Effect of Dispersing Agents and Substitution on the Dyeing and Spectroscopic Properties of Disperse Dyes.

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Summary: A number of monoazo disperse dyes were prepared and milled with different dispersing agents in a finely divided form as dispersions. The average particle size of all dispersions were measured to be under 1μm for all dyes studied. The efficiencies of dispersing agents used were in order : Ligninsulphonate > Berol > Tamol > Monolans. Low concentrations of Tamol were required for S1 type of dyes as compared to S2 type. The capability to withstand high temperature (130°C) during dyeing was determined by the change in average particle size which increased after heating but remained under 1 μm except for Berol which showed no remarkable changes in particle size. The fastness properties studied should higher values for A2-D2 series which have cyano-ethyl group in their coupling component than A1-D1 series with hydroxyl group in their structure. On the whole fastness value to wash, light and heat of basic dyes S1 (3-4) and S2 (4-4.5) series increased with the introduction of electron withdrawing groups in the dye structure and remained around 5. The effect of substitution also showed bathochromic and hypsochromic shift from 8 to 25 nm . The effect of dispersants on the colour properties of dyes studied were in order: Ligninsulphonate > Tamol > Monolan >Berol. All the dyes showed a good co-relationship between the data obtained during these investigations.

Introduction

Disperse dyes have been available for almost 75 years. Originally introduced for the coloration of cellulose acetate, they were now almost exclusively used for colouring polyester fibre, the world production of which had grown enormously over the last 40 years.Disperse dyes are used in aqueous dyebaths in the form of fine dispersion, because their solubility in water is very low, even at high temperatures. During manufacture dispersing agents are incorporated into the dye powders to confer the for dyeing properties required of commercial dyestuff [1,2].

Two groups of investigators, McDowell and Weingarten and McGregor & Peters reported that several parallel processes undergo in the dyeing of polyester [3,4]. Important aspect of dyeing with disperse dyes includes the state of dye in the dyebath during dyeing , their solubility in aqueous medium, the stability of their dispersion obtained and the rate of dyeing are all affected by the type and concentration of the dispersing agents. It has been shown experimentally that dispersing agent can also diffuse into polyester substrate.The rate of dissolution of dye in the dyebath affects the instantaneous concentration of dye that can be adsorbed at the fibre surface, and subsequently diffuse into the fibre[5-7].

The solubility of disperse dyes in water depend on their particle size which have a high surface energy and tend to increase in size as the free energy of the system decreases. As a result, the average particle size of the disperse dye in solution changes and the number of large particles increases [8-10]. The methods for measuring solubility of disperse dyes and their behaviour in the dyebath and the environment have been described by Baughman and Perenich [11]. Influence of auxiliries in dyeing polyester with disperse dyes, the effect of several dispersing agents, carriers and levelling agents on dyebath exhaustion was examined colorimetrically in HT dyeing machine at 130°C and liquor ratio of 25:1 [12].

The effect of cation type on lignosulphonate dispersant performance in disperse dye system performance was studied by Dilling [13] while Brunger *et al.*, studied the influence of temperature and anionic dispersing agents and found that the hydrotropic interaction caused an increase in the dispersed component [14]. Smimov *et al.* investigated the effect of non-ionic surfactants (Monoalkyl phenol ethoxylates) on the state of disperse dyes. The relationship between the nature of the disperse dye and the concentration of the surfactant in which the colloidal particles are formed are also explained. The influence of dispersing agents on the solubility of a micellar disperse dye by non-ionic surfactants has been reported as well by various investigators such as Knopf & Schollineyer, Weingarten, Knox & Weigman and Braun who spectrophotometrically determined the influence of dispersing agents by this method [15-20].

According to Erik Kissa the stability of the dispersion to flocculation and sedimentation depends on the attractive and repulsive forces between the dye particles, which in turn depend on the interactions at the water-dispersant-dye interfaces and the particle size of the dye. Consequently an adsorbed amphiphilic dispersant lowers the dye-water interfacial tension by rendering the dye particles hydrophilio and it stabilizes the dispersion by steric and electrostatic mechanism [20]. In case of polyester a high rate of heating requires considerable stability of the disperse dye in the dye bath to prevent faults. A novel method of fractional pressure filtration to test disperse dyes under high-temperature conditions has been mentioned by Jaroslav and co-workers to avoid this defect [21].

