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ORIGINAL ARTICLE

Disperse dyes based on 2-aminothiazole derivatives for cellulose triacetate fabric

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2-Amino-4-(*p*-nitrophenyl)-5-nitrothiazole;
Cellulose triacetate;
Dyeing;
Exhaustion;
Fixation;
Fastness

Abstract A range of azo disperse dyes was prepared by coupling diazotized 2-amino-4-(*p*-nitrophenyl)-5-nitrothiazole with various substituted arylamines. Spectral properties in the infrared and visible range of the dyes obtained were investigated. All the dyes, when applied on cellulose triacetate fabric as 2% shade, showed fairly good to very good light fastness and very good to excellent fastness to washing, perspiration, rubbing and sublimation. All the dyes gave a wide range of reddish brown to indigo shades with very good depth and levelness on fabric. The purity of dyes was checked by thin layer chromatography. The percentage dyebath exhaustion and fixation on fabric was reasonably good and acceptable.

1. Introduction

Monoazo disperse dyes with thiazole diazo components have been intensively investigated to produce bright and strong colour shades ranging from red to greenish blue on synthetic fiber. These results led to commercial products to replace the conventional azobenzene disperse dyes (Colour Index, 1971). Most heterocyclic dyes of technical interest for application to textiles are derived from diazo components consisting of five-membered rings containing one sulphur heteroatom and to which a diazotizable amino group is directly attached, the ring may also possess one or more nitrogen heteroatoms. The discovery of the fusion reaction between *p*-toluidine and sulphur to give dehydrothio-*p*-toluidine in 1887 constitutes the beginning of thiazole dyestuff technology. Colour Index described various basic, direct, vat and disperse dyes wherein thiazole nucleus occurs (Annen et al., 1987).

Before 1950, almost all the disperse blue dyes used were prepared from the anthraquinone class and had the limitations of poor dischargeability and sensitivity to oxide of nitrogen. Derivative of 2-aminothiazole has a long history of use as heterocyclic diazo components for disperse dyes (Shuttleworth and Weaver, 1990). Blue dischargeable monoazo derivatives based on 2-amino-5-nitrothiazole caught the attention of dye chemists in the 1950. With colourants (Hu et al., 1987) such as C.I. Disperse Blue 339 having been produced commercially since then, 2-aminothiazole containing nitro groups are prized for their bathochromism and high tinctorial strength relative

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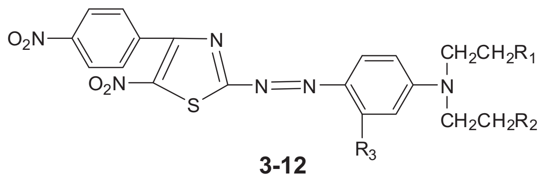
to their carbocyclic analogues (Schwander, 1982). These properties, which have aided the rise to prominence of such dyes as replacement for blue anthraquinone colourants (Egli, 1991) were first reported by Dickey nearly 40 years ago (Dickey et al., 1959). 2-Amino-5-nitrothiazole could be used to produce bright blue dyes with adequate light fastness combined with excellent dischargeability, gas fastness and dyeability on hydrophobic fabric. The commercial success of dyes for cellulose triacetate, which were derived from 2-amino-5-nitrothiazole, resulted in considerable interest in this class of dyes. Early dyes showed moderate light fastness on cellulose triacetate and polyesters, and light fastness on polyamides was very poor. Dyes with increased light fastness and/or sublimation fastness were prepared from aniline type coupling components containing one or more *N*-alkyl groups substituted with cyano (Gosei Senryo Gijutsu Kenkyu Kumiai, 1983a), amylcarbonyloxy (Gosei Senryo Gijutsu Kenkyu Kumiai, 1983b), alkoxy (Mitsubishi Chemical Industries Co. Ltd., 1979a,b), sulphato (Sumitomo Chemical Co. Ltd., 1981), diphenylamine (Erwin et al., 1991), pyridinium (Parton, 1978), dicarboximide (Weaver and Straley, 1970), l-naphthylamine (Modena and Risaliti, 1977) and *N*-alkyl-1,2,3,4-tetrahydroquinolines (Gosei Senryo Gijutsu Kenkyu Kumiai, 1984) were used as coupling components. These coupler types have the advantages of providing dyes, which have a neutral or green cast when exposed to artificial light, whereas the corresponding dyes from *N*-alkylaniline couplers have an extremely red cast. The improved fastness to light and sublimation provided by 3-acylaminoaniline type coupling components was not overlooked and dyes were patented (Nippon Kayaku Co. Ltd., 1979; Peter, 1979; Mitsubishi Chemical Industries Co. Ltd., 1979a,b; Gosei Senryo Gijutsu Kenkyu Kumiai, 1982). Greenish blue dyes can be prepared by choosing a coupler containing electron donating groups such as 5-acetamido-2-methoxyaniline derivatives. Additional early work on the 2-thiazolylazo dyes resulted in violet dyes from 2-amino-4-trifluoromethyl-5-carbalkoxythiazole (Towne and Hill, 1956), 2-amino-5-alkylsulphonylthiazole (Merian, 1961), 4-halo-5-formylthiazole (Egli, 1979) and even more bathochromic dyes from 2-amino-4-alkylsulphonyl-5-nitrothiazole (Towne et al., 1958).

