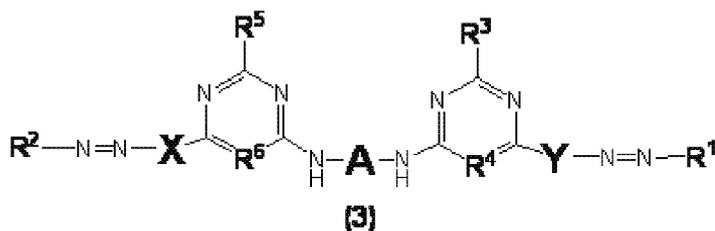
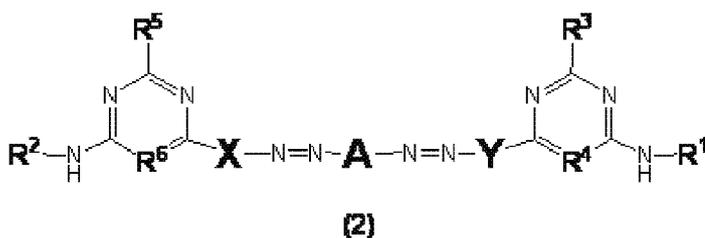
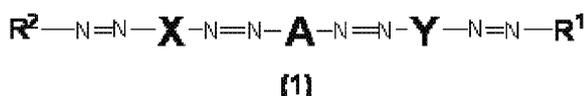




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- Declarations under Rule 4.17:**
— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

[Continued on next page]

(54) Title: NOVEL REACTIVE DYES, THERE MIXTURES AND PROCESSES THEREOF



(57) Abstract: The present invention relates to polyazo reactive dyes comprising of stilbene or diaminodiphenylsulfone derivatives of formula (1), Formula (2) and Formula (3). Where, A= 4,4'-diaminostilbene-2,2'-disulphonic acid; 4:4'-Diaminodiphenylsufone; 3:3'-Diaminodiphenylsulfone which can be applied as single dye or as mixture with other compatible dyestuffs for dyeing a wide variety of fibre materials selected from, cellulose, polyamide or protein fibres and yield dyeings having good allround fastness properties.

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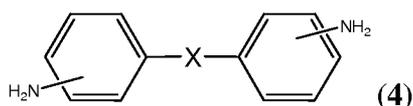
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*
 - *of inventorship (Rule 4.17(iv))*
- Published:**
- *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

NOVEL REACTIVE DYES, THERE MIXTURES AND PROCESSES THEREOF**Field of the Invention**

The present invention relates to polyazo reactive dyes comprising of stilbene or diaminodiphenylsulfone derivatives and processes for the preparation thereof.

5 Background of the invention and prior art

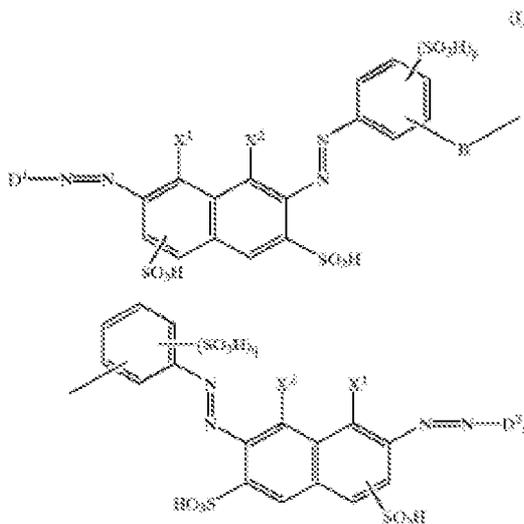
Diaminodiphenyl derivatives of the formula (4) are very widely used and well known intermediate in the dyestuff chemistry. These intermediates are mainly explored for the synthesis of Direct and Acid Dyes.



10 X= -CH=CH-; SO₂; -NH-SO₂-; -NHCO-; -CO-... etc.

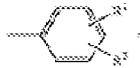
As such these intermediates has very limited or no utilization in the synthesis of Reactive Dyes. Some of the following patent literatures represent the some specific reactive dye molecules based on these intermediates.

15 US patent 6013775 discloses polyazo compounds which are useful as dyes for dyeing material or synthetic substrates and is provide by the formula



Where one of the two radicals X1 and X2 is hydroxyl and the other is amino,
p and q are each independently of the other 0 or 1,

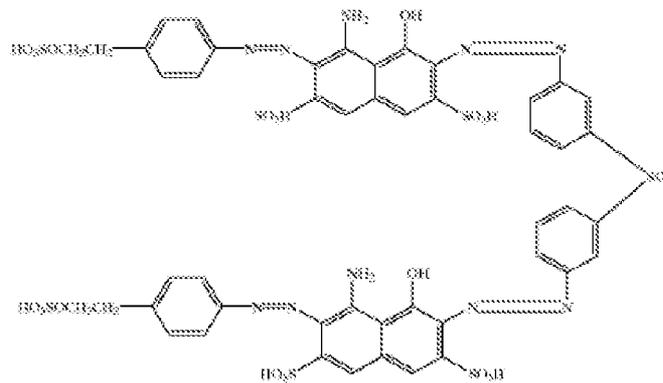
D1 and D2 are each independently of the other a radical of the formula



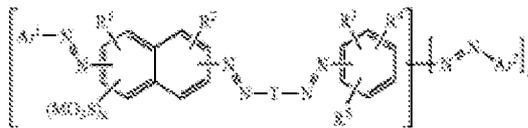
And B is a bridge member are prepared using novel sulfonamide intermediates and are useful as dyes for dyeing natural or synthetic substrates. It is further disclosed that B is

- 5 -SO₂-NH-A¹-NH-SO₂-, -SO₂-N(Alk)-A¹-NH-SO₂-, -SO₂-N(Alk)-A¹-N(Alk)-SO₂-,
 -SO₂-N(Alk)-A¹-O-SO₂-, -SO₂-O-A¹-O-SO₂-, -SO₂-N(Alk)-SO₂-N(Alk)-SO₂-, -SO₂-NH-A²-
 NH-SO₂-, -SO₃- or SO₂,

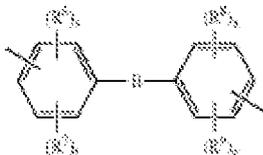
Further column 17 & 18 disclose compound of the formula,



- 10 Most closest prior art US2008047079 discloses polyazo dyes of the formula



Wherein T is a radical of the general formula



wherein B is a bridging element of the formula

- 15 -NH-, -CO-, -SO₂-, -CH=CH-, -CH₂-CH₂-, -NH-CO-, -NH-SO₂-, -SO₂-NH-SO₂- or a direct
 bond. The main objective of US2008047079 is to provide better solution for dyeing leather to

overcome issue with most commonly used acid and direct dyes with polyazo reactive dyes which can have good affinity and fixation on leather. Although claim 11 of US2008047079 mentioned general formula 1 which is very wide and in subsequent claims it was limited to specific substituents and in particular with radical T it disclosed only –NH-, –NH-CO- and -NH-SO₂-. Other patent literature discloses use of these intermediate in the synthesis of Bis, tris, tetra and poly azo Direct and Acid dyes such as; EP0013750; US5272259; US4390470; US2056539; EP0498217; US5785718; US4169832; EP2022828 and US5431723.

Objects of the Invention:

10 It is an object of the present invention to provide bis, tris, tetra and poly azo reactive dyes based on derivatives of 4, 4'-diaminostilbene-2, 2'-disulphonic acid; 4:4'-Diaminodiphenylsufone and 3:3'-Diamino diphenyl sulfone of the respective formula (1) to obtain novel black, blue, red, brown and yellow reactive dyes with very deeper shades and overall good fastness properties particularly washing fastness and light fastness.

15 It is another object of the present invention to provide reactive azo dyes based on derivatives of 4,4'-diaminostilbene-2,2'-disulphonic acid; 4:4'-Diaminodiphenylsufone and 3:3'-Diamino diphenyl sulfone of the respective formula (2) with excellent fastness properties especially washing fastness and light fastness.

It is yet another object of the present invention to provide reactive azo dyes based on derivatives of 4,4'-diaminostilbene-2,2'-disulphonic acid; 4:4'-Diaminodiphenylsufone and 3:3'-Diamino diphenyl sulfone of the respective formula (3) with excellent fastness properties and very good build up.

It is a further object of the present invention to provide a process for the preparation of compounds of formula (1), Formula (2) and Formula (3).

25 It is a further object of the present invention to apply as single dye or as mixture, or in combination with other compatible dyestuffs containing vinylsulfone and/or heterocyclic reactive groups, preferably applied in dichromatic or trichromatic combinations, to achieve very deep shades, and excellent fastness properties.

1:5/1:8-Diamino naphthalene

1:5/1:8-Dihydroxy naphthalene

and similar diamino, amino hydroxy and dihydroxy benzene and naphthalene derivatives;

wherein X and Y are not simultaneously 1-Amino-8-Hydroxy naphthalene-3:6-disulphonic acid (H acid);

5 acid (H acid);

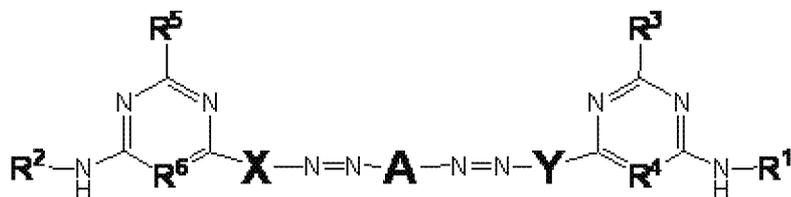
R^1 & R^2 = Amino benzene or naphthalene derivatives containing at least one or more vinylsulphone reactive group with or without $-SO_3H$, alkyl, alkoxy and halo substituent on benzene or naphthalene ring.

R^3 & R^5 = May be same or different in combination of Cl; F; C1-C4 Alkoxy, $-NH_2$, $-NHCN$, -

10 C1-C4 alkylamine, Alkyl amino sulfone derivatives, alkyl amino acids, alkyl amino sulphonic acid derivatives etc.

R^4 & R^6 = N, CH, C-Cl.

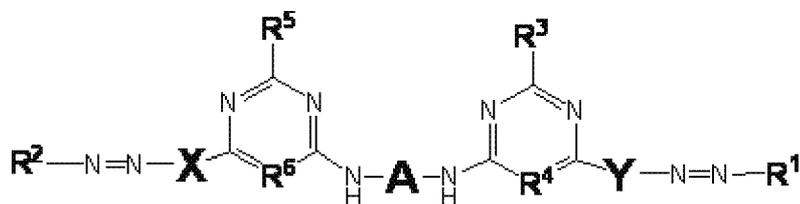
According to another aspect of the present invention there is provided polyazo dyes of the formula (2) and mixtures thereof,



(2)

15

According to another aspect of the present invention there is provided polyazo dyes of the formula (3) and mixtures thereof,



(3)

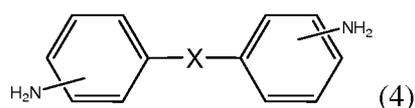
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According to yet another aspect of the invention there is provided a process for the preparation of compounds of formula (1), formula (2) and formula (3).

Detailed Description of the present invention

The present invention describes a new and unique class of polyazo dyes comprising of stilbene or diaminodiphenylsulfone derivatives, processes for preparing said dyes, and methods for applying these dyes to fibers.

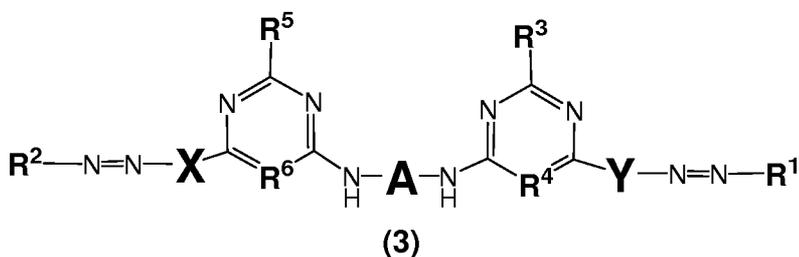
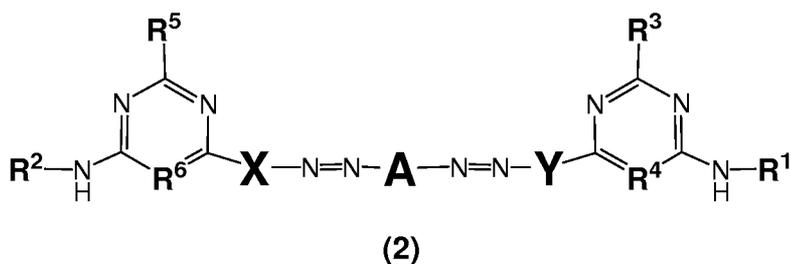
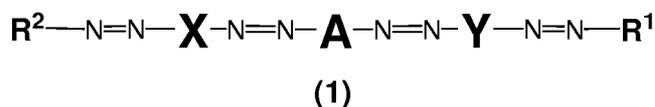
In its most basic embodiment the dyes of the present invention have the structure of formula (4)



10 X= -CH=CH-; SO₂; -NH-SO₂-; -NHCO-; -CO-... etc.

which is further substituted with azo groups and amino groups which are further substituted.