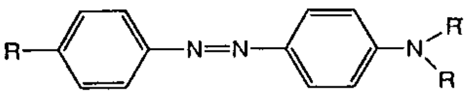
This paper presents the effect of different dispersing agents on the reduction of particle size and consequent dyeing properties. The effect of substitution in the diazo as well as coupling reagents on the fastness and spectroscopic properties are also described.

Result and Discussion

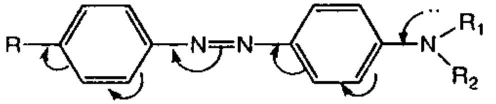
In order to study the effect of dispersing agents on the dyeing and spectroscopic properties, several disperse dyes having the general structure formula (1) were synthesised and purified by the conventional method of diazotization and coupling. These dyes were milled in sand mill in the presence of the various dispersing agents and their effects on particle size reduction and various dyeing properties have been recorded in Tables (1-9).

The data presented in Table-1 shows λ_{max} values of parent and other dyes. It is obvious that 2-Cl and 2-CN substitution exert a pronounced bathochromic shift from 8-25 nm. The presence of (2,6-dichloro and dibromo) substituents at *ortho* to the azo group resulted in the displacement of the visible band to a shorter wavelength and reduction in intensity,in analogy with the reported effect of multiple substituents in such diazo components where steric crowding occurs and the molecule is forced to adopt the non-polar structure. Although the powerful electron-attracting nature of the nitro group in the conjugated 4-position compensates to some extent any steric crowding effects at the 2,6-positions [22, 23].

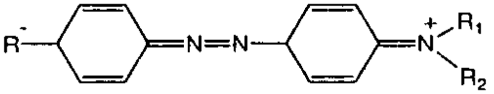
The substituents in the basic structure of 4-aminoazobenzene (1) cause bathochromic or hypsochromic shift, depending upon the nature of terminal groups. Thus, presence of a nuclear electron-withdrawing group R in dyes S1 and S2 facilitates the migration of electron density from the alkyl substituted donor amino group, towards the azo group. Thus, the parent system (1) may be regarded



(1)



(2)



(3)

as a resonance hybrid of two extreme canonical structures (2 ↔3) of different energies.

Structure (2) is a fairly close approximation to the ground state of the molecule whereas , the high energy dipolar structure (3) can be taken as a reasonable approximation to the excited state. Electron withdrawal by R leads to preferential stabilization of the excited state and a consequent bathochromic shift of the visible absorption band. However, inductive electron withdrawal by the CH_2CH_2CN group leads to a reduction in the electron-releasing tendency of the terminal nitrogen atom and a consequent hypsochromic shift of the visible absorption band. The hypsochromic influence of the cyanoethyl group more than compensates for the bathochromic effect of the terminal bridge so that the λ_{max} values of these dyes are at somewhat shorter wave lengths than those of analogous compounds derived from 4-aminoazobenzene. Thus, λ_{max} values reported in Table-1 can be explained and are in agreement with the investigations on analogues of 4-aminoazobenzene [24].

Table-1: Effect of substitution in general structural formula on values of λ_{max} of disperse dyes.

Dye ref No.	X	Y	R	R1	R2	λ_{max} (nm)	$\Delta\lambda_{max}$ (nm)
S1	H	H	NO_2	C_2H_5	C_2H_4OH	515	—
S2	H	H	NO_2	C_2H_5	C_2H_4CN	488	-
A1	CN	H	NO_2	C_2H_5	C_2H_4OH	540	25
A2	CN	H	NO_2	C_2H_5	C_2H_4 CN	500	12
B1	Br	Br	NO_2	C_2H_5	C_2H_4OH	476	-39
B2	Br	Br	NO_2	C_2H_5	C_2H_4 CN	452	-36
C1	Cl	Cl	NO_2	C_2H_5	C_2H_4OH	480	-35
C2	Cl	Cl	NO_2	C_2H_5	C_2H_4CH	457	-31
D1	Cl	H	NO_2	C_2H_5	C_2H_4OH	523	14
D2	Cl	H	NO_2	C_2H_5	C_2H_4 CH	496	8

Table-2: Dispersing agents used in the present investigation

Agent no.	Name	Description
1	Tamol NNO	Naphthalene sulphonic acid condensate
2	Monolan	Ethylene Oxide-propylene Oxide Co-polymer
3	Berol	
4	Lignin sulphonate	

Effeciency of dispersants

The average particle size of crude disperse dyes without milling were determined and are indicated in Table-3 . The efficiencies of dispersing agents were determined by milling dyes with each dispersing agent in 0.025 to 0.50 dispersant/dye weight ratio for 30 minutes at given pH and temperature. The reduction in average particle size after milling at the given ratios are indicated in Table-4 which shows that the lignin sulphonate/dye weight ratio which gave dispersions with minimum average particle size , range from 0.02 to 0.05 for the dyes studied except for B1 which gave high values of average particle size even at high concentrations of dispersing agent.

