

## **Effect of Benzoylation on Properties of Acid Dyes Derived from H-Acid on Nylon 6. 6**

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**ABSTRACT:**Twelve dyes were synthesized by diazotizing six primary aromatic amines, which were subsequently coupled with H-acid(1-naphthol-8-amino-3,6-disulphonic acid).Each of these amines was also diazotized and coupled with benzoylated H-acid.The colours obtained were mainly pink, red and orange. The various dyes synthesized were applied onto a Nylon 6.6. The molecular weights of the dyes, as well as their molar extinction coefficients were calculated and their solubility in water was determined. Their maximum absorption wavelength was measured in water. The fastness properties of the dyes were also investigated. They had good fastness properties.Benzoylated acid dyes give brighter shades and high wet fastness properties on nylon 6.6, due to their high molecular weight. They also have good exhaustion properties.

**Key words:**Acid dye, Diazotization, Benzoylation, Exhaustion and Extinction coefficient.

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### **I. Introduction**

Acid dyes are water soluble anionic dyes and are applied primarily to fibres such as wool, silk, and nylon, all of which contain basic groups. Although, some acid dyes stain cellulose fibre considerably, none are sufficiently substantive to be of commercial value for colouring cellulosic material [1].

Chemically, the acid dyes consist of azo(including metal-complex azo)compound.The colour range is very bright, although the metal complex types are relatively dull.They are directly substantive to wool, silk, nylon from neutral or acid dye baths.The dyes have good migrating properties but low wet fastness. The ability of acid dyes to give level dyeing on nylon material is influenced not only by the factors common to all dye-fibre combination but, in particular, by physical and chemical variations in the fibre.[2]

The problem of achieving level dyeing, free from ‘barreness’ on continuous filament materials is still considerable.Further problems which may be encountered include relatively poor build up and incompatibility in mixtures, arising from low saturation values and differences in anion affinity. [3]

The nylon fibres are long –chain polymers with reoccurring amide (-CONH-) groups as an integral part of the main chain [1]. The amineend – groups are the functional sites in nylon for the adsorption of anionic dyes [3, 4].

### **II. Materials and Methods**

#### **General information**

All the chemicals used in the synthesis of the dyes were of analytical grade and were used without further purification. Melting points were determined by the open capillary method. The Visible absorption spectra were measured using a Milton Roy spectrophotometer 21D.

### **III. Synthesis of Dyes**

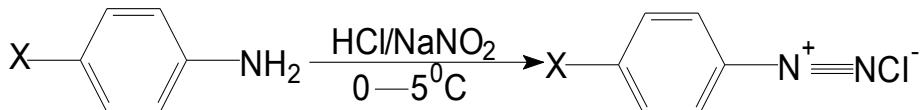
The process simply involves diazotisation and coupling. The procedure for diazotisation varies with basicity of the aromatic amine used before the coupling[3]. The six primary aromatic amines used were 4-amino benzoic acid ( $I_1$ ), sulphanilic acid ( $I_2$ ), aniline ( $I_3$ ),para-anisidine( $I_4$ ), 4-chloroaniline ( $I_5$ )and 4-nitroaniline( $I_6$ ).

#### **Diazotisation of aniline, p- anisidine and 4 - aminobenzoic acid:**

The amines (0.0365mol, 0.4g aniline) and (0.00365mol, 0.5g p-anisidine and 4- aminobenzoic acid) were respectively dissolved in concentrated HCl (0.09125moles, 3.33ml)and cooled to 0-5°C in an ice bath equipped with a magnetic stirrer. Sodium nitrite (0.7g, 0.00673 moles) dissolve in 10ml of distilled water was added drop wisely over a period of 30 minutes while stirring for another 45 minutes. Urea (0.5g) was then added to the mixture and stirring was continued for another 10 minutes to achieve complete diazotization.

#### **Diazotization of p-chloro aniline, sulphanilic acid and p- nitro aniline:**

The amine (0.0365mol, 0.5g) was dissolve in hot concentrated HCl (0.09125moles, 3.33ml) and cooled very rapidly to 0-5°C in an ice bath equipped with a magnetic stirrer by addition of ice to obtain a fine suspension of the amine-hydrochloride. Sodium nitrite (0.7g) dissolve in 10ml of distilled water was added drop wisely over a period of 30 minutes while stirring for another 45 minutes. Urea (0.5g) was then added to the mixture and stirring was continued for another 10 minutes to achieve complete diazotization.

