

## Stilbene Based Direct Dyes-effect of Fixing Agents on the Fastness and Colour Properties

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**Summary:** The dyed cotton fabrics after dyeing are usually treated with different auxiliaries to impart desirable properties according to their commercial uses in industries. An attempt has been made to improve the wash fastness and colour properties of eleven non-benzidine direct dyes based on 4,4'-diaminostilbene-2,2'-disulphonic acid. The effectiveness of three fixing agents used was determined by comparing the properties of treated and untreated dyed substrate. All the three fixing agents showed beneficial effects on these properties as assessed by ISO CO 5 wash fastness and on the colour properties like tristimulus values, CIE L\*a\*b\* co-ordinates, chromaticity co-ordinates and Munsell values. Use of these fixing agents improved the wash fastness of these dyes on cotton as well as the brightness and strength of the colour in a similar pattern.

### Introduction

Direct dyes are anionic in nature, have substantivity for cellulosic fibres and are normally applied from an aqueous dyebath containing an electrolyte. They are also used on their blends to impart medium shades of moderate to good light fastness but poor to moderate wet fastness. Their most attractive feature is the essential simplicity of the dyeing process, but a separate aftertreatment to enhance wet fastness is necessary for most direct dyeings[1].

Schmidt has investigated the treatment of textile material with cationic agent after dyeing with direct dyes. He used substances based on formaldehyde condensation products for improving the wet fastness properties of direct dyeings but found them unsuitable. However, these substances demonstrated considerably better fastness without undesirable secondary effects, particularly when cationic softeners were used with the cationic agents [2]. Similarly polyacrylamide, a cationic dye-fixing agent, has been found by Shukla and Mathur to control the bleeding of dyeings of direct dyes on cotton during washing [3].

Golob and co-workers illustrated an ecological and colorimetric analysis of reactant-fixable direct dye aftertreatments. Viscose fabric was dyed with direct dyes and aftertreated with mono-, di- and trifunctional fixatives. The aftertreatment baths were ecologically analysed using COD and BOD methods. The effect of various fixing agents on wet fastness

and on shade changes was assessed colorimetrically [4].

Fluoroheterocyclic-quaternary-ammonium salts can be used as fixing agents for anionic dyes also showed a marked improvement in the colour yield of dyeing and enhanced wetfastness properties on cellulosic materials with substantive dyes [5].

Cationic surfactants are quaternary N compounds which are basically long-chain fatty amines, imidazolines, polyethylene imines and resins of dicyanodiamide, fatty amides and alkanolamides, benzyl trimethyl ammonium chloride, heterocyclic compounds such as pyridine, piperazine, piperidine and certain ethoxylated fatty amines. Such materials are used as well for the aftertreatment of direct dyes to improve wet fastness [6].

Notable improvements in the wet fastness of direct dyeing on cellulosic fibres can be brought about by means of aftertreatment. Of the several aftertreatments which have been practised over many decades, that which involves treatment with a cationic fixing agent ' is currently most popular.

Direct dyes made from benzidine and its derivatives have been withdrawn from manufacture due to the occurrence of carcinoma of bladder in operatives. An intensive search has been undertaken to develop non-benzidine direct dyes from less hazardous 4,4'-diaminostilbene-2,2'-disulphonic acid

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as the alternative of carcinogen diamines. The purpose of the work presented in this paper is to examine the effectiveness of typical commercial cationic fixing agents on the wash fastness of these non-benzidine direct dyes synthesised in our laboratory

### Results and Discussion

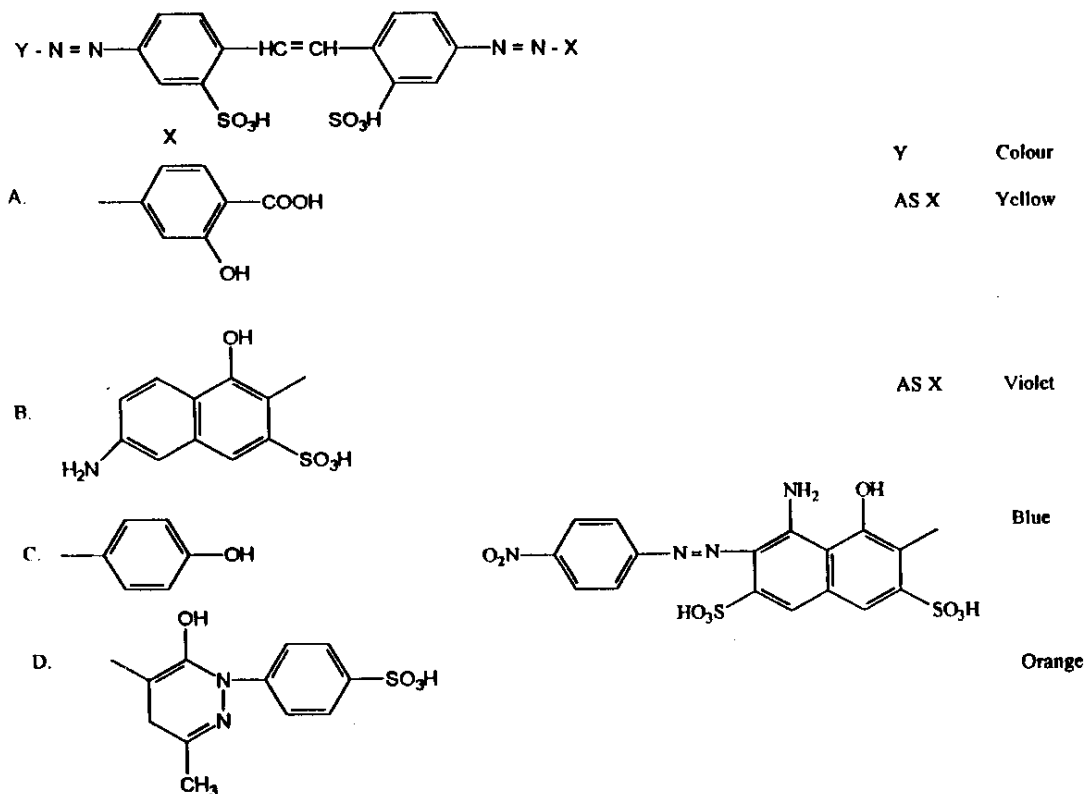
A variety of disazo, trisazo and tetrazo direct dyes were prepared by coupling bis-diazotized 4,4'-diaminodiphenylstilbene disulphonic acid with different coupling agents in acid and alkaline media to yield products in various colour and shades (Scheme-1). The coupling agents used are: salicylic acid, *meta*-aminophenol, pyrazolone resorcinol, *meta*-amine and hydroxy naphthalene sulphonic acid (H-acid and J-acid). For the preparation of tetrazo and trisazo dyes the disazo dyes containing amino group in the coupling agent were again diazotized and then coupled with another coupling agent (see scheme-1 and experimental part for detail). Effect of fixing

