Asian Journal of Chemistry; Vol. 23, No. 2 (2011), 717-719

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Nano Silicagel Supported by Phosphoric Acid for Synthesis of Azoic Dyes Based on Naphthol

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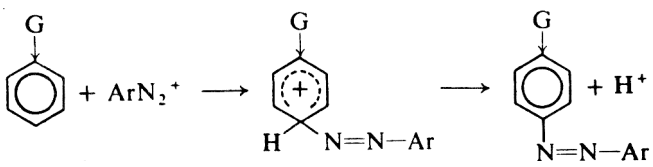
(*Received*: 11 March 2010; *Accepted*: 30 September 2010) AJC-9146

Synthesis of some azoic dyes based on α-naphthol requires special conditions such as low temperature, use of dense acids and high pressure. Aside from great expenses and difficulties in preparing conditions of solution, depreciation of dye-making devices due to the application of dense acids is regarded as another problem in this system. This paper tries to use a new method to remove these difficulties. Producing dyes using solid acids appears to be more effective than applying aqueous ones. One of the advantages of this system is the reduction of device corrosion, prevention of any damaging to the environment, an increase in efficiency and simplicity of the method. Applying this method, some azoic dyes based on α-naphthol, in room temperature and atmosphere pressure, were synthesized in high per cent and in a short time. The structure of the synthesized dye was investigated by FTIR. The synthesized dye was then used for dyeing some textile fibers in order to identify the best condition for dye absorbing and for studying the quality of these dyes on fabrics. Consequently, washing fastness test, staining test, light fastness were done. The results show that synthesized dyes are placed in acidic dyes category.

Key Words: α-Naphthol, Diazonium salt, Nano silicagel, Azoic dye.

INTRODUCTION

Azoic dyes are the largest group of dyes that contain more than 50 % of produced dyes of the world. -N=N- group has low alkaline properties but the alkaline properties of this group are not more than those of water, that it is because of the resonance and implant effect of benzene cycles[1]. In recent years, great efforts have been made to replace anthraquinone dyes by azoic ones with the same properties. The reaction of coupling aromatic component to diazonium salts occurs in neutral or low acidic places in water and solvents. On the other hand, α-naphthol and β-naphthol (and same components), prefer to couple to diazonium salts in alkaline place under the same conditions (**Scheme-I**)[2,3].



Scheme-I: Coupling of aromatic diazonium salt with benzene group

Diazonium cation can both chemically and electrochemically reduce. Most of the components have the ability of being exposed to oxidation/reduction and attack of electrophilic/electrophobic simultaneously. This ability of diazonium cations is used for electrophilic reaction[4]. Solid acids have many advantages over other catalyzers, such as reduction of reactor and container corrosion and prevention of the environmental problems. Solid acids are able to prevent the production of derivative products and pleonastic materials or reduce them to the lowest possible point[5]. In this paper, by using silicagel in the scale of nano supported by dry phosphoric acid as an acidic environment, diazonium salt was produced.

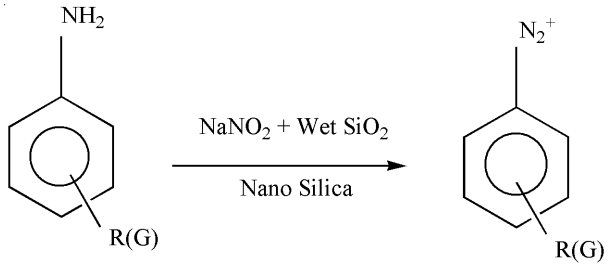
EXPERIMENTAL

The materials which were used in this study were dense phosphoric acid (H_3PO_4), sodium nitrite ($NaNO_2$), silicagel, nano silicagel 20 (Aldrich), aminobenzoic acid, α-naphthol ($C_{10}H_{10}O$), acetone (C_3H_6O).

Preparation of the solid acidic base: Phosphoric acid (9.8 mL) was dried by sodium sulphate and P_2O_5. Mean while, 5 g nano silicagel is put in the oven for 1 h in 80-100 ºC. Then, it was to be blended in a vacuum concal flask for 10 h in order to support dry phosphoric acid on activated nano silicagel. The upcoming white powder was nano silicagel supported by phosphoric acid[6].

