**SYNTHESIS, CHARACTERISATION AND APPLICATION
PROPERTIES OF SOME NOVEL ACID AZO DYES.****Dr. D.G.Patel and N.K.Prajapati***

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ABSTRACT

Novel acid azo dyes have been prepared by the coupling of diazo solution of 4-methyl Aniline with 1-(4-N-acetyl amino) 2-methyl phenyl, 2-chloro ethanone. The resultant product were hydrolysis by refluxing with ethanol containing for 4-5 hours. The coupling

compound of various aromatic acid 1a-1g with above diazonium salt soln. The resultant 2a-2g dyes were characterized by spectral techniques, *i.e.*, elemental analysis, IR, UV—visible spectroscopy. The dyeing performance of all the dyes was evaluated on wool and nylon fabrics and studies their light and washing fastness properties.

KEYWORDS: acid azo dye, UV—visible spectroscopy, light fastness, washing fastness.

INTRODUCTION

Out of different classes of dyes, azo dyes constitute the largest group of colorants used in industry.^[1] Azo dyes do not occur in nature and are produced only through chemical synthesis.^[2] The emergence of diverse classes of synthetic dyes including azo-dye occurred due to constant effort to find specific dye or a particular class of dye for application on diverse materials of industrial importance mainly textile fibres, aluminium sheet, leather, electro optical devices, ink – jet printers etc.^[3]

While phenols are well established intermediates for the synthesis of various commercial dyes^[4-8], they are marketed in the form of azo-acid dyes *etc.* All of these dyes having

phenolic motif, containing hydroxyl group as an auxochrome group. Such auxochromic(-OH) and chromophoric (C=O) group containing compound The area in which the acid azo dyes formation based on this compound may yield the dyes with good hue properties. Hence, in continuation of our earlier work^[9-10], it was thought interesting to explore the field of acid azo dyes based on 1-(4-N-acetyl amino) 2-methyl phenyl 2-chloro ethanone. The proposed synthetic route is shown in Scheme 1.

MATERIALS AND METHODS

All the chemicals used were of analytical reagent grade and were used without further purification, All the product were synthesized and characterized by their spectral analysis, All Chemicals and solvents like acetone, ethanol, NaNO₂, NaOH, sodium acetate were purchased from S.D.fine chemicals (india).

Melting points were taken by open capillary tube and are uncorrected. The UV-Visible spectra were recorded in DMF using Shimadzu A-200 Spectrophotometer and C,H,N of all disperse dyes were estimated by the means of a carlo Erba elemental analyzer (Italy) The characteristic data of different molecules were studied their light, wash fastness properties and further study applied on wool fibers and nylon fibers.

EXPERIMENTAL

Synthesis of acid azo dyes: First 4-methyl aniline was dissolve in a mixture of anhydrous acetone and pyridine in 250ml flask then added dropwise to a mixture of 1-(4-N-acetyl amino) 2-methyl phenyl 2-chloro ethanone and sodiumbicarbonate as an accepter. The reaction mixture is set aside over night. Then resultant product were hydrolysis by refluxing with ethanol containing HCl for 4-5 hours. The cool solution was dilute with water and was mass just alkaline with conc.NH₃ solution (d= 0.880) to give yield 1--(4-amino-2-methyl phenyl)2-(N-4-methyl phenyl) ethanone. Diazotization of various aromatic acid was performed by a reported method.^[11-13] The yield was dissolved in HCl with stirring and the solution cooled to 0-5 °c in an ice-bath. A solution of sodium nitrite (0.01 mole) in 5ml water cooled to 0 °c then was added. The excess nitrous acid was neutralized with sulfamic acid/urea (1.0 gm) and the mixture was filtered to get the clear diazonium salt solution. 1a-1g coupling component was dissolved in NaOH (15 ml) and then solution cooled 0-5 °c To this well stirred solution the above diazonium salt solution was added slowly so that temperature did not rise above 0-5 °c while maintaining the pH 4-5 by the action of sodium acetate solution (10% w/v) the mixture was stirred for 3 hrs. at 0-5 °c. After

completion of the reaction the solid material was filtered, washed and dried it. So 2a-2g acid azo dyes were prepared.

RESULTS AND DISCUSSION

The acid azo dyes obtained from this compounds are shown in Scheme-I The observed bands in the IR spectra for each dye are shown in Table-I.