In case of Tamol low concentrations are required to disperse dyes with S1 series as compared to S2 series of all dyes with the exception of B1.This may probably be due to the presence of sulphonic groups in these two dispersants, which facilitates solubilization of the dyes. Perhaps that is why, higher concentrations of dispersants like Monolan and Berol, which do not have sulphonic groups in their structure reduce the particle size under 1μm for the stable dispersion of the dyes used both at low as well as at higher temperature.

Stability of dispersions

In analogy with Skelly's work, the stabilities of different disperse dyes were determined using different dispersing agents at 130°C. It is obvious that all dispersants showed some increase in average particle size which remained under 1 μm. However, Berol showed no significant changes on heating with any dye. On the whole, the dispersions were stable as were assessed visually and by dyeing the polyester fabric [25].

Table-3: Particle size distribution of disperse dyes before milling

Dye Ref #	Under 4.0 µm %	Under 4.0-3.5 µm %	Under 3.5-3.0 µm %	Under 3.0-2.5 µm %	Under 2.5-2.0 µm %	Under 2.0-1.5 µm %	Under 1.5-1.0 µm %	Under 1.0-0.5 µm %	Under .05-00 µm %	Median Particle size µm
S1	100	12.0	12.0	06.7	06.7	04.5	02.5	01.3	00.8	5.70
S2	100	60.4	41.6	41.6	41.6	41.6	38.8	21.7	09.5	3.70
A1	100	70.0	62.1	52.9	40.9	25.8	15.3	07.5	00.9	2.90
A2	100	44.4	32.8	19.2	08.7	02.2	02.0	00.0	00.0	4.39
B1	100	53.9	52.5	42.9	33.4	20.9	09.5	02.3	00.5	3.37
B2	100	22.8	22.8	14.2	11.3	07.0	04.3	02.2	01.3	5.29
C1	100	54.0	51.4	42.9	33.3	20.9	09.5	02.2	00.4	3.40
C2	100	72.8	66.5	59.7	53.5	45.7	34.2	20.6	05.4	2.28
D1	100	72.2	59.8	48.6	43.0	33.5	22.0	10.7	03.5	3.07
D2	100	67.6	59.7	47.3	44.6	36.1	26.7	14.3	05.2	3.11

Table-4: Effect of dispersant/ dye weight ratio on average particle size of various disperse dyes after milling.

Dye ref No	Lignin sulphonate	Average particle size (µm)	Tamol	Average particle size (µm)	Berol	Average particle size (µm)	Monolan	Average particle size(µm)
S1	0.020	0.32	0.100	0.42	0.020	0.75	0.10	0.81
S2	0.025	0.26	0.033	0.41	0.025	0.71	0.10	0.79
A1	0.025	0.28	0.100	0.26	0.025	0.27	0.10	0.82
A2	0.050	0.26	0.025	0.2	0.040	0.25	0.10	0.78
B1	0.010	1.02	0.100	1.60	0.020	0.36	0.10	0.89
B2	0.033	0.34	0.025	0.39	0.025	0.26	0.10	0.86
C1	0.020	0.32	0.010	0.26	0.020	0.28	0.10	0.82
C2	0.033	0.28	0.033	0.25	0.020	0.27	0.10	0.77
D1	0.020	0.48	0.100	0.28	0.025	0.38	0.10	0.85
D2	0.025	0.45	0.033	0.24	0.040	0.34	0.10	0.84

Table-5: Effect of heating (130°C) on the average particle size of dispersions at given dispersant/dye weight ratio.

