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Synthesis and Application of Vinylsulphone Disperse Reactive Dyes for Polyester

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Abstract: Disperse dyes contain around 30-60% of dispersing agents as well as dyeing with disperse dyes require around 2-5 gpl of dispersing agent for faultless dyeing of polyester and other hydrophobic fibres. Dispersing agents are not taken up by the fibres and large quantity of dispersing agent creates unavoidable load on the effluent treatment. Vinyl sulphone disperse reactive dyes seem to have an acceptable solution to this existing problem. These dyes can work in absence of dispersing agents and can be called as dispersant free disperse dyes.

In this work, vinylsulphone disperse reactive dyes were synthesized by using vinylsulphone based diazo compounds with the different coupling components like N,N Diethylaniline Acetanide; N (3-diethylamino) phenyl; Acetanide N (3-diethytlamino)-4-methoxy] phenyl and N,N Dicynoethylaniline. The synthesized dye were applied successfully on Polyester with level dyeing, good build-up and desired colour yield. The dyeing was dependent on the pH and the optimum pH was found to be 5 similar to that employed in conventional polyester dyeing. The fastness properties obtained are good and comparable with the conventional dyes.

Keywords : Ecofriendly, Effluent load, Vinylsulphone disperse reactive dyes, Dispersant free disperse dyes, Polyester.

1. Introduction

The historical development of the synthetic dyestuffs dates back to1856, when eighteen year old, W.H. Perkin discovered the synthesis of Mauveine, a basic dye, by accident, while he was engaged in the study of the action of potassium dichromate on aniline sulphate[1].

The development of disperse dyes for dyeing secondary cellulose acetate fibres in the early 1920s was a major technological breakthrough. Their major use today is for the coloration of polyester, the most important group of synthetic fibres[2].

Disperse dyes are used in aqueous dyebaths in the form of fine dispersions, because their solubility in water is very low, even at high dyeing temperatures. During manufacture, dispersing agents are incorporated into the dye powders to confer the dyeing properties. One important aspect of dyeing with disperse dyes is the state of dye in the dyebath during dyeing. Dye particles in the finely divided dispersion acts as a dye reservoir. The solubility of disperse dyes, though small, is also a very important factor. In addition, the stability of the dye dispersion, the equilibrium between dye dispersion and dye in true solution in the dyebath, and the rate of dyeing are all affected by the type and concentration of the disperse dyes. During dyeing, the kinetics of dye dissolution is more significant than those governing solubilisation. Equilibrium solubilisation of disperse dyes is attained in aqueous solutions of surfactants and dispersant agents at 130ºC over a relatively long period[3]. The dispersing agents are divided into two classes according the chemical point of view, such as surfactants and water-soluble polymer & oligomers. These are contained in dyes is usually anionic polyelectrolytes[4].

In the conventional disperse dyeing of polyester, dispersing agents are usually added to increase the dispersion stability and solubility of disperse dyes. However, after the dyeing process is finished, they are not adsorbed onto polyester and discharged as effluents with the residual dyeing liquor, which increases the COD and BOD values of the effluent[5,6].

One of the severe problem encountered in dyeing of polyester at high temperatures with disperse dyes in poor dispersion stability and its consequences: inadequate levelness and unacceptable reproducibility[7].

The development of new disperse dyes must take into account the effect that dyeing effluent will have on the environment, and aim to minimise such pollution. These objectives are not mutually exclusive but interrelated; they must all be taken into account in any dye development program[8].

Recently, we have synthesised various vinylsulphone disperse reactive dyes using diazo components having vinylsulphone group with different couplers in the range of orange such as yellow, orange, red. The correlation between the dye structure and spectral properties were discussed. After the complete hydrolysis of these dyes in dyebath during dyeing or beforehand, these dyes can be used as dispersant free disperse dyes for polyester and performance properties were also investigated.

2. Experimental

2.1 Materials and apparatus

Ready for dyeing polyester (100%) substrate (weight 70 gm/m^2, Ends per inch 105 & Picks per inch 94) was purchased from Piyush Sydicate, Mumbai, India.

