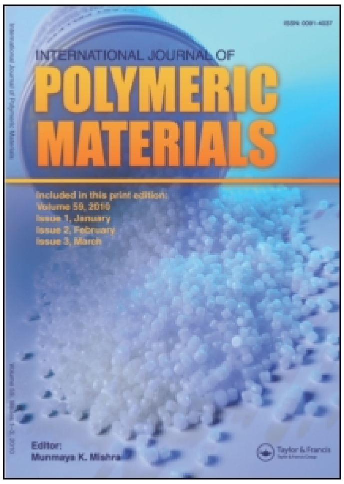

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Azo Dyes Based on Phenol—Furfural Oligomers

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Azo Dyes Based on Phenol – Furfural Oligomers

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A series of new oligomeric disperse and acid azo-phenol furfural dyes were prepared by coupling various aromatic diazonium salts to phenol-furfuraldehyde (PF), *m* cresolfurfuraldehyde (CF) and resorcinol-furfuraldehyde (RF) oligomers. They were characterized in terms of their softening points, colour, solubility, IR and UV-VIS spectra and thermogravimetric properties. Their dyeing on polyester, nylon and wood resulted in yellow, orange, and brown to red shades with good to excellent light fastness and washing fastness properties.

Keywords: Azo dyes; phenol; furfural; high fastness

INTRODUCTION

Phenolics are known as matrix resins or binding resins for various applications. The main advantages of phenolics are their easy availability and some of their excellent properties, such as high thermal stability, excellent acid resistance, high fire retardancy, *etc.* One such area of using phenolic resins as coupling component in the formation of azo dyes or pigments has received little attentions both academically and industrially in spite of above advantages. Only few instances [2–4] about the use of phenolic resins are coupling components in the azo dyes formation have been patented. One of our authors (H.S.P) have recently worked upon "Azo dyes based on

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phenolic oligomers" [5]. These dyes are reported to have been used in dyeing of synthetic and natural fibres and metallized dyes are applied.

Hence in extension of this work [5], the present communication comprises the synthesis of oligomers based on condensation of phenol, *m*-cresol, and resorcinol, respectively, with furfural, coupling of various diazonium salts to each of these three oligomers and evaluation of the properties of the resultant oligomeric disperse and acid azophenol furfural dyes.

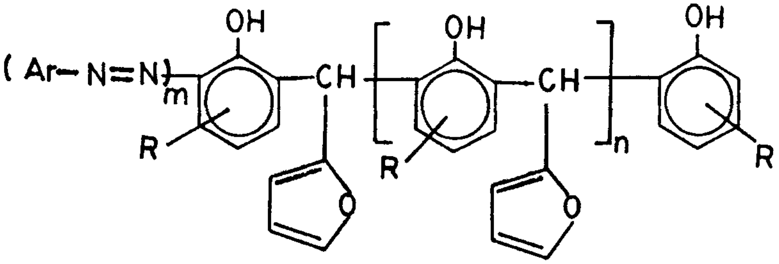

FIGURE 1 $m=2$, $n=2$ or 3, R = H, CH_3, OH, Ar = Corresponds to amines 1 – 21.

EXPERIMENTAL

Materials

Phenol, *m*-cresol and resorcinol were of analytical grade and distilled or crystallized prior to use. Furfural and oxalic acid were of laboratory grades. For diazonium salt preparation, the aromatic amines of analytical grade presented in Table I were employed.

Polyester (PET), Nylon 66, and Wool (100%) were obtained from local market.

Synthesis of Phenol-furfuraldehyde (PF) and *m*-cresol-furfuraldehyde (CF) Oligomers

In a 2l three necked round bottom flask a mixture of phenol (or *m*-cresol) (1 mol.), furfural (0.5 mol.), and oxalic acid (2.0 g) was taken and heated gradually on free flame. When the exothermic reaction set