Dye ref No	Lignin (sulphonate)	Average particle size (µm)	Tamol	Average particle size (µm)	Berol	Average particle size (µm)	Monolan	Average particle size(µm)
S1	0.020	0.52	0.100	0.57	0.020	0.30	0.10	0.87
S2	0.025	0.48	0.033	0.53	0.025	0.28	0.10	0.82
A1	0.025	0.44	0.100	0.31	0.025	0.32	0.10	0.84
A2	0.050	0.37	0.025	0.29	0.040	0.29	0.10	0.80
B1	0.010	3.92	0.100	4.90	0.020	0.41	0.10	0.95
B2	0.033	0.64	0.025	0.47	0.025	0.31	0.10	0.89
C1	0.020	0.48	0.010	0.41	0.020	0.33	0.10	0.88
C2	0.033	0.42	0.033	0.35	0.020	0.31	0.10	0.85
D1	0.020	0.68	0.100	0.36	0.025	0.44	0.10	0.88
D2	0.025	0.59	0.033	0.30	0.040	0.40	0.10	0.83

Dyeing properties

Polyester cloth was used to study the dyeing properties such as fastness to light , wash and dry heat. As shown in Table-6 the light fastness of dyes with A2-D2 series have higher values than the dyes of A1-D1 series. The light fastness of 4-aminoazobenzene dyes depend on the substituents present as well as on the main chromogen. It has been found that variations in the terminal alkyl groups in dye structure have a significant effect on the fastness to light. High fastness to light on polyester fibre can be associated with the presence of on N-β-cyano-ethyl group in series A2-D2. The reason for this phenomenon may be attributed to the fact that the cyano is an electron withdrawing group and reduces the basicity of the tertiary amino group of the coupling component. This reduces the susceptibility of these dyes to oxidative degradation resulting in improvement fastness to light. In other words the possibility of degradation is not initiated at the basic amino group which results in improvement of fastness to light. The hydroxyl group on the other hand is an electron-donor having a lone pair of

Table-6: Effect of light , washing and dry heat on various disperse dyes

Dye Ref. No.	Light fastness	Wash fastness			Fastness dry heat		
		Change in colour	Staining Cootton	Staining Polyester	Change in colour	Staining Cotton	Staining Polyester
S1	3/4	4/5	4/5	4/5	4	4	3
S2	4.5	4/5	5	5	4.5	4	3
A1	4.5	5	5	5	5	4/5	4
A2	5	5	5	5	5	4/5	4
B1	4	5	5	5	4/5	4/5	3/4
B2	5	5	5	5	5	4/5	4
C1	4	5	5	5	5	4/5	4
C2	5	5	5	5	5	4	4
D1	4	5	5	5	5	4	4
D2	5	5	5	5	5	4	4

electrons on oxygen atom, which increases the basicity of the amino group and therefore initiates the degradation at the basic amino group, and thus lowers the light fastness. The light fastness of the disperse dyes synthesised is also improved due to the polarity of the structure caused mainly by the presence of electron-attracting substituents (NO_2, Cl, Br and CN) in the diazo component of dye molecule.

Fastness to dry heat is important as disperse dyes being non-ionic in most cases may melt and vaporize when heated. A relationship exists between vapour pressure and both molecular weight and polarity of dyes. Fastness to heat increases with increase in relative molecular mass or polarity of the dye molecules. Increase in molecular weight is introduced by substitution through diazo and coupling components and the ability of substituent groups to form hydrogen bonds with the fibre can be very significant. The results of heat fastness dyes are presented in Table-6 the fastness of dye of S1 and S2 type are in the range of 3-4, whereas A1-D1 and A2-D2 dye series showed an increase in fastness from 4-5, which may be attributed to their high molecular weights. These results are in conformity with observations of Halla , who pointed out that variation in terminal substituents have a marked effect on fastness to heat than nuclear substutents [26].

Colour assessment

In general, by simple substitution variation in the diazo component of the basic dye structure both of S1 and S2 type of dyes, affords the range of different colours. Table-1 shows the effect of different substituents on the λ_{max} of A to D series as compared with basic 4-aminoazobenzene dyes. The basic structure has λ_{max} 515 nm for S1. In A1-D1 series the results for different categories are: 540 nm for 2-cyano; 523 nm for 2-chloro; 480 nm for 2,6-dichloro and 476 nm for 2,6-dibromo.On the other hand, in S2 series, the basic structure has λ_{max} value of 488 nm. The λ_{max} for A2-D2 series are as follows : 500nm for 2-cyano, 496 nm for 2-chloro, 457 nm for 2,6-dichloro and 452 nm for 2,6-dibromo. Similar substitution effects on the colour, dyeing and fastness properties of aminoazobenzene are reported by Peters [27].

