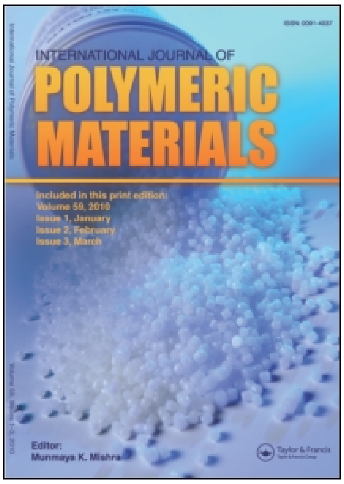

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Arylene Azo-naphthol-furfuraldehyde Oligomer Dyes (Part-2)

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A series of oligomeric acid 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 wool, silk and nylon-6,6 assessed. Dyeings on wool, silk and nylon-6,6 resulted in yellow, orange and brown to red colourations having excellent fastness to light and washing.

Keywords: Azo dyes; oligomers; properties; spectra

INTRODUCTION

Whilst naphthols are well established intermediates for the synthesis of dyes, the use of naphthol-furfuraldehyde condensates as coupling components in the formation of acid azo dyes and pigments has received no 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 acid azo dyes based on the use of naphthol-furfuraldehyde condensates as a coupling components.

EXPERIMENTAL

Materials

1- and 2-naphthols were of 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). Wool was supplied by Kiran threads, Vapi, India and Wool and Nylon-6,6 were supplied 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.

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 untill the viscous mass was obtained. The thick viscous resin was washed with large amount of water and was kept in the vacuum desicator. The yield was 75% and it was designated as 1-NF oligomer. (Fig. 1).

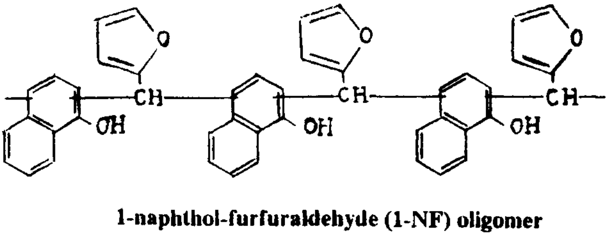
2-Naphthol-furfuraldehyde (2-NF) Oligomer

In a round bottom flask (1 lit.) a mixture of 2-naphthol (2 mole), furfural (1 mole) and potassium carbonate was heated untill 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. (Fig. 1).

Characterization data for 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



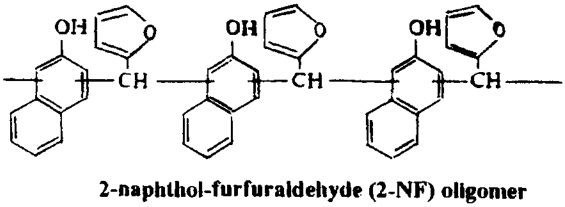


FIGURE 1 Structure of naphthol oligomers.

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 (*i.e.*, No. of azo groups per one polymer molecule) of the dyes was determined by following the method for simple azo dyes. In this method the polymer sample was reduced by $TiCl_3$ and number of azo groups were determined by calculating used $TiCl_3$ [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 Analyser at

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*)	$\bar{M}n$ *estimated by VPO*
			C		*H*			
			Cal.	*Found*	*Cal.*	*Found*		
(1-NF)	Brown	162–165	80.89	79.9	4.49	4.35	150	800
(2-NF)	Light Brown	172–174	80.89	80.58	4.49	4.40		700

Where VPO = Vapour Pressure Osmometry.

a heating rate of 10°C/min. The number average molecular weight of all the oligomeric acid dyes were estimated both by VPO and nonaqueous conductometric titration method. In VPO method the DMF was used as a solvent and benzil was used as a calibrant. The temperature was 70°C ± 0.1°C. In nonaqueous conductometric titration, pyridine was used as a solvent and NaOMe was used as a titrant. The $\bar{M}n$ (by VPO method) of 1-NF and 2-NF are represented in Table I.

Dyeing of Wool, Silk and Nylon-6,6 with Oligomeric Acid Azo-NF Dyes

A known quantity of each oligomeric azo-NF dye (Tabs. II and III) was taken into water and was adjusted at required pH. Wool, silk 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 [8].

