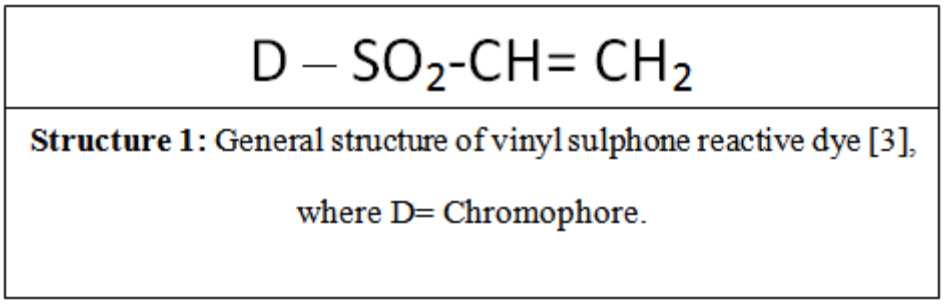
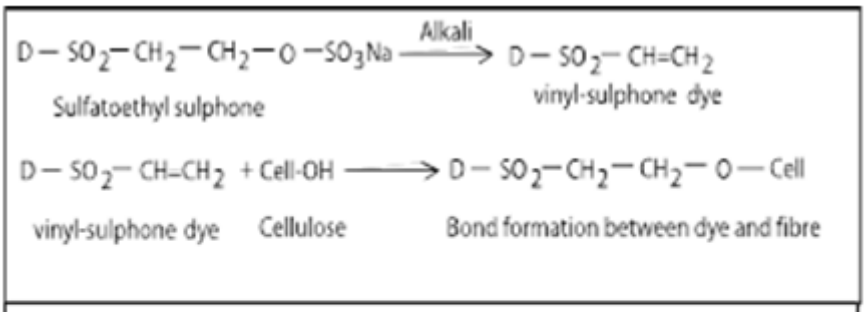
I. Introduction

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 the dyes reactive dyes are mostly used for dyeing cotton substrate. Reactive dyes contain different types of reactive groups such as vinyl sulphone, mono-chlorotriazine, bis-monochlorotriazine, monofluorotroazine, bis-monofluorotriazine, etc. 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, material to liquor ratio i.e. M:L, etc.) and hampers to achieve greater level of right-first-time and higher productivity. 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 [1]. 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 [2]. 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. Vinyl sulphone is mono-functional reactive group and mono-chlorotriazine / vinylsulphone is hetero bi-functional reactive group. Vinyl sulphone reactive group undergo nucleophilic addition reaction and mono-chlorotriazine/vinyl sulphone reactive group undergo nucleophilic substitution reaction with cotton fibre under alkaline condition. The general structure of vinyl sulphone reactive dye are given below:



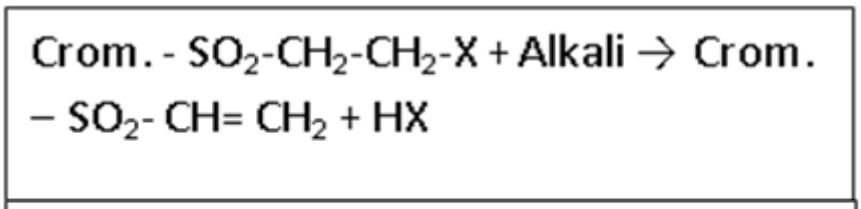
Structure 1: General structure of vinyl sulphone reactive dye [3], where D= Chromophore.

The reactive group that has had the greatest impact on the market is the 2-sulfooxyethylsulfonyl group [4]. 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 as an elimination-addition sequence.



