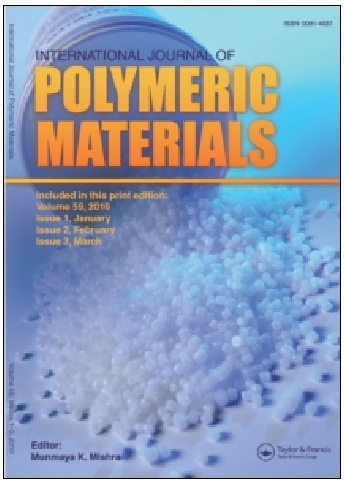

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2-Aryl Azo Benzothiazole Resorcinol Formaldehyde Oligomer Dyes

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A series of Oligomeric azo dyes has been prepared by coupling various diazonium salt of Benzothiazoles to Resorcinol-formaldehyde (RF) oligomer. They were evaluated in terms of their softening points, yield, colour, solubility and U.V.-Visible spectra. Structure property relationships are discussed and dyeing on polyester PET, Nylon-6,6 and wool assessed. Dyeing on polyester, Nylon-6,6 and wool resulted in yellow, Orange and brown to red colourations having excellent fastness to light and washing.

Keywords: Azo dyes; polyester PET; Nylon-6,6; wool; light and washing fastness

1. INTRODUCTION

Whilst Phenol/Naphthols are well established intermediates for the synthesis of dyes. The use of Resorcinol-formaldehyde condensates as coupling components in the formation of azo dyes and pigments have received little attention. However, the use of phenolic resins as 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 author (HSP) recently studied the oligomeric dyes in this direction [4–6]. The present work compries some azo dyes based on the use of Resorcinol-formaldehyde condensates as a coupling components.

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2. EXPERIMENTAL

2.1. Materials

Resorcinol was analytical grade and was crystalised from ethanol prior to use. Formaldehyde and Oxalic acid were of laboratory grade. For diazonium salt preparation various Benzothiazoles were used (see foot note Tab. I).

Polyester (PET) (100%) was supplied by Mafatlal fabrics Ahmedabad India, and Nylon-6,6 and wool were obtained from local market.

2.2. Synthesis of Resorcinol-Formaldehyde Oligomer

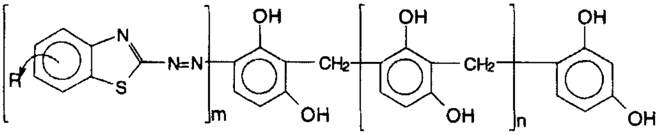
Resorcinol-Formaldehyde (RF) oligomers were prepared by the method reported by one of the author (HSP) [4]. The specificational RF oligomers are as follows:

Colour and physical state: Brown thick liquid.

Effect at Room Temperature: Hardened after six months stored well in vaccum desiccator.

$\overline{Mn} = 625$, estimated by VPO, $30 \pm 1°C$, Acetone

GENERAL STRUCTURE



Where $m = 2$ and $n = 2$ or 3. Where R is (1) R = H, (2) R = 4-NO_2, (3) R = 6-NO_2, (4) R = 4-OCH_3, (5) R = 6-OCH_3, (6) R = 6-CH_3, (7) R = 4-Cl, (8) R = 6-Cl, (9) R = 4-CH_3.

2.3. Synthesis of Various 2-Amino Benzothiazoles

0.1 mole aryl amine and 0.22 mole ammonium thiocyanate was taken in solution of 0.1 mole bromine in acetic acid and the reaction was carried out for 24 hours and the product was isolated from HCl and

TABLE I Characterisation of Oligomeric AZO-RF Dyes

Oligomeric Azo-Rf					*Mean*				*Dyeing on polyester*		*Dyeing on nylon*		*Dyeing on wool*	
Dyes[a]	*Colour*	*Softening point (°C)*	*Nitrogen found (%)*	*Sulphur found (%)*	*number of Azo*	*Yield (%)*	$\overline{Mn}$ *by VPO*	λ_{max} *(nm)*	*Light fastness*	*Washing fastness*	*Light fastness*	*Washing fastness*	*Light fastness*	*Washing fastness*
AN-1	Light brown	112	8.9	6.7	1.9	85	949	456.5	4	5	4	4	4	4
AN-2	Brown	128–130	10.8	6.2	1.93	75	1039	350	3–4	4–5	3	4–5	3	3–4
AN-3	Orange	113–115	10.9	6.3	1.94	79	1030	357	3–4	4–5	3	4–5	3–4	3
AN-4	Yellow	123–125	8.3	6.3	1.95	80	1009	456	4–5	4–5	4	4–5	3	4
AN-5	Reddish brown	122	9	6.4	1.9	85	1000	467	3–4	4–5	4	4	4	4–5
AN-6	Orange	132–135	8.6	6.5	1.94	82	977	461	4	4–5	3–4	4	3–4	4
AN-7	Light yellow	110–112	8.3	6.3	2.00	77	1017	468.5	3	5	3–4	4–5	4	4
AN-8	Brown	118–120	8.4	6.3	1.96	79	1010	459	3	4–5	3	4	4	3–4
AN-9	Orange	125–127	8.7	6.6	1.98	80	970	396	4	4–5	3	4–5	4	4

[a] Amines are used as a diazo components. (**1**) 2-Amino Benzothiazole, (**2**) 2-Amino-4-Nitro Benzothiazole, (**3**) 2-Amino-6-Nitro Benzothiazole, (**4**) 2-Amino-4-Methoxy Benzothiazole, (**5**) 2-Amino-6-Methoxy Benzothiazole, (**6**) 2-Amino-6-Methyl Benzothiazole, (**7**) 2-Amino-4-Chloro Benzothiazole, (**8**) 2-Amino-6-Chloro Benzothiazole, (**9**) 2-Amino-4-Methyl Benzothiazole.