Meta base vinylsulphone, Para base vinylsulphone diazo compounds were supplied by Chemistar Intermediates Pvt. Ltd., Ahmedabad, India. N,N Diethylaniline Acetanide; N (3-diethylamino) phenyl; Acetanide, N (3-diethytlamino)-4-methoxy] phenyl and N,N Dicynoethylaniline couplers were supplied by Spectrum dyes & chemicals Pvt. Ltd., Surat, Gujarat, India.

Sodium nitrate, Sodium carbonate, Hydrochloric acid (HCl), Sulphamic acid, Sodium acetate and Sodium chloride were of analytical grade and purchased from S.D. fine chem. Ltd. Mumbai. All dyeings were carried out using Flexi dyer machine (Rossari Labtech, Mumbai, India). Melting points were determined using DSC- 60 Differential Scanning Calorimeter, Shimadzu, Kyoto, Japan.

The dispersibility was evaluated by filtering time and filter residue of vinylsulphone disperse reactive dyes under standard conditions in aqueous media using the AATCC Test Method 146-2006.

As shown in Table 1, according to filter residue, all the dyes showed good dispersibility in aqueous media. All dyes showed very good filteration time except B which took 51 sec which is also under the standard norm of 60 sec.

Table 1: Filtration of Synthesized Dyes

Dye	Filter Rating	
	Filteration Time (sec)	Filter Residue Scale
A	30	4-5
B	51	4
C	27	4
D	35	4-5

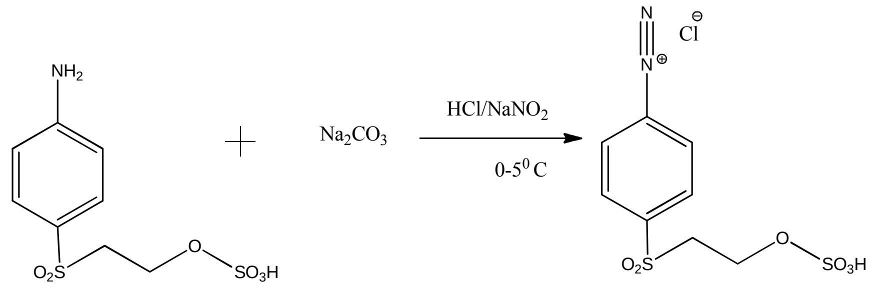
2.2 Synthesis of dyes

2.2.1 Diazotisation

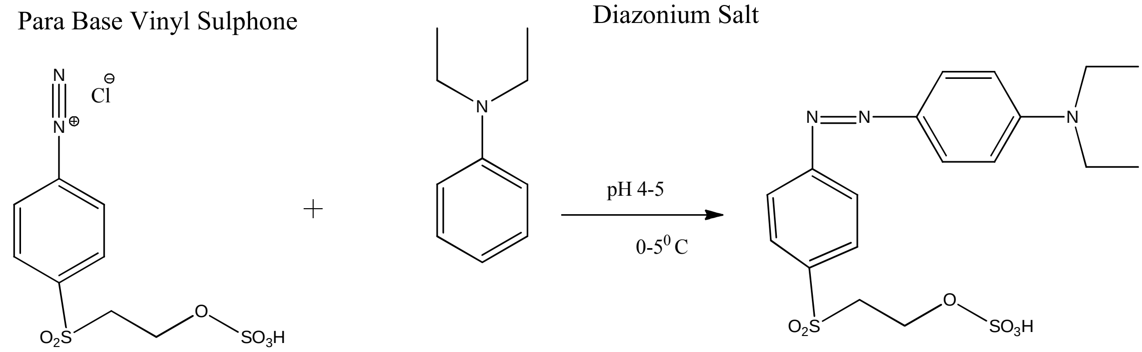
Vinyl sulphone based diazo (0.017794 mol) was dissolved in water and solution of Na_2CO_3 (0.035588 mol) at 0-5º C was added to it. Then added concentrated hydrochloric acid (0.062279 mol) and sodium nitrite (0.017794 mol) to the above solution, slowly under constant stirring at 0-5ºC and the diazotisation was continued for 3-4 hr. Checked the reaction completion by the starch paper.