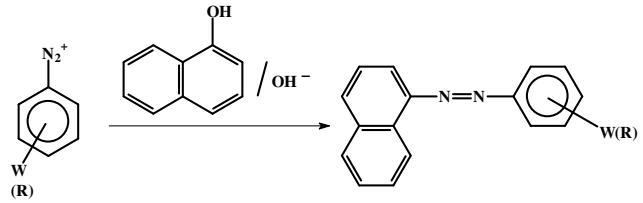
Synthesis of diazonium salt: 10 mmol of primary material (aromatic amine) was weighted and solved in acetone so that a yellow aqueous solution revealed itself. Then, 10 mmol sodium nitrite was weighted and added to it. 0.05 g of prepared nano

silicagel (supported by phosphoric acid) was added afterwards. In the next step, the solution was well blended. To perform the aimed reaction, 0.05 g wet silicagel was added in order to make diazonium salt (**Scheme-II**)[7,8].



Scheme-II: Diazonium creation

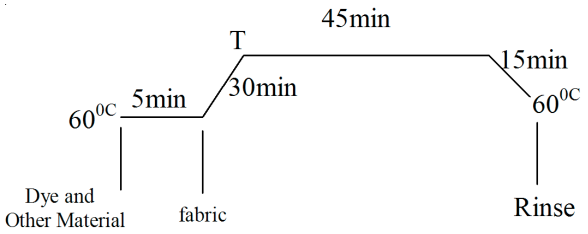
Azo coupling: 1 g of α-naphthol was measured and blended with 5 % sodium hydroxide. Then it was volumed up to 100 mL by addition of distilled water. 2 mL alkaline α-naphthol was added to aqueous solution of diazonium salt. The next step was blending. During 30-90 s the dye of azoic group revealed itself which had a red-base colour. The synthesized dyes were listed in Table-4. **Scheme-III** illustrates the coupling of α-naphthol with diazonium salt[9,10].



Scheme-III: Diazonium coupling with α-naphthol

Dyeing process: In order to further investigate the synthesized dyes, polyester, acrylic, nylon and acetate were dyed with synthesized dyes based on the graph in **Scheme-IV** and Table-1. The dyeing temperature for polyester was 130 and 75 ºC for acetate. Washing and light fastness test were done after dyeing[11].

All dyed samples were washed according to the functions presented in Table-2 and their dyeing wastewater and washing wastewater were kept for the study of dye exhaustion.



Scheme-IV: Dyeing graph

TABLE-1
DYEING RECIPE

Used material	Amount
Dye	1.5%
Acetic acid	10 % (pH = 5.5)
L:R	40:1

TABLE-2
WASHING BATH RECIPE AFTER DYEING

Used material	Amount
Detergent	3 %
Temperature	60 ºC
Time	20 min
L:R	30:1

Fastness testing: Washing fastness of the dyed samples was tested according to the ISO 105-CO3 method. The samples were washed in a standard soap solution at 60 ºC for 0.5 h, keeping liquor to material ratio as 1:50. Light fastness was tested according to the ISO 105-BO2 method. The dyeing were exposed to light[12].

RESULTS AND DISCUSSION

Structure of synthesis dyes: Fourier transition infrared spectra (FTIR) of synthesized dye are shown in Figs. 1 and 2 By the peaks of these figures, it is possible to obtain the structure of synthesized dyes as it has been depicted in Table-3.

In Fig. 1, the peak of 3376 cm^{-1} is for -OH functional group in sample A-1. The peaks of 1601-1409 cm^{-1} refer to aromatic cycles and peak of 1543 cm^{-1} is for -N=N- functional group. 1221 cm^{-1} shows C-N functional group and 848 cm^{-1} shows -COOH functional group in compound.

TABLE-3
DIAZO DYES BASE ON α-NAPHTHOL

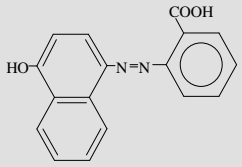
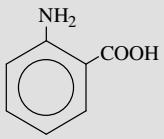
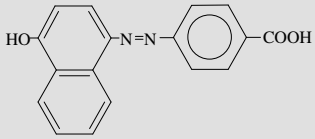
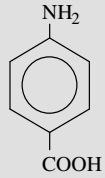
Yield (%)	Product	Amine name	Structure of amine	Dye code
95		2-Amino benzoic acid		A-1
95		4-Amino benzoic acid		A-2

TABLE-5
RESULTS OF LIGHT AND WASHING FASTNESS AND STAINING

Dye code	Good type	Light fastness	Washing fastness	Staining test					
				Wool	Acrylic	Nylon	Polyester	Cotton	Viscose
A-1	Nylon	5	4.0	4.0	4.5	4.0	3	3.0	3.0
	Acrylic	7	4.5	4.5	4.5	4.0	4	3.0	3.4
	Polyester	5	4.0	4.0	4.0	4.0	4	4.0	4.0
	Acetate	3	4.0	4.0	4.5	4.0	3	3.0	3.0
A-2	Nylon	6	4.5	4.0	5.0	4.5	4	4.0	5.0
	Acrylic	7	5.0	5.0	5.0	5.0	5	4.5	5.0
	Acetate	6	5.0	5.0	5.0	5.0	5	4.5	5.0