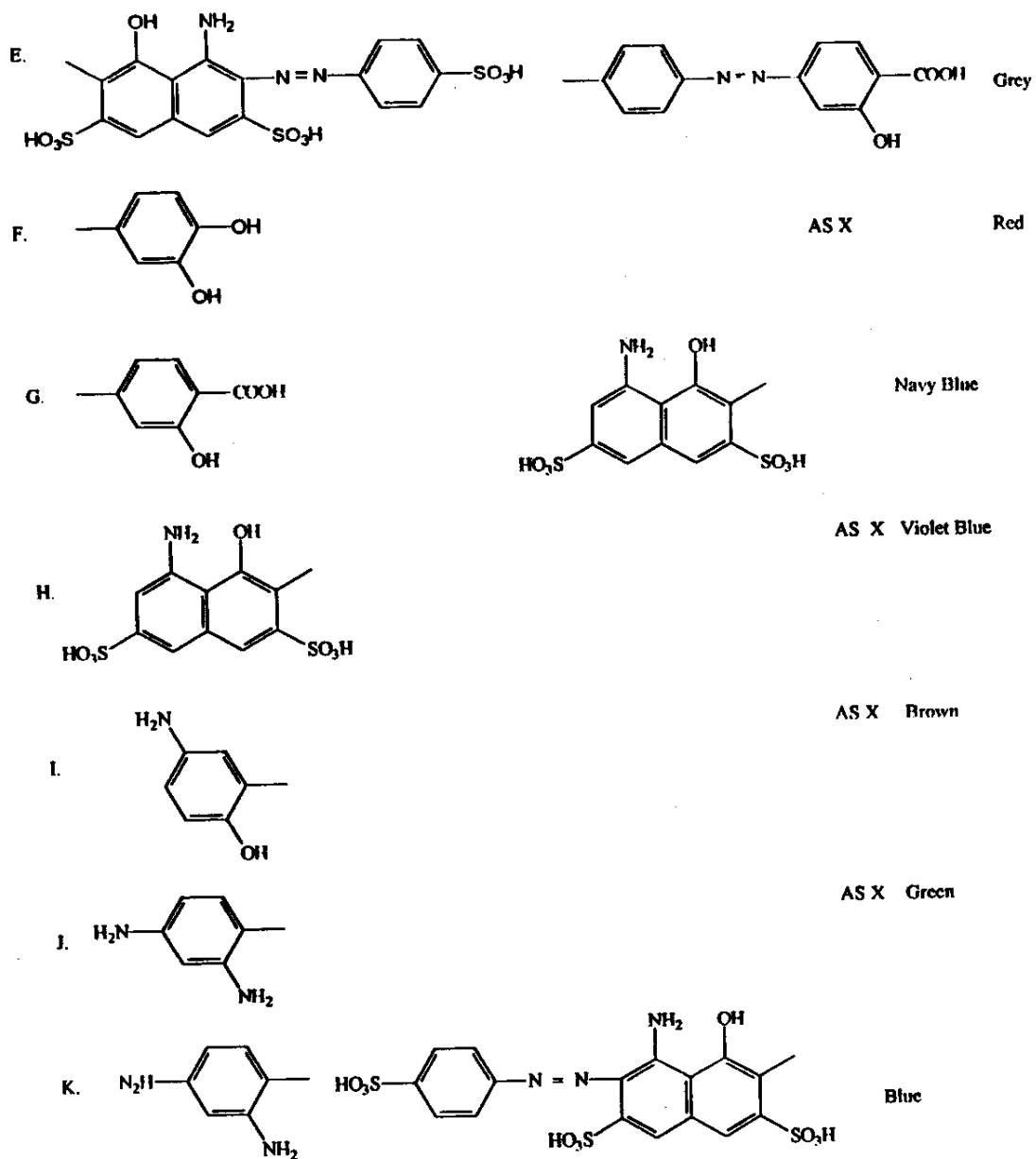
agents on the fastness and colour properties of the dyes synthesised is described below:

