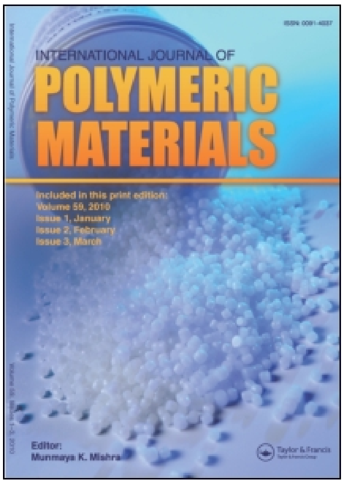

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Arylene Azo-Naphthol-Furfuraldehyde Oligomer Dyes

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A series of oligomeric azo dyes has been prepared by coupling various aromatic diazonium salts to 1-naphthol-furfuraldehyde (1-NF) and 2-naphthol-furfuraldehyde (2-NF) oligomers. They were evaluated in terms of their softning points, yield, colour, solubility and UV-Vis spectra. Structure-property relationships are discussed and dyeings on polyester PET and nylon-6,6 assessed. Dyeings on polyester and nylon-6,6 resulted in yellow, orange and brown to red colourations having excellent fastness to light and washing.

Keywords: Azo dyes; polyester; PET; nylon-6,6; light fastness; washing

INTRODUCTION

Whilst napthols are well established intermediates for the synthesis of dyes, the use of naphthol-furfuraldehyde condensates as coupling components in the formation of azo dyes and pigments has received little attention. However the use of phenolic resins as a coupling components in the azo dyes has been reported [1–3] and the products are stated to be useful in the dyeing of synthetic and natural fibres, and also of leather. They are stated to have good fastness properties. One of the authors (HSP) recently studied the oligomeric dyes in this direction [4–6]. Hence in continuation of this work [4–6] the present

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work comprises some azo dyes based on the use of naphthol-furfuraldehyde condensates as a coupling components.

EXPERIMENTAL

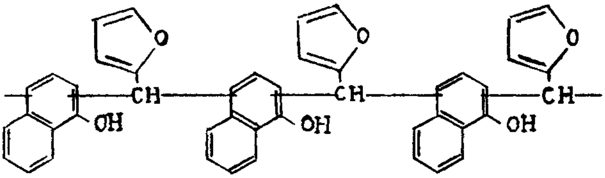
Materials

1- and 2-naphthols were analytical grade and were crystallised from ethanol prior to use. Furfuraldehyde and oxalic acid were of laboratory grade. For diazonium salt preparation, analytical grade arylamines were used (see footnote, Tab. II).

Polyester PET (100%) was supplied by Mafatlal Fabrics, Ahemdabad, India and nylon-6,6 by Vareli Fabrics, Surat, India.

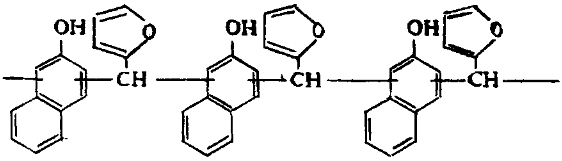
Synthesis of Naphthol-furfuraldehyde Oligomers

1-naphthol-furfuraldehyde (1-NF) and 2-naphthol-furfuraldehyde (2-NF) oligomers were prepared by the following methods. (Schemes I and II).



I– 1-naphthol-furfuraldehyde (1-NF) oligomer

SCHEME I



II– 2-naphthol-furfuraldehyde (2-NF) oligomer

SCHEME II

1-Naphthol-furfuraldehyde (1-NF) Oligomer

In a round bottom flask (1.0 lit) a mixture of 1-naphthol (2.0 mole), furfural (1.0 mole), potassium carbonate (2.0 gm.) was heated until the viscous mass was obtained. The thick viscous resin was washed with large amount of water and was kept in the vacuum desiccator. The yield was 75% and it was designated as 1-NF oligomer.

2-Naphthol-furfuraldehyde (2-NF) Oligomer

In a round bottom flask (1 lit) a mixture of 2-naphthol (2 mole), furfural (1 mole) and potassium carbonate was heated until the thick lumps were obtained. It was purified and was kept in vacuum desicator. The yield was 75% and was designated as 2-NF oligomer.

Characterization data of these oligomers are reported in Table I.

Synthesis of Oligomeric Arylene Azo-naphthol-furfuraldehyde Dyes

1-NF (or 2-NF) oligomer (0.1 mole) was dissolved in 10% aq. NaOH (75 ml) and the pH of the liquor was adjusted to 10 – 10.5. The solution was then cooled to 0°C and the appropriate diazonium liquor was added to it dropwise whilst maintaining the temperature at 0°C and pH 10 – 10.5. After coupling was complete the reaction mixture was stirred for 1 hr. at 0°C and then acidified to pH 5.5. The precipitated product was filtered, washed with water dried, and Soxhlet-extracted with ether to remove any monoazo dye resultant from the presence of any residual naphthol in the oligomer.