TABLE I Aromatic amines for the preparation of diazonium salts

No.	*Aromatic amine*
1.	Aniline
2.	*p*-Aminophenol
3.	*p*-Toludine
4.	*p*-Nitroaniline
5.	*p*-Chloroaniline
6.	*m*-Nitroaniline
7.	α-Naphthylamine
8.	*p*-Anisidine
9.	*p*-Aminosalicylic acid
10.	*p*-Aminobenzoic acid
11.	Sulfanilic acid
12.	8-Amino-1-napththol-3,6-disulfonic acid (H-acid)
13.	6-Amino-1-napththol-3-sulfonic acid (J-acid)
14.	7-Amino-1-napththol-3,6-disulfonic acid (γ-acid)
15.	8-Amino-1,3,6-napththalene-trisulfonic acid (Koch's acid)
16.	8-Amino-1-napththalene sulfonic acid (Peri acid)
17.	2-Amino-1-napththalene sulfonic acid (Tobias acid)
18.	6-Amino-2-napththalene sulfonic acid (Brooner's acid)
19.	5-Amino-1-napththalene sulfonic acid (Laurent's acid)
20.	Naphthonic acid
21.	8-Amino-1-napththol-5,7-disulfonic acid (Chicago acid)

in the flame was removed. The reaction was kept for 15 – 20 min., then it was refluxed for 1.5 h. The resultant mixture was then distilled under reduced pressure (13–20 hPa) at 90–100°C to remove unreacted phenol (or *m*-cresol) furfural and water as much as possible. The resulting thick liquid was collected and kept in a vaccum desiccator. The yield was 85% (75% for CF).

Synthesis of Resorcinol-furfuraldehyde (RF) Oligomer

In a 21 three necked round bottom flask a mixture of resorcinol (1 mol.), furfural (0.5 mol.), oxalic acid (2.0 g) and benzene (500 ml.) was taken and refluxed at 80–82°C for 3 h. The resultant reaction mixture was then distilled under reduced pressure (13–20 hPa) at 90–100°C, to remove benzene, furfural and water as much as possible. The resulting thick liquid was collected and kept in a vaccum desiccator. The yield was 80%.

Analyses of PF, CF and RF Oligomers

All oligomers were thick liquids. C and H contents of each oligomer agreed with the structure proposed earlier. The free phenol in these oligomers were 2–3%. The $\bar{M}_n$ and efflux viscosity time (t) of the oligomers were:

$$\mathrm{PF} : \bar{M}_n = 520, \quad 5 = 108\,\mathrm{s}$$
$$\mathrm{CF} : \bar{M}_n = 560, \quad t = 38\,\mathrm{s}$$
$$\mathrm{RF} : \bar{M}_n = 700, \quad t = 80\,\mathrm{s}$$

Synthesis of diazonium salt solution

The diazonium salt solutions of aromatic amines (Tab. I) were prepared by a literature method [6].

Synthesis of Oligomeric disperse and acid Azo-phenol Furfural dyes

To a cooled (0°C) alkaline solution (pH 10–10.5) of the phenol furfural oligomer (0.1 mol) the diazonium salt solution or suspension (amines 1–8 yield clear diazo solutions while amines 9–21 yield diazo suspensions) was added dropwise at such a rate that the reaction proceeded at low temperature (exothermic reaction) while maintaining the pH between 10 and 10.5. The completion of azo coupling was established from starch-iodide paper. The reaction mixture was then stirred for one hour at 0–5°C and then acidified to pH 5.5–6.0. The precipitated disperse dye (from amines 1–8) was then filtered, washed throughly with hot water and dried. The precipitated acid dye (from amines 9–21) seperated as a pasty mass and was stirred well with 20 g of NaCl and heated on water bath for 13 min. The dye was Soxhlet extracted with ether (Ethanol for acid dyes) to purify from adventitious products to presumably due to the formation of simple dye from the coupling of di-azo compounds with the free phenol present in oligomer. The oligomeric azo-phenol furfural dye was dissolved in an appropriate solvent and re-precipitated by addition of water. The yield was about 85%.

MEASUREMENTS

The elemental analysis of the phenol furfural oligomers and of oligomeric azo-phenol furfural dyes were performed with an elemental analyzer Carlo Erba (C,H,N elemental analyzer), Italy.

The free furfural and free phenols in the oligomers were determined according to the methods reported in literature [7].