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

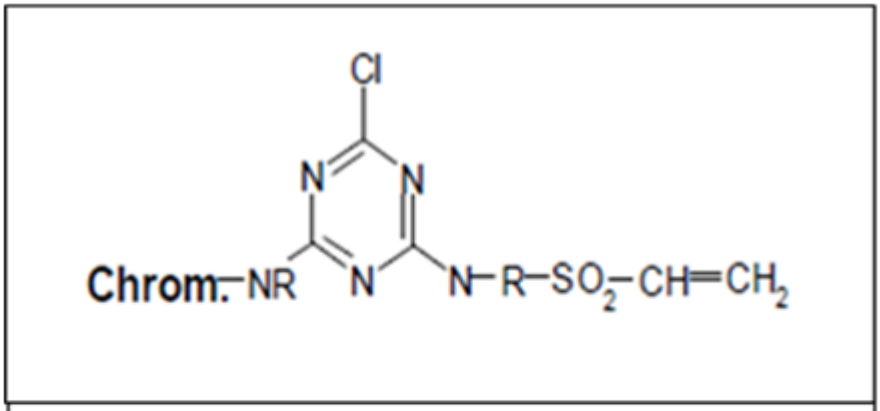
Reactive vinyl sulphones are also prepared from 2-chloroethylsulfonyl derivatives, which lead to the desired intermediates by elimination of hydrogen chloride [4]:



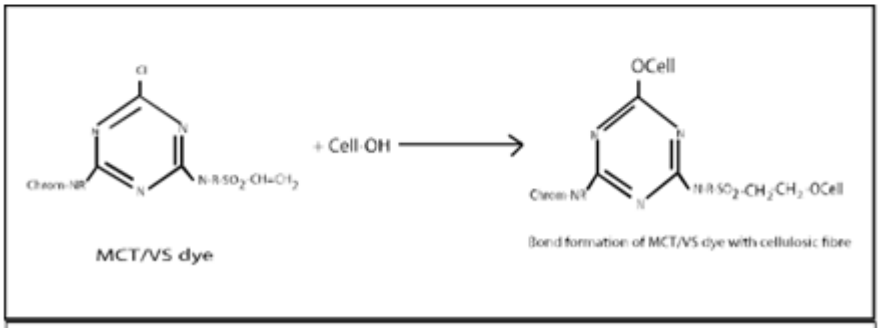
Reaction 2: Vinyl sulphone dye formation from 2-chloroethylsulfonyl derivative

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 [5]. These dyes are applicable by a wide variety of batch wise and continuous processes [3].

Warm- and cold-dyeing double-anchor dyes are prepared by incorporating halotriazinyl and vinylsulphonyl reactive anchors [4]. This type of dye employed a masked vinyl sulphone and a monochlorotriazine in the same molecule. The bond between the triazine ring and a fiber is stable under basic conditions, whereas that to the vinylsulphonyl group is stable to acid [4]. A combination of the two anchor systems therefore produces a dye with good fastness over a wide pH range [4]. These dyes were designed primarily for exhaust dyeing, with the triazinyl group being used to enhance substantivity (generally in the 30–60% range) and exhaustion. Fixation to cellulosic fibre dependent upon substantivity, reactivity, diffusibility and also the positions of the reactive groups. Two reactive groups of different reactivity offer a wider temperature range for application (MCT 80 °C; VS 50 °C), thereby favoring shade reproducibility, and this is a useful feature when the temperature distribution in the dye bath is not uniform. These dyes are also claimed to show minimal sensitivity to electrolyte, alkali and liquor ratio. Omura has argued that the presence of MCT and VS groups in a molecule is no guarantee of temperature insensitivity during dyeing [6]. The general structure of MCT/VS reactive dye is given below:



Structure 2: General structure of monochlorotriazine/vinyl sulphone reactive dye [5].



Reaction 3: Reaction involved in bond formation between MCT/VS dye and cellulose.