#### After Treatment with Cationic Fixing Agents

The wet fastness properties (washings) of dyeings with direct dyes are not sufficient for many end uses. Therefore, some improvements are brought about by after treatment to confer improved fastness. There are various methods of improving the washing fastness of direct dyes on cellulosic fibre fabrics. The most widely used method involves the application of a cationic dye fixing agent subsequent to dyeing in a separate bath [7]. The fixing agent (I) are quaternary ammonium salts which when dissolved in water, ionise into long cations and small anions. On the other hand, when a direct dye is dissolved in water, it ionises into long coloured anions and small sodium ions. When the dye fixing agent solution is applied after dyeing with the direct dye, the long ions of opposite ionic charge combine with one another to form an insoluble complex inside the fibre and due to

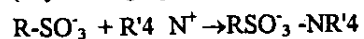
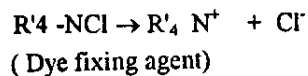
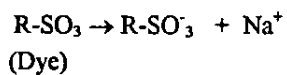
General Structure of Azo Dyes



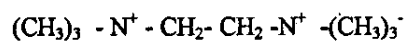


Scheme 1. Shows general structure and structural formula for X and Y.

insolubility of the complex the washing fastness is improved. The reaction follows as :



Fixing agent (II) is a polymerised quaternary ammonium salt (polycationic) having basic structure as :



Whereas fixing agent (III) is a polyethylene polyamine based resin having basic structure as: -NH-  
 $\rightarrow (CH_2-CH_2-NH)_n-CH_2-CH_2-N$

### Wash Fastness

The wash fastness was determined by ISO CO<sub>2</sub> standard method and the assessment were made with grey scale. The data for both treated and untreated dyeings are presented in Table-7. As indicated in Table the aftertreatment improved the fastness of eleven dyes on cotton in terms of change in shade from 3 to 4-5 grade of grey scale. Highest changes were obtained with fixing agent (III). This behaviour can be attributed to the forces of attraction between cationic sites in the fixing agent structure and anionic sulphonic acid groups present in the structure of dye molecule which make the dye more resistance to washing.

The values for loss in colour due to staining on cotton were also determined for treated and untreated samples before and after washing fastness test and the results are also summarized in Table-7. The changes are observed from 1-2 to 4-5 grade of grey scale for untreated and treated samples.

Generally speaking the effectiveness of the three fixing agent on wash fastness of dyed samples is in the order: Fixing agent (III) > Fixing agent (II) > Fixing agent (I)

### Colour Measurement

CIE LAB colour space represents the colour in a three dimensional space based on the Munsell

system. The Cartesian (L\* a\* b\*) values in CIE LAB colour space represent a three -dimensional system with three perpendicular axes representing lightness/darkness (L\*), redness/greeness (a\*) and yellowness/blueness (b\*) respectively. The colour difference  $\Delta E$  concept is based on the cumulative effect of differences in the three individual components.

The corresponding colorimetric data for the eleven dyeings are presented in Table-6 before and after wash fastness respectively. The comparison in terms of  $\Delta E$  is presented in Table-8 for the three fixing agents and when they are mutually compared the fixing agent (III) afforded better results for treated and NIL samples, although changes appeared followed the same pattern as for fixing agent (I) and (II). The reason for this improvement can be attributed to the largest molecular size of fixing agent (III) as compared to (II) and (I) and also having larger number of the substitutes capable of hydrogen bond formation and therefore the lower is the magnitude of dye removal under the influence of washing solution. All the three fixing agents used are cationic in nature and it is postulated that this improved wash fastness could be attributed to: The formation of a large molecular size dye-cationic agent of reduced aqueous solubility within the fibre and/or the formation of a 'layer' of the polymeric cationic fixing agent at the periphery of the dyed fibre.

Table-1: Aftertreatment with fixing agent (1)-Effect on the colour properties of dyed samples before washing fastness test.