According to one embodiment, there is provided polyazo dyes based on the formula (1), formula (2) and formula (3),



15 Where, A= 4,4'-diaminostilbene-2,2'-disulphonic acid; (DASDSA)
4:4'-Diaminodiphenylsufone; (4,4'-DADPS)

3:3'-Diaminodiphenylsulfone (3,3'--DADPS)

X & Y are same or different in combination of followings

1-Amino-8-Hydroxy naphthalene-3:6-disulphonic acid. (H acid)

1-Amino-7-Hydroxy naphthalene-3:6-disulphonic acid.

5 1-Amino-7-Hydroxy naphthalene-6-sulphonic acid.

7-Amino-1-naphthol-3-sulfonic acid (Gamma acid)

N-Methyl-Gamma acid

2-Amino-5-hydroxy-7-naphthalenesulfonic acid (J acid)

1-Hydroxy-6-(methylamino)-3-naphthalenesulfonic acid (N-methyl J-acid)

10 1-Hydroxy-6-(2'-Carboxy ethyl amino)-3-naphthalenesulfonic acid

1-Hydroxy-6-(2'-sulfo ethyl amino)-3-naphthalenesulfonic acid

And similar N-substituted alkyl derivatives.

1:3-Diamino benzene (m- phenylenediamine)

1:4-Diamino benzene (p- phenylenediamine)

15 2:5-Diamino benzene sulphonic acid (PPDSA)

2:4-Diamino benzene sulphonic acid (MPDSA)

1:3-Diamino benzoic acid

2:4-Diamino toluene

3:4-Diamino toluene

20 1:3-Dihydroxy benzene,

1:5/1:8-Diamino naphthalene

1:5/1:8-Dihydroxy naphthalene

and similar diamino, amino hydroxy and dihydroxy benzene and naphthalene derivatives;

wherein in formula (1), X and Y are not simultaneously 1-Amino-8-Hydroxy naphthalene-

25 3:6-disulphonic acid (H acid);

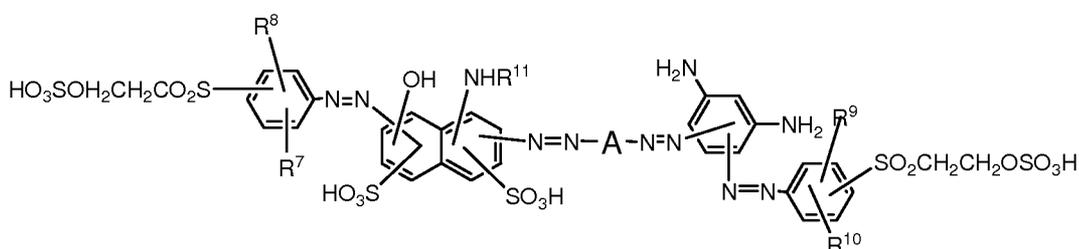
R^1 & R^2 = Amino benzene or naphthalene derivatives containing at least one or more vinylsulphone reactive group with or without $-SO_3H$, alkyl, alkoxy and halo substituent on benzene or naphthalene ring.

8

R^3 & R^5 = May be R^3 & R^5 are same or different in combination of Cl; F; C1-C4 Alkoxy, -NH₂, -NHCN, -C1-C4 alkylamine, Alkyl amino sulfone derivatives, alkyl amino acids, alkyl amino sulphonic acid derivatives etc.

R^4 & R^6 = N, CH, C-Cl.

5 The poly azo dyes of formula 1 are preferably selected from formula (1')



Where, A = 4,4'-diaminostilbene-2,2'-disulphonic acid; (DASDSA)

4:4'-Diaminodiphenylsulfone; (4,4'-DADPS)

3:3'-Diaminodiphenylsulfone (3,3'-DADPS)

10 R^7 , R^8 , R^9 and R^{10} = May be same or different in combination of -H, -SO₃H, alkyl and halo.

R^{11} = -CH₂CH₂COOH, -CH₂CH₂CN, -CH₂CH₂CONH₂, -CH₂COOH, -CH₂CH₂SO₃H, -CH₂CH(CH₃)COOH, -CH₂CH₂OSO₃H, -CH₂CH₂COCH₃, -CH₂CH₂COOC₂H₅,

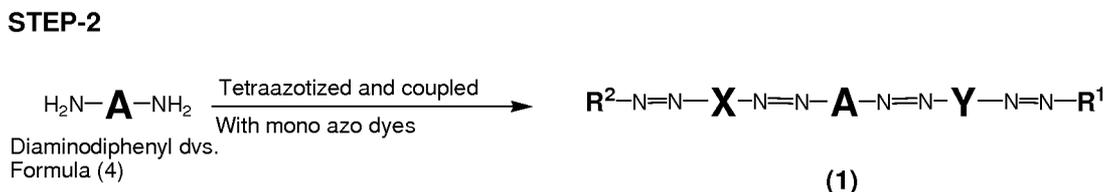
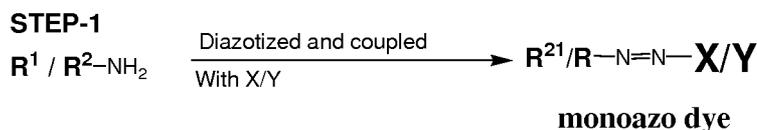
and also their mixtures with each or one another.

15

In another embodiment, there is provided a process for the preparation of compounds of formula (1), formula (2) and formula (3).

While diamino diphenyl derivative as described by formula (4) is tetraazotized and coupled with mono azo dyes obtained by coupling of diamino, amino hydroxyl or dihydroxy benzene & naphthalene derivatives with diazotized primary aromatic amine containing at least one vinylsulphone reactive group under appropriate condition to get novel reactive dyes of formula (1) having very high optical density and excellent build up and all around fastness properties.

20



In another embodiment, Bisazo amino/hydroxyl intermediate may be linked to suitable chromophores through a suitable heterocyclic reactive intermediate which may or may not be prior substituted or subsequently condensed with any of the substituent described as R³ and/or R⁵ to get novel reactive dyes of formula (2) having very excellent build up and all around fastness properties.

The following examples of linking compounds serve to illustrate this embodiment without in any way limiting the range of possible linking components: cyanuric chloride, cyanuric fluoride, trifluoro chloropyrimidine, trifluoro pyrimidine.

STEP-1

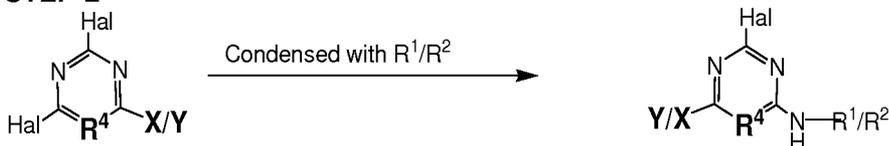


Hal= Cl or F
 R⁴= N, CH, C-Cl

Heterocyclic linking component

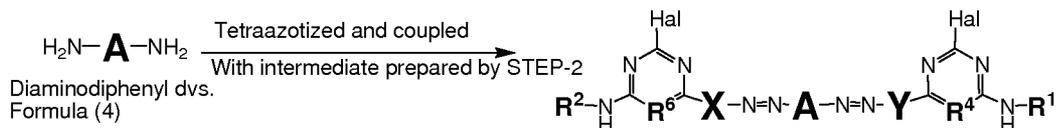
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STEP-2

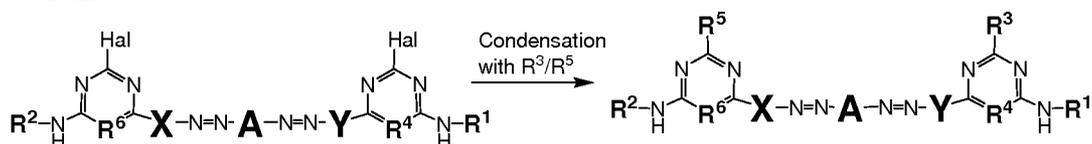


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STEP-3



STEP-4

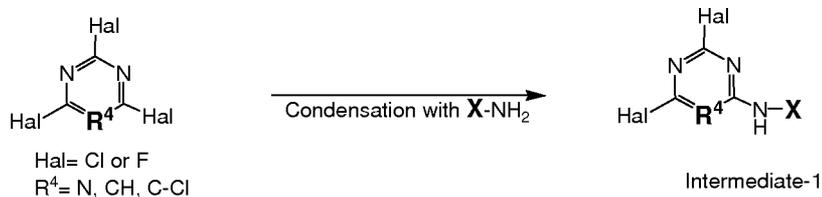


(2)

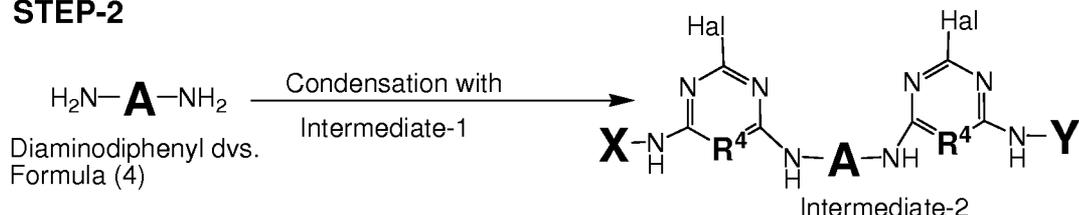
In yet another embodiment, diamino diphenyl derivative as described by formula (4) may be linked with diamino, amino hydroxyl or dihydroxy benzene & naphthalene derivatives through a suitable bifunctional intermediate heterocyclic reactive intermediate which may or may not be prior substituted or subsequently condensed with any of the substituent described as R⁴.

The following examples of linking compounds serve to illustrate this embodiment without in anyway limiting the range of possible linking components: cyanuric chloride, cyanuric fluoride, trifluoro chloropyrimidine, trifluoro pyrimidine. This is further coupled with diazotized amino benzene or naphthalene derivatives containing at least one or more vinylsulphone reactive group to get novel reactive dyes of formula (3) having very high optical density and excellent build up and all around fastness properties.

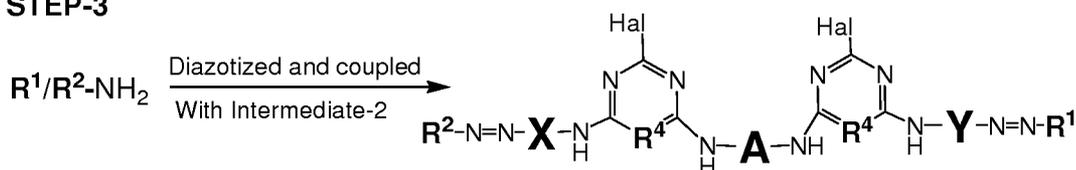
STEP-1



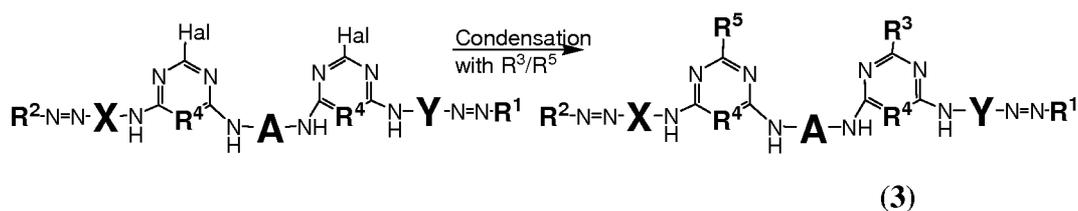
STEP-2



STEP-3



STEP-4



5 All novel reactive dyes described as formula(1), formula(2) and formula(3) can be applied as single dye or as mixtures or in combination with other compatible dyestuffs containing vinylsulfone and/or heterocyclic reactive groups, preferably applied in dichromatic or trichromatic combinations, to achieve very deep shades, and excellent fastness properties.