$\bar{M}_n$ of phenol furfural oligomers as well as oligomeric azo-phenol furfural were estimated both by vapour pressure osmometry (DMF, 70 ± 1°C) and non aqueous conductometric titration [8, 9] (In pyridine against standard sodium methanolate). The number of azo groups of azo-phenol furfural dyes was estimated by a method reported earlier [10].

IR spectral characteristics of oligomeric dye samples were estimated in KBr pellets on a Perkin Elmer 983 spectrophotometer.

Visible spectra of all the oligomeric dyes were recorded in DMF on a Beckman DK-2A spectrophotometer.

Thermogravimetric analysis of oligomeric azo-RF dyes (dispersed dyes) and all oligomeric azo-acid dyes were carried out on a DuPont TGA 983 analyzer, in air at a heating rate of 10 K/min.

Dyeing of Polyester and Nylon Fibres with Oligomeric disperse azo-dyes

A known quantity of each oligomeric dispersed azo-phenol furfural dye (Tab. III) was taken in a water along with the same quantity of Dodamol, a dispersing agent, 2–3 drops of wetting agent (2% Sodium Lauryl sulphate solution) and the dispersion of the azo-phenol furfural dye particles in water was prepared by vibration for 2 h. An exact quantity of dispersion containing 0.04 g of the dye in 100 ml water was used for dyeing synthetic fibres (2 g weight of each fibre) so as to get 1% shade of the dye on fibres. The material to liqour (M:L) ratio was maintained at 1:50 at 90°C.

Dyeing of Nylon and Wool with Oligomeric acid azo-phenol Furfural dyes

For dyeing, wool and nylon were scoured in soap (0.2%) solution containing amonia (0.1% w/v) at 40–50°C for 10 min, washed with water, squeezed and dried. The treated wool and nylon fibres were heat set for 5 min at 85°C in a dilute acid solution, the pH value was adjusted with dilute sulphuric acid at pH 3 for wool and pH 5 for nylon.

Dyeing conditions (amount of dye, water and fibre and M:L ratio) were the same for the oligomeric disperse azo-dyes. The dye bath was constantly revolving in a thermostated bath at 85°C. The dyeing was continued upto the equilibrium. The fastness properties were determined according to the international standards [11].

RESULTS AND DISCUSSIONS

High molecular weight compounds are used as pigments rather than dyes due to their poor dyeability on the fibres [12]. Phenol–furfural polymers are feared for their poor dyeability and therefore it was planned to obtain the oligomers of low molecular weight from condensation of phenol, *m*-cresol, resorcinol respectively with furfural.

Perusal of literature has revealed that phenol–furfural oligomers have been extensively employed in the veritable applications and hence many synthetic methods of their formation are available [1]. Based on the studies of novel dyes, the synthesis of phenol–furfural, *m*-cresol–furfural and resorcinol–furfural oligomers have been modified to suit the azo coupling reactions for a number of amino compounds to achieve suitable oligomers in the present study, several variables namely molar ratios of reactants, temperature, catalyst and reaction time have been optimised in the synthesis. Thus phenol–furfural (PF), *m*-cresol–furfural (CF) and resorcinol (RF) oligomers were synthesized for the dye formation as mentioned in experimental part. It was observed that three oligomers were thick liquids and remain liquid for several months during storage in a desiccator (*i.e.*, the eflux for flow viscosity of oligomer did not change during its storage), but on standing at room temperature in ambient atmosphere each oligomer started to solidify, it is preassumed that some extent of cross-linking might have occured under atmosphere conditions. No further evidences are reported for such cross-linking. All the phenolic oligomers have lower $\bar{M}_n$ (*i.e.*, DP 4 or 5) indicating that they have possible reactive sites for electrophilic substitution reactions such as azo coupling. With this view the attempt was made successfully to couple the diazo salts to these three phenolic resins.