IR spectra of all seven series of acid azo dyes contain aromatic nuclei, azo group and hydroxyl group. The band appeared from 1030 to 1275 cm^{-1} due to primary -OH group, The strong band at 1575 to 1640 cm^{-1} appeared in the spectra are considered for the presence of azo (-N=N-) group. The bands around of 660 to 1180 cm^{-1} are attributed to the presence of -SO₃OH group. In the spectra of dyes obtained from aniline derivatives side chain attached to the tertiary nitrogen The broad band around 3430-3540 comprises to primary amine stretching. The weak bands observed 2890-and 2950 cm^{-1} which is attributed to the -CH₂ stretching vibration.

The IR spectra of all dyes comprise the important bands due to initial diazo component. The bands due to -CH₃ stretching 2905-2930 and 1320-1475 cm^{-1} and -CO of -COCH₂ aniline (-CH₃). The other bands due to presence of coupling component are their respective positions. The elemental of C,H,N confirmed by Table: II.

The visible absorption spectroscopic properties of the all dyes were recorded in DMF. Absorption maximum (λ_{max}), Intensities' ($\log \epsilon$), dyeing assessment of acid azo dyes on Wool and Nylon fabrics are shown in Table-III, The absorption maximum (λ_{max}) of all the dyes falls in the range 407-487 nm in DMF. The values of the logarithm of molar extinction coefficient ($\log \epsilon$) of all the dyes were in the range of 3.645-4.783, consistent with their medium absorption intensity The disperse azo dyes were applied at a 2% dye bath on nylon and wool fabrics and gave various shade implied in Table-III.

Table: I. Structure of the Coupling component and corresponding of novel azo dyes.

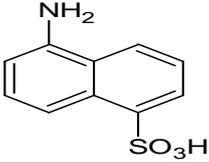
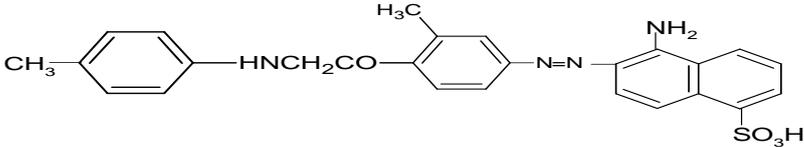
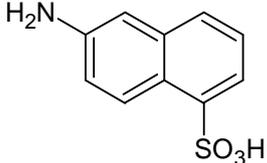
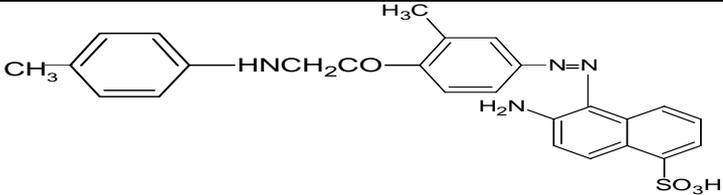
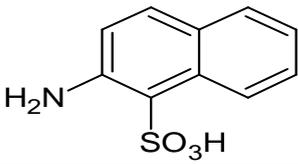
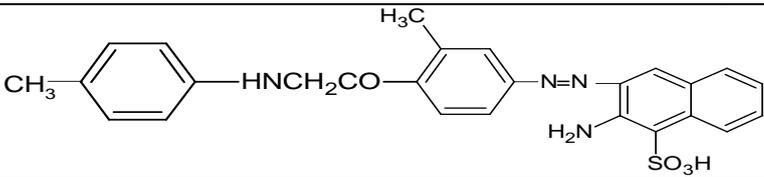
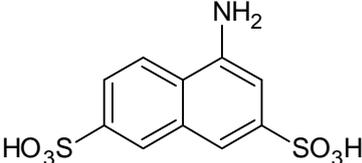
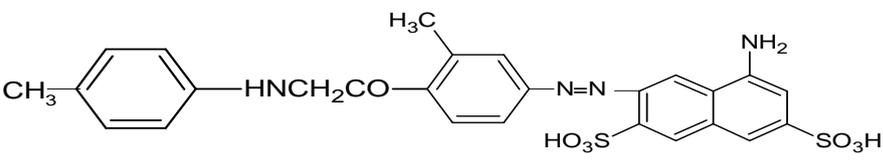
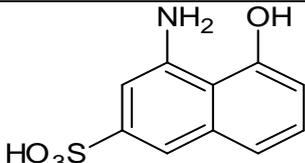
