

## Application of bisphenol as a coupler in the synthesis of azo dyes and its assessments on vegetable tanned leather

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### ABSTRACT

Bisphenol-A has successfully been used as a coupler in the synthesis of some azo dyes with P-phenylenediamine and 4-aminophenol as the diazo components. The dyes exhibited a wide range of visible absorptions ranging from maroon to orange with characteristic absorption bands at 640.00 nm and 490.00 nm respectively. The results obtained from the calculation of the RF value indicates that the dye synthesized from 4-aminophenol is heavier with RF value 0.78 the dye synthesized from p-phenylenediamine serving as the diazo components has the least RF values 0.72 and 0.76 respectively. The fastness properties on dyed vegetable tanned leather showed very good fastness indicative of a great potential in future application of these dyes in colour technology.

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### KEYWORDS

Bisphenol-A;  
Synthesis;  
Fastness;  
Tanned leather.

### INTRODUCTION

Dyes are color substances capable of application in aqueous or non-aqueous solution or in an aqueous dispersion to a substrate, so that the substrate acquires a colored appearance. These substrates are usually leather, paper, fur, plastic material, wax, hair and textile materials. Most of the colored substances owe their color to the presence of organic substances that absorb light of a given wavelength within the visible portion of the spectrum and this property is not destroyed by pulverization. For a dye to be suitable for use, the colored material must have the following desirable properties; intense colour, solubility in water, ability to vaporize on heating,

Substantivity for the substrate and reactivity (6). The two main parts of dye which are responsible for color are known as; the chromophores and auxochromes. The chromophores are the conjugated system of atoms on which the dye is built, e.g. azobenzene, anthraquinone, triarylmethane, and phthalocyanine. Attachment of one or more auxochromes is necessary to develop the required intense color. Auxochromes are either electron-accepting groups such as  $-\text{NO}_2$ ,  $\text{C}=\text{O}$ , or electron donating group such as  $-\text{NH}_2$ ,  $-\text{OH}$ ,  $-\text{OCH}_3$  etc.

Bisphenol-A (BPA) is an organic compound with the chemical formula  $(\text{CH}_3)_2\text{C}(\text{C}_6\text{H}_4\text{OH})_2$ . It is a dysfunctional building block of several important polymers and polymer additives.

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The chemistry of bisphenol is determined by the phenolic OH groups, the aromatic nuclei, and the bridge segment. Hence, they primarily undergo the same reactions as similarly substituted monophenols, i.e. esterification and etherification at the OH group, and substitution and hydrogenation of the aromatic nucleus. Because of their bifunctionality, they are useful in the synthesis of high molecular weight linear polyesters (2, 5). This work is to explore the possibility of using bisphenol-A as a coupler in the synthesis of azo dyes with different aromatic amines such as P-phenylenediamine and 4-aminophenol, the use of these dyes in the coloration of leather material and the determination of the fastness properties of the dyed leather to parameters such as alkaline, acid, rubbing, light and wash fastness.

### EXPERIMENTAL METHODS

#### Reagents/materials

Bisphenol-A, acetone, sodium nitrite, sodium hydroxide, p-phenylenediamine, 4-aminophenol, p-anisidine, 3-nitroaniline, hydrochloric acid, ethanol, acetic acid, antibumping granules, glycerol, distilled water, ice block, sodium hydroxide, formic acid, vegetable tanned leather, 9100 Electrothermal Melting Point Apparatus, Jenway 6305 Spectrophotometer and Uv-visible spectrophotometer,

#### Synthesis of the dyes

##### Synthesis of p-disazo-bis (bisphenol)

Exactly 2.00 g of P-phenylenediamine was weighed and dissolved in 30.00 ml of 2.00 M solution of HCl, the temperature of the mixture was cooled to 0-5°C in ice bath. 50.00 ml of 1.00 M of cold solution of sodium nitrite was added drop-wise with continuous stirring for 15 minutes to form the diazonium salt. The diazonium salt solution of p-phenylenediamine was added drop-wise to exactly 1.98 g of bisphenol dissolved in 25.00 ml of 2.00 M sodium hydroxide solution. The mixture was stirred vigorously for one hour and left overnight. It was then filtered and dried. Recrystallization of the dye was carried out from hot-boiling water.

##### Synthesis of bisphenol-azo-p-phenolate

Exactly 2.00 g of 4-aminophenol was weighed and dissolved in 30.00 ml of 2.00 M solution of HCl, the temperature of the mixture was cooled to 0-5°C in ice bath. 50.00 ml of 1.00 M of cold solution of sodium nitrite was added drop-wise with continuous stirring for 15 minutes to form the diazonium salt. The diazonium salt solution of 4-aminophenol was added drop-wise to exactly 1.98 g of bisphenol dissolved in 25.00 ml of 2.00 M sodium hydroxide solution. The mixture was stirred vigorously for one hour and left overnight. It was then filtered and dried. Recrystallization of the dye was carried out from hot-boiling water.