10 **Application:**

The present invention provides a process for dyeing from aqueous bath and printing of fiber materials with the dyes of the present invention.

In particular, cellulose, natural cellulose fibers such as cotton, linen or hemp, especially cotton, and regenerated cellulose such as viscose or lyocell, polyamide fibers such as nylon 6, nylon 6.6 or protein fibers such as wool, silk or leather are preferred fiber materials.

The dyes are also suitable for dyeing and printing of fiber blends containing the mentioned cellulose, polyamide or protein fiber materials.

The dyes of the invention can be applied to and fixed on the fiber material in various ways, in particular in the form of aqueous dye solutions and print pastes. They are suitable for known

application techniques which are established for the application of reactive dyes, in particular exhaust method, padding method, whereby the material is impregnated with aqueous, salt containing or salt free solutions of the dyes, and fixed after alkali treatment or in presence of alkali with or without heating, and printing methods, conventional or digital (ink jet) printing.

5

After fixing, the dye and prints are rinsed and thoroughly washed with cold or hot water containing auxiliary agents such as detergents or surfactants that promote the wash-off of unfixed portions.

Coloration in deep shades is often a challenge, especially when high fastness to washing, contact and perspiration is concerned. All known dyes have limitations in this respect.

The present dyes are of from Yellow to Black colour and are especially suitable for dyeing in deep shades, applied as single dye or as mixture in the present invention, or in combination with other compatible dyestuffs containing vinylsulfone and/or heterocyclic reactive groups, preferably applied in dichromatic or trichromatic combinations, while exhibiting superior properties in coloration technology compared to known mixtures of state of the art, with regard to achieving very deep shades, and excellent fastness properties.

Examples of suitable alkali used for fixation include alkali hydroxide, alkali carbonate, alkali silicate, of which sodium hydroxide, sodium carbonate, sodium silicate are preferred.

The amount of dye applied in the dyebath can vary according to the desired depth of shade, generally an amount of 0.01 to 10 % per weight of fabric is suitable, and in particular 0.2 to 8% per weight of fabric is preferred.

The dyebath may contain additions of auxiliaries such as inorganic salt, preferably sodium chloride or sodium sulfate, to support the exhaustion of the dyes onto the fiber material, and in padding process urea, and in printing applications thickening pastes such as alginate thickenings.

In exhaust dyeing process, the preferred procedure is dyeing from an aqueous batch, in the presence of 20-100 g/L salt, sodium chloride or sodium sulfate, and a liquor ratio of 1:2 to 1:50, preferably 1:3 to 1:30, at a dyebath pH of 7-13, preferably 9-11, and at a temperature of 40-90°C, preferably 70-90 °C.

The dyeing obtained with the dyes of the present invention has excellent fixation yield and excellent build-up. The obtained dye-fiber bond is of high stability not only in the acid but also in the alkaline range, also good light fastness and very good wash fastness, even in deep shades, as well as good contact fastness to water and perspiration.

5 Moreover, the dyeing obtained with the dyes of the first part of the present invention represents formula (1) are dischargeable and can be applied in discharge printing.

Leather is dyed using dyeing procedure described in US2008047079 for comparative study.

Example: 1

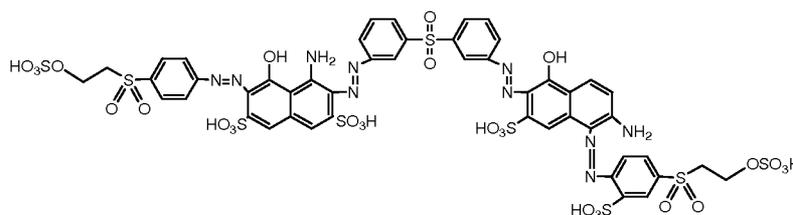
(A) 28.8 parts of 2-[(4-Aminophenyl)sulfonyl]ethyl hydrogensulfate (p-VS ester) are
10 introduced into 400 parts of ice-water and 15 parts of 30% Hydrochloric acid with small amount of wetting agent under efficient stirring, cool the reaction mass to 0-5°C with ice. A solution of 7.3 parts of Sodium Nitrite in 25 parts of water is added slowly in 10-15 minutes. Check reaction mass for excess of nitrite and stir for 2 hrs. After two hrs excess nitrite is destroyed by addition sulfamic acid. Add 32 parts of 1-amino-8-hydroxy naphthalene-3,6-
15 disulphonic acid at 0-5°C and stir for 4-5 hrs at 0-5°C until coupling is complete.

(B) 34.5 parts of 4-Amino-3-sulfophenyl-2'-sulfatoethylsulfone (SulphoVS ester) are introduced into 400 parts of ice-water and 15 parts of 30% Hydrochloric acid with small amount of wetting agent under efficient stirring, cool the reaction mass to 0-5°C with ice. A solution of 7.3 parts of Sodium Nitrite in 25 parts of water is added slowly in 10-15 minutes.
20 Check reaction mass for excess of nitrite and stir for 2 hrs. After two hrs excess nitrite is destroyed by addition sulfamic acid. Add 24 parts of 2-amino-5-hydroxy-7-naphthalenesulphonic acid at 0-5°C and stir for 4-5 hrs at 0-5°C until coupling is complete.

(C) 15.2 parts of 3,3'-Diaminodiphenylsulfone are charged into 400 parts of water, stir for 15-30 minutes and slowly adjust pH 7-7.5 with caustic soda lye to obtain clear solution. Add
25 7.3 parts of sodium nitrite and stir to dissolve. This solution is added slowly over a period of 2-3 hrs in 800 parts ice and 30 parts of 30% Hydrochloric acid keeping temperature below 5°C with ice as needed. After completion of addition continue stirring at 0-5°C with excess of nitrite for another 2 hrs. Destroy excess nitrite with sulfamic acid.

14

(D) Add coupling mass (A) to above tetra azo solution (C) at 0-5°C in 30 minutes. Stir further 30 minutes at 0-5°C temperature and then adjust pH 2.5-3.0 with 20% soda ash solution. Stir further at this pH and let temperature raises up to 10-15°C till coupling is completed. When first coupling is completed again cool down to 5-10°C and add coupling mass (B) in 30 minutes at 5-10°C, stir for further 30 minutes without adjusting pH. After 30 minutes raise pH up to 6.0-6.5 with 20% soda ash solution and maintain at this pH till completion of coupling. Finally dye of formula (1-A) is isolated by filtration after salting out or by drying reaction mass at low temperature.



10

(1-A)

The product (1-A) obtained as dark blue powder which dyes cotton in very deep navy blue shade with good all around fastness properties.

Example-2:

The dyestuffs of the formula 1 are synthesized using same method as described in Example-1 to get following dyes described in table 1:

15



(1)

Table 1

A	X	R2	Y	R1	λ Max	SHADE
4,4'- Diaminostilbene -3,3'-disulphonic acid	1-amino-8- hydroxy naphthalene- 3,6-disulphonic acid	2-[(4- Aminophenyl) sulfonyl]ethyl hydrogen sulfate	2-amino-5- hydroxy -7- naphthalenesul phonic acid	2-[(4- Aminophenyl) sulfonyl]ethyl hydrogen sulfate	642	Navy
4,4'- Diaminostilbene -3,3'-disulphonic	1-amino-8- hydroxy naphthalene-	2-[(4- Aminophenyl) sulfonyl]ethyl	2-amino-5- hydroxy -7- naphthalenesul	4-Amino-3- sulfophenyl 2- sulfatoethylsul	666	Navy

acid	3.6-disulphonic acid	hydrogen sulfate	phonic acid	fone		
4,4'-Diaminostilbene-3.3'-disulphonic acid	2-Amino-5-hydroxy-7-naphthalenesulfonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-Amino-5-hydroxy-7-naphthalenesulfonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	518	Rubine
4,4'-Diaminostilbene-3.3'-disulphonic acid	7-Amino-1-naphthol-3-sulfonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	7-Amino-1-naphthol-3-sulfonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	510	Red
3,3'-diaminodiphenyl sulfone	1-amino-8-hydroxy naphthalene-3.6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-amino-5-hydroxy-7-naphthalenesulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	605	Navy
3,3'-diaminodiphenyl sulfone	2-Amino-5-hydroxy-7-naphthalenesulfonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	2-Amino-5-hydroxy-7-naphthalenesulfonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	526	Red Brown
3,3'-diaminodiphenyl sulfone	1-amino-8-hydroxy naphthalene-3.6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	7-Amino-1-naphthol-3-sulfonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	570	Red Brown
3,3'-diaminodiphenyl sulfone	1-amino-8-hydroxy naphthalene-3.6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	1-Hydroxy-6-(2'-Carboxyethylamino)-3-naphthalenesulfonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	530	Red
4,4'-diaminodiphenyl sulfone	1-amino-8-hydroxy naphthalene-3.6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-Amino-5-hydroxy-7-naphthalenesulfonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	625	Navy
4,4'-diaminodiphenyl sulfone	1-amino-8-hydroxy naphthalene-3.6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	7-Amino-1-naphthol-3-sulfonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	579	Red Brown
4,4'-diaminodiphenyl sulfone	1-amino-8-hydroxy naphthalene-3.6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	1-Hydroxy-6-(2'-Carboxyethylamino)-3-naphthalenesulfonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	539	Red

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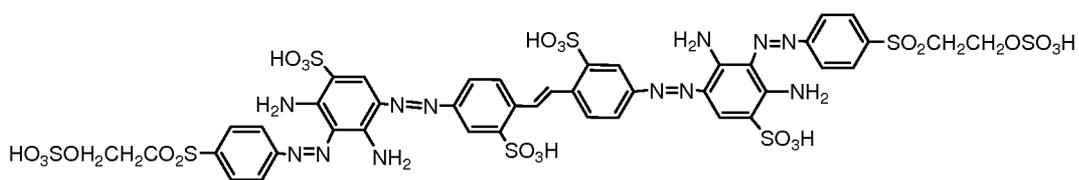
4,4'-diaminodiphenyl sulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	2-Amino-5-hydroxy-7-naphthalenesulfonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	645	Navy
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Example-3:

(A) 28.8 parts of 2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate are introduced into 400 parts of ice-water and 15 parts of 30% Hydrochloric acid with efficient stirring, cool the reaction mass to 0-5°C with ice. A solution of 7.3 parts of Sodium Nitrite in 25 parts of water is added slowly in 10-15 minutes. Check reaction mass for excess of nitrite and stir for 2 hrs. After two hrs excess nitrite is destroyed by addition sulfamic acid. Add 18.6 parts of 2,4-diaminobenzene sulphonic acid at 0-5°C and stir for 4-5 hrs at 0-5°C until coupling is complete.

(B) 19 parts of 4,4'-Diaminostilbene-3,3'-disulphonic acid are charged into 400 parts of water, stir for 15-30 minutes and slowly adjust pH 7-7.5 with caustic soda lye to obtain clear solution. Add 7.3 parts of sodium nitrite and stir to dissolve. This solution is added slowly over a period of 2-3 hrs in 800 parts ice and 30 parts of 30% Hydrochloric acid keeping temperature below 5°C with ice as needed. After completion of addition continue stirring at 0-5°C with excess of nitrite for another 2 hrs. Destroy excess nitrite with sulfamic acid.

(C) Add solution (A) to above tetra azo solution (B) at 0-5°C in 30 minutes. Stir further 5-6 hrs maintaining 0-5°C temperature and then adjust pH 6-6.5 with 20% soda ash solution. Stir further at this pH and temperature till coupling is completed. Finally dye of formula (1-B) is isolated by filtration after salting out or by drying reaction mass at low temperature.



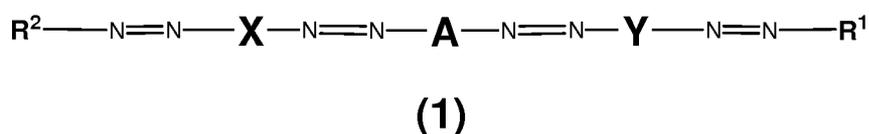
(1-B)

The product (1-B) obtained as orange coloured powder which dyes cotton in very deep orange shade with good all around fastness properties.