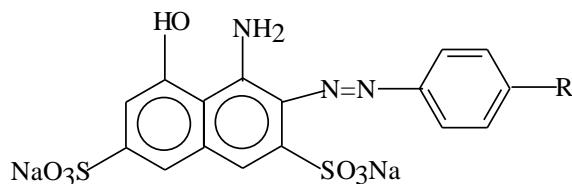


X = COOH, SO<sub>3</sub>H, H, OCH<sub>3</sub>, Cl, NO<sub>2</sub>

Scheme showing diazotisation of primary aromatic amine

**Synthesis of dyes I<sub>1</sub>- I<sub>6</sub>: Coupling of the diazotised amines to H-acid(1-naphthol-8- amino-3, 6-disulphonic acid).**

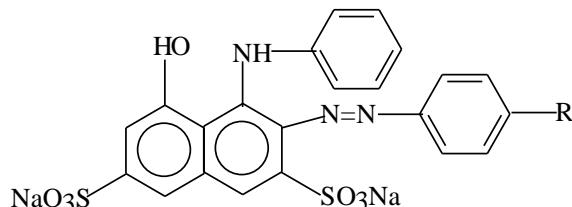
0.05moles(14.8g) of H-acid was dissolved in 50cm<sup>3</sup>of distilled water containing 0.5g of sodium hydroxide (NaOH) and 5.0g of sodium carbonate(Na<sub>2</sub>CO<sub>3</sub>) in 250ml beaker. The prepared solution of H-acid was coupled with diazotised solution of the various amines(immersed in an ice bath) drop wisely over a period of 30minutes and the temperature maintained at 0-5°C. Stirring was then continued for another 60 minutes. The resultant dye produced was filtered and dried at 50 °C in an electric/drying oven. The resultant dye yieldwas determined by weighing on a weighing balance.



General structure of dyes derived from H-acid.

**Synthesis of dyes II<sub>1</sub>- II<sub>6</sub>: Coupling with n-benzoyl H-acid (n-benzoyl-1-naphthol-8- amino-3, 6-disulphonic acid).**

The process is the same as described in (B) above except that the various diazotised amines were coupled to benzoylated H-acid which was used as the coupling component.



General structure of dyes derived from benzoylated H-acid

**Dyeing and fastness properties measurement**

The dyes synthesised were applied on Nylon 6.6 fabric using the 'dye master machine' to ensure efficient stirring in an unsealed tube. 1% stock solution of each dye was prepared by dissolving 1g of dye sample in 100ml of distilled water. The volume of dye required was 1ml to give 2% depth of shade on weight of fabric. This was done at a pH of 2-3 and a dye bath liquor ratio of 50: 1. The percentage exhaustionwas determined by the usual method [4],wash fastness properties were determined by the standard (I. S. O. 3) procedure[6] and [7]. The results are summarized in Table 3.

#### IV. Results and discussion

**Synthesis of dyes**

Six dyes were obtained using H-acid as coupling component (I), while six dyes were also obtained using N-Benzoyl H-acid as coupling component (II).The different dyes synthesised possess distinct characteristics.The structures of the dyes synthesised are planar thus,can lie flat against the polymermolecules.Their planarityaccounts for their good substantivity for hydrophobic fibres. They are also soluble in water due to the presence of solubilising groups [8].

**Table 1:** Physical characteristics of the dyes

Dyes	Molar mass(gmol <sup>-1</sup> )	Solubility in water	%yield	Colour of dyed material
I <sub>1</sub>	468	soluble	91.2	Purple
I <sub>2</sub>	504	soluble	71.3	Pink
I <sub>3</sub>	424	sparingly soluble	85.3	Orange
I <sub>4</sub>	438	soluble	62.0	Pink
I <sub>5</sub>	458.5	soluble	89.0	Purple
I <sub>6</sub>	469	soluble	83.0	Purple
II <sub>1</sub>	572	soluble	92.4	Red
II <sub>2</sub>	608	soluble	98.0	Red
II <sub>3</sub>	528	soluble	85.0	Pink
II <sub>4</sub>	544	soluble	82.0	Purple
II <sub>5</sub>	562.8	soluble	89.0	Red
II <sub>6</sub>	573	soluble	83.0	Red

In Table 1, the dyes were found to be soluble in water. This is because acid dyes are water soluble anionic dyes which possess one or two solubilizing or hydrophobic groups[1]. The dyes also have high molar extinction coefficient of above values of 10,000 which is a characteristic of a good dye [9].