Dye Ref#	Tristimulus values			CIE Lab			Chromaticity Co-ordinates		Munsell Renotation		
	Y	X	Z	L*	a*	b*	x	y	Hue	Lightness	Value
A	22.83	30.77	04.20	54.51	33.54	55.89	0.5413	0.4011	3.16YR	05.32	11.62
NIL	21.45	30.31	03.39	54.89	34.20	56.45	0.5323	0.3949	3.21YR	05.58	11.49
B	02.39	02.79	02.74	17.13	18.25	00.49	0.3544	0.3038	2.34 R	01.68	01.55
NIL	01.98	02.23	02.57	17.41	18.62	00.56	0.3522	0.3017	2.46 RP	01.72	01.37
C	09.40	23.54	06.53	42.55	-43.12	-09.98	0.5279	0.3485	5.17 R	04.44	10.47
NIL	08.46	22.34	06.38	42.70	-43.45	-10.31	0.5218	0.3445	5.29 R	04.61	10.29
D	12.96	20.44	09.78	43.45	40.04	24.98	0.5165	0.3275	5.93 R	04.24	10.27
NIL	12.45	20.05	09.37	43.80	41.45	25.01	0.5118	0.3245	6.01 R	04.78	10.08
E	08.44	08.53	11.14	34.27	01.96	-03.13	0.3078	0.3032	1.81 P	03.39	00.75
NIL	07.79	08.17	10.88	34.88	02.23	-03.23	0.3034	0.3002	1.89 P	03.71	00.69
F	03.19	04.04	01.95	20.46	13.93	12.19	0.4417	0.3494	2.51YR	02.02	03.48
NIL	02.87	03.89	01.74	20.78	14.12	12.49	0.4400	0.3474	2.60YR	02.36	03.43
G	02.77	02.78	04.49	18.85	00.99	-06.41	0.2784	0.2796	5.42PB	01.85	01.41
NIL	02.53	02.51	04.08	19.09	01.18	-06.74	0.2768	0.2748	5.57PB	02.31	01.36
H	03.61	03.80	07.05	22.18	03.73	-11.89	0.2674	0.2501	6.96PB	02.17	02.55
NIL	03.23	03.58	06.89	22.83	03.96	-12.07	0.2627	0.2496	7.08PB	02.44	02.38
I	10.23	11.22	05.84	37.98	08.79	19.85	0.4163	0.3795	7.50YR	03.7	03.50
NIL	09.97	10.89	05.36	38.25	08.90	20.12	0.4111	0.3748	7.68YR	04.01	03.44
J	03.69	03.10	05.02	22.43	-08.44	-03.01	0.2665	0.3168	6.59BG	02.20	02.23
NIL	03.34	02.65	04.81	22.61	-08.35	-03.22	0.2624	0.3124	6.67BG	02.45	01.98
K	02.27	02.14	03.19	16.66	-01.66	-03.09	0.2887	0.3001	6.27B	01.62	00.91
NIL	02.08	01.88	02.98	16.84	-01.83	-03.38	0.2815	0.2986	6.34B	01.78	00.67

Table-2: Aftertreatment with fixing agent (11)-Effect on the colour properties of dyed samples before washing fastness test.

Dye Ref.#	Tristimulus values			CIE Lab			Chromaticity Co-ordinates		Munsell Renotation		
	Y	X	Z	L*	a*	b*	x	y	Hue	Lightness	Value
A	22.55	30.42	03.61	54.03	33.85	55.15	0.5387	0.3990	3.01YR	05.44	11.77
NIL	21.45	30.31	03.39	54.89	34.20	56.45	0.5323	0.3949	3.21YR	05.58	11.49
B	02.29	02.44	02.70	17.11	18.25	00.42	0.3582	0.3097	2.26 R	01.60	01.43
NIL	01.98	02.23	02.57	17.41	18.62	00.56	0.3522	0.3017	2.46 RP	01.72	01.37
C	09.15	22.86	06.81	42.33	-42.69	-10.14	0.5299	0.3496	5.79 R	04.18	10.16
NIL	08.46	22.34	06.38	42.70	-43.45	-10.31	0.5218	0.3445	5.29 R	04.61	10.29
D	13.04	20.36	09.98	43.15	39.87	24.21	0.5166	0.3275	5.93 R	04.24	10.27
NIL	12.45	20.05	09.37	43.80	41.45	25.01	0.5118	0.3245	6.01 R	04.78	10.08
E	07.94	08.41	11.31	34.01	01.89	-03.03	0.3079	0.3032	1.73 P	00.82	03.45
NIL	07.79	08.17	10.88	34.88	02.23	-03.23	0.3034	0.3002	1.89 P	03.71	00.69
F	03.09	03.99	02.11	20.26	13.76	12.01	0.4408	0.3507	2.43YR	02.12	03.57
NIL	02.87	03.89	01.74	20.78	14.12	12.49	0.4400	0.3474	2.60YR	02.36	03.43
G	02.88	02.79	04.53	18.39	00.74	-06.21	0.2785	0.2796	5.36PB	01.93	01.49
NIL	02.53	02.51	04.08	19.09	01.18	-06.74	0.2768	0.2748	5.57PB	02.31	01.36
H	03.44	03.74	06.95	22.35	03.63	-11.76	0.2799	0.2501	6.77PB	02.34	02.43
NIL	03.23	03.58	06.89	22.83	03.96	-12.07	0.2627	0.2496	7.08PB	02.44	02.38
I	10.03	10.98	05.67	37.71	08.54	19.13	0.2668	0.3795	7.40YR	03.59	03.61
NIL	09.97	10.89	05.36	38.25	08.90	20.12	0.4111	0.3748	7.68YR	04.01	03.44
J	03.45	02.86	04.95	22.23	-08.03	-02.99	0.4148	0.3168	6.38BG	02.34	02.01
NIL	03.34	02.65	04.81	22.61	-08.35	-03.22	0.2624	0.3124	6.67BG	02.45	01.98
K	02.12	01.94	03.02	16.49	-01.46	-02.98	0.2647	0.3149	6.09B	01.53	00.82
NIL	02.08	01.88	02.98	16.84	-01.83	-03.38	0.2815	0.2986	6.34B	01.78	00.67

Table-3: After treatment with fixing agent (111)-Effect on the colour properties of dyed samples before washing fastness test.