All the oligomeric disperse azo-phenol furfural dyes (listed in Tab. II) were soluble in common organic solvents. However, the oligomeric acid azo-phenol furfural dyes (listed in Tab. III) were soluble completly in water and in organic solvents like 1,4-dioxane, DMF and DMSO. It has been reported that the simple phenol based dyes are soluble in common organic solvents [11] including ether. Few of disperse dyes based on PF and CF are in form of semi solid while others are solid powders which softened in the range of 95°C–210°C depending upon the nature of oligomeric dye. All the oligomeric acid dyes didnot soften below 300°C. Nitrogen contents of all the oligomeric azo-phenol furfural dyes indicate that there may be two azo groups present per oligomer chain. This agrees with estimated azo group contents in each series of oligomeric azo phenolic dyes. The nitrogen and azo contents of each oligomeric azo-phenol furfural dyes also agree with their corresponding $\bar{M}_n$ values.

The IR spectra of all oligomeric azo-phenol furfural dyes comprise the important characteristic bands of azo groups and phenolic moieties, a broad band at 3600–3400 cm^{-1} due to γ_{OH}, medium broad bands at 2925 and 2850 cm^{-1} attributed to asymmetric and symmetic — CH–bridges of phenolics and the bands at 1625 and 1450 cm^{-1} arising from the azo group. All the spectra comprise the band in the double bond region due to aromatic rings. Other bands due to the presence of substituents on the arylazonium moiety are observed at their respective positions. In the IR spectra of the oligomeric acid azo-phenol furfural dyes, the streching bands at 1250, 1050 and 650 cm^{-1} appeared disernibly, which may be attributed to the presence of — SO_3H — groups.

The UV-Vis spectra of all the azo-phenol furfural dyes were obtained in DMF solution. The maximum wavelength (λ_{max}) of their absorption and the corresponding extinction coefficient of selected azo-phenol furfural dyes are presented in Tables II and III. The wavelength of maximum absorption is attributed to the excitation of azo groups in the dye, which is observed around 370 – 590 nm.

TABLE II Characteristics of oligomeric disperse azo-phenol furfural dyes[a]

Oligomeric disperse azo-phenolic dye[b]	*Softening range* (°C)	*Nitrogen content* (%)	*Mean number of azo groups*	$\bar{M}_n$	*Colour*	*λmax* (*nm*)	*log E*	*Dyeing on nylon*		*Dyeing on wool*	
								Light fastness	*Wash fastness*	*Light fastness*	*Wash fastness*
PF-5	96–98	7.77	2	728	yellow	370	5.14	3 to 4	4	2 to 3	4
PF-6	116–118	7.54	2	828	brown	574	4.13	1 to 2	3 to 4	3 to 4	4
PF-7	Semisolid	8.02	2	653	yellow	513	4.21	3 to 4	3	3	3
CF-4	67–69	8.59	2	832	yellow	394	5.33	3	3 to 4	4 to 5	4 to 5
CF-5	108–109	7.08	1.9	838	yellow	381	4.79	3 to 4	4	4 to 5	4
CF-7	Semisolid	6.85	1.8	870	brown	522	4.45	1 to 2	3 to 4	3 to 4	4 to 5
RF-1	194–196	6.68	1.9	885	yellow	418	4.61	2 to 3	3 to 4	4	4
RF-3	176–178	6.39	1.8	910	light yellow	444	4.43	4 to 5	4	3 to 4	3
RF-6	159–160	7.34	1.95	970	yellow	392	4.74	3 to 4	4	5	3 to 4
RF-8	110–111	6.16	1.9	935	Reddish yellow	441	4.64	4	2 to 3	3 to 4	4

[a] Characteristics of those Azo-phenol furfural dyes not mentioned here can be supplied by the authors.

[b] The number indicates the amines (listed in Tab. I) used for diazo components.