II. Material And Methods

2.1 Material: 100% Cotton Single Jersey scoured and bleached Knit fabric of 180 GSM was used.

2.2 Chemicals and auxiliaries 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.

2.3 Dyes used:

Table no 1: Investigated reactive groups of reactive dyes

Functionality	Reactive Group	Reactive dye	Brand name	Manufacturer
Mono-functional	vinyl sulphone	Remazol Yellow RR	Remazol	Dystar
		Remazol Briliant Red F3B (CI Reactive Red 180)		
		Remazol Blue BB (CI Reactive Blue 220)		
Hetero-bifunctional	monochlorotriazine vinylsulphone	Drimarine Yellow CL-2R	Drimarine	Clarient (Now Archroma)
		Drimarine Red CL-5B		
		Drimarine Blue CL-BR		

2.4 Dyeing: Exhaust dyeing method was used for dyeing cotton fabric. Two different shades: light (0.3% owf) and dark (2.1% owf) shades were dyed. Dyeing with Procion and Remazol dye have been done by using same recipe.

Table no 2: Recipe of dyeing (Light shade)

Dyes/Chemicals	Recipe -1 (Standard)	Recipe -2	Recipe -3	Recipe -4	Recipe - 5	Recipe -6	Recipe -7	Recipe -8	Recipe -9	Recipe -10	Recipe -11
Remazol Yellow RR	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/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	60°C	60°C	60°C	60°C	60°C	60°C	60°C	60°C	60°C	60°C	60°C

Table no 3: Recipe of dyeing (Dark shade)

Dyes/Chemicals	Recipe -1 (Standard)	Recipe - 2	Recipe - 3	Recipe - 4	Recipe - 5	Recipe - 6	Recipe - 7	Recipe - 8	Recipe - 9	Recipe - 10	Recipe - 11
Remazol Yellow RR	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 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	12.8g/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	60°C	60°C	60°C	60°C	60°C	60°C	60°C	60°C	60°C	60°C	60°C

2.5 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.
- Then dyeing continued at mentioned temperature for required time.
- Dye samples were unloaded.

Aftertreatment:

- 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 is cold rinsed for 5 minutes.

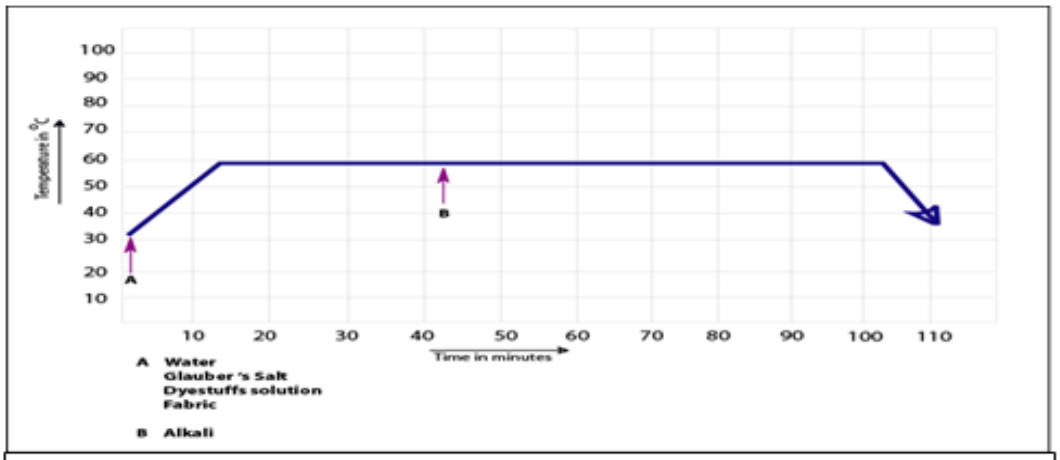


Fig 1. Dyeing curve of VS and MCT/VS reactive groups containing reactive dye with standard recipe.

III. Result

Spectrophotometric evaluation has been done by using Datacolor 600^{TM} Spectrophotometer (made in: USA) and color difference value (DE*) of samples have been used for characterization of reactive groups. The sensitivity of a reactive dye may be determined by the color difference value (DE*) between the standard sample and the sample dyed with variation of conditions (salt concentration, alkali concentration, exhaustion time variation, fixation time variation and M:L). The higher the color difference (DE* value) between the samples the higher will be the sensitivity and lower will be the robustness. For convenience of result discussion a grading system (Table 4) for sensitivity has been introduced.