As shown in Tables 7-11, the lightness L of dyes were reduced in the case of Ligninsulphonate and Tamol showing that the depth of colour has been increased . Increase in Munsell chroma also shows that the colours are stronger than the parent dyes. With Monolan and Berol the lightness L are increased showing that the colours are lighter than the parent dyes where Munsell renotation showed a decrease in chroma i.e. the colour is weaker than the parent dyes. The results of Munsell value are also in agreement with these results. On the whole, the effect of dispersing agents on the colour properties of dyes are in the order: Ligninsulphonate > Tamol > Monolan > Berol. Examination of the data given in Table-1 and Tables-7-10 shows that the λ_{max} values of disperse dyes are in reasonable agreement with the Y, x, y co-ordinates and Munsell renotations and the observed colours of the dyes varied from orange to red.

Experimental

Materials

Disperse dyes were prepared in the laboratory without dispersing agents.They were dried, rubbed and again dried to constant mass. The dispersing agents used are described in Table-2. For dyeing standard 100% polyester fabric was used .

Equipment

The particle size distribution of the disperse dyes was determined using a HORIBA Centrifugal Automatic Particle Analyzer .The colour assessment was made using a Z- 80-11 Colour Measuring System (Nippon Denshoku IND.Co.Ltd.) .The visible spectra were recorded on Hitachi Spectrophotometer

Procedure :

The amines used in the synthesis of disperse dyes are:A. 4-nitro-2-cyanoaniline; B: 2,6-dibromo-

Table-7: Effect of substitution on the colorimetric properties of disperse dyes.

Dye	Tristimulus value			CIE LAB				Colour Co-ordinates		Munsell Renotation	
ref. No.	Y	X	Z	L	a	b	Y	x	y	hue value/	chroma
S1	14.15	20.74	4.21	35.2	39.51	15.09	14.15	0.5009	0.3104	8.22R	6.51/10.95
S2	20.34	30.19	4.98	40.39	35.60	22.98	20.34	0.4879	0.3468	1.60YR	7.91/11.14
A1	14.6	23.71	10.26	38.22	43.83	10.84	14.46	0.4880	0.3007	2.95R	4.06/9.98
A2	8.65	14.87	14.79	30.12	29.87	1.58	8.65	0.3699	0.2483	2.3R	3.55/7.35
B1	45.37	25.37	5.98	38.83	15.56	15.41	45.37	0.3796	0.3595	10YR	6.27 /6.01
B2	34.55	32.55	19.37	55.34	14.99	14.39	34.50	0.4121	0.3600	6.34YR	7.97/6.50
C1	29.78	40.08	20.18	51.67	19.71	16.17	29.78	0.4076	0.3341	8.51R	6.01 / 7.99
C2	32.01	32.86	29.73	49.37	28.74	14.51	32.01	0.4112	0.3169	7.17R	5.98 / 8.01
D1	9.24	21.94	8.99	30.75	31.93	7.78	9.24	0.4430	0.3215	4.08R	3.96 / 10.15
D2	13.89	14.23	10.86	36.35	44.32	10.34	13.89	0.4565	0.3195	7.2R	5.1 / 12.01

Table –8: Effect of Ligninsulphonate as dispersing agent on the colorimetric properties of disperse dyes.

Dye	Tristimulus value			CIE LAB				Colour Co-ordinates		Munsell Renotation	
ref. No.	Y	X	Z	L	a	b	Y	x	y	hue value/	chroma
S1	12.54	20.33	5.29	32.91	40.11	14.58	12.54	0.4759	0.2860	5.93R	6.36/12.01
S2	17.80	27.30	4.70	37.48	37.02	20.38	17.80	0.4329	0.2823	7.21R	7.29 /13.11
A1	11.17	17.97	7.75	30.28	33.94	08.60	11.17	0.3992	0.2481	2.60R	5.26 / 11.07
A2	11.15	16.05	14.46	37.30	24.38	-02.06	11.15	0.2144	0.2805	04.48RP	3.17 / 7.94
B1	20.68	23.59	11.68	30.12	08.61	10.97	20.68	0.1846	0.[illegible]621	1.64YR	6.47 /6.97
B2	29.79	36.02	19.20	50.34	20.57	15.95	29.79	0.3600	0.2767	8.40R	8.01 / 6.06
C1	32.22	35.40	16.95	66.33	14.28	18.37	32.22	0.3171	0.2612	2.83YR	6.32 /7.32
C2	25.26	35.68	18.00	46.97	15.19	18.06	25.26	0.2929	0.2408	4.04R	5.55 / 8.37
D1	11.03	17.21	08.01	32.49	35.11	06.08	11.03	0.4959	0.3180	3.50R	3.77 /8.84
D2	14.64	23.99	06.01	37.18	43.65	16.96	14.64	0.5070	0.3095	6.19R	4.09 /11.79

Table-9: Effect of Monolan as dispersing agent on the colorimetric properties of disperse dyes.