Dye Ref. #	Tristimulus values			CIE Lab			Chromaticity Co-ordinates		Munsell Renotation		
	Y	X	Z	L*	a*	b*	x	y	Hue	Lightness	Values
A	22.92	30.64	04.11	53.99	33.39	55.61	0.5426	0.4009	2.71YR	05.50	11.53
NIL	21.45	30.31	03.39	54.89	34.20	56.45	0.5323	0.3949	3.21YR	05.58	11.49
B	02.53	02.61	02.90	17.09	18.06	00.51	0.3568	0.3097	2.11 R	01.56	01.50
NIL	01.98	02.23	02.57	17.41	18.62	00.56	0.3522	0.3017	2.46 RP	01.72	01.37
C	09.33	23.14	06.69	42.23	-42.82	-10.09	0.5283	0.3475	5.10 R	04.52	10.35
NIL	08.46	22.34	06.38	42.70	-43.45	-10.31	0.5218	0.3445	5.29 R	04.61	10.29
D	13.25	20.59	10.01	43.38	40.17	24.55	0.5154	0.3275	5.84 R	04.59	10.34
NIL	12.45	20.05	09.37	43.80	41.45	25.01	0.5118	0.3245	6.01 R	04.78	10.08
E	08.27	08.71	11.46	33.95	01.78	-03.25	0.3056	0.3032	1.85 P	03.62	00.71
NIL	07.79	08.17	10.88	34.88	02.23	-03.23	0.3034	0.3002	1.89 P	03.71	00.69
F	03.33	04.41	02.35	20.09	13.55	12.26	0.4431	0.3474	2.39YR	02.27	03.53
NIL	02.87	03.89	01.74	20.78	14.12	12.49	0.4400	0.3474	2.60YR	02.36	03.43
G	02.59	02.62	04.34	18.11	01.02	-06.30	0.2801	0.2796	5.21PB	02.24	01.43
NIL	02.53	02.51	04.08	19.09	01.18	-06.74	0.2768	0.2748	5.57PB	02.31	01.36
H	03.58	03.91	07.18	22.03	03.41	-11.52	0.2649	0.2517	6.82PB	02.39	02.48
NIL	03.23	03.58	06.89	22.83	03.96	-12.07	0.2627	0.2496	7.08PB	02.44	02.38
I	10.42	11.01	05.71	37.58	08.49	19.48	0.4150	0.3795	7.61YR	03.79	03.55
NIL	09.97	10.89	05.36	38.25	08.90	20.12	0.4111	0.3748	7.68YR	04.01	03.44
J	03.72	02.99	05.18	22.17	-08.27	-02.64	0.2633	0.3168	6.44BG	02.40	02.11
NIL	03.34	02.65	04.81	22.61	-08.35	-03.22	0.2624	0.3124	6.67BG	02.45	01.98
K	02.18	02.26	03.11	16.31	-01.62	-02.73	0.2839	0.3025	6.19B	01.46	00.73
NIL	02.08	01.88	02.98	16.84	-01.83	-03.38	0.2815	0.2986	6.34B	01.78	00.67

Such a mechanism would serve to lower the rate at which the dye diffused out of the dyed substrate during washing and thus improve wash fastness [14-17]. The three cationic fixing agents varied in their ability to washdown of the dyes studied which can be explained by their different

chemical constitution.

#### Experimental

##### Fabric

Scouring and bleached, fluorescent brightener-free woven cotton (150 g/m) was used.

Table-4: Aftertreatment with fixing agent (I)-Effect on the colour properties of dyed samples after washing fastness test.