Table no 4: Grading system depending on DE* value

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

The following table 5 and 6 have been found by comparing the samples in spectrophotometer:

Table no 5: Color difference of VS for different shade

Criteria	**Light shade**		**Dark shade**	
	DE*	**Sensitivity**	**DE***	**Sensitivity**
Low Salt	0.58	High	0.58	Medium
More Salt	1.22		0.76	
Low Alkali	0.74	High	0.36	Low
High Alkali	1.29		0.46	
Low Exhaustion Time	0.67	Medium	0.03	Low
High Exhaustion Time	0.73		0.34	
Low Fixation Time	0.52	High	1.3	High
High Fixation Time	1.08		0.34	
Low M:L	1.02	High	0.49	Low
High M:L	0.32		0.39	

From table 5 it is seen that in case of VS reactive group for light shade salt sensitivity is high, pH sensitivity is high, exhaustion time sensitivity is medium, fixation time sensitivity is high and M:L sensitivity is high. But for dark shade salt sensitivity is medium, alkali sensitivity is low, exhaustion time sensitivity is low, fixation time sensitivity is high and M:L sensitivity is low. So it can be said that 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 remains high in both shade% which means that the vinyl sulphone dye is highly fixation time sensitive.

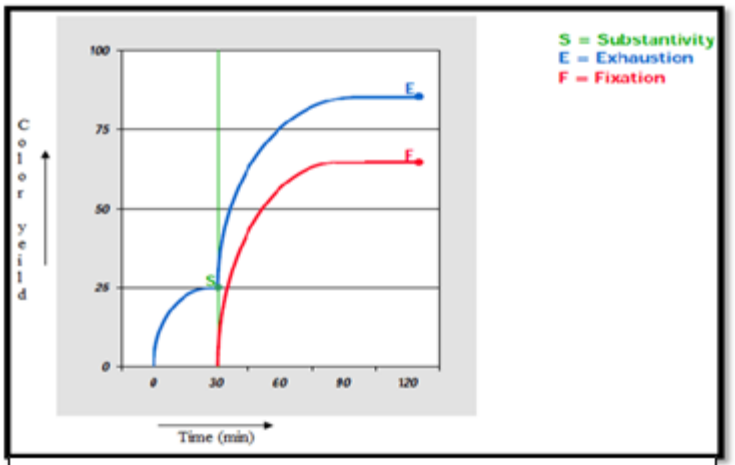


Fig 2. Color yield – time curve of VS reactive group of reactive dye [5].

Vinyl sulphone dyes have moderate reactivity and lower substantivity [fig. 2]. The substantivity can be increased by increasing the pH upto 11 [7]. 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.

Table no 6*:* Color difference of MCT/VS for different shade

Criteria	Light shade		Dark shade	
	DE*	**Sensitivity**	**DE***	**Sensitivity**
Low Salt	0.62	Medium	0.87	Medium
More Salt	0.74		0.41	
Low Alkali	0.6	Medium	0.65	Medium
High Alkali	0.72		0.71	
Low Exhaustion Time	0.29	Low	0.22	Medium
High Exhaustion Time	0.46		0.58	
Low Fixation Time	0.68	Medium	0.71	Medium
High Fixation Time	0.3		0.19	
Low M:L	0.49	Medium	0.57	Medium
High M:L	0.66		0.76	

From table 6 it is seen that for 0.3% shade salt sensitivity is medium, alkali sensitivity is medium, exhaustion time sensitivity is low, fixation time sensitivity is medium and M:L sensitivity is medium. But for 2.1% shade salt sensitivity is medium, alkali sensitivity is medium, exhaustion time sensitivity is medium, fixation time sensitivity is medium and M:L sensitivity is medium. So it can be said that in all the parameters except exhaustion time the performance is similar with increased shade% i.e. salt sensitivity is unchanged, pH sensitivity remains unchanged, fixation time sensitivity remains low and also M:L sensitivity remain low. But only exhaustion time sensitivity becomes medium when shade depth is 2.1%. It does not show high sensitivity. Though small amount of fluctuation is seen in case of exhaustion time variation it can be said that in case of 0.3% shade the sensitivity is low which means that performance is improved and sensitivity is decreased in this case than 2.1% shade where sensitivity is medium.