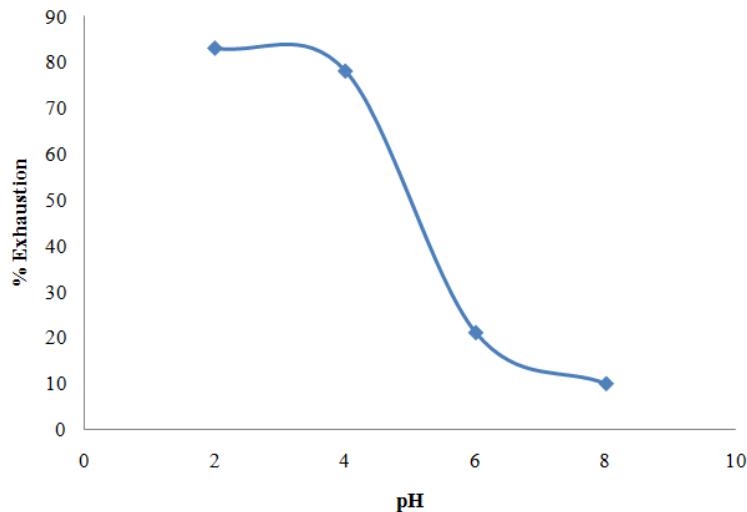
The UV/visible spectra of the synthesised dyes in distilled water were determined as shown in Table 2. The dyes obtained using N-Benzoyl H-acid (II) give higher maximum wavelength in the same solvent, higher molar extinction coefficient, and greater bathochromic shift when compared with the dyes from H-acid. However, the benzoylated dyes (II<sub>3</sub>, II<sub>4</sub>, II<sub>5</sub>) are hypsochromic because of the reduction in electron donating strength of the dyes, as free amino acids group in the dye has been substituted with benzoyl group. The reasons for the differences in the behaviour of the electron withdrawing groups are that dyes derived from H-acid can exist either in hydrazone form or in the azo form. For the hydrazone form, the diazo component is the donor part while it is the acceptor part for the azo form. Hydroxyazo types are charge transfer(CT) chromophores, and the influence of substitutions on the light absorption is of importance.

**Table 2:** Spectroscopic properties of the Dyes

Dye	$\lambda_{\text{max}}$ (nm)	Absorbance	Conc.(mol/dm <sup>3</sup> )	Extinction coefficient (dm <sup>3</sup> mor <sup>-1</sup> cnr <sup>-1</sup> )
I <sub>1</sub>	506	1.356	$2.14 \times 10^{-4}$	63365
I <sub>2</sub>	526	1.335	$1.98 \times 10^{-4}$	67424
I <sub>3</sub>	544	1.229	$2.36 \times 10^{-4}$	52076
I <sub>4</sub>	646	1.189	$2.28 \times 10^{-4}$	52149
I <sub>5</sub>	628	1.159	$2.18 \times 10^{-4}$	53165
I <sub>6</sub>	514	1.297	$2.13 \times 10^{-4}$	60892
II <sub>1</sub>	568	1.252	$1.18 \times 10^{-4}$	106101
II <sub>2</sub>	640	1.318	$1.16 \times 10^{-4}$	113620
II <sub>3</sub>	496	1.317	$1.89 \times 10^{-4}$	69683
II <sub>4</sub>	606	1.341	$1.84 \times 10^{-4}$	72880
II <sub>5</sub>	594	1.114	$1.78 \times 10^{-4}$	62584
II <sub>6</sub>	572	1.382	$1.75 \times 10^{-4}$	78971