Dye ref	Tristimulus value			CIE LAB				Colour Co-ordinate		Munsell Renotation	
. No.	Y	X	Z	L	a	b	Y	x	y	hue value/	chroma
S1	15.16	25.25	5.65	37.57	46.07	17.71	15.16	0.5105	0.3061	6.27 R	6.58 / 9.96
S2	21.09	32.86	5.06	41.92	41.90	23.14	21.09	0.4543	0.2950	7.49 R	8.02 / 10.12
AI	14.84	24.11	10.43	38.89	44.57	11.02	14.84	0.4962	0.3058	3.00R	4.37 / 11.05
A2	10.26	15.69	11.71	22.07	30.95	-05.76	10.26	0.3869	0.2480	4.42RP	3.72 / 8.46
B1	13.75	20.10	06.30	32.41	27.46	13.88	13.75	0.3816	0.2622	6.11R	5.01 / 8.38
B2	37.37	42.31	24.45	43.71	15.26	17.62	37.37	0.3454	0.3015	2.41YR	8.11 / 6.37
C1	32.31	42.99	21.17	57.45	32.44	18.72	32.31	0.4062	0.3287	7.92R	6.34 / 7.39
C2	30.88	39.86	20.12	52.92	29.31	17.75	30.88	0.3978	0.3082	6.86R	5.99 / 7.98
D1	12.40	19.63	08.59	36.48	36.62	09.80	12.40	0.4450	0.2840	3.15R	4.27 / 11.12
D2	16.37	26.81	07.12	37.12	43.51	16.48	16.37	0.4480	0.2735	5.07 R	5.20 / 11.73

Table-10: Effect of Tamol as dispersing agent on colorimetric properties of disperse dyes

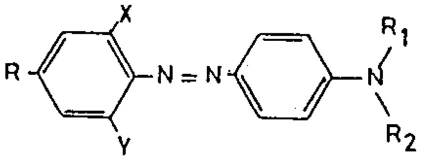
Dye Ref.	Tristimulus value			CIELAB				Colour Co-ordinate		Munsell Renotation	
No.	Y	X	Z	L	a	b	Y	x	y	hue value/	chrom
S1	16.64	24.80	06.52	33.43	30.55	15.61	16.64	0.3471	0.23[illegible]5	5.40R	5.52 / 12.18
S2	21.06	30.80	05.53	39.43	33.89	21.46	21.06	0.3959	0.27[illegible]8	7.29R	5.86 / 13.16
A1	16.60	25.30	13.81	36.76	35.67	07.59	16.60	0.3694	0.2474	1.22R	3.89 / 11.12
A2	06.24	18.13	12.71	43.70	21.60	03.73	06.24	0.2829	0.20[illegible]4	0.09YR	3.90 / 7.45
B1	30.03	33.66	23.13	43.71	10.97	10.63	30.03	0.3158	0.2465	3.38YR	6.87 / 5.99
B2	37.66	43.56	27.89	53.77	13.80	12.93	37.66	0.3165	0.3165	4.33YR	7.07 / 6.63
C1	28.72	36.24	18.44	58.16	24.80	15.75	28.72	0.3688	0.2923	7.16R	5.18 /8.01
C2	29.20	36.63	19.22	48.23	25.13	15.82	29.20	0.3536	0.27[illegible]4	6.62R	5.09 / 8.58
D1	11.56	17.87	08.09	36.33	32.09	09.06	11.56	0.4170	0.2698	3.17R	4.09 / 9.82
D2	19.18	28.30	09.34	37.15	33.12	08.74	19.18	0.3599	0.2431	4.94R	4.98 / 12.34

Table-11: Effect of Berol as dispersing agent on the colorimetric properties of disperse dyes