2.2.2 Coupling

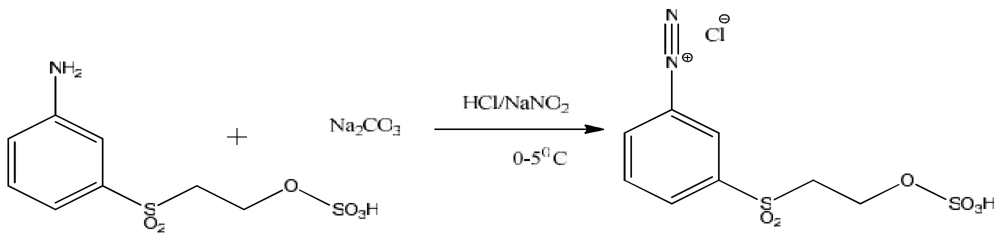
One to the coupling component namely N,N Diethylaniline (0.017794 mol); Acetanide, N (3-diethylamino) phenyl (0.017794 mol); Acetanide, N (3-diethytlamino)-4-methoxy] phenyl (0.017794 mol) and N,N Dicynoethylaniline (0.017794 mol) was dissolved in water and 35% hydrochloric acid at room temperature. The prepared diazonium salt liquor and meshed ice were added to the corresponding coupling component solution and the temperature was maintained between 0-5°C. The solution was stirred for 2-3 hr and allowed to reach room temperature. Sodium acetate solution (1M) was added to adjust the pH between 4 and 5. After, saturated sodium chloride solution was added to the above solution; the precipitate formed was filtered and dried in a vacuum oven at room temperature. The yield of synthesised dyes is 2.21gm, 2.85gm, 2.45gm and 2.23gm respectively.



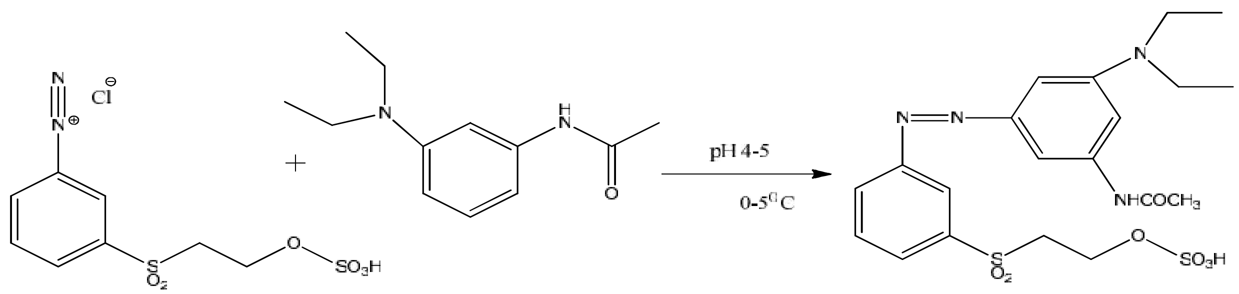
Para Base Vinyl Sulphone   Diazonium Salt



Diazonium Salt   N,N - Diethylaniline   Synthesised Dye A (Orange)



Meta Base Vinyl Sulphone   Diazonium Salt



Diazonium Salt   Acetanide N- (3 diethylamino) phenyl   Synthesised Dye B (Orange)