Dye Ref#	Tristimulus values			CIE Lab			Chromatic Co-ordinates		Munsell notation		
	Y	X	Z	L*	a*	b*	X	Y	Hue	Hightness	Value
A	23.08	29.16	03.06	54.89	34.20	55.59	0.5323	0.3949	3.46YR	05.32	01.62
NIL	21.67	30.91	03.16	56.24	34.89	54.41	0.5011	0.3991	3.28YR	05.49	11.35
B	02.16	01.98	01.96	17.41	18.62	00.48	0.3597	0.3353	2.78RP	01.28	01.69
NIL	02.08	02.23	02.03	20.11	19.91	00.23	0.3998	0.3319	2.53RP	01.82	01.48
C	09.4	21.89	06.01	42.70	-42.45	-09.12	0.5289	0.3501	5.19R	04.44	10.58
NIL	08.55	22.27	06.45	44.80	-41.98	-09.79	0.5119	0.3523	5.34R	04.79	10.32
D	13.12	20.78	07.89	43.80	41.45	25.01	0.5118	0.3231	5.93R	04.74	10.48
NIL	12.88	21.42	08.05	46.09	43.16	23.13	0.5198	0.3358	6.17R	04.87	10.20
E	08.46	08.78	13.01	34.88	02.28	-03.32	0.3011	0.3111	2.13P	03.39	00.98
NIL	07.97	09.08	13.41	37.16	03.39	-03.97	0.3121	0.3087	1.96P	03.83	00.71
F	03.18	03.89	01.28	20.78	14.12	12.49	0.4492	0.4081	2.09YR	02.27	03.75
NIL	02.96	04.12	01.66	23.41	15.08	11.99	0.4781	0.4109	2.67YR	02.41	03.49
G	03.01	02.98	04.11	19.99	01.18	-03.38	0.3211	0.3108	5.28PB	02.09	01.68
NIL	02.66	03.27	04.55	22.69	01.47	-02.31	0.3198	0.3181	5.61PB	02.46	01.40
H	03.94	03.79	06.54	22.33	04.04	-11.78	0.2799	0.2628	6.89PB	02.17	03.16
NIL	03.62	04.02	07.11	24.28	04.44	-12.97	0.2711	0.2699	7.15PB	02.52	02.43
I	12.25	10.19	04.65	38.25	08.90	20.12	0.4271	0.3899	7.50YR	03.71	03.98
NIL	10.15	11.28	05.14	41.45	09.35	19.65	0.4318	0.3929	7.73YR	04.16	03.49
J	03.74	02.63	05.08	22.61	-08.35	-03.22	0.2891	0.3409	6.36BG	02.20	02.77
NIL	03.47	02.99	05.83	25.63	-09.41	-03.89	0.2838	0.3476	6.73BG	02.56	02.49
K	02.27	01.99	03.17	16.84	-01.83	-03.27	0.3216	0.3296	6.09B	01.36	00.91
NIL	02.18	02.16	03.42	19.28	-02.25	-03.92	0.3101	0.3318	6.32B	01.82	00.72

Table-5: Aftertreatment with fixing agent (II)-Effect on the colour properties of dyed samples after washing fastness test.

Dye Ref#	Tristimulus values			CIE Lab			Chromatic Co-ordinates		Munsell Renotation		
	Y	X	Z	L*	a*	b*	x	y	Hue	Lightness	Value
A	23.39	31.39	03.00	53.89	34.25	55.76	0.5453	0.4045	3.19YR	05.25	11.56
NIL	21.67	30.91	03.16	56.24	34.89	54.41	0.5011	0.3991	3.28YR	05.49	11.35
B	02.56	02.78	01.18	16.71	18.25	00.42	0.4067	0.3484	2.44R	01.45	01.60
NIL	02.08	02.23	02.03	20.11	19.91	00.23	0.3998	0.3319	2.53RP	01.82	01.48
C	09.36	22.51	08.52	41.48	-42.69	-10.14	0.5473	0.3613	5.21R	04.49	10.54
NIL	08.55	22.27	06.45	44.80	-41.98	-09.79	0.5119	0.3523	5.34R	04.79	10.32
D	13.27	21.32	08.83	42.88	40.87	24.21	0.5382	0.3412	6.09R	04.34	10.31
NIL	12.88	21.42	08.05	46.09	43.16	23.13	0.5198	0.3358	6.17R	04.87	10.20
E	08.71	09.46	08.11	33.29	01.90	-03.03	0.3231	0.3197	1.85P	03.19	00.80
NIL	08.71	07.97	09.08	37.16	03.39	-03.97	0.3121	0.3087	1.96P	03.83	00.71
F	03.35	04.29	01.73	19.75	15.08	11.99	0.4951	0.4231	2.59YR	02.08	03.62
NIL	02.96	04.12	01.66	23.41	15.08	11.99	0.4781	0.4109	2.67YR	02.41	03.49
G	02.88	03.46	04.99	17.45	00.84	-03.78	0.3287	0.3263	5.55PB	02.08	01.49
NIL	02.66	03.27	04.55	22.69	01.47	-02.31	0.3198	0.3181	5.61PB	02.46	01.40
H	03.84	04.18	07.64	21.89	03.96	-12.07	0.2859	0.2717	6.89PB	02.21	02.64
NIL	03.62	04.02	07.11	24.28	04.44	-12.97	0.2711	0.2699	7.15PB	02.52	02.43
I	10.69	11.85	05.44	37.02	08.54	20.12	0.4452	0.4059	7.57YR	03.75	03.63
NIL	10.15	11.28	05.14	41.45	09.35	19.65	0.4318	0.3929	7.73YR	04.16	03.49
J	04.25	03.37	06.21	21.67	-08.03	-03.45	0.2972	0.3539	6.66BG	02.19	02.51
NIL	03.47	02.99	05.83	25.63	-09.41	-03.89	0.2838	0.3476	6.73BG	02.56	02.49
K	02.77	02.59	03.96	16.08	-01.98	-02.98	0.3211	0.3407	6.41B	01.42	01.10
NIL	02.18	02.16	03.42	19.28	-02.25	-03.92	0.3101	0.3318	6.32B	01.82	00.72

### Material

4,4'-Diaminodiphenylstilbene-2,2'-disulphonic acid was used as the amine which was bis-diazotized by the standard method of diazotization and was coupled with different coupling agents as given in Scheme-I.

### Purification of Dyes

The crude dyes were purified by Thin-layer chromatography on kiesel gel 60 silica gel plates (Merck) deposited on glass plates with a layer of thickness of 0.2mm. The dyes were introduced as 0.1% solutions and the plates were developed with

Table-6: Aftertreatment with fixing agent (III)-Effect on the colour properties of dyed samples after washing fastness test.