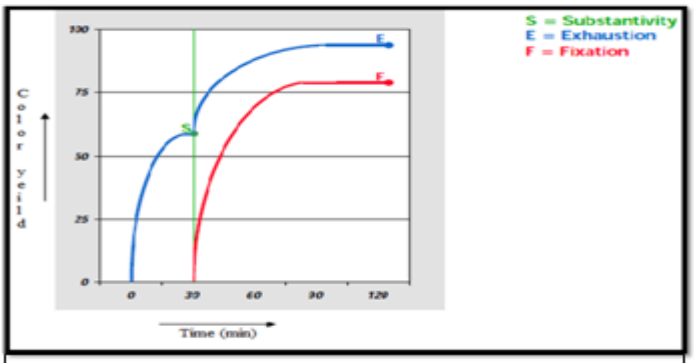


Fig 3. Color yield – time curve of MCT/VS reactive group of reactive dye [5].

Reactivity of MCT/VS dye is medium and the substantivity is also medium [fig 3]. Substantivity is increased with decreasing temperature and pH. The reactivity of reactive dye is dependent on their leaving group. The bond energy of Cl is 77kcal/gm [8]. The higher the bond energy of leaving group, it needs drastic condition for dyeing. Here addition and substitution reaction takes place for covalent bond formation between reactive dye with cellulose. For the presence of both triazine group and vinyl sulphone group there is flexibility in dyeing temperature and they shows medium sensitivity which is not dependent on pH change for changing shade%.

3.3 Comparison between the investigated reactive groups:

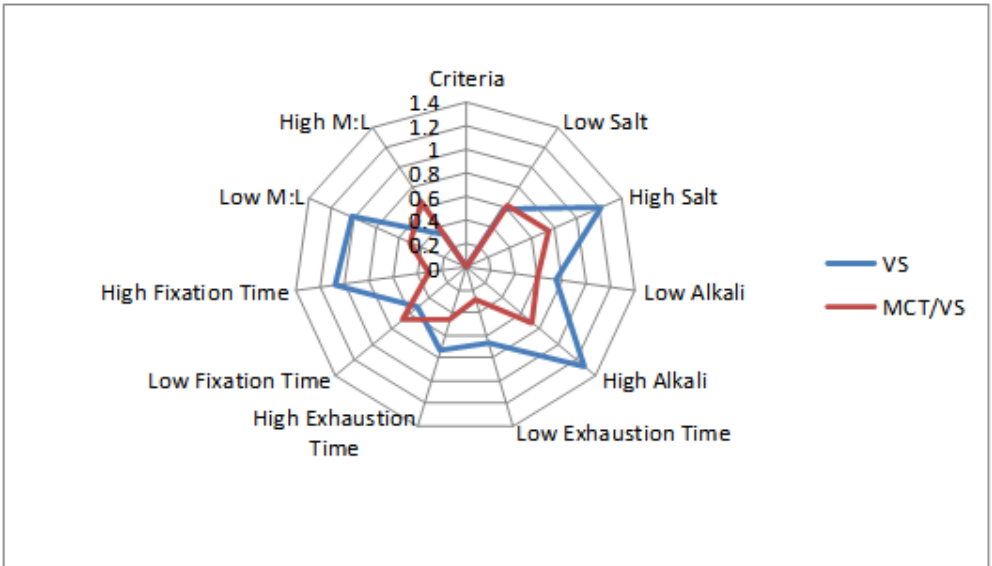


Fig 4. Sensitivity curve of VS and MCT/VS reactive groups of reactive dye to different variables (Light shade).