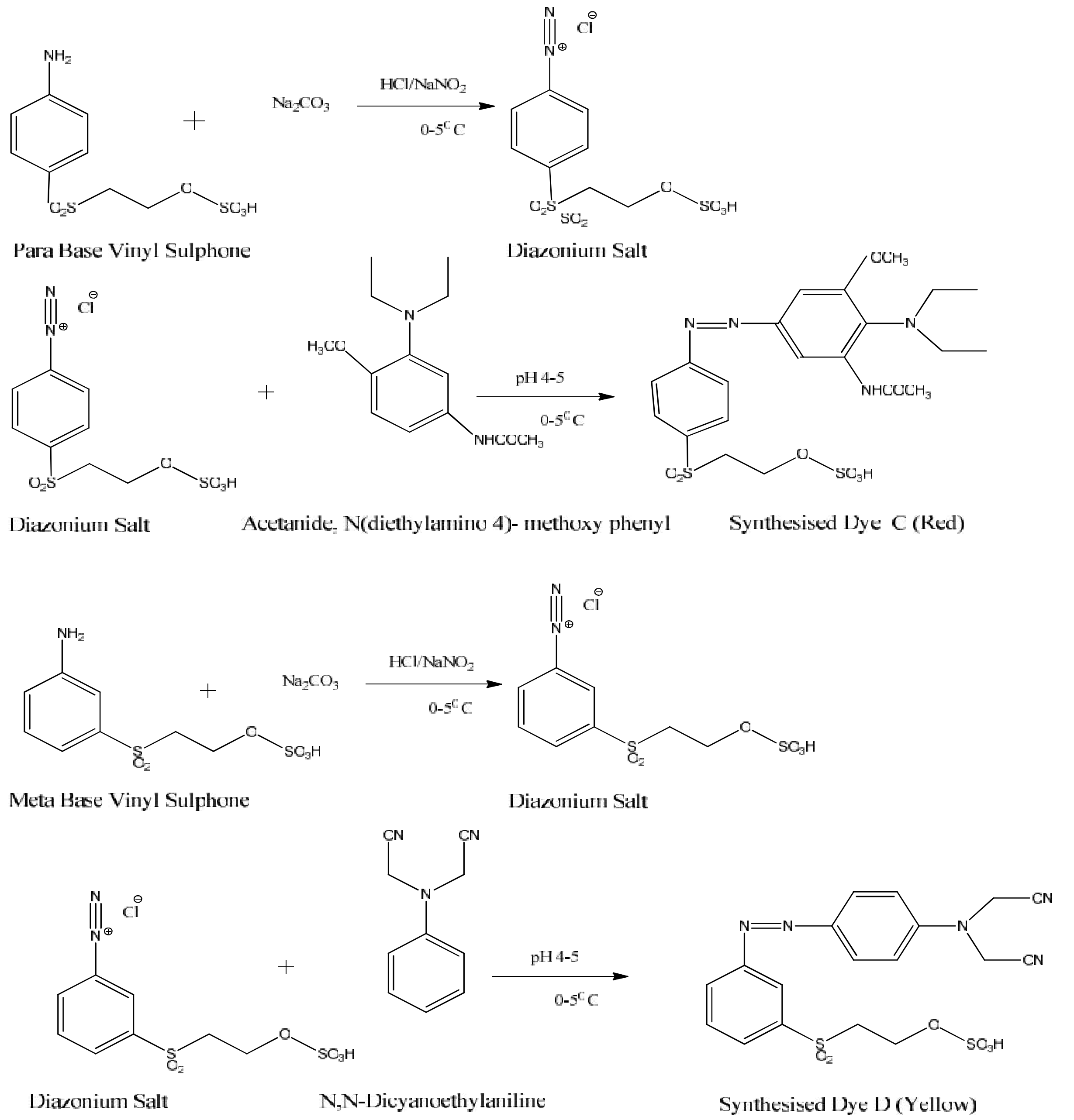


Figure 1: Synthesis of vinyl sulphone disperse reactive dyes

2.3 Dyeing of polyester

Polyester fabric was dyed in a Flexi dyer dyeing machine at M: L 1:20. The dyebaths were prepared with the synthesised dyes without using any dispersing agent and maintained at pH 4-5 by acetic acid. The dyebath temperature was raised at a rate of 1°C/min to 130°C, maintained at this temperature for 60 min, and rapidly cooled to 60°C. The dyeings were rinsed and then reduction cleared in an aqueous solution of 2 g/l sodium hydroxide and 2 g/l sodium hydrosulphite at 80°C for 30 min.