##### Determination of the melting point of the dyes

The melting point of each dye was determined with the use of 9100 Electrothermal Melting Point Apparatus.

##### Separation of the synthesized dyes using thin layer chromatography

The synthesized dyes were separated by spotting the dyes on a chromatographic plates and thereafter, the spotted plates was placed inside a chromatographic tank containing equal volume of ethanol and acetone mixed together. As the plate was soaked in the mixed solvents to a point near the applied dyes, the solvent was observed to move up against gravity carrying alongside the different color components of the dyes. The color separations were observed at different spots, the distance moved by the solvent and that of the spotted dyes was measured and the RF value(s) was calculated.

##### Ultra violet-visible spectroscopy of the dyes

The Jenway 6305 Spectrophotometer was used, the cell to be used for the Uv-Visible Spectroscopy was washed thoroughly with distilled water. Distilled water was used to calibrate the instrument at the wavelength of 400.00 nm. Thereafter, 0.001 g of each dye was diluted with 10.00 ml of distilled water and 5.00 ml of the diluted dyes was measured and placed in the cell. The absorbance of the dyes was determined within the visible region (i.e. 400.00-750.00 nm) and the wavelength of maximum absorption ( $\lambda_{mas}$ ) of each dye was extrapolated from the graph.

### Dyeing of vegetable tanned leather

The vegetable tanned leather was cut at 5.00 × 4.00 cm and labeled A, B, C and D. The samples were each weighed and placed in separate conical flask containing 2.00 % of each synthesized dyes in water. The leather samples were agitated for about an hour at a temperature of 40°C after which the dye penetration was checked and ascertained. The dye was fixed using 4.00 % formic acid in each flask respectively. The fixing was carried out for 30 minutes after which the dyed leather were rinsed with distilled water, horsed up to drain, dried, staked and toggled (6, 7).

### Assessment of dyed substrate

#### Light fastness (fastness to sunlight)

This method is intended for the determination of the resistance of the colour of leather to the action of ordinary day light. This test was carried out in accordance with the Society of Leather Technologist and Chemists (Official Method of Analysis, 1996).

A piece of the dyed leather 5.00 x 2.00 cm was half covered with cardboard paper such that half of the length was covered. This was exposed to day light for ten days for 8 hours daily at an average temperature of 32°C. The change in colour was compared to the uncovered and exposed leather respective, using the standard grey scale.

#### Alkaline fastness

This was carried out in order to determine the resistance of leather to action of alkaline

3.00 x 3.00 cm of the dyed leather was dipped in sodium bicarbonate solution for 60 minutes and dried at room temperature without rinsing, the change in colour was determined using the standard grey scale.

#### Acid fastness

This was carried out in order to determine the resistance of leather to action of acid

3.00 x 3.00 cm of the dyed leather was dipped in a solution of acetic acid for 60 minutes and dried at room temperature without rinsing, the change in colour was determined using the standard grey scale.

### Wash fastness

This was carried out to assess the leather resistance to prolonged action of water

3.00 x 3.00 cm of the dyed leather was dipped into a solution made by 5.00 g (0.5%) of detergent powder into 200.00 cm<sup>3</sup> of distilled water. This was placed in water bath and the temperature was allowed to rise to 40°C. This was vigorously stirred for about 30 minutes and the leather was rinsed with distilled water and dried. The change in colour was assessed by the standard grey scale.

### Rub fastness

This is intended for determining the behavior of the surface of leather on rubbing with felt. The leather to be tested is rubbed with pieces of standard wool felt under a given pressure with a given number of forward and backward motions.

3.00 x 3.00 cm pieces of the leather sample were cut and dipped on a rub fastness tester (machine model STM). The number of rubs on a fixed position was varied to assess the degree of fastness to rubbing. The change in colour of the felt and the leather was assessed with the standard grey scale (7).