TABLE III Characteristics of oligomeric acid azo-phenol furfural dyes[a]

Oligomeric acid azo-phenolic dye[b]	Sulphur content (%) found	Nitrogen content (%) found	Mean number of azo groups	$\bar{M}_n$ by VPO	Colour	λ max (nm)	log E	Dyeing on nylon		Dyeing on wool	
								Light fastness	Wash fastness	Light fastness	Wash fastness
PF-11	8.22	7.2	1.9	852	yellow	359	5.12	3 to 4	4 to 4	5	5
PF-14	6.59	5.9	1.9	1012	reddish brown	433	4.64	4	4	5	5
PF-21	10.63	4.8	2	1299	red	539	4.43	4	3 to 4	4 to 5	4
CF-13	6.95	5.4	1.9	1147	red	508	4.26	4 to 5	4	5	4 to 5
CF-18	6.38	5.6	1.9	1132	orange	369	5.46	5 to 6	5	5	5
CF-20	6.27	5.7	2	1152	orange	402	4.16	5	5	4 to 5	4 to 5
RF-12	9.42	4.11	1.93	1330	reddish brown	465	4.32	5	4 to 5	4 to 5	4 to 5
RF-17	5.44	4.78	1.92	1140	violet	342	4.52	5	4 to 5	5	4 to 5
RF-19	5.6	4.9	1.97	1145	orange	465	4.34	4	4 to 5	5	5
RF-20	5.88	4.82	1.94	1210	reddish brown	398	4.91	5 to 6	4 to 5	5	4

[a] Characteristics of those Azo-phenol furfural dyes not mentioned here can be supplied by the authors.

[b] The number indicates the amines (listed in Tab. I) used for diazo components.

[c] Conductometric titration curves were not sharp.

The variations in λ_{max} may be attributed to the structural variations in the oligomers and the amine coupling components.

TGA measurements reveal that the solid powder oligomeric disperse dyes start their decomposition between 150–170°C, weight loss being completed between 190 to 220°C depending upon the structural variation. The oligomeric acid azo-phenol furfural dyes start their decomposition between 200 to 225°C and have lost 75 – 85% weight at 700°C depending upon the structural variations. The results also show that the oligomeric acid dyes are thermally more stable than oligomeric disperse dyes. This may be due to the presence of the acid group in the oligomeric dye. It is further evidenced that the decomposition of all the oligomeric dyes may justify that they are the independent entitiy of the dye.

The oligomeric disperse dyes and acid dyes were dyed on polyesters, nylon and wool fibres at 1% shade gave yellow, brown red and orange shades (Tabs. II and III). They resulted in a variety of attractive hues on the dyed fibres. The results of percentage dyebath exhaution and fixation of all the dyes varied from 75–100% depending upon the nature of oligomeric dye while it was observed in simple arylazo (phenol, cresol and resorcinol) [12] dyes the exhaustion and fixation varied from 60–80%.

The light fastness properties of all azo-phenol furfural oligomeric disperse and acid dyes (Tabs. II and III) were determined according to international standards (ISO) [10]. Examination of the data reveals that the light fastness of all three disperse and acid azo-PF, azo-CF and azo-RF dyes on polyester, nylon and wool fibres were particularly appreciable. The light fastness of oligomeric disperse dyes varied from 2–3 (moderate) on polyester fibre and 3–4 (good) on nylon fibre. Similarly the light fastness of oligomeric acid dyes varied from 4–6 (very good) on wool and 3–5 (good) on nylon fibres, most of disperse dyes have 3 (good) and 4 (very good) rating on polyester and nylon and acid dyes have 4 (very good) and 5 (very good) rating on nylon and wool respectively. The wash fastness of all disperse and acid dyes varied from 3–5 on polyester, nylon and wool fibres. It can be concluded that the light fastness of dyeing by oligomeric disperse and acid azo-phenol furfural dyes on polyester, nylon and wool varies from poor to very good compared to moderate results for dyeing by simple azo-phenol dyes. A difference is also observed between wash fastness of the produced oligomeric dyes and that of simple azo-phenol dyes, which was slightly higher for oligomeric dyes.

It is interesting to note that most of polymeric dyes reported earlier [13] have been dyed on various textiles but they formed patches on fibre. In this study of oligomeric disperse and acid azo dyes, the dyeing on fibre is completed in short time (1.5 h on polyester, 45 min on nylon and 30 min on wool) and at low temperature. Fixation is also high and most important is that no patches were observed on fibres. It was also noted that the semi solid disperse azo dyes of PF and CF can be employed on dyeing without any difficulty, but minor patches on the fibre were formed.

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