2.4 Colour Strength

The colour properties of the dyed samples were determined with Spectra Scan 5100+ under the illuminant D65 using 10^o standard observer. The K/S values were determined using expression;

$$K/S = \frac{(1-R)^2}{2R}$$

where, R is the reflectance at complete opacity, K is the Absorption coefficient & S is the Scattering coefficient

Dyed fabrics were simultaneously evaluated in terms of CIELAB colour space (L*, a* and b*) values. In general, the higher the K/S value, the higher the depth of the colour on the fabric. L* corresponds to the brightness (100 represents white, 0 represents black), a* to the red–green coordinate (+ve represents red, -ve represents green) and b* to the yellow–blue coordinate (+ve represents yellow, -ve represents blue). As a whole, a combination of all these enables one to understand the tonal variations.

Four locations on the dyed fabric were arbitrarily chosen and L*, a* and b* values were measured by spectrophotometer. The CIEL*a*b* colour difference between any two points was calculated. The levelling properties of the dyes on polyester fabric were assessed using the mean of 5 such colour difference results [5].

The exhaustion of dye on the polyester fabric was also measured by DMF extraction method (30 min at 150°C). The absorbance of the solution extracted was determined using UV-VIS 8500 spectrophotometer. The percentage exhaustion was calculated using equation:

Exhaustion (%) = C_t/C_0 *100

Where, C_t is the amount of dye extracted from a dyed fabric at time t and C_0 is the amount of dye in the initial dyebath.

2.4 Fastness test

The colour properties of the dyed samples were determined with Spectra Scan 5100+ under the illuminant D65 using 10° standard observer. Rubbing fastness of the dyed samples was determined by using automatic Crockmeter (World Traders & Co. Bombay) using the standard ISO 105 X 12 method. Sublimation fastness (Sublimation fastness tester, RBE Electronics Engg. Pvt. Ltd. Mumbai, India) of the polyester dyed samples were tested on Sublimation tester using the ISO 105- F04 method. The light fastness of the dyed samples was tested on Q-Sun Xenon Test Chamber using the AATCC 16-2004 method. Washing fastness testing was done by the standard method ISO 2-105-C10: 2006(E). The shade change, together with staining of adjacent fabrics, was rated according to appropriate SDC grey scales.

3. Result and discussion

3.1 Synthesis of dyes

The dyes A-D were synthesised by coupling of the diazotised compounds as illustrated in Figure 1. The melting points of synthesised dyes are 441.52°C, 498.57°C, 543.63°C and 463.49 °C respectively.

3.2 Spectral properties of dyes

The Table 2 shows the spectral data of synthesised dyes A-D. The absorption maxima of the dyes varied from 420 to 530, which was yellow to red shade.

Table 2: The spectral data of synthesised dyes (Measured in DMSO)

Dye	λ_{max} (nm)
A	470
B	480
C	530
D	420

3.3 Dyeing Properties

The exhaustion % at different pH of dyebath is given in Table 3 of dye A-D. The trend in exhaustion % remained same for all the dyes for polyester dyeing and good colour yields were obtained. The maximum colour yield was observed at pH 5 for all the dyes and was of the tune of 90%. The colour yields at pH 7 and 8 were lower than those at pH 5 and also the dyeings showed some unlevelness. Therefore, the optimum pH condition for dyeing was concluded as pH 5. At pH 4, colour yield was low due to the low conversion rate of the soluble dye into the insoluble vinylsulphone form. The colour yield on the polyester fabric increased continuously throughout the whole dyeing procedure, implying gradual increase in the conversion of dye. The low dye uptake and poor leveling at pH 10 can be attributed to the rapid conversion of dye causing a collapse in the dyebath dispersion stability. Thus the exhaustion of dybath in terms of exhaustion % was highly dependent on the pH of the dyebath with maximum exhaustion of 90.7%; 89.8%; 91% and 91.2% respectively for dye A-D obtained at pH 5 [5].