RESULTS AND DISCUSSION

Infusible compounds of the type studied have been used as pigments rather than dyes due to their pool 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 wool 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 (~25°C) for the flow viscosity of 1-NF oligomer remained constant during this storage period. 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),

TABLE II Characterization of azo-1-NF acid dyes

Oligomeric azo-1-NF dyes **a**	*Colour*	*Nitrogen %*		*Mean No. of azo groups*	*Yield*	*$\bar{M}n$ by VPO*	λ_{max}	*log ε*	*Dyeing on wool*		*Dyeing on silk*		*Dyeing on nylon*	
		Cal.	*Found*						*LF*	*WF*	*LF*	*WF*	*LF*	*WF*
1-NF-**1**	Pink	3.73	3.81	1.94	85	1470	462.0	4.62	3 to 4	4	4	4	4 to 5	6
1-NF-**2**	Petal	4.18	4.27	1.92	88	1310	467.0	4.59	4	5	4	4	5	6
1-NF-**3**	Light Jaipur Pink	3.75	3.81	1.91	80	1470	470.5	4.46	4	5	4 to 5	4 to 5	5	5
1-NF-**4**	Pink	4.16	4.19	2.00	91	1310	474.0	4.52	4 to 5	6	3 to 4	3 to 4	5	5
1-NF-**5**	Signal Red	4.24	4.38	1.95	92	1280	487.5	4.56	4 to 5	6	4	4	5	4
1-NF-**6**	Plate Shell Pink	4.21	4.38	1.93	86	1275	360.0	4.08	3 to 4	4	4	4	3 to 4	5
1-NF-**7**	Candy Pink	4.26	4.38	1.96	84	1289	478.0	4.42	4	5	4 to 5	4 to 5	4	5

LF = Light Fastness; WF = Wash Fastness. **a** = Amines used as diazo components: **1**, H-Acid; **2**, Y-Acid; **3**, Chicago-Acid; **4**, J-Acid; **5**, Tobias-Acid; **6**, Laurents-Acid; **7**, Brooner-Acid.

TABLE III Characterization of azo-2-NF acid dyes

Oligomeric azo-2-NF dyes **a**	Colour	Nitrogen %		Mean No. of azo groups	Yield	$\bar{M}n$ by VPO	λ_{max}	log ε	Dyeing on wool		Dyeing on silk		Dyeing on nylon	
		Cal.	Found						LF	WF	LF	WF	LF	WF
2-NF-**1**	Mushroom	3.73	3.85	2.00	90	1230	469	4.61	4 to 5	5	4	5	4 to 5	5
2-NF-**2**	Chandan Light	4.18	4.25	1.95	88	1070	364	4.62	4 to 5	6	4	5	5	6
2-NF-**3**	Jaipur Pink	3.75	3.85	1.91	89	1225	472	4.46	4	5 to 6	4	5	5	6
2-NF-**4**	Bluish Pink	4.16	4.11	1.94	91	1070	511	4.62	3 to 4	5	3 to 4	4	4	5
2-NF-**5**	Tractor Orange	4.24	4.35	2.00	84	1040	480	4.49	4	5	4	5	4	5
2-NF-**6**	P.O.Red	4.21	4.35	1.91	86	1035	505	4.45	4	5	5	6	3 to 4	5
2-NF-**7**	Merrie Pink	4.26	4.38	1.93	90	1040	476	4.32	4 to 5	4	4	5	5	4

LF = Light Fastness; WF = Wash Fastness. **a** = Amines used as diazo components: **1**, H-Acid; **2**, Y-Acid; **3**, Chicago-Acid; **4**, J-Acid; **5**, Tobias-Acid; **6**, Laurents-Acid; **7**, Brooner-Acid.

which also emphasize the probable hetrogeneous nature of the products due to reaction proceeding at the ortho position, the more probable para position, or a combination of the two. All the oligomeric acid azo-NF dyes listed in Tables II and III were soluble in solvents such 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 acid azo-NF dyes could be non-hetrogeneous and, on the premise [8–11] that simple naphthol-based azo dyes are soluble in solvents such as ether, ethanol, 1,4-dioxane, DMF and DMSO, the oligomeric acid 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 acid 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 acid azo-NF dyes.

The UV-Visible spectra of the acid 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 λ_{max} being attributed to structural variations in the oligomer and to the nature of arylamine used as a diazo component. The thermal stability of the acid 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 acid 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 acid azo-NF dyes were dyed on wool, silk 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 wool, silk 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]. This difference was probably attributed to molecular size considerations. Results for the percentage fixation of the oligomeric dyes in the dyeing of the wool, silk and nylon-6,6 indicated that the oligomeric dyes showed higher values (70–90%) than simple azo dyes (60–80%).

The light fastness of the oligomeric acid azo-NF dyes are shown in Tables II and III. The light fastness of both the acid azo-1-NF and acid azo-2-NF dyes on wool, silk and nylon-6,6 fibres varied from moderate to good on wool and silk 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 acid 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 uneven 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 wool and silk, 45 min on nylon-6,6) and at low temperatures, uniform dyeings were obtained.

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