Example-4:

The dyestuffs of the formula 1 are synthesized using same method as described in Example-1 to get following dyes described in table 2:

5

**Table 2**

A	X	R2	Y	R1	λ Max	SHADE
4,4'- Diaminostilben e-3.3'- disulphonic acid	2.4- Diaminobenze nesulphonic acid	2-[(4- Aminophenyl)sul fonyl]ethyl hydrogen sulfate	2.4- Diaminobenze nesulphonic acid	2-[(4- Aminophenyl)sul fonyl]ethyl hydrogen sulfate	470	Orange
4,4'- Diaminostilben e-3.3'- disulphonic acid	2.4- Diaminobenze nesulphonic acid	4-Amino-3- sulfophenyl 2- sulfatoethylsulfo ne	2.4- Diaminobenze nesulphonic acid	4-Amino-3- sulfophenyl 2- sulfatoethylsulfo ne	475	Orange
4,4'- Diaminostilben e-3.3'- disulphonic acid	2.4- Diaminobenze nesulphonic acid	2-Methoxy-4-(2- sulfatoethylsulfo nyl)aniline	2.4- Diaminobenze nesulphonic acid	2-Methoxy-4-(2- (2- sulfatoethylsulfo nyl)aniline	462	Orange
4,4'- Diaminostilben e-3.3'- disulphonic acid	1:3-Diamino benzoic acid	4-Amino-3- sulfophenyl 2- sulfatoethylsulfo ne	1:3-Diamino benzoic acid	4-Amino-3- sulfophenyl 2- sulfatoethylsulfo ne	484	Orange
4,4'- Diaminostilben e-3.3'- disulphonic acid	2.4- Diaminobenze nesulphonic acid	2-[(4- Aminophenyl)sul fonyl]ethyl hydrogen sulfate	1.3- Diaminobenze ne	4-Amino-3- sulfophenyl 2- sulfatoethylsulfo ne	484	Orange
4,4'- Diaminostilben e-3.3'- disulphonic acid	1.3- Diaminobenze ne	4-Amino-3- sulfophenyl 2- sulfatoethylsulfo ne	1.3- Diaminobenze ne	4-Amino-3- sulfophenyl 2- sulfatoethylsulfo ne	504	Red Brown

4,4'-Diaminostilbene-3,3'-disulphonic acid	1,3-Diaminobenzene	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	1:3-Diaminobenzoic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	488	Red Brown
4,4'-Diaminostilbene-3,3'-disulphonic acid	1:3-Diaminotoluene	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	1:3-Diaminotoluene	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	502	Red Brown
3,3'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2,4-Diaminobenzenesulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	420	Yellow
3,3'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	2,4-Diaminobenzenesulphonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	427	Yellow
3,3'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	2-Methoxy-4-(2-sulfatoethylsulfonyl)aniline	2,4-Diaminobenzenesulphonic acid	2-Methoxy-4-(2-sulfatoethylsulfonyl)aniline	412	Yellow
3,3'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	1:3-Diaminobenzoic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	434	Yellow
3,3'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	1,3-Diaminobenzene	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	434	Yellow
3,3'-diaminodiphenylsulfone	1,3-Diaminobenzene	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	1,3-Diaminobenzene	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	455	Orange
3,3'-diaminodiphenylsulfone	1,3-Diaminobenzene	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	1:3-Diaminobenzoic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	438	Orange
3,3'-diaminodiphenylsulfone	1:3-Diaminotoluene	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	1:3-Diaminotoluene	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	453	Orange
4,4'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2,4-Diaminobenzenesulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	432	Yellow

4,4'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	2,4-Diaminobenzenesulphonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	439	Orange
4,4'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	2-Methoxy-4-(2-sulfatoethylsulfonyl)aniline	2,4-Diaminobenzenesulphonic acid	2-Methoxy-4-(2-sulfatoethylsulfonyl)aniline	424	Yellow
4,4'-diaminodiphenylsulfone	1:3-Diaminobenzoic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	1:3-Diaminobenzoic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	448	Orange
4,4'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	1,3-Diaminobenzene	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	448	Orange
4,4'-diaminodiphenylsulfone	1,3-Diaminobenzene	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	1,3-Diaminobenzene	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	468	Orange
4,4'-diaminodiphenylsulfone	1,3-Diaminobenzene	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	1:3-Diaminobenzoic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	446	Orange
4,4'-diaminodiphenylsulfone	1:3-Diaminotoluene	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	1:3-Diaminotoluene	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	465	Orange

Example-5:

- (A) 86.3 parts of 4-Amino-3-sulfophenyl 2-sulfatoethyl sulfone are introduced into 800 parts of ice-water and 30 parts of 30% Hydrochloric acid with efficient stirring, cool the reaction mass to 0-5°C with ice. A solution of 17 parts of Sodium Nitrite in 50 parts of water is added slowly in 10-15 minutes. Check reaction mass for excess of nitrite and stir for 2 hrs. After two hrs excess nitrite is destroyed by addition sulfamic acid. Add 26 parts of 1,3-diaminobenzene at 0-5°C and stir for 5-6 hrs at 0-5°C until coupling is complete.
- (B) 72 parts of 2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate are introduced into 1000 parts of ice-water and 37 parts of 30% Hydrochloric acid with efficient stirring, cool the reaction mass to 0-5°C with ice. A solution of 18 parts of Sodium Nitrite in 50 parts of water is added slowly in 15-30 minutes. Check reaction mass for excess of nitrite and stir for 2 hrs.

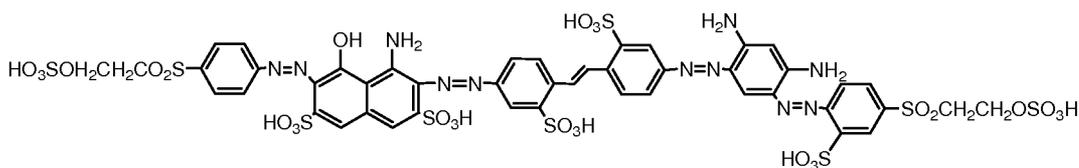
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After two hrs excess nitrite is destroyed by addition sulfamic acid. Add 80 parts of 1-amino-8-hydroxy naphthalene-3,6-disulphonic acid at 0-5°C and stir for 5-6 hrs at 0-5°C until coupling is complete.

5 (C) 95 parts of 4,4'-Diaminostilbene-3,3'-disulphonic acid are charged into 1000 parts of water, stir for 15-30 minutes and slowly adjust pH 7-7.5 with caustic soda lye to obtain clear solution. Add 37 parts of sodium nitrite and stir to dissolve. This solution is added slowly over a period of 2-3 hrs in 1200 parts ice and 150 parts of 30% Hydrochloric acid keeping temperature below 5°C with ice as needed. After completion of addition continue stirring at 0-5°C with excess of nitrite for another 2 hrs. Destroy excess nitrite with sulfamic acid.

10 (D) Add solution (A) to above tetra azo solution (B) at 0-5°C in 30 minutes. Stir further 30 minutes and then maintaining 0-5°C temperature slowly adjust pH up to 3.5 to 4.0 with 20% sodium carbonate solution. Stir further at this pH for another 7-8 hrs and let temperature rises up to 20-25°C till coupling is completed. Check with TLC and it should show very little presence of solution (A) when OK proceed further for second coupling.

15 (E) Cool reaction mass (D) to 10°C with ice and slowly charge solution (B) in 30 minutes and further stir at 5-10°C for 30 minutes and then adjust pH 6.0-6.5 with 20% sodium carbonate solution. Maintain at this temperature and pH for 6-7 hrs for completion of coupling. Finally dye of the formula 1-C is isolated by filtration after slating out or directly dried.



(1-C)

The product (1-C) obtained as black powder and dyes cotton in very deep black shade with excellent build up and good fastness properties.

Example-6:

25 The dyestuffs of the formula 1 are synthesized using same method as described in Example-1 to get following dyes described in table as shown in table 3:



(1)

Table 3

A	X	R2	Y	R1	λ Max	SHADE
4,4'- Diaminostilbene- 3.3'-disulphonic acid	1-amino-8- hydroxy naphthalene- 3.6- disulphonic acid	2-[(4- Aminophenyl)sulfo nyl]ethyl hydrogen sulfate	1:3-Diamino benzoic acid	4-Amino-3- sulfophenyl 2- sulfatoethylsulf one	605	Black
4,4'- Diaminostilbene- 3.3'-disulphonic acid	1-amino-8- hydroxy naphthalene- 3.6- disulphonic acid	2-[(4- Aminophenyl) sulfonyl]ethyl hydrogen sulfate	1.3- Diaminoben zene	4-Amino-3- sulfophenyl 2- sulfatoethylsulf one	638	Black
4,4'- Diaminostilbene- 3.3'-disulphonic acid	1-amino-8- hydroxy naphthalene- 3.6- disulphonic acid	4-Amino-3- sulfophenyl 2- sulfatoethylsulfone	1.3- Diaminoben zene	4-Amino-3- sulfophenyl 2- sulfatoethylsulf one	665	Black
4,4'- Diaminostilbene- 3.3'-disulphonic acid	1-amino-8- hydroxy naphthalene- 3.6- disulphonic acid	4-Amino-3- sulfophenyl 2- sulfatoethylsulfone	1.3- Diaminoben zene	2-[(4- Aminophenyl)s ulfonyl]ethyl hydrogen sulfate	600	Black
4,4'- Diaminostilbene- 3.3'-disulphonic acid	1-amino-8- hydroxy naphthalene- 3.6- disulphonic acid	2-[(4- Aminophenyl)sulfo nyl]ethyl hydrogen sulfate	1.3- Diaminoben zene	2-[(4- Aminophenyl)s ulfonyl]ethyl hydrogen sulfate	660	Olive green
4,4'- Diaminostilbene- 3.3'-disulphonic acid	1-amino-8- hydroxy naphthalene- 3.6- disulphonic acid	2-[(4- Aminophenyl)sulfo nyl]ethyl hydrogen sulfate	1:3-Diamino toluene	4-Amino-3- sulfophenyl 2- sulfatoethylsulf one	638	Black
4,4'- Diaminostilbene- 3.3'-disulphonic acid	1-amino-8- hydroxy naphthalene- 3.6- disulphonic acid	2-[(4- Aminophenyl)sulfo nyl]ethyl hydrogen sulfate	1:3-Diamino toluene	2-[(4- Aminophenyl)s ulfonyl]ethyl hydrogen sulfate	636	Black

4,4'-Diaminostilbene-3,3'-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2,4-Diaminobenzenesulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	640	Olive green
3,3'-diaminodiphenyl sulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	1:3-Diaminobenzene	4-Amino-3-sulphophenyl 2-sulfatoethylsulfone	578	Black
3,3'-diaminodiphenyl sulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	1:3-Diaminotoluene	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	594	Black
3,3'-diaminodiphenyl sulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	1:3-Diaminobenzoic acid	4-Amino-3-sulphophenyl 2-sulfatoethylsulfone	580	Black
4,4'-diaminodiphenyl sulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	1:3-Diaminotoluene	4-Amino-3-sulphophenyl 2-sulfatoethylsulfone	596	Black
4,4'-diaminodiphenyl sulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	1:3-Diaminotoluene	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	603	Black
4,4'-diaminodiphenyl sulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	1:3-Diaminobenzoic acid	4-Amino-3-sulphophenyl 2-sulfatoethylsulfone	597	Black

Example-7:

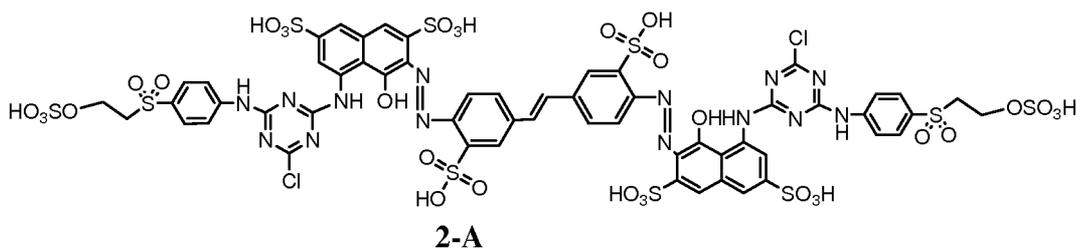
(A) 55.9 parts of Cyanuric Chloride slurry is prepared by charging under stirring in 600 parts of water at 0-5°C. To this slurry slowly charge solution of 94.8 parts of 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid dissolved in 800 ml of water under neutral

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conditions in 2 hrs. Stir further 3-4 hrs at 0-5°C and check TLC to ensure absence of 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid. Slowly charge 83.5 parts of 2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate and stir for another 5-6 hrs at 25-30°C and adjust pH 3 with 20% sodium carbonate solution. Then slowly raise pH up to 5 – 5.5 and temperature also rises up to 45°C and further stir for 2 hrs for completion of condensation.