Ammonia treatment. The product was recrystallised from rectified spirit [12–14].

2.4. The Diazotization of Variously Substituted 2-Amino Benzothiazole [15]

The substituted 2-Amino Benzothiazole used were diazotised using $NaNO_2$ and sulphuric acid mixture at 0–5°C temperature.

2.5. Synthesis of Oligomeric Azo Resorcinol-Formaldehyde Dyes

RF 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 (*i.e.*, Benzothiazole derivative) was added to it dropwise whilst the maintaining the temperature at 0°C and pH 10–10.5. After coupling was complete the reaction mixture was stirred for one hour at 0°C and then acidified to pH 5.5. The precipitated product was filtered wash with water, dried and soxhlet-extrated with ether to remove any mono azo dye resultant from the presence of any residue Resorcinol in the oligomers.

2.6. Characterisation

Elemental analysis of RF oligomers and oligomeric azo-RF dyes was carried out on an elemental analyser (Carlo Erba, Italy). The mean number of azo groups of the dyes was determined by known methods [4–7]. Visible spectra were recorded on Backman DK-2A spectrophotometer and the thermal stability of the dyes were assessed on a Du Pont 951.

Thermal 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 non-aqueous conductometric titration method. The Mn (by VPO method) of RF are represented as stated above.

2.7. Dyeing of Polyester PET, Nylon-6,6 and Wool with Oligomeric Azo-RF Dyes

A known quantity of each oligomeric Azo-RF dyes (Tab. I) was taken into DMF, together with the same quantity of Dodamal (dispersing agent), 2 – 3 drops of wetting agent (2% lauryl sulphate) solution and dispersion of the azo-RF dye was the prepared using Ultrasonic Vibration of two hours polyester PET and Nylon0-6,6 and wool (2.0 gm) were coloured at 2% depth using a liquor ratio 1:50 and dyeing temperature for polyester 130°C, nylon 90°C and wool 90°C. Fastness properties of the dyes were determined according to recognized procedures [5 – 8].

3. RESULT AND DISCUSSION

Infusible compounds of type studied have been used as pigments rather then dyes due to their poor dye abilities [6 – 9] Resorcinol-Formaldehyde oligomers are known to have poor dye ability and it was therefore attempted to obtained oligomers of low molecular weight from the condensation of Resorcinol with Formaldehyde.

Phenol – formaldehyde oligomers can be utilized in various application and many synthetic methods for their formation are available [7 – 10]. The synthesis of Resorcinol-formaldehyde oligomers has received less attention. To provide suitable oligomers for this present study a number of variables in the synthesis *i.e.*, molar ratio on polyester PET, Nylon and wool of reactants, temperature, catalysts and reaction time were optimized. The RF oligomer was obtained as a thick liquid which remained in this form even after six to seven months of storage in vaccum desiccator. The effux time at room temp. (~ 32°C) for the flow viscocity of RF oligomer remained constant during this storage period.

The C and H contents for Resorcinol-formaldehyde oligomers are in agreement with proposed structure which also emphesize the probable heterogenous nature of the products due to reaction proceeding of the ortho position the more probable para position or a combination of two.

All the oligomeric Azo-RF dyes listed in Table I were soluble in solvent as ethanol, 1:4 dioxane, DMF and DMSO. As the RF condensates are the mixture of different molecular RF oligomeric chains and traces of free Resorcinol. The resulting Azo-RF dyes could be nonheterogeneous and on the premise [8 – 11] that simple Resorcinol based azo dyes are soluble in solvent such as ether, ethanol, 1:4 dioxane, DMF and DMSO. The oligomeric Azo-RF 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-RF dye. The values of Nitrogen content of the Azo-RF dyes indicate that there may be two azo group present per oligomer chain. This is in agreement with the estimated azo group content of samples in this series of oligomeric Azo-RF dyes.

The U.V.-Visible spectra of the Azo-RF dyes were recorded in DMF absorption – maximum is shown in Table I. 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 from table variations in λ_{max} being attributed to structural variations in the oligomers and to the nature of Benzothiazole amine used as a diazo component. The thermal stability of the Azo-RF dyes was also assessed in terms of the loss in weight at different temperatures at the constant heating rate of 10°C/mm in air. This showed that the Azo-RF 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-RF dyes were dyed on polyster PET an Nylon-6,6 and wool fibres at 2% depth of shade and gave the yellow to brown shades implied in Table I. The dyebath exhaustion of the oligomeric dyes in the dyeing of polyester PET and Nylon-6,6 and wool fibres was low (30 – 40%) as compared with the values of 60 – 70% of simple aryl azo phenols, cresol, naphthols [8 – 11]. This difference was probably attributed to molecular size consideration results for the percentage fixation of the oligomeric dyes in the dyeing of the polyester PET, Nylon-6,6 and wool indicates that oligomeric dyes showed higher values (70 – 80%) than simple azo dyes (60 – 70%).

The fastness Properties of the oligomeric Azo-RF dyes are shown in Table I. The light fastness of Azo-RF dyes on polyester PET and Nylon-6,6 and wool fibres varied from moderate to good on polyester PET and good to very good on Nylon-6,6 and good to wool fibre. 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 dyeing produced from the oligomeric Azo-Rf 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-RF dyes described in the present work and particularly when the dyeings were carried out for relatively short periods (1.5 hr on polyester PET, 45 min on Nylon-6,6, 45 min on wool) at low temperatures level dyeing were obtained.

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