Dye Ref#	Tristimulus values			CIE Lab			Chromaticit Co-ordinates		Munsell Renotation		
	Y	X	Z	L*	a*	b*	x	y	Hue	Lightness	Value
A	22.92	32.46	03.65	52.28	33.09	55.94	0.5328	0.4095	3.31YR	05.38	11.48
NIL	21.67	30.91	03.16	56.24	34.89	54.41	0.5011	0.3991	3.28YR	05.49	11.35
B	02.53	02.46	01.63	16.05	17.91	00.33	0.4187	0.3500	2.68RP	01.35	01.78
NIL	02.08	02.23	02.03	20.11	19.91	00.23	0.3998	0.3319	2.53RP	01.82	01.48
C	09.33	23.01	05.14	40.83	-43.27	-10.10	0.5498	0.3691	5.58R	04.58	10.59
NIL	08.55	22.27	06.45	44.80	-41.98	-09.79	0.5119	0.3523	5.34R	04.79	10.32
D	13.65	22.21	08.63	42.01	42.89	22.49	0.5400	0.3474	6.43R	04.23	10.45
NIL	12.88	21.42	08.05	46.09	43.16	23.13	0.5198	0.3358	6.17R	04.87	10.20
E	08.46	10.88	13.93	33.05	02.65	-03.18	0.3291	0.3208	2.05P	03.44	00.82
NIL	07.97	09.08	13.41	37.16	03.39	-03.97	0.3121	0.3087	1.96P	03.83	00.71
F	03.33	03.91	02.01	18.39	14.93	12.17	0.4809	0.4289	2.92YR	02.01	03.74
NIL	02.96	04.12	01.66	23.41	15.08	11.99	0.4781	0.4109	2.67YR	02.41	03.49
G	02.59	03.89	05.11	16.87	01.76	-03.40	0.3211	0.3288	5.85PB	02.00	01.51
NIL	02.66	03.27	04.55	22.69	01.47	-02.31	0.3198	0.3181	5.61PB	02.46	01.40
H	04.31	04.37	07.76	21.17	04.25	-12.44	0.2889	0.2798	7.38PB	02.12	02.71
NIL	03.62	04.02	07.11	24.28	04.44	-12.97	0.2711	0.2699	7.15PB	02.52	02.43
I	11.63	11.82	05.62	36.73	09.09	19.10	0.4342	0.4079	7.87YR	03.99	03.69
NIL	10.15	11.28	05.14	41.45	09.35	19.65	0.4318	0.3929	7.73YR	04.16	03.49
J	04.46	03.26	06.37	20.13	-09.01	-03.14	0.2913	0.3582	6.89B	02.03	02.62
NIL	03.47	02.99	05.83	25.63	-09.41	-03.89	0.2838	0.3476	6.73BG	02.56	02.49
K	02.94	03.99	06.37	15.99	-02.09	-03.11	0.3156	0.3463	6.56B	01.31	01.28
NIL	02.18	02.16	03.42	19.28	-02.25	-03.92	0.3101	0.3318	6.32B	01.82	00.72

Table-7 Effect of Fixing Agent Treatment on Washing Fastness of Dyed Samples

After treatment with Fixing agent (I)	Change In Shad	Staining on cotton	After treatment with Fixing agent (II)	Change In Shade	Staining on cotton	After treatment With Fixing agent (III)	Change In Shade	Staining on cotton
NIL	3-4	3-4	NIL	3-4	3-4	NIL	3-4	3-4
A	4	4	A	4	4	A	4-5	4-5
NIL	3	1-2	NIL	3	1-2	NIL	3	1-2
B	4	3-4	B	4	3-4	B	4-5	4
NIL	3	1-2	NIL	3	1-2	NIL		1-2
C	4	3-4	C	4	4-5	C	4-5	4
NIL	3-4	3-4	NIL	3-4	3-4	NIL	3-4	3-4
D	4	3-4	D	4	3-4	D	4-5	4
NIL	3-4	2-3	NIL	3-4	2-3	NIL	3-4	2-3
E	4	3-4	E	4	3-4	E	4-5	4
NIL	3-4	3-4	NIL	3-4	3-4	NIL	3-4	3-4
F	4	4	L^	4	4-5	F	4-5	4-5
NIL	3-4	3-4	NIL	3-4	3-4	NIL	3-4	3-4
G	4	4	G	4	4-5	G	4-5	4-5
NIL	3	3	NIL	3	3	NIL	3	3
H	3-4	3-4	H	3-4	4-5	H	4	4
NIL	3-4	3-4	NIL	3-4	3-4	NIL	3-4	3-4
I	4	4	I	4	4	I	4-5	4-5
NIL	3-4	3-4	NIL	3-4	3-4	NI	3-4	3-4
J		4	J	4	4	J	4-5	4
NIL	3-4	3-4	NIL	3-4	3-4	NIL	3-4	3-4
K	4	4	K	4	4-5	K	4-5	4-5

butanol:dimethyl formamide (DMF): 25% ammonia (4:2:3.5 V/V). The purified fraction was scraped off the plates and DMF was added to elute the dyes. Silica gel was removed by filtration and dye was isolated by distillation and was characterized by IR and visible spectrophotometry.