(B) 57 parts of 4,4'-Diaminostilbene-3,3'-disulphonic acid are charged into 800 parts of water, stir for 15-30 minutes and slowly adjust pH 7-7.5 with caustic soda lye to obtain clear solution. Add 21.3 parts of sodium nitrite and stir to dissolve. This solution is added slowly over a period of 2-3 hrs in 1200 parts ice and 90 parts of 30% Hydrochloric acid keeping temperature below 5°C with ice as needed. After completion of addition continue stirring at 0-5°C with excess of nitrite for another 2 hrs. Destroy excess nitrite with sulfamic acid.

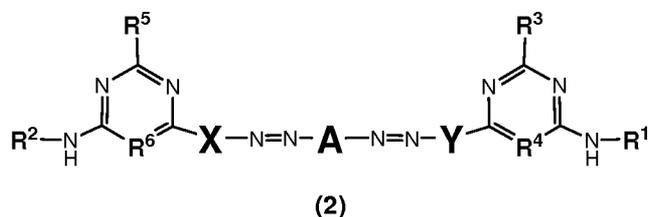
Now, charge reaction mass (A) to tetraazo (B) at 0-5°C in 30-40 minutes without adjusting pH further stir for 30 minutes and then adjust pH to 3.5-4 with 20% sodium carbonate solution and maintain pH and temperature for 1-2 hrs. After 2 hrs again adjust pH to 6.5-7.0 with 20% sodium carbonate solution and stir for 1-2 hrs at 0-5°C at this pH. Check for TLC and spot test for completion of coupling. When coupling is completed product of formula 2-A is either isolated by filtration after slating out or directly dried.



The product (2-A) obtained as blue powder and dyes cotton in bright blue shade with excellent fixation yield of 80% on exhaust dyeing with excellent build up and ISO 105 C03 washing fastness- staining on cotton 4 and on polyamide 4-5.

Example-8:

The dyestuffs of the formula 2 are synthesized using same method as described in Example-7 to get following dyes described in table 4:



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Table 4

A	X	Y	R1	R2	R3	R4	R5	R6	λ Max	Shade
4,4'-Diaminostilbene-3,3'-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	Cl	N	Cl	N	579	Blue
4,4'-Diaminostilbene-3,3'-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-Methoxy-5-methyl-4-(b-sulfatoethyl sulfonyl)aniline	Cl	N	Cl	N	580	Blue
4,4'-Diaminostilbene-3,3'-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-Methoxy-5-sulpho-4-(2-sulfatoethyl sulfonyl)aniline	Cl	N	Cl	N	579	Blue
4,4'-Diaminostilbene-3,3'-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-Methoxy-5-methyl-4-(b-sulfatoethyl sulfonyl)aniline	2-Methoxy-5-sulpho-4-(2-sulfatoethyl sulfonyl)aniline	Cl	N	Cl	N	583	Blue
4,4'-Diaminostilbene-3,3'-disulphonic acid	2-Amino-5-hydroxy-7-naphthalene sulfonic acid	2-Amino-5-hydroxy-7-naphthalene sulfonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen	Cl	N	Cl	N	528	Rubine

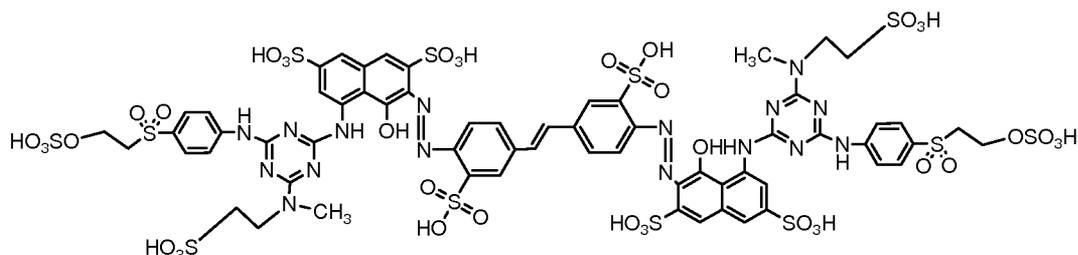
	nesulfonic acid		hydrogen sulfate	sulfate							
4,4'-Diaminostilbene-3,3'-disulphonic acid	2-Amino-5-hydroxy-7-naphthalenesulfonic acid	2-Amino-5-hydroxy-7-naphthalenesulfonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-Methoxy-5-methyl-4-(b-sulfatoethylsulfonyl)aniline	Cl	N	Cl	N	526	Rubine	
4,4'-Diaminostilbene-3,3'-disulphonic acid	2,4-Diaminobenzenesulfonic acid	2,4-Diaminobenzenesulfonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	Cl	N	Cl	N	458	Orange	
4,4'-Diaminostilbene-3,3'-disulphonic acid	2,4-Diaminobenzenesulfonic acid	2,4-Diaminobenzenesulfonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-Methoxy-5-methyl-4-(b-sulfatoethylsulfonyl)aniline	Cl	N	Cl	N	462	Orange	
4,4'-Diaminostilbene-3,3'-disulphonic acid	7-Amino-1-naphthol-3-sulfonic acid	7-Amino-1-naphthol-3-sulfonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	Cl	N	Cl	N	552	Red	
3,3'-diaminodiphenylsulfone	1-amino-8-hydroxynaphthalene-3,6-disulphonic acid	1-amino-8-hydroxynaphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	Cl	N	Cl	N	510	Red	
3,3'-diaminodiphenylsulfone	1-amino-8-hydroxynaphthalene-3,6-disulphonic acid	1-amino-8-hydroxynaphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-Methoxy-5-methyl-4-(b-sulfatoethylsulfonyl)aniline	Cl	N	Cl	N	506	Red	
3,3'-diaminodiphenylsulfone	1-amino-8-hydroxynaphthalene-3,6-disulphonic acid	1-amino-8-hydroxynaphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-Methoxy-4-(2-sulfatoethylsulfonyl)aniline	Cl	N	Cl	N	506	Red	

3,3'-diaminodiphenylsulfone	1-amino-8-hydroxynaphthalene-3,6-disulphonic acid	1-amino-8-hydroxynaphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-Methoxy-5-sulpho-4-(2-sulfatoethylsulfonyl)aniline	Cl	N	Cl	N	511	Red
4,4'-diaminodiphenylsulfone	1-amino-8-hydroxynaphthalene-3,6-disulphonic acid	1-amino-8-hydroxynaphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	Cl	N	Cl	N	524	Red
4,4'-diaminodiphenylsulfone	1-amino-8-hydroxynaphthalene-3,6-disulphonic acid	1-amino-8-hydroxynaphthalene-3,6-disulphonic acid	2-Methoxy-5-sulpho-4-(2-sulfatoethylsulfonyl)aniline	2-Methoxy-5-sulpho-4-(2-sulfatoethylsulfonyl)aniline	Cl	N	Cl	N	524	Red

Example-9: Product synthesized in Example-7 and 8 were further condensed with 2-(methylamino)ethanesulphonic acid maintaining 7.5 pH at 85-90°C monitor condensation reaction by TLC and when OK clarify the reaction mass and spray dried.

5

The product (2-B) obtained blue powder and dyes cotton in bright blue shade with excellent fixation yield which provide excellent build up and good fastness properties.



10 Here, in place of 2-(methylamino)ethanesulphonic acid, Cyanamide, Mercaptoacetic acid, 2-Amino ethanesulphonic acid, ammonia, C1-C4alkyl amine, etc were used and products were evaluated.

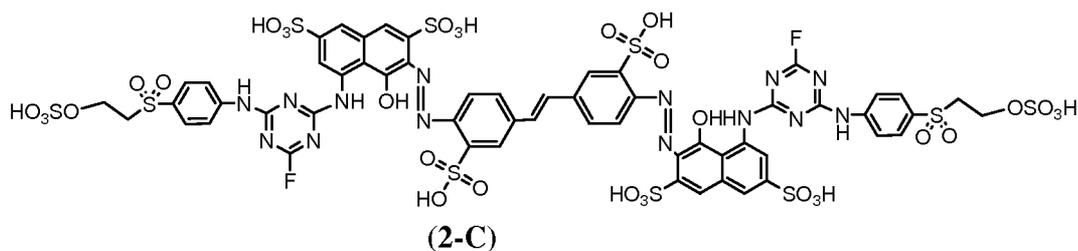
Example-10:

15 (A) 94.8 parts of 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid are dissolved in 800 ml of water under neutral conditions, and the solution is cooled down to 0-5. 42 parts of

2,4,6-trifluoro-1,3,5-triazine are added drop wise at this temperature in the course of 20 minutes, during which the pH of the reaction solution is kept weakly acid to Congo red by the simultaneous addition of 2N sodium hydroxide solution. After addition of a mixture of 83.5 parts of 2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate in 500 parts of water which
 5 has been adjusted to pH 5 the pH of the reaction mixture is initially briefly kept weakly acid to Congo red and then at 5-6 by the constant addition of 2N sodium hydroxide solution. At the same time the temperature is raised to 20-25°C in the course of 2 to 3 hours.

(B) 57 parts of 4,4'-Diaminostilbene-3,3'-disulphonic acid are charged into 800 parts of water, stir for 15-30 minutes and slowly adjust pH 7-7.5 with caustic soda lye to obtain clear
 10 solution. Add 21.3 parts of sodium nitrite and stir to dissolve. This solution is added slowly over a period of 2-3 hrs in 1200 parts ice and 90 parts of 30% Hydrochloric acid keeping temperature below 5°C with ice as needed. After completion of addition continue stirring at 0-5°C with excess of nitrite for another 2 hrs. Destroy excess nitrite with sulfamic acid.

(C) Now, charge reaction mass (A) to tetra azo solution (B) to coupled at 0-10°C and pH
 15 6.5. After the coupling reaction at pH 8 has ended the reaction mixture is clarified and the resultant reactive dye of the formula (2-C) is isolated at pH 7 by filtration after slating it out from reaction mass or directly dried.



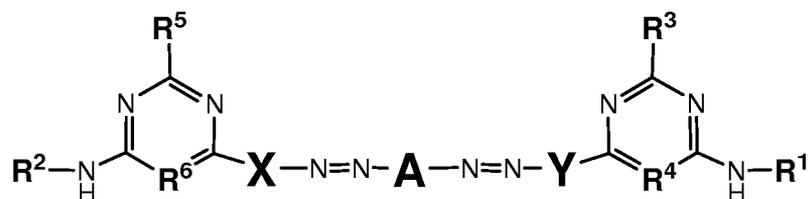
20

The product (2-C) obtained as blue powder and dyes cotton in bright blue shade with excellent build up and good fastness properties.