Characterization

Elemental analysis of NF oligomers and oligomeric azo-NF dyes was carried out on an Elemental Analyser (Carlo Erba, Italy). The efflux viscocity time of the 1-NF oligomer was measured at room temperature (~ 32°C) using a B:5-1733 flow cup. The mean number of azo groups of the dyes was determined by known methods [4 – 7]. Visible spectra were recorded on Beckman DK-2A spectrophotometer and the thermal stability of the dyes were assessed on a Du Pont 951 Thermal

TABLE I Characterization of naphthol-furfuraldehyde (NF) oligomers

Naphthol-furfuraldehyde oligomer	*Colour*	*Softning point (°C)*	*Elemental analysis (%)*				*Efflux viscosity time(s) at room temp. (32°C)*	$\overline{Mn}$ *estimated by VPO*
			C		*H*			
			Calcd	*Found*	*Calcd*	*Found*		
(1-NF)	Brown	162–165	80.89	79.9	4.49	4.30	150	800
(2-NF)	Light Brown	172–174	80.58	79.7	4.48	4.40	–	700

where VPO = Vapour Pressure Osmometry.

Analyser at a heating rate of 10°C/min. The number average molecular weight of all the oligomeric disperse dyes were estimated both by VPO and nonaqueous conductometric titration method. The $\overline{Mn}$ (by VPO method) of 1-NF and 2-NF are represented in Table I.

Dyeing of Polyester PET and Nylon-6,6 with Oligomeric Azo-NF dyes

A known quantity of each oligomeric azo-NF dye (Tabs. II and III) was taken into water, together with the same quantity of Dodamol (dispersing agent), 2–3 drops of wetting agent (2% lauryl sulphate solution) and a dispersion of the azo-NF dye was then prepared using ultrasonic vibration of 2 hrs. Polyester PET and nylon-6,6 (2.0 gram) were coloured at 1% depth using a liquor ratio of 50 : 1 and a dyeing temperature of 90°C fastness properties of the dyes were determined according to recognized procedures [5–8].

RESULTS AND DISCUSSION

Infusible compounds of the type studied have been used as a pigments rather than dyes due to their poor dyeability properties [6–9]. Naphthol-furfuraldehyde oligomers are known to have poor dyeability and it was therefore attempted to obtain oligomers of low molecular weight from the condensation of 1- and 2-naphthols with furfuraldehyde.

Phenol-furfuraldehyde oligomers can be utilized in various applications and many synthetic methods for their formation are available [7–10]. The synthesis of naphthol-furfuraldehyde oligomers has received less attention. To provide suitable oligomers for this present study, a number of variables in the synthesis, *i.e.*, molar ratios on both polyester PET and nylon-of reactants, temperature, catalysts and reaction time were optimized. The 1-NF oligomer was obtained as a viscous liquid, which remained in this form even after six to seven months of storage in a vacuum desiccator. The efflux time at room temperature (~32°C) for the flow viscosity of 1-NF oligomer remained constant during this storage period.

TABLE II Characterization of oligomeric azo-1-NF dyes

Oligomeric Azo-1-NF dyes[a]	*Colour*	*Softning point (°C)*	*N (%) found*	*Mean number of azo groups*	*Yield (%)*	*$\overline{Mn}$ by VPO*	*λ max (nm)*	*log E*	*Dyeing on polyester*		*Dyeing on nylon*	
									Light fastness	*Wash fastness*	*Light fastness*	*Wash fastness*
1-NF-1	Pinkish brown	145–150	5.48	1.90	90	1010	500	4.52	5	5	4 to 5	4
1-NF-2	Light brown	150–153	5.00	1.80	91	1110	504	4.48	4 to 5	5	4	4 to 5
1-NF-3	Reddish brown	180–185	5.33	2.00	95	1040	534	4.33	5 to 6	6	3 to 4	3 to 4
1-NF-4	Pinkish brown	200–225	5.20	1.90	93	1070	525	4.41	5 to 6	6	4	4
1-NF-5	Brown	180–190	5.01	1.80	88	1105	470	4.51	5	5	4	4
1-NF-6	Orange	190–210	5.29	1.90	90	1040	460	4.43	4	5	4 to 5	4
1-NF-7	Brown	200–205	5.13	2.00	85	1080	470	4.39	5	6	3 to 4	3 to 4

[a] Amines used as diazo components: 1, aniline; 2,1-naphthyl amine; 3, *p*-toludine; 4, *p*-anisidine; 5, 2-amino-5-chloro-toluene; 6, *p*-aminophenol; 7, *p*-chloroaniline.