## RESULTS AND DISCUSSION

### Diazotization and coupling reactions

The synthesis of some azo dyes using bisphenol-A as a coupler with different aromatic amines such as P-phenylenediamine and 4-aminophenol was carried out. The TABLE 1 represents the reaction scheme involving the diazotization and coupling reactions. The first column of the Table represents the diazotization reaction of the aromatic amines (P-phenylenediamine and 4-aminophenol) to form the diazonium ion. This was carried out by reacting the aromatic amines with sodium nitrite in an acidic medium. The temperature of the reaction was cooled and maintained to 0-5°C in ice bath. The completion of the diazotization reaction was confirmed with a blue coloration of starch iodide paper to form diazonium ions of the amines. This diazonium ion was immediately coupled with the coupling agent

TABLE 1 : Reaction scheme

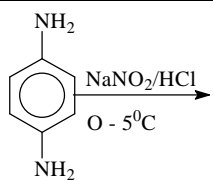
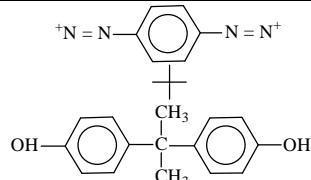
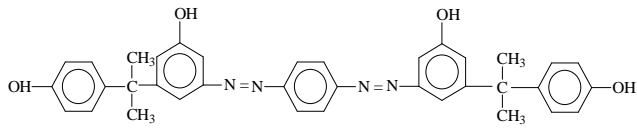
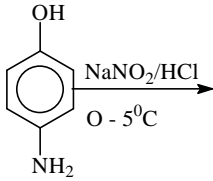
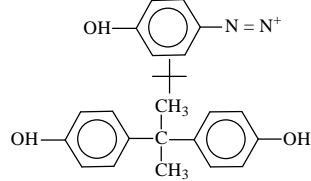
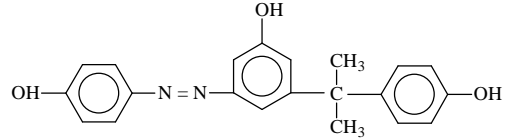
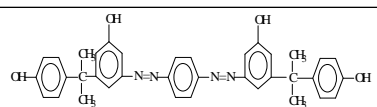
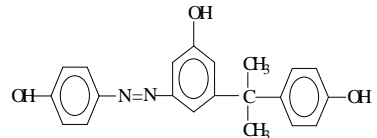
S/No	Diazotization Reaction	Coupling Reaction	Dyes
1			
2			

TABLE 2 : Characteristic of the synthesized dyes

S/No	Dye structures	Dye names	Melting points (°C)	TLC	RF Value	Recrystallization Solvent	Appearance
1		p-disazo-bis(bisphenol)	161	Two spot	0.72, 0.76	Water	Maroon
2		Bisphenol-azo-p-phenolate	156	One spot	0.78	Water	Orange

(bisphenol-a solution) as represented in the second reaction of the second column on TABLE 1 to give the dye which is represented in the third column of TABLE 1 below.

### Characterization of the synthesized dyes

TABLE 2 represents the general characterization of the synthesized dyes comprising of the proposed dye structures with proposed dye names. It also comprises of the melting point, the thin layer chromatographic separations of the dyes, the recrystallization solvents and the color appearance of the dyes.

The close similarities in the range of the melting point of the synthesized dyes can be accounted for by the backbone symmetry which is bisphenol (100-200°C). This shows that the dye melts as the backbone melts.

The recrystallization of the various dye produced was possible with hot boiling distilled water, although methanol, methylated spirit, ethanol and acetic acid could be used. But the choice of water dur-

ing the study was based purely on solubility.

### Thin layer chromatography

The thin layer chromatography was carried out to analyze the dye synthesized. Some showed one spot indicating that there were no impurities in the dye, while some showed two spots due to the presence of impurities. The dye synthesized from the diazonium salt of P-phenylenediamine showed two spots for thin layer chromatography (TLC) which makes it to be impure and gives a maroon color dye. The other synthesized dye showed one spot for TLC which implies that the dye is pure with different characteristic orange colour dye from the diazonium salt of 4-aminophenol as represented in TABLE 2.

The heavier the dye, the less the distance moved and the more the adherent to the substrate or the absorbent. The retention factor (RF values) of each dye was calculated using the equation below:

$$\text{RF Value} = \frac{\text{Distancemovedbydye}}{\text{Thedyefront}}$$

The results obtained from the calculation of the

TABLE 3

Dye name	Light fastness	Wash fastness	Acid fastness	Alkaline fastness	Rub fastness
p-disazo-bis(bisphenol)	4	3	4	4	4
Bisphenol-azo-p-phenolate	4	4	4	3	4