From fig. 4 it is seen that MCT/VS dye shows medium sensitivity in all parameters except exhaustion time variation where it shows low sensitivity and VS dye shows medium and high sensitivity in different parameters and also fluctuation is seen here. So the order of sensitivity is: **VS > MCT/VS.**

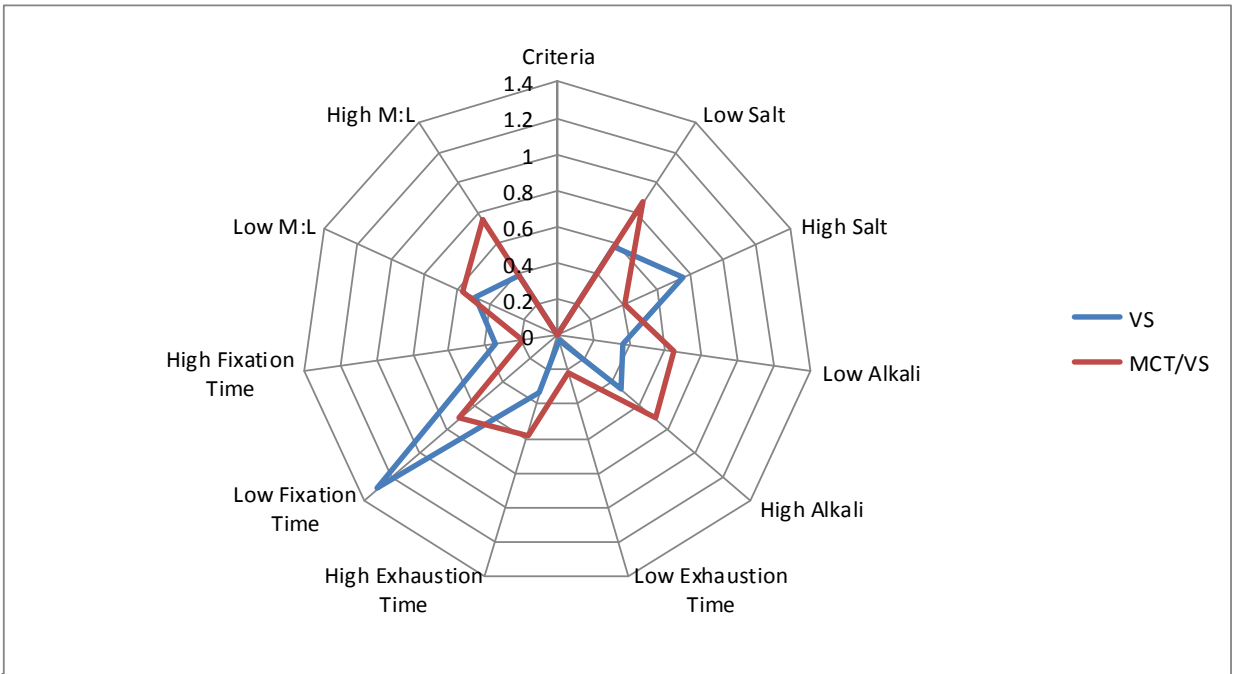


Fig 5. Sensitivity curve of VS and MCT/VS reactive groups of reactive dye to different variables (Dark shade)

From fig. 5 it is seen that for 2.1% shade MCT/VS dye shows medium sensitivity. VS dye shows lower and medium sensitivity in different parameters except low fixation time which shows high sensitivity and it also shows fluctuation of sensitivity. So, the order of sensitivity is: **VS > MCT/VS**

IV. Conclusion

From the comparison of light shade and dark shade it can be said that VS reactive group is more sensitive than the MCT/VS reactive group in different parameters. As a result MCT/VS dye can be used for robust dyeing.

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