#### Effect of pH on dye exhaustion

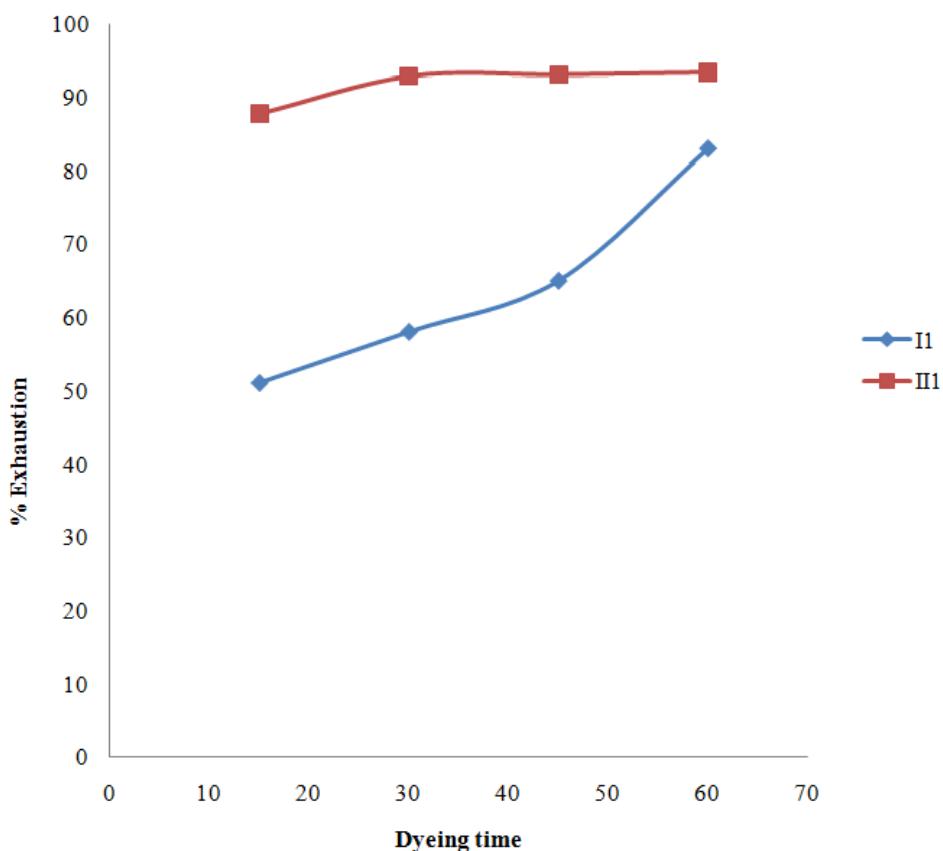
Figure 1 gives the percentage exhaustion of dye on nylon 6.6 fabric. Dye I<sub>1</sub> gave a high percentage exhaustion of 83% at pH of between 2-3, as the pH increases to 8, the percentage exhaustion drops. This is because, acid dyes absorbed better at lower pH range. In an acid bath, ionization of the carboxylic acid is depressed leaving a net positive charge on the fibre. The positive charges are neutralized initially by the moving acid anions which are then gradually displaced by the large and hence more slowly diffusely dye anions. However, as the pH of the dye liquor falls below 3-4 (when excess dye is present), the amount of dye uptake by the nylon begins to increase again and no saturation value is approached [3]. This phenomenon is attributed to protonation of the amide (-CONH-) groups in the main chain of the polymer and consequent adsorption of the acid dye anions [9].



**Fig. 1:** Effect of pH on dye exhaustion

#### **Effect of time on dye exhaustion**

Subsequent dyeing was carried out at pH of 2-3, while the time was varied at 15 minutes, 30 minutes, 45 minutes and 1 hour respectively. Results show that the higher the time, the higher the rate of dye absorption and subsequently the deeper the shade. Almost all the dyes gave high exhaustion at higher temperature. This may be due to the fact that, initially the dye is absorbed on the surface of the fabric and with longer time it slowly diffuses into the fibre to give level dyeing. Thus, the longer the dyeing time the better the dye diffusion and consequently the higher the percentage exhaustion. The high percentage exhaustion with increased in dyeing time in the above listed dyes may be due to the presence of sulphonate groups which enhances the solubility of the dyes in solution thus making them available to the fibres [5]. Dyes derived from N-Benzoyl H-acid (II) gave better exhaustion than corresponding dye from H-acid (I). The values are attributed to the increase in kinetic energy of the dye molecules at high temperature. Also, as the temperature increases, the nylon fibres swells thereby increasing the accessibility of the originally more difficult to penetrate crystalline region.



**Fig. 2:** Effect of dyeing time on exhaustion  
**Table 3:** Wash fastness rating of the dyes on nylon 6.6

Dyes	Change in colour	Staining on white
I <sub>1</sub>	4	4
I <sub>2</sub>	4	3-4
I <sub>3</sub>	3	2-3
I <sub>4</sub>	4	4-5
I <sub>5</sub>	4	4-5
I <sub>6</sub>	4	4-5
II <sub>1</sub>	4	3-4
II <sub>2</sub>	4	4-5
II <sub>3</sub>	4	4-5
II <sub>4</sub>	4	4-5
II <sub>5</sub>	4	4-5
II <sub>6</sub>	4	4

From Table 3, it is discovered that, dyes derived from N-Benzoyl H-acid showed the highest wash fastness where five out of six have ratings of 4-5 and little staining on the undyed fabric. This is most likely due to the additional benzene ring on the coupling component that may increase the planarity of the dyes and thus surface area of possible contact of the dye molecules themselves and the fibre.

## V. Conclusion

The results of the study showed that acid dyes gave a comparatively varying absorption wavelength, as a result of the effect of the different substituents groups. This also led to the varying fastness properties on the fabric. Bathochromic colours were observed by increasing the conjugation of the coupler ring. The dyes provided a wide range of deep and bright shades on nylon, although dyes from N-Benzoyl H-acid gave brighter shades and colour. These dyes have good exhaustion properties and level dyeing. Their synthesis is generally convenient, economical and environmentally friendly.

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