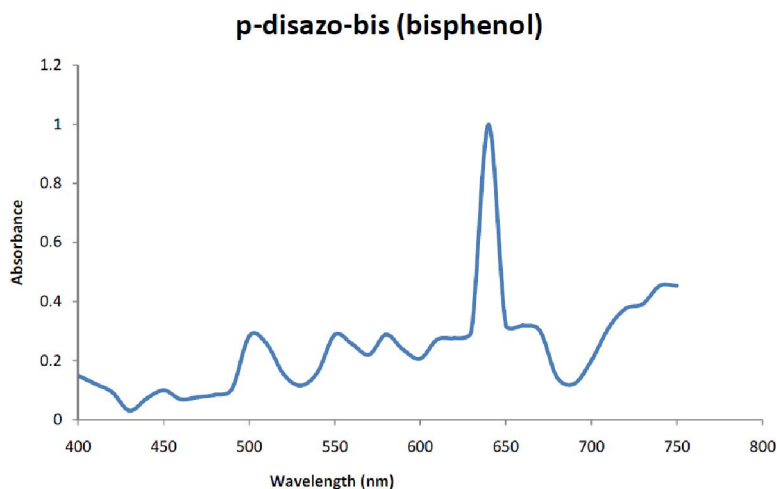


Figure 1 : UV/Visible Spectroscopy of p-disazo-bis (bisphenol)

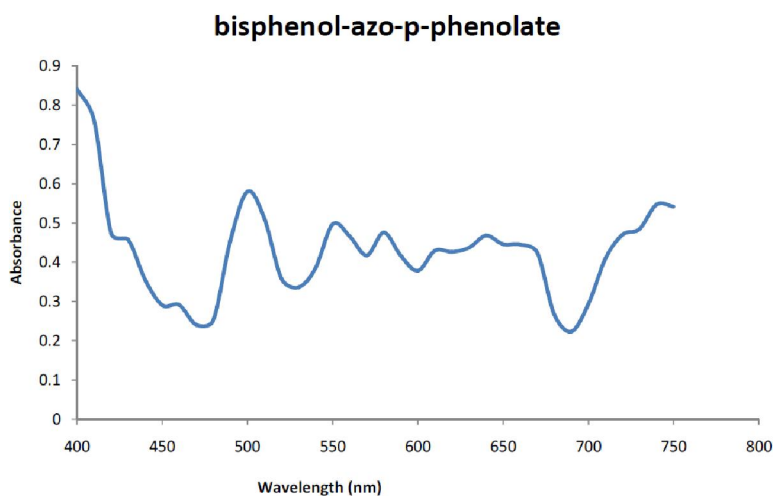


Figure 2 : UV/Visible Spectroscopy of bisphenol-azo-p-phenolate

RF value as represented in TABLE 2 indicates that the dye synthesized from 4-aminophenol is heavier with RF value 0.78 while the dye from p-phenylenediamine has the least molecular weight with RF values 0.72 and 0.76 respectively.

#### Fastness properties of the synthesized dyes on vegetable tanned leather

TABLE 3 gives the results of the fastness properties of dyed leather with the synthesized dyes to external parameters. This comprises of the light fastness, wash fastness, acid fastness, rub fastness and alkaline fastness of the synthesized dyes respectively.

The fastness property ranges from good to very good for each dyed leather material, indicated by the grey scale 3 and 4 respectively. This can be attributed to photostability and affinity effect.

#### Key:

1 = Poor 2 = Fair 3 = Good  
4 = Very good 5 = Excellent

#### Ultraviolet/visible spectroscopy of synthesized dyes

The ultra-violet and visible regions of the spectrum are used to determine the molecule present in the sample. From the result obtained in Figure 1 and

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2 respectively, the plot of absorbance against wavelength, it shows that the compounds are conjugated and are colored because of their  $\lambda_{\max}$  (nm), and their absorption in the visible region above 400.00 nm of the electromagnetic spectrum. The results obtained from the Ultraviolet/Visible spectroscopy of the dyes indicates that p-disazo-bis (bisphenol) absorbs at the  $\lambda_{\max}$  640.00 nm while bisphenol-azo-p-phenolate absorbs at the  $\lambda_{\max}$  490.00 nm respectively. The multiplicity of the  $\lambda_{\max}$  (nm) indicates that the mixtures of color of closely related compounds may be present in the synthesized dye products, (1)

### CONCLUSION

Bisphenol which hitherto have been used as a monomer in synthesis of resinous substances for plastic and medical technology has now been used successfully as a coupler in the synthesis of azo dyes with different aromatic amines. It gave different variety of colours, due to the fact that most of the dyes produced have different primary aromatic amines. The synthesized dye possesses different visible absorption properties that span the visible spectrum (maroon to orange).

The dyes are solids with similar melting temperature respectively due to the backbone symmetry and the directory position. The dye from the diazonium salt of P-phenylenediamine showed two components with RF values of 0.72 and 0.76 respectively. This can be attributed to the possible forma-

tion of monoazo and disazo derivatives. While the dye from 4-aminophenol showed absorption characteristic value as one component. The light, wash, rub, acid and alkaline fastness for the dyes on vegetable tanned leather ranges from good to very good indicative of the potential of these dyes for the coloration of leather.

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