Example-11:

25 The dyestuffs of the formula 2 are synthesized using same method as described in Example-9 to get following dyes described in table 5:

28



(2)

Table 5

A	X	Y	R1	R2	R3	R4	R5	R6	λ Max	SHA DE
4,4'- Diaminostilbene-3,3'- disulphonic acid	1-amino-8- hydroxy naphthalene- 3,6- disulphonic acid	1-amino-8- hydroxy naphthalen e-3,6- disulphonic acid	2-[(4- Aminophen yl)sulfonyl]e thyl hydrogen sulfate	2-[(4- Aminophen yl)sulfonyl]e thyl hydrogen sulfate	F	N	F	N	575	Blue
4,4'- Diaminostilbene-3,3'- disulphonic acid	1-amino-8- hydroxy naphthalene- 3,6- disulphonic acid	1-amino-8- hydroxy naphthalen e-3,6- disulphonic acid	2-[(4- Aminophen yl)sulfonyl]e thyl hydrogen sulfate	2-[(4- Aminophen yl)sulfonyl]e thyl hydrogen sulfate	F	C	F	C	570	Blue
4,4'- Diaminostilbene-3,3'- disulphonic acid	1-amino-8- hydroxy naphthalene- 3,6- disulphonic acid	1-amino-8- hydroxy naphthalen e-3,6- disulphonic acid	2-[(4- Aminophen yl)sulfonyl]e thyl hydrogen sulfate	2-[(4- Aminophen yl)sulfonyl]e thyl hydrogen sulfate	F	C- Cl	F	C- Cl	575	Blue
4,4'- Diaminostilbene-3,3'- disulphonic acid	2-Amino-5- hydroxy-7- naphthalene sulfonic acid	2-Amino-5- hydroxy-7- naphthalen esulfonic acid	2-[(4- Aminophen yl)sulfonyl]e thyl hydrogen sulfate	2-[(4- Aminophen yl)sulfonyl]e thyl hydrogen sulfate	F	N	F	N	525	Rubi ne
4,4'- Diaminostilbene-3,3'- disulphonic acid	2-Amino-5- hydroxy-7- naphthalene sulfonic acid	2-Amino-5- hydroxy-7- naphthalen esulfonic acid	2-[(4- Aminophen yl)sulfonyl]e thyl hydrogen sulfate	2-[(4- Aminophen yl)sulfonyl]e thyl hydrogen sulfate	F	C	F	C	520	Rubi ne
4,4'- Diaminostilbene-3,3'- disulphonic acid	2-Amino-5- hydroxy-7- naphthalene sulfonic acid	2-Amino-5- hydroxy-7- naphthalen esulfonic acid	2-[(4- Aminophen yl)sulfonyl]e thyl hydrogen sulfate	2-[(4- Aminophen yl)sulfonyl]e thyl hydrogen sulfate	F	C- Cl	F	C- Cl	526	Rubi ne

4,4'-Diaminostilbene-3,3'-disulphonic acid	7-Amino-1-naphthol-3-sulfonic acid	7-Amino-1-naphthol-3-sulfonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	F	N	F	N	550	Red
4,4'-Diaminostilbene-3,3'-disulphonic acid	7-Amino-1-naphthol-3-sulfonic acid	7-Amino-1-naphthol-3-sulfonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	F	C	F	C	548	Red
4,4'-Diaminostilbene-3,3'-disulphonic acid	7-Amino-1-naphthol-3-sulfonic acid	7-Amino-1-naphthol-3-sulfonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	F	C-Cl	F	C-Cl	552	Red
3,3'-diaminodiphenylsulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	F	N	F	N	515	Red
3,3'-diaminodiphenylsulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	F	C	F	C	510	Red
3,3'-diaminodiphenylsulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	F	C-Cl	F	C-Cl	514	Red
4,4'-diaminodiphenylsulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	F	N	F	N	523	Red
4,4'-diaminodiphenylsulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	F	C	F	C	518	Red

4,4'- diaminodiph enylsulfone	1-amino-8- hydroxy naphthalene- 3,6- disulphonic acid	1-amino-8- hydroxy naphthalen e-3,6- disulphonic acid	2-[(4- Aminophen yl)sulfonyl]e thyl hydrogen sulfate	2-[(4- Aminophen yl)sulfonyl]e thyl hydrogen sulfate	F	C- Cl	F	C- Cl	522	Red
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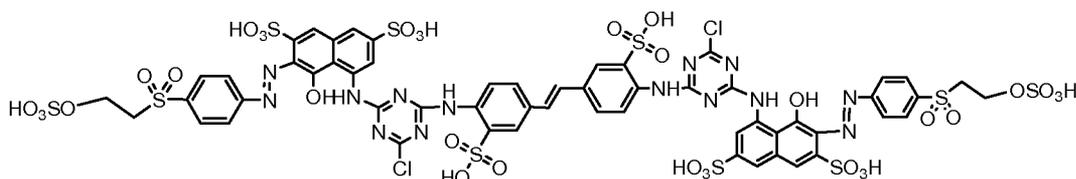
Example-12:

(A) 55.9 parts of Cyanuric Chloride slurry is prepared by charging under stirring in 600 parts of water at 0-5°C. To this slurry slowly charge solution of 94.8 parts of 1-amino-8-
5 hydroxynaphthalene-3,6-disulfonic acid dissolved in 800 ml of water under neutral conditions in 2 hrs. Stir further 3-4 hrs at 0-5°C and check TLC to ensure absence of 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid.

(B) 85.4 parts of 2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate are introduced into 500 parts of ice-water and 65 parts of 30% Hydrochloric acid with efficient stirring, cool the
10 reaction mass to 0-5°C with ice. A solution of 21 parts of Sodium Nitrite in 50 parts of water is added slowly in 15-30 minutes. Check reaction mass for excess of nitrite and stir for 2 hrs. After two hrs excess nitrite is destroyed by addition sulfamic acid.

Add this diazo solution to solution (A) at 0-5°C and stir for 30 minutes and raise pH up to 6.5-7.0 and check spot test for completion of coupling reaction. After coupling test is ok use
15 this reaction mass for further condensation.

(C) Add 57 parts of 4,4'-Diaminostilbene-3,3'-disulphonic acid in to above coupling mass and stir 2-3 hrs at room temperature at pH 3.0 and then slowly raise pH up to 5.0-5.5 and also raise temperature up to 40-45°C, stir further for 2-3 hrs and confirm completion of condensation by TLC. On completion of condensation product of the formula 3(A) is isolated
20 by filtration after slating out from reaction mass or directly dried.

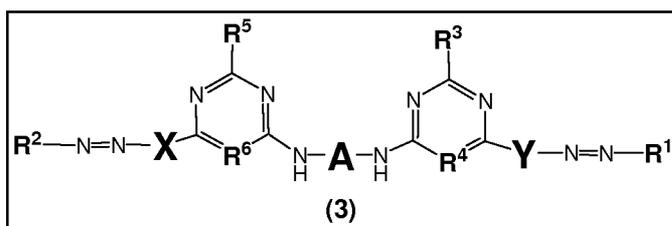
**3-A**

31

The product of the formula (3-A) is obtained as red powder and dyes cotton in very deep bright red shade having fixation yield of 82% on exhaust dyeing and ISO 105 C03 washing fastness –staining on cotton 4 and on polyamide 4-5.

5 **Example-13:**

The dyestuffs of the formula 3 are synthesized using same method as described in Example-11 to get following dyes described in table 6:



15

Table 6

A	X	Y	R1	R2	R3	R5	R6	λ Max	SHADE
4,4'-Diaminostilbene-3,3'-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	Cl	Cl	N	516	Red
4,4'-Diaminostilbene-3,3'-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	Cl	Cl	N	512	Red
4,4'-Diaminostilbene-3,3'-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-Methoxy-5-methyl-4-(b-sulfatoethylsulfonyl)aniline	2-Methoxy-5-methyl-4-(b-sulfatoethylsulfonyl)aniline	Cl	Cl	N	530	Red

4,4'-Diaminostilbene-3,3'-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-Methoxy-4-(2-sulfatoethylsulfonyl)aniline	2-Methoxy-4-(2-sulfatoethylsulfonyl)aniline	Cl	Cl	N	550	Red
4,4'-Diaminostilbene-3,3'-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-Methoxy-5-sulpho-4-(2-sulfatoethylsulfonyl)aniline	2-Methoxy-5-sulpho-4-(2-sulfatoethylsulfonyl)aniline	Cl	Cl	N	567	Red
4,4'-Diaminostilbene-3,3'-disulphonic acid	2-Amino-5-hydroxy-7-naphthalene sulfonic acid	2-Amino-5-hydroxy-7-naphthalene sulfonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	Cl	Cl	N	454	Dull Orange
4,4'-Diaminostilbene-3,3'-disulphonic acid	2,4-Diaminobenzenesulphonic acid	2,4-Diaminobenzenesulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	Cl	Cl	N	417	Yellow
4,4'-Diaminostilbene-3,3'-disulphonic acid	2,4-Diaminobenzenesulphonic acid	2,4-Diaminobenzenesulphonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	Cl	Cl	N	400	Yellow
4,4'-Diaminostilbene-3,3'-disulphonic acid	2,4-Diaminobenzenesulphonic acid	2,4-Diaminobenzenesulphonic acid	2-Methoxy-5-methyl-4-(b-sulfatoethylsulfonyl)aniline	2-Methoxy-5-methyl-4-(b-sulfatoethylsulfonyl)aniline	Cl	Cl	N	397	Yellow
4,4'-Diaminostilbene-3,3'-disulphonic acid	2,4-Diaminobenzenesulphonic acid	2,4-Diaminobenzenesulphonic acid	2-Methoxy-4-(2-sulfatoethylsulfonyl)aniline	2-Methoxy-4-(2-sulfatoethylsulfonyl)aniline	Cl	Cl	N	396	Yellow
4,4'-Diaminostilbene-3,3'-disulphonic acid	7-Amino-1-naphthol-3-sulfonic acid	7-Amino-1-naphthol-3-sulfonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	Cl	Cl	N	508	Red

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4,4'-Diaminostilbene-3,3'-disulphonic acid	7-Amino-1-naphthol-3-sulfonic acid	7-Amino-1-naphthol-3-sulfonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	Cl	Cl	N	468	Red
3,3'-diaminodiphenylsulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	Cl	Cl	N	525	Red
3,3'-diaminodiphenylsulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	Cl	Cl	N	513	Red
3,3'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	2,4-Diaminobenzenesulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	Cl	Cl	N	427	Yellow
3,3'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	2,4-Diaminobenzenesulphonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	Cl	Cl	N	379	Yellow
3,3'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	2,4-Diaminobenzenesulphonic acid	2-Methoxy-5-methyl-4-(b-sulfatoethylsulfonyl)aniline	2-Methoxy-5-methyl-4-(b-sulfatoethylsulfonyl)aniline	Cl	Cl	N	442	Yellow
3,3'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	2,4-Diaminobenzenesulphonic acid	2-Methoxy-4-(2-sulfatoethylsulfonyl)aniline	2-Methoxy-4-(2-sulfatoethylsulfonyl)aniline	Cl	Cl	N	420	Yellow
4,4'-diaminodiphenylsulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	Cl	Cl	N	517	Red

4,4'-diaminodiphenylsulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	Cl	Cl	N	514	Red
4,4'-diaminodiphenylsulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-Methoxy-5-methyl-4-(b-sulfatoethylsulfonyl)aniline	2-Methoxy-5-methyl-4-(b-sulfatoethylsulfonyl)aniline	Cl	Cl	N	581	Red
4,4'-diaminodiphenylsulfone	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	1-amino-8-hydroxy naphthalene-3,6-disulphonic acid	2-Methoxy-4-(2-sulfatoethylsulfonyl)aniline	2-Methoxy-4-(2-sulfatoethylsulfonyl)aniline	Cl	Cl	N	517	Red
4,4'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	2,4-Diaminobenzenesulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	Cl	Cl	N	408	Yellow
4,4'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	2,4-Diaminobenzenesulphonic acid	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	4-Amino-3-sulfophenyl 2-sulfatoethylsulfone	Cl	Cl	N	443	Yellow
4,4'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	2,4-Diaminobenzenesulphonic acid	2-Methoxy-5-methyl-4-(b-sulfatoethylsulfonyl)aniline	2-Methoxy-5-methyl-4-(b-sulfatoethylsulfonyl)aniline	Cl	Cl	N	441	Yellow
4,4'-diaminodiphenylsulfone	2,4-Diaminobenzenesulphonic acid	2,4-Diaminobenzenesulphonic acid	2-Methoxy-4-(2-sulfatoethylsulfonyl)aniline	2-Methoxy-4-(2-sulfatoethylsulfonyl)aniline	Cl	Cl	N	419	Yellow

Example-14:

- (A) 94.8 parts of 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid are dissolved in 800 ml of water under neutral conditions, and the solution is cooled down to 0-5°C. 42 parts of 2,4,6-trifluoro-1,3,5-triazine are added drop wise at this temperature in the course of 20 minutes, during which the pH of the reaction solution is kept weakly acid to Congo red by

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the simultaneous addition of 2N sodium hydroxide solution. After addition of a mixture of 57 parts of 4,4'-Diaminostilbene-3,3'-disulphonic acid in 500 parts of water which has been adjusted to pH 6-6.5 the pH of the reaction mixture is initially briefly kept weakly acid to Congo red and then at 5-6 by the constant addition of 2N sodium hydroxide solution. At the

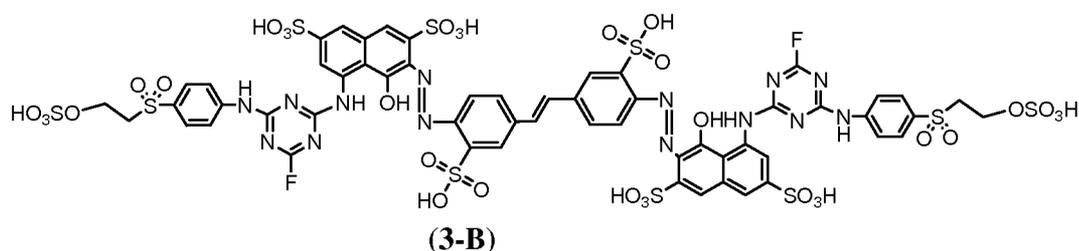
5 same time the temperature is raised to 20-25°C in the course of 2 to 3 hours.