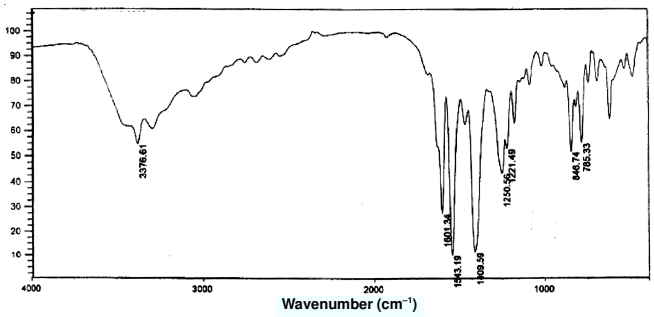


Fig. 1. FTIR of sample A-1 (primary aromatic amine name: 2-aminobenzoic acid/coupling function: α-naphthol)

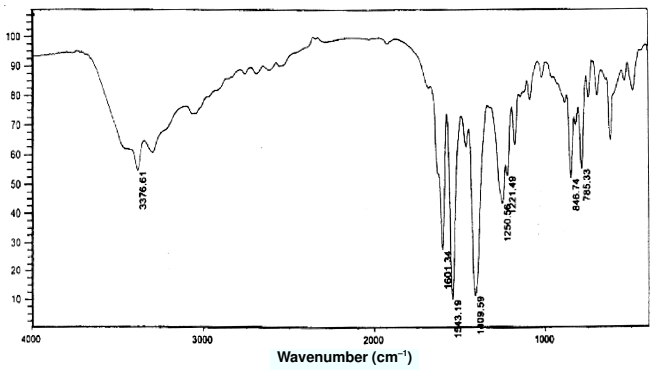


Fig. 2. FTIR of sample A-2 (primary aromatic amine name: 4-aminobenzoic acid/coupling function: α-naphthol)

Peaks of Fig. 2 show some functional groups of sample A-2. The peaks of 3381 cm^{-1} are for -OH functional group, 1406-1599 cm^{-1} for aromatic cycles, 1543 cm^{-1} is for -N=N- functional group and 849 for -COOH functional group.

Dye ability of synthesized dyes: Polyester, acetate, nylon and acrylic were dyed with 4 synthesized dyes. Afterwards, the washing wastewater was investigated by the absorbing spectrophotometer device. Using the results of spectroscopy and calibration equation, dye concentration of washing and dyeing wastewater was calculated. With these results and knowing the primary amount of dye bath and with regard to eqn. 1, exhaustion of samples can be calculated. The results are presented in Table-4.

TABLE-4
SYNTHESIZED DYE ABSORPTION EQUATIONS AND EHAUSTION

Absorption equations	Acetate	Acrylic	Polyester	Nylon	Sample
	Exhaustion (%)				Dye
Abs = 10.84 × C + 0.05	58.20	56.80	47.50	79.60	A-1
Abs = 3.31 × C – 0.02	29.20	27.60	28.10	53.10	A-2

$$E\,(\%) = \left[A - \frac{(B+C)}{A} \right] \times 100 \quad (1)$$

A = primary dye concentration in dye bath, B = concentration of dye in dyeing wastewater, C = concentration of dye in washing wastewater.

With regard to the good dye exhaustion of samples, A1 and A2 dyes, on nylon, they can be grouped in acidic dyes. -COOH functional group of these dyes demonstrales their anionic nature. Further, the results from washing fastness and staining test of these dyes on the different fabrics (Table-5) show that the latter dyes are acidic.

Dyed samples were tested for light and washing fastness to check for the study quality dye fastness of samples. The results are shown in Table-5.

Conclusion

Synthesis of some azoic dyes based on α-naphthol requires special conditions. Not only does this lead to high expenses and many difficulties in special conditions of reaction, but also depreciation of dye-making devices due to the application of dense acids is regarded as another problem in this system. To overcome these problems, it is common to use solid acids because of their benefits.

Some azo dyes based on α-naphthol can be provided by the use of silicagel base (supported by phosphoric acid) in room temperature, with a high output, in a short time and above all, with no use of dense liquid acids.

The results of the tests identified different functional groups and structures of dyes that can be grouped in the acidic dye category. It could be drawn from the results that using this new method in order to synthesize the dyes based on α-naphthol is economical and harmless to the environment due to the elimination of dense liquid acids.

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