Cationic fixing agents purchased from the market are named as NEOFIX RBC (fixing agent I), NEOFIX R-755 (fixing agent II) and CHEMRIT-RND (fixing agent III).

#### Dyeing of Fabric

All the dyeings (4% owf fabric) were carried out in sealed stainless steel dyeing tubes of 200 mL capacity and housed in a Roche laboratory dyeing machine. At 25:1 liquor ratio, 5 g cotton pieces was added to the dye bath and after the addition of sodium chloride (9 g), the temperature was raised to 98°C during 30 minutes and dyeing was continued for 1hr. Thereafter, the dyebath temperature was lowered to room temperature and the samples were drawn out of the tubes and rinsed with tap water.

Table-8 Aftertreatment with fixing agent- Effect on the colour loss of untreated and treated samples before and after washing with water in terms of CIE Lab difference ( $\Delta E$ )

Dye Ref #	Fixing Agent (I)		Fixing Agent (II)		Fixing Agent (III)	
A A*	9.25	9.79	11.85	12.01	13.85	14.17
B B*	8.43	8.94	9.26	9.78	12.83	13.01
C C*	6.99	7.27	10.36	10.85	13.23	13.79
D D*	9.01	9.45	10.99	11.24	13.65	13.9
E E*	9.48	9.83	12.05	12.85	12.35	12.74
F F*	8.89	9.11	9.69	10.05	13.49	13.78
G G*	8.05	8.46	11.29	11.73	11.93	12.15
H H*	9.76	10.13	9.83	10.21	11.69	12.58
I I*	8.35	8.73	10.09	10.42	13.11	13.53
J J*	7.65	8.12	9.02	9.55	12.65	12.89
K K*	7.35	7.98	8.76	9.11	12.13	12.48

\*values are for sample after washing

#### After Treatment With the Cationic Fixing Agent

Each of the three cationic agents was applied at 4% owf fabric to the 4% dyeings, using a 25:1 liquor ratio, in a sealed stainless steel dyeing tubes (200 mL capacity) and housed in a Roche laboratory dyeing machine. The temperature of bath was raised to 40°C and after 30 minutes the samples were drawn out of the dyeing tubes.

#### Fastness Determination

The wash fastness test of the dyeings was carried out following ISO CO<sub>5</sub> standard method [10]. In this test disazo, trisazo and polyazo structures and those with the highest affinity have structures in which the groups that are soap solution was prepared containing 5 g/L and 2 g/L sodium carbonate in distilled water. Each of the specimen (4cm x 5cm) was cut and placed between two adjacent white cotton fabric of the same dimensions and then stitched together. 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 in Launderometer which consists of a water bath containing a rotatable shaft which supports, radially, stainless steel container (75± 5 mm x 125 ± 10 mm high) of capacity 500 ± 50 mL, the bottom of the containers being 45 ±10 mm from the centre of the shaft. The shaft/container assembly is rotated at a frequency of 40 ± 2 min<sup>-1</sup>. The temperature of the water bath is thermostatically controlled to maintain the test solution at the prescribed temperature ± 2°C. The washing was continued at this temperature for 30 minutes. The composite 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 summarized in Table-4.

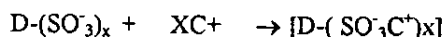
#### Colour Measurement

The tristimulus values Y X Z and the corresponding CIE L\*, a\*, b\*, chromaticity coordinates x, y and Munsell renotation of the dyed samples were measured using (Z- (80 II) colorimeter. Each fabric sample was folded to realise a total of four thicknesses of fabric. A total of three measurements were made of each sample, from which the average value was calculated.

#### Conclusions

Direct dyes are anionic but have higher molecular masses and more linear structures. Most direct dyes have most likely to interact (via hydrogen bonds) with hydroxyl groups are spaced at intervals corresponding approximately to the hydroxyl group spacing in cellulose.

Cationic fixing agents aftertreatment results in the improvement of fastness to washing due to the formation of a cation-anion complex having limited solubility in water, either within the fibre or at the fibre surface. A general study of the interaction of direct dyes and cationic fixing agent in aqueous solution is shown as follows:



#### References

1. C.C. Cook, *Rev. Prog. Coloration*, **12**, 73 (1982).
2. R. Schmidt, *Tekstil*, **34**, 999 (1985).
3. S.R. Shukla and M. Mathur, *Indian Text. J.*, **66**, (1994).
4. V. Golob, S. Jeler and J. Donlagic, IFATCC Congress Book of Papers, pp 374 (1996).
5. CGY, BP, 1, 545, 027 (1976).
6. H.D. Pratt, *Am. Dyestuff Rep.*, **79**, 24 (1991).
7. V.A. Shenai and N.M. Saraf " Chemistry of Organic Textile Chemicals ", 2<sup>nd</sup> Ed. pp 277. (1995).
8. S.M. Burkinshaw and G.W. Collins, *Dyes and Pigments*, **29**, 323 (1995)
9. S.M. Burkinshaw and G.W. Collins *Dyes and Pigments*, **29**, 323 (1995)
10. Standard Methods for the determination of the colour fastness of textiles and leather, 4<sup>th</sup> Ed (Bradford: SDC, 1978).