During the last 15 years, the level of interest as indicated by the patent literature has grown in the field of thiazolylazo disperse dyes (Tsien et al., 1995; Sens and Etzbach, 1994; Beckmann et al., 1994). There has been a considerable growth in the volume of data reporting outside of patent literature (Sekar, 1994; Peters and Gbadamosi, 1995; Bello et al., 1995; Desai et al., 1995; Bello, 1995; Griffihs and Riepl, 1998; Chikhalia and Desai, 1998; Rangnekar et al., 1998; Hallas and Choi, 1999; Towns, 1999; Bajpai et al., 2000; Rangnekar and Malankar, 2000; Elkholy et al., 2001; Helal, 2001, 2004; Yao, 2001; Sonawane and Rangnekar, 2002; Georgiadou and Tsatsaroni, 2002; El-Mossalomy and Ibrahim, 2002; Kaparir et al., 2004; Saylam et al., 2008; Helal et al., 2008; Abdet-Latif et al., 2009). Earlier we had studied the disperse dyes based on 2-aminothiazole derivatives (Maradiya and Patel, 2000, 2001a,b,c,d,e, 2002a,b, 2003; Maradiya, 2002, 2004a,b, 2009, 2010).

The encouraging results prompted to extend the study on thiazole moiety. Hence, a series of monoazo dyes of general formula shown in Fig. 1 were synthesized and tested as disperse dyes for cellulose triacetate fabric. In addition to the characterization of the dyes, an evaluation of their technical properties and a colour assessment was performed.



3-12

Figure 1 General structure of dyes **3**–**12**; **3** $R_1 = R_2 = OH$, $R_3 = H$; **4** $R_1 = R_2 = OAc$, $R_3 = H$; **5** $R_1 = R_2 = OH$, $R_3 = H$; **6** $R_1 = R_2 = OH$, $R_3 = Cl$; **7** $R_1 = R_2 = OH$, $R_3 = NHAc$; **8** $R_1 = R_2 = OAc$, $R_3 = CH_3$; **9** $R_1 = R_2 = Cl$, $R_3 = H$; **10** $R_1 = R_2 = CN$, $R_3 = H$; **11** $R_1 = R_2 = CN$, $R_3 = CH_3$; **12** $R_1 = R_2 = CN$, $R_3 = Cl$.

2. Experimental

2.1. Materials and methods

All of the chemicals used were of commercial grade and were further purified by crystallization and distillation. All solvents used were either of analytical grade or redistilled commercial grade.

*2.2. Preparation of 2-amino-4-phenylthiazole (**1**)*

The title compound was synthesized by the following method.

Bromine (160 g, 2.0 mol) was added dropwise with stirring to acetophenone (120 g, 1.0 mol) and thiourea (152 g, 2.0 mol). The mixture was heated overnight on the steam bath, diluted with 2.5 l hot water (85 °C), stirred, and filtered hot. The filtrate was cooled, made slightly basic with concentrated ammonium hydroxide, and filtered. The solid residue recrystallized from ethanol gave 126 g (71%) yield of 2-amino-4-phenylthiazole, m.p. 143–144 °C, literature m.p. 144–145 °C (see Scheme 1).

*2.3. Preparation of 2-amino-4-(p-nitrophenyl)-5-nitrothiazole (**2**)*

The title compound was synthesized by the following method.

To 47 ml (0.88 mol) of concentrated sulphuric acid in a 100 ml three-necked flask, 8.8 g (0.05 mol) of 2-amino-4-phenylthiazole was added at 10–14 °C with stirring. The stirred solution was treated at 3–5 °C over a period of 30 min with a mixture of 7.0 g (0.11 mol) of fuming nitric acid (sp. gr. 1.49–1.50) and 6 ml of concentrated sulphuric acid, stirring was continued for 15 min at this temperature. After the stirred reaction mixture warmed to room temperature, it was allowed to stand overnight, protected from moisture and the reaction mixture was poured into 500 ml of an ice–water mixture, yielding a reddish solid, which was collected on a filter. The product was washed with cold water, then with saturated sodium acetate solution until it was neutral to Congo Red paper and then the product was washed with water. The crude product has m.p. 221–226 °C, weight 10.5 g (78%). A sample recrystallized from a benzene–ethyl alcohol mixture melted with decomposition at 249–251 °C, literature m.p. 250–251 °C (see Scheme 1).

2.4. Preparation of 2-[4′-[N,N-bis(2-hydroxyethyl)amino] phenylazo]-4-(4″-p-nitro phenyl)-5-nitrothiazole (3)

Synthesis of **3** involves two steps.