Table 3: Effect on pH on exhaustion (%) value of dye A-D on polyester fabric (1% owf, M: L 1:20)

pH	Exhaustion (%)			
	A	B	C	D
4	78.1	77.1	78.5	79.5
5	90.7	89.8	91.0	91.2
6	88.3	87.0	88.4	88.1
7	79.0	78.6	77.9	79.1
8	74.5	75.0	74.8	75.2
9	67.7	68.5	66.7	69.2
10	61.5	60.3	59.8	61.7

Figure 2 shows the build-up of the dyes at pH 5 in terms of K/S values at various depths of dyeing such as 0.5% to 3%. Dyes A-D exhibited good build-up on the polyester and the colour strength of these dyes reached saturation at depth of dyeing of 2.0% owf with no distinct increase in K/S values at 3% owf depth of dyeing.

The colour data as shown in Table 4 is in agreement with the spectral data in Table 2. The dyes gave yellow, orange and red hues on polyester fabrics.

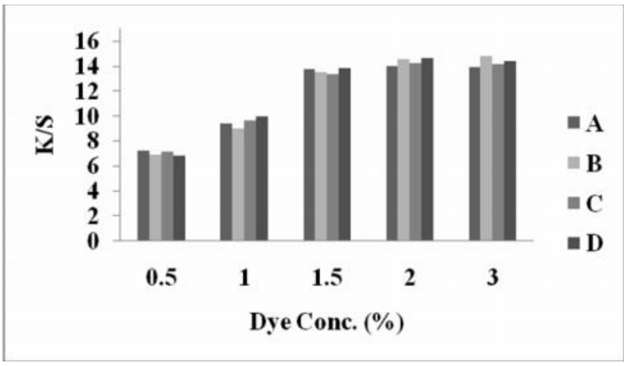


Figure 2: Colour build-up of dyes A-D on polyester fabric (pH 5, M: L 1:20)

Table 4: The colour data of dyes A-D on polyester fabrics

Dye	CIEL*a*b* values			Colour name
	L*	a*	b*	
A	58.635	35.290	64.135	Orange
B	61.618	37.817	67.317	Orange
C	38.376	53.080	10.242	Red
D	77.598	0.313	46.409	Yellow

Table 5: Colour differences between four points of polyester fabric

Dye	Colour differences					
	1	2	3	4	5	Average
A	0.504	0.409	0.256	0.607	0.540	0.463
B	0.296	0.341	0.452	0.167	0.332	0.317
C	0.088	0.215	0.097	0.193	0.212	0.161
D	0.451	0.671	0.521	0.337	0.390	0.474

Table 5 gives the average of 5 results for the colour differences at four random locations on polyester fabric. All the dyes showed very small colour differences between locations, showing that leveling was good [5].

3.4 Fastness properties

The Colour fastness tests were carried out for all the dyeings done at pH 5, which was obtained as the optimum pH of dyeing. The results of the wash fastness tests for dyes A-D on polyester are summarised in Table 5 and showed good to excellent wash fastness. Table 6 shows the results of light and rubbing fastness tests. The rubbing and sublimation results were good and light fastness was moderate to good.

Table 5: The wash fastness of dyes A-D (1% owf) on polyester fabric

Dye	Change in colour	Staining					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
A	4-5	4-5	4-5	4	5	5	4-5
B	4-5	4	4-5	3-4	4-5	5	4
C	4-5	4-5	5	4-5	5	5	4-5
D	4-5	4-5	5	4-5	5	5	4-5

Table 6: The rubbing, light and sublimation fastness of dyes A-D (1% owf) on polyester fabric

Dye	Fastness			
	Rubbing		Light	Sublimation
	Dry	Wet		
A	4-5	4-5	4-5	4-5
B	4-5	4	3-4	4
C	4-5	4	4-5	4-5
D	4-5	4-5	4-5	4-5

4.Conclusion

Polyester fabrics were successfully dyed with the synthesised dyes without using dispersing agent. The colour yield on polyester was dependent on the dyeing pH and the optimum result was obtained at pH 5 similar to that employed in conventional polyester dyeing. Therefore no modification of dyeing process is needed for the application of synthesised dyes. The dyes gave yellow to red hues on polyester and showed good build-up and leveling properties. The dyes exhibited good to excellent wash fastness while rubbing; sublimation and light fastness results were good and moderate to good and mainly dependent on the structure of dyes. This research clearly shows the use of vinylsulphone disperse reactive dyes as dispersant- free dyes for dyeing of polyester.

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