Dye ref.	Tristimulus value			CIELAB			Colour Co-ordinates			Munsell Renotation	
No.	Y	X	Z	L	a	b	Y	x	y	hue value/	chrom
S1	18.12	25.84	02.84	36.46	30.09	17.75	18.12	0.3770	0.2611	6.68R	7.51 / 9.55
S2	24.64	32.04	08.47	38.69	22.15	19.19	24.64	0.2985	0.2294	1.06YR	8.02 / 10.40
A1	19.87	28.57	17.80	40.11	32.71	06.78	19.87	0.3484	0.2380	0.75R	4.06 / 10.37
A2	12.72	18.54	14.87	40.06	27.04	00.22	12.72	0.3186	0.2180	5.64RP	4.56 / 6.73
B1	22.28	24.93	17.13	32.41	08.10	07.87	22.28	0.1825	0.1583	0.522YR	6.4 0/ 4.78
B2	40.56	45.23	29.24	57.01	15.36	13.40	40.56	0.3333	0.2833	2.95 YR	8.01 / 6.32
C1	30.45	38.37	19.53	58.16	26.26	16.68	30.45	0.3905	0.3095	7.58R	6.31 / 8.15
C2	31.48	37.67	17.80	51.36	26.50	16.71	31.48	0.4209	0.3107	6.66 R	6.13 / 7.25
D1	13.38	20.16	11.09	41.38	30.39	06.73	13.38	0.3527	0.2336	1.43R	4.69 / 9.80
D2	20.25	28.81	11.15	37.01	29.22	13.82	20.25	0.3234	0.2273	4.56R	5.75 / 10.97

4-nitroaniline; C: 2,6-dichloro-4-nitroaniline and D: 2-chloro-4-nitroaniline. The coupling reagents used in the synthesis of dyes are N-ethyl-N-(β-hydroxyethyl) aniline and N-ethyl-(-β-cyanoethyl) aniline.

All the dyes were prepared by the conventional method of diazotization and coupling and the dyes thus obtained are numered as AI-DI and A2 -D2 respectively.The parent dyes numbered as SI-S2 have general structure formula as given below:



(1)

All the dyes developed were purified and their λ_{max} were determined in dimethyl formamide by spectrophotometer.The values of R, R1, R2, X and Y in the general structural formula (1) for parent and other dyes are given in Table-1.

Effect of Dispersants

The dispersants aids wetting of the dye particles by water and stablizes the dispersions by coating the dye particles with a protective steric and electronegative barrier.To determine the effect of the dispersant concentration on the efficiency of sand milling, dye was milled with various amounts of dispersant (ligninsulphonate), ranging from 0.05 to 0.50 dispersant/dye weight ratio. The ratio at which maximum reduction in average particle size obtained were used for further studies. The similar procedure has been followed for other dispersing agents and the results of this study are shown in Table-4.

Milling Procedure

The sand milling equipment (VOLRATH) consisted of a 250ml stainless steel cylindrical shell of dimension (length 24 cm , diameter 9.8 cm) and a stainless steel disk with a shaft , driven by an electric motor. The lower part of the mill is perforated and is fitted with a wire guaze of 150 mesh. The dye S1 and dispersing agent (10g with 0.02 dispersant/dye weight ratio), 20 ml of water (or proportionally less if a wet filter cake was milled) were transferred to the stainless steel beaker. Milling was started and 200g of sand (ottawa Silica Co.)were added over a period of 3-5 minutes. During milling the temperature of the slurry was maintained at 40-50°C and the milling was continued for a period of ½ hr. The slurry was filtered through ordinary filter paper by vacuum suction and the sand was washed on the filter paper with minimum quantity of water (10-15ml). The pH of the milled dispersions ranged from 5.0-6.9. During milling the samples were drawn and were filtered through Whatman No.2 filter papers under vacuum and the progress of grinding was monitored visually by the fineness of the residue received on the filter papers. The particle size of the samples drawn was determined by Horiba CAPA particle size analyzer and grinding continued till constant values of particle size was obtained. The slurry was transferred to spray dryer (Buchimini made in Switzerland) which gave fine powder of dye which was stored in sample bottles. The same procedure was used for all dyes with different dispersing agents at the given dispersant/dye weight ratio.

Stability of dispersions

As the dispersing agent absorbs on the surfaces of the particles in the clusters, the particles acquire like electric charges that cause the repellant forces to become greater than the forces of attraction which finally leads to spontaneous dispersion. Once a dispersion is obtained , the aim is to maintain its stability throughout further processing and application. The term 'stable' signifies that the total number and the size of the suspended particles remain unchanged.

In evaluating dispersing agents for dye manufacture, the main interest lies in determining the ability of these products to improve the degree of dispersity and their stabilizing effect. The stability of dye dispersions at given dispersant/dye ratio were conducted at 130°C in pots of dyeing machine (Roche) without fibrous material being present. After 1hr the dispersions were cooled at room temperature and their average particle size were determined and are given in Table-5.