TABLE III Characterization of oligomeric azo-2-NF dyes

									Dyeing on polyester		*Dyeing on Nylon*	
Oligomeric Azo-2-NF dyes[a]	*Colour*	*Softning point (°C)*	*N (%) found*	*Mean number of azo groups*	*Yield (%)*	$\overline{M}n$ *by VPO*	*λ max (nm)*	*log E*	*Light fastness*	*Wash fastness*	*Light fastness*	*Wash fastness*
2-NF-1	Orange	142–154	7.00	1.90	85	800	485	4.31	5	6	3 to 4	3 to 4
2-NF-2	Pink	170–173	6.18	1.80	83	900	510	4.44	5 to 6	6	4	4
2-NF-3	Safron	175–180	6.77	1.90	80	830	494	4.36	5	5 to 6	4 to 5	4
2-NF-4	Reddish brown	165–170	6.47	1.90	89	855	530	4.14	5	5	4	4
2-NF-5	Orange	170–180	6.18	1.80	88	900	490	4.26	5	5	4	4
2-NF-6	Yellow orange	160–165	6.71	2.00	89	830	470	4.08	6	5	4	3 to 4
2-NF-7	Orange	150–160	6.40	1.80	90	865	474	4.19	5	5	4	3 to 4

[a] Amines used as diazo components: 1, aniline; 2,1-naphthyl amine; 3, *p*-toludine; 4, *p*-anisidine; 5,2-amino-5-chloro-toluene; 6, *p*-aminophenol; 7, *p*-chloroaniline.

The C and H contents (Tab. I) for both the 1-NF and 2-NF oligomers are in agreement with the proposed structures (I and II), which also emphasize the probable hetrogeneous nature of the products due to reaction proceeding of the ortho position, the more probable para position, or a combination of the two.

All the oligomeric azo-NF dyes listed in Tables II and III were soluble in solvents as ethanol, 1,4-dioxane, DMF and DMSO. As the NF condensates are the mixtures of different molecular NF oligomeric chains and traces of free naphthol, the resulting azo-NF dyes could be non-hetrogeneous and, on the premise [8–11] that simple naphthol-based azo dyes are soluble in solvants such as ether, ethanol, 1,4-dioxane, DMF and DMSO, the oligomeric azo-NF dyes were Soxhlet-extracted with ether–ethanol (1:1) to remove both the simpler dyes resulting from traces of any low molecular-weight oligomeric azo-NF dye. The values of the nitrogen content of the azo-NF dyes indicate that there may be two azo groups present per oligomer chain. This is in agreement with the estimated azo group content of samples in this series of oligomeric azo-NF dyes.

The UV-Visible spectra of the azo-NF dyes were recorded in DMF. Absorption maximum and extinction coefficients are shown in Tables II and III. It is apparent that the wavelength of maximum absorption is relatable to the azo groups in the compounds and it is observed within the region 375–525 nm, variations in λmax being attributed to structural variations in the oligomer and to the nature of arylamine used as a diazo component. The thermal stability of the azo-NF dyes was also assessed in terms of the loss in weight at different temperatures at a constant heating rate of 10°C/min in air. This showed that the azo-NF dyes began to decompose at around 190°C, with weight loss being complete at around 220°C depending on the structural variations.

The oligomeric azo-NF dyes were dyed on polyester PET and nylon-6,6 fibres at 1% depth of shade and gave the yellow to brown shades implied in Tables II and III. The dyebath exhaustion of the oligomeric dyes in the dyeing of polyester PET and nylon-6,6 fibres was low (30–50%) as compared with the values of 70–80% of simple arylazo-phenols, -cresols, -resorcinols, or -naphthols [8–11]. These difference was probably attributed to molecular size considerations. Results for the percentage fixation of the oligomeric dyes in the dyeing of the polyester PET and nylon-6,6 indicated that the oligomeric dyes showed higher values (70–90%) than simple azo dyes (60–80%).

The last fastness of the oligomeris azo-NF dyes are shown in Tables II and III. The light fastness of both the azo-1-NF and azo-2-NF dyes on polyester PET and nylon-6,6 fibres varied from moderate to good on polyester PET and good to very good on nylon-6,6, the majority of the dyes are having higher ratings. The washing fastness (neutral detergents) varied from moderate (3) to very good (5) for nylon-6,6 fibres. Compared with simpler azo-phenol dyes [8], the dyeings produced from the oligomeric azo-NF dyes had more moderate light fastness, but slightly higher washing fastness. It is of interest to note that most of the polymeric dyes previously reported [8–11], when dyed on various textiles, gave somewhat unlevel colourations. With the azo-NF dyes described in the present work, and particularly when the dyeings were carried out for relatively short periods (1.5 h on polyester PET, 45 min on nylon-6,6) and at low temperatures, level dyeings were obtained.

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