(B) 85.4 parts of 2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate are introduced into 500 parts of ice-water and 65 parts of 30% Hydrochloric acid with efficient stirring, cool the reaction mass to 0-5°C with ice. A solution of 21 parts of Sodium Nitrite in 50 parts of water is added slowly in 15-30 minutes. Check reaction mass for excess of nitrite and stir for 2 hrs.

10 After two hrs excess nitrite is destroyed by addition sulfamic acid.

Add this diazo solution to solution (A) at 0-5°C and stir for 30 minutes and raise pH up to 6.5-7.0 and check spot test for completion of coupling reaction. After the coupling reaction at pH 8 has ended the reaction mixture is clarified and the resultant reactive dye of the formula (3-B) is isolated at pH 7 by filtration after slating it out from reaction mass or directly dried.

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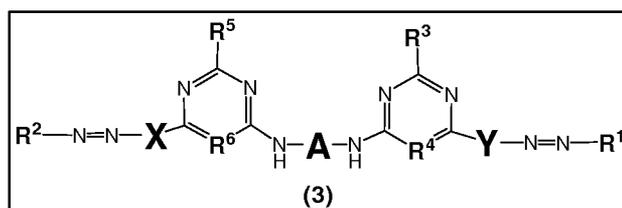
The product (3-B) obtained as blue powder and dyes cotton in bright red shade with excellent
20 build up and good fastness properties.

Example-15:

The dyestuffs of the formula 2 are synthesized using same method as described in Example-13 to get following dyes described in table 7:

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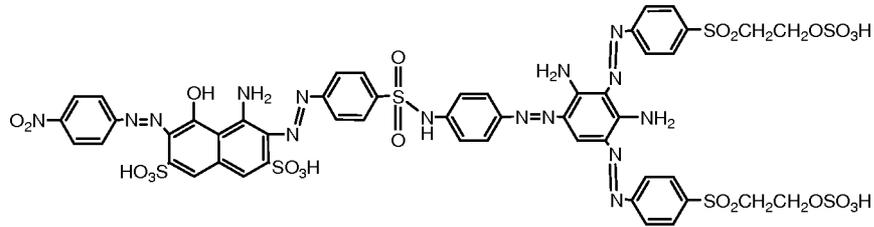
Table 7

A	X	Y	R1	R2	R3	R5	R6	λ Max	SHAD E
4,4'- Diaminostilbene-3,3'- disulphonic acid	1-amino-8- hydroxy naphthalene- 3,6- disulphonic acid	1-amino-8- hydroxy naphthalene- 3,6- disulphonic acid	2-[(4- Aminophen- yl)sulfonyl]e- thyl hydrogen sulfate	2-[(4- Aminophenyl) sulfonyl]ethyl hydrogen sulfate	F	F	N	515	Red
4,4'- Diaminostilbene-3,3'- disulphonic acid	1-amino-8- hydroxy naphthalene- 3,6- disulphonic acid	1-amino-8- hydroxy naphthalene- 3,6- disulphonic acid	2-[(4- Aminophen- yl)sulfonyl]e- thyl hydrogen sulfate	2-[(4- Aminophenyl) sulfonyl]ethyl hydrogen sulfate	F	F	C	512	Red
4,4'- Diaminostilbene-3,3'- disulphonic acid	1-amino-8- hydroxy naphthalene- 3,6- disulphonic acid	1-amino-8- hydroxy naphthalene- 3,6- disulphonic acid	2-[(4- Aminophen- yl)sulfonyl]e- thyl hydrogen sulfate	2-[(4- Aminophenyl) sulfonyl]ethyl hydrogen sulfate	F	F	C- Cl	516	Red
4,4'- Diaminostilbene-3,3'- disulphonic acid	2,4- Diaminoben- zenesulphon- ic acid	2,4- Diaminoben- zenesulphon- ic acid	2-[(4- Aminophen- yl)sulfonyl]e- thyl hydrogen sulfate	2-[(4- Aminophenyl) sulfonyl]ethyl hydrogen sulfate	F	F	N	415	Yellow
4,4'- Diaminostilbene-3,3'- disulphonic acid	2,4- Diaminoben- zenesulphon- ic acid	2,4- Diaminoben- zenesulphon- ic acid	2-[(4- Aminophen- yl)sulfonyl]e- thyl hydrogen sulfate	2-[(4- Aminophenyl) sulfonyl]ethyl hydrogen sulfate	F	F	C	412	Yellow
4,4'- Diaminostilbene-3,3'- disulphonic acid	2,4- Diaminoben- zenesulphon- ic acid	2,4- Diaminoben- zenesulphon- ic acid	2-[(4- Aminophen- yl)sulfonyl]e- thyl hydrogen sulfate	2-[(4- Aminophenyl) sulfonyl]ethyl hydrogen sulfate	F	F	C- Cl	415	Yellow
3,3'- diaminodiph- enylsulfone	1-amino-8- hydroxy naphthalene-	1-amino-8- hydroxy naphthalene-	2-[(4- Aminophen- yl)sulfonyl]e	2-[(4- Aminophenyl) sulfonyl]ethyl	F	F	N	529	Red

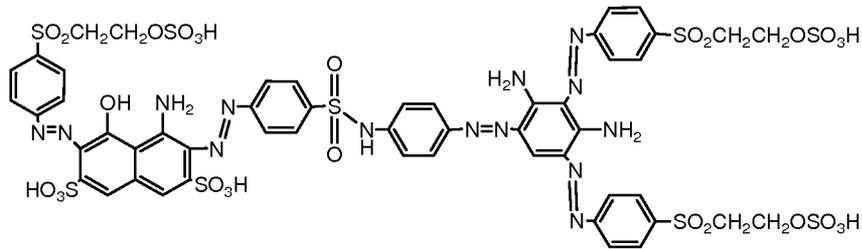
	3.6-disulphonic acid	3.6-disulphonic acid	thyl hydrogen sulfate	hydrogen sulfate					
3,3'-diaminodiphenylsulfone	1-amino-8-hydroxy naphthalene-3.6-disulphonic acid	1-amino-8-hydroxy naphthalene-3.6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	F	F	C	523	Red
3,3'-diaminodiphenylsulfone	1-amino-8-hydroxy naphthalene-3.6-disulphonic acid	1-amino-8-hydroxy naphthalene-3.6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	F	F	C-Cl	527	Red
4,4'-diaminodiphenylsulfone	1-amino-8-hydroxy naphthalene-3.6-disulphonic acid	1-amino-8-hydroxy naphthalene-3.6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	F	F	N	520	Red
4,4'-diaminodiphenylsulfone	1-amino-8-hydroxy naphthalene-3.6-disulphonic acid	1-amino-8-hydroxy naphthalene-3.6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	F	F	C	518	Red
4,4'-diaminodiphenylsulfone	1-amino-8-hydroxy naphthalene-3.6-disulphonic acid	1-amino-8-hydroxy naphthalene-3.6-disulphonic acid	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	2-[(4-Aminophenyl)sulfonyl]ethyl hydrogen sulfate	F	F	C-Cl	522	Red

Comparative Examples

- The following dyestuffs are used as comparative examples:
 DYE-1 is known from US2008/0047079 A1, example 1.
 DYE-2 is known from US2008/0047079 A1, example 2.
 DYE-3 is from Example 5
 DYE-4 is from Example 6
 DYE-5 is from Example 6

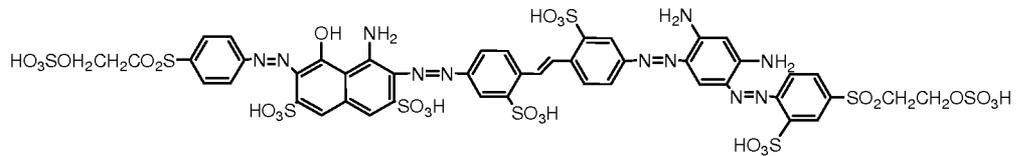


DYE-1

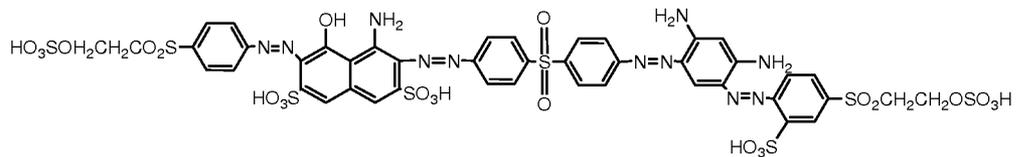


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DYE-2

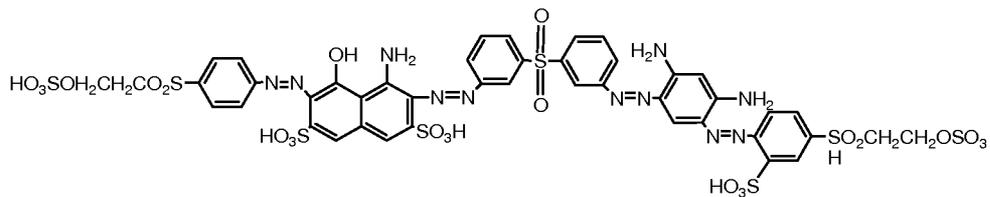


DYE-3



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DYE-4



DYE-5

15 In the following table advantages of the dyestuffs of the present invention are illustrated. In the table, ISO105-C06 is 60 °C washing fastness and ISO 105 B02 fastness is Color Fastness to Light. All fastness tests are obtained from dyeing in 1/1 standard depth with dyes

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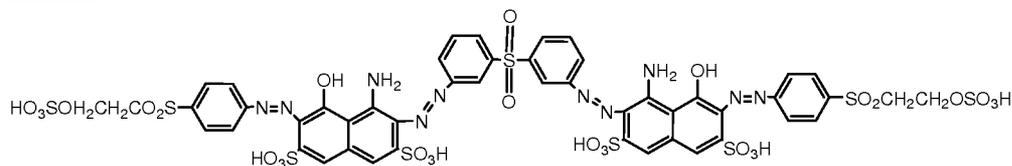
of the present invention of formula in comparison with structural similar known dyestuffs. In the fastness test, the staining of adjacent cotton and polyamide fabric is assessed. On the assessment scale used, 5 denote to no staining whatsoever and 1 denotes to substantial staining.

- 5 Fixation yield refers to the degree of fixation on cotton relative to the total amount of dyestuff applied in the dye bath in exhaust dyeing, carried out according to the dyeing examples 1 and 2.

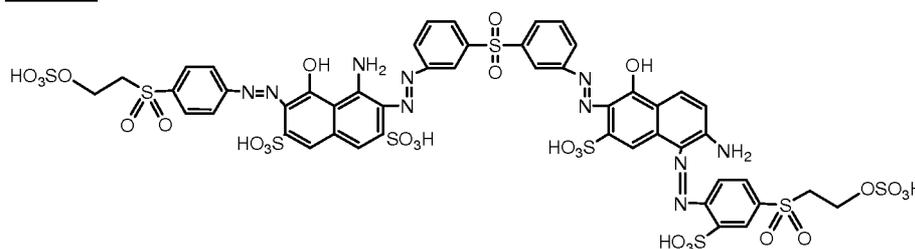
	Shade	Fixation	Wash fastness (ISO 105 C06) CO/PA	Light fastness (ISO 105 B02)
DYE-1	Olive	60%	4/4	2-3
DYE-2	Olive	65%	4/4-5	3
DYE-3	Black	82%	3-4/4-5	5
DYE-4	Black	70%	4/3-4	3-4
DYE-5	Black	70%	4/4-5	3-4

- 10 The table shows that fastnesses and fixation yields and Light fastness of the dyes of the present invention are superior compared to similar dyes of closest the state of the art. In particular DYE-3 which represents Example-5 of present invention having one additional chromophore resulting in more deeper dyeing shade and also shows significant improvement in fixation yield on cotton fabrics and light fastness.

- 15 2. The following dyestuffs are used as comparative examples:
DYE-6 is known from US2000/6013775 example 1.
DYE-7 is from Example 1.

DYE-6

DYE-7



In the following table advantages of the dyestuffs of the present invention are illustrated.