Dyeing polyester with disperse dyes

Polyester fabric was dyed with disperse dyes at a high temperature of about 130°C using a high temperature dyeing machine by the following procedure:

200 mgs of dispersant/dye mixture which showed maximum reduction in average particle size was taken in mortar, a few drops of water were added in it. It was then ground with a pestle to form a very fine paste followed by dilution with 200mL warm water (dye stock solution 0.1%). The fabric 3.5 gm was wetted with water and transferred to dyeing pot containing dye (2%, 70 mL of 0.1% dye stock solution) in 50:1 liquor: fabric ratio. The pH of dyeing solution was maintained at 4.5 to 5 with ammonium acetate and formic acid. Now the dyeing pots were fitted in the dyeing machine and the temperature of the machine was slowly raised to 130°C at the rate of 2°C/minute and maintained for 60 minutes. The bath temperature was then decreased to 50°C at the same rate. The specimens were then removed from the dyeing pots, rinsed with cold water and finally dried in an oven at 60°C.

After treatment

Reduction clearing was carried out by treatment for 20minutes at 75°C in an aqueous solution containing sodium hydroxide, 5ml/L and sodium hydrosulfite (85%), 2g/L, using a liquor ratio of 20:1. The treated sample was then rinsed thoroughly in water and allowed to dry in the open air .

Wash fastness test:

The washing fastness test was carried out following ISO CO5 procedure [28]. In this test soap solution was prepared containing 5g/L soap and 2g/L sodium carbonate in distilled water. Each of the specimen (4cm x 5 cm) was cut and placed between two adjacent white fabrics of the same dimensions and then stitched together . For polyester fabric, one of the adjacent fabrics was made of polyester, while the second piece was cotton. The composite was then placed in the container and necessary amount of soap solution previously heated to 60°C was added to give a liquor ratio of 50:1. Washing was carried out on water bath at this temperature for 30 minutes. The composites were then removed, rinsed, opened , dried and finally assessed with the aid of grey scales. The change in colour of the specimen and the staining of the adjacent fabrics was assessed with the grey scale. The results obtained are summerized in Table-6.

Fastness to dry-heat

This method is intended for determining the resistance of the colour on polyester and was carried out by following ISO-105 stadard procedure [28]. The specimen (10cm x 4cm) was placed between the two adjacent fabrics of polyester fibre and sewed along one of the shorter sides. Placed the composite specimen in the oven and left it there for 30s at 210°C. Removed the composite specimen and left it for 4h in air at room temperature (27°C) at relative humidity of 65 %.

Assessed the change in colour of the specimen with the grey scale and the staining of the adjacent fabrics against pieces of the adjacent fabrics similarly treated in the absence of a specimen (Table-6).

Fastness to day light

This test was also carried out by following ISO BO 1 standard procedure [28]. An area of the material (strips of cloth) not less than 1cm x 6cm were arranged parallel in a card .An opaque cover was laid across the middle third of the specimen. The card was mounted on the exposure rack sloping at an angle from the horizontal and covered with window glass to protect the specimens from rain and other elements of the weather.Exposed the rack to day light for 110 hr. The effect of light was followed by removing the cover and inspecting the specimen frequently. Regardless of the character of the change, the assessment was based upon the magnitude of the visual contrast between the specimen covered and original one. The fastness rating of the specimen is the number of grey scale which corresponds to the contract between the original and the faded sample (Table –6).

Assessment of colour

The colour of the dyed fabric were assessed by measuring the tristimulus values, colour co-ordinance and and Munsell renotations by using a Z 80-11 colour measuring systems.The data showing the effects of substitution and dispersing agents on these values is presented in Tables 7-10.

Conclusion

Disperse dyes were prepared and their dispersions were obtained by milling them with different dispersing agents. The dispersion properties like stability at room and high temperature (130°C) were also determined. The data presented showed that Ligninsulphonate and Tamol being ionic dispersants affect the ionic strength of the aqueous medium and therefore stabilise the dilute dispersions by electrostatic repulsion. This factor is less marked in case of Monolan and Berol which are not ionic dispersants.The forementioned dispersants have good solubilizing effect because of the sulphonic group present and therefore influence the diffusion of the dye into the polyester and facilitate the mechanism of the entire dyeing process at high temperature (130°C). The substitution variations in the diazo component of basic dye S1 and S2 types demonstrated the facility with which a range of colours developed. The substitution in the nucleus as well as in the terminal amino group increased the fastness properties as compared to the basic structure. Thus , these studies provide a base for assessing dyes and to apply the information obtained to develop new disperse dyes with better colour properties, levelling action and fastness properties.

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