5 In the table, ISO105-C06 is 60 °C washing fastness and ISO 105 B02 fastness is Color Fastness to Light. All fastness tests are obtained from dyeing in 1/1 standard depth with dyes of the present invention of formula in comparison with structural similar known dyestuffs. In the fastness test, the staining of adjacent cotton and polyamide fabric is assessed. On the assessment scale used, 5 denote to no staining whatsoever and 1 denotes to substantial staining.

10 Fixation yield refers to the degree of fixation on cotton relative to the total amount of dyestuff applied in the dye bath in exhaust dyeing, carried out according to the dyeing examples 1 and 2.

	Shade	Fixation	Wash fastness (ISO 105 C06) CO/PA	Light fastness (ISO 105 B02)
DYE-6	Navy	60%	3/4	2-3
DYE-7	Navy	70%	4/4-5	3-4

15

The table shows that fastnesses and fixation yields and Light fastness of the dyes of the present invention are superior compared to similar dyes of closest the state of the art.

Dyeing Example 1:

100 parts per weight of cotton fabric is introduced at a temperature of 60 °C into a dyebath containing 800 parts of water, 30 parts per weight of sodium chloride, and 5 parts per weight of the dyestuff of Example 1-6. After 30 min at 60°C, 10 parts per weight of sodium carbonate is added, and the dyeing temperature is maintained at 60 °C for another 45 min.

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The dyed fabric is then rinsed in a fresh bath of 2000 parts warm water, neutralized by adding 1 part per weight of acetic acid, and soaped in another fresh bath of 2000 parts of water in presence of a conventional detergent for 5 min. at 95°C, and dried. A dyeing with excellent fixation yield and overall good fastness property is obtained.

5

Dyeing Example 2:

100 parts per weight of cotton fabric is introduced at a temperature of 80 °C into a dye bath containing 1000 parts of water, 60 parts per weight of sodium chloride, and 5 parts per weight of the dyestuff of example 7-14. Start heating at 1.5°C/minute and raise temperature up to 80°C and after 10 minutes at 80°C, add 15 parts per weight of sodium carbonate, the dyeing temperature is maintained at 80 °C for 60 min, then the dyed fabric is rinsed and soaped in the same manner as outlined in dyeing example 1. A deep dyeing with excellent fixation yield with overall good fastness property is obtained.

15

CLAIMS

1. A polyazo dye of the formula 1,

**(1)**

Where, A= 4,4'-diaminostilbene-2,2'-disulphonic acid; (DASDSA)
 4:4'-Diaminodiphenylsufone; (4,4'-DADPS)
 3:3'-Diaminodiphenylsulfone (3,3'--DADPS)

X & Y are same or different in combination of followings,

- 10 1-Amino-8-Hydroxy naphthalene-3:6-disulphonic acid. (H acid)
 1-Amino-7-Hydroxy naphthalene-3:6-disulphonic acid.
 1-Amino-7-Hydroxy naphthalene-6-sulphonic acid.
 7-Amino-1-naphthol-3-sulfonic acid (Gamma acid)
 N-Methyl-Gamma acid
- 15 2-Amino-5-hydroxy-7-naphthalenesulfonic acid (J acid)
 1-Hydroxy-6-(methylamino)-3-naphthalenesulfonic acid (N-methyl J-acid)
 1-Hydroxy-6-(2'-Carboxy ethyl amino)-3-naphthalenesulfonic acid
 1-Hydroxy-6-(2'-sulfo ethyl amino)-3-naphthalenesulfonic acid
 And similar N-substituted alkyl derivatives.
- 20 1:3-Diamino benzene (m- phenylenediamine)
 1:4-Diamino benzene (p- phenylenediamine)
 2:5-Diamino benzene sulphonic acid (PPDSA)
 2:4-Diamino benzene sulphonic acid (MPDSA)
 1:3-Diamino benzoic acid
- 25 2:4-Diamino toluene
 3:4-Diamino toluene
 1:3-Dihydroxy benzene,
 1:5/1:8-Diamino naphthalene

1:5/1:8-Dihydroxy naphthalene

and similar diamino, amino hydroxy and dihydroxy benzene and naphthalene derivatives;

wherein X and Y are not simultaneously 1-Amino-8-Hydroxy naphthalene-3:6-disulphonic acid. (H acid);

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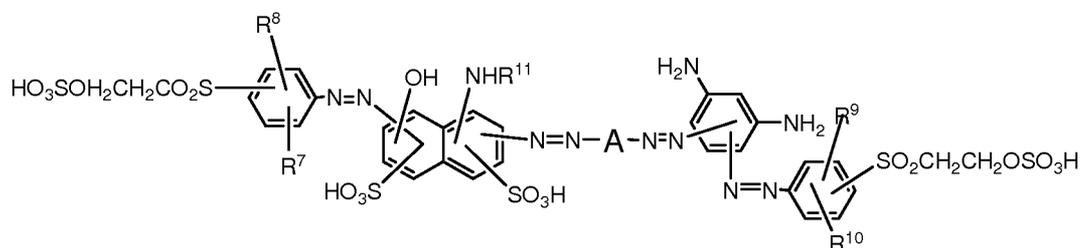
R^1 & R^2 = Amino benzene or naphthalene derivatives containing at least one or more vinylsulphone reactive group with or without $-SO_3H$, alkyl, alkoxy and halo substituent on benzene or naphthalene ring;

R^3 & R^5 = May be R^3 & R^5 are same or different in combination of Cl; F; C1-C4 Alkoxy, $-NH_2$, $-NHCN$, $-C1-C4$ alkylamine, Alkyl amino sulfone derivatives, alkyl amino acids, alkyl amino sulphonic acid derivatives etc; R^4 & R^6 = N, CH, C-Cl; and their mixtures with each or one another.

10

2. The poly azo dyes according to Claim 1 wherein the compound of formula 1 is preferably of formula (1')

15



Where, A = 4,4'-diaminostilbene-2,2'-disulphonic acid; (DASDSA)
 4:4'-Diaminodiphenylsufone; (4,4'-DADPS)
 3:3'-Diaminodiphenylsulfone (3,3'-DADPS)

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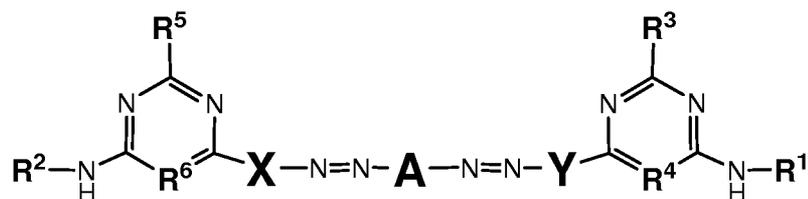
R^7 , R^8 , R^9 and R^{10} = May be same or different in combination of $-H$, $-SO_3H$, alkyl and halo;

R^{11} = $-CH_2CH_2COOH$, $-CH_2CH_2CN$, $-CH_2CH_2CONH_2$, $-CH_2COOH$, $-CH_2CH_2SO_3H$, $-CH_2CH(CH_3)COOH$, $-CH_2CH_2OSO_3H$, $-CH_2CH_2COCH_3$, $-CH_2CH_2COOC_2H_5$; and their mixtures with each or one another.

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3. A poly azo dye of formula (2),

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(2)

Where, **A**= 4,4'-diaminostilbene-2,2'-disulphonic acid; (DASDSA)

4:4'-Diaminodiphenylsufone; (4,4' -DADPS)

3:3'-Diaminodiphenylsulfone (3,3'--DADPS)

5 X & Y are same or different in combination of followings,

1-Amino-8-Hydroxy naphthalene-3:6-disulphonic acid. (H acid)

1-Amino-7-Hydroxy naphthalene-3:6-disulphonic acid.

1-Amino-7-Hydroxy naphthalene-6-sulphonic acid.

7-Amino-1-naphthol-3-sulfonic acid (Gamma acid)

10 N-Methyl-Gamma acid

2-Amino-5-hydroxy-7-naphthalenesulfonic acid (J acid)

1-Hydroxy-6-(methylamino)-3-naphthalenesulfonic acid (N-methyl J-acid)

1-Hydroxy-6-(2'-Carboxy ethyl amino)-3-naphthalenesulfonic acid

1-Hydroxy-6-(2'-sulfo ethyl amino)-3-naphthalenesulfonic acid

15 And similar N-substituted alkyl derivatives; 1:3-Diamino benzene (m-phenylenediamine)

1:4-Diamino benzene (p- phenylenediamine)

2:5-Diamino benzene sulphonic acid (PPDSA)

2:4-Diamino benzene sulphonic acid (MPDSA)

20 1:3-Diamino benzoic acid

2:4-Diamino toluene

3:4-Diamino toluene

1:3-Dihydroxy benzene,

1:5/1:8-Diamino naphthalene

25 1:5/1:8-Dihydroxy naphthalene

and similar diamino, amino hydroxy and dihydroxy benzene and naphthalene derivatives;

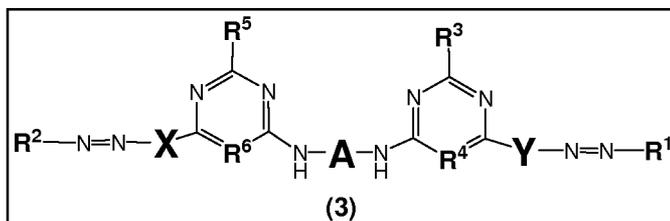
R^1 & R^2 = Amino benzene or naphthalene derivatives containing at least one or more vinylsulphone reactive group with or without $-SO_3H$, alkyl, alkoxy and halo substituent on benzene or naphthalene ring;

R^3 & R^5 are same or different and is selected from Cl; F; C1-C4 Alkoxy, $-NH_2$, $-NHCN$, $-C1-C4$ alkylamine, Alkyl amino sulfone derivatives, alkyl amino acids, alkyl amino sulphonic acid derivatives etc;

R^4 & R^6 = N, CH, C-Cl;

and their mixtures with each or one another.

4. A poly azo dye of formula (3),



Where, **A** = 4,4'-diaminostilbene-2,2'-disulphonic acid; (DASDSA)

4:4'-Diaminodiphenylsufone; (4,4'-DADPS)

3:3'-Diaminodiphenylsulfone (3,3'-DADPS)

X & **Y** are same or different in combination of followings,

1-Amino-8-Hydroxy naphthalene-3:6-disulphonic acid. (H acid)

1-Amino-7-Hydroxy naphthalene-3:6-disulphonic acid.

1-Amino-7-Hydroxy naphthalene-6-sulphonic acid.

7-Amino-1-naphthol-3-sulfonic acid (Gamma acid)

N-Methyl-Gamma acid

2-Amino-5-hydroxy-7-naphthalenesulfonic acid (J acid)

1-Hydroxy-6-(methylamino)-3-naphthalenesulfonic acid (N-methyl J-acid)

1-Hydroxy-6-(2'-Carboxy ethyl amino)-3-naphthalenesulfonic acid

1-Hydroxy-6-(2'-sulfo ethyl amino)-3-naphthalenesulfonic acid

And similar N-substituted alkyl derivatives.

46

- 1:3-Diamino benzene (m- phenylenediamine)
 1:4-Diamino benzene (p- phenylenediamine)
 2:5-Diamino benzene sulphonic acid (PPDSA)
 2:4-Diamino benzene sulphonic acid (MPDSA)
- 5 1:3-Diamino benzoic acid
 2:4-Diamino toluene
 3:4-Diamino toluene
 1:3-Dihydroxy benzene,
 1:5/1:8-Diamino naphthalene
- 10 1:5/1:8-Dihydroxy naphthalene
 and similar diamino, amino hydroxy and dihydroxy benzene and naphthalene derivatives;
 R^1 & R^2 are Amino benzene or naphthalene derivatives containing at least one or more vinylsulphone reactive group with or without $-SO_3H$, alkyl, alkoxy and halo substituent on benzene or naphthalene ring;
- 15 R^3 & R^5 are same or different and is selected from Cl; F; C1-C4 Alkoxy, $-NH_2$, $-NHCN$, $-C1-C4$ alkylamine, Alkyl amino sulfone derivatives, alkyl amino acids, alkyl amino sulphonic acid derivatives etc;
 R^4 & $R^6 = N, CH, C-Cl$;
- 20 and their mixtures with each or one another.
5. A process for dyeing and printing fiber materials which comprises treating the fiber materials with dyes of formula (1), formula (2) and formula (3) according to any of the preceding claims.
6. The process according to claim 5, wherein the fiber material is selected from cellulose fibers, cotton or regenerated cellulose, viscose or Lyocell, a polyamide fiber, nylon 6
- 25 or nylon 66 or a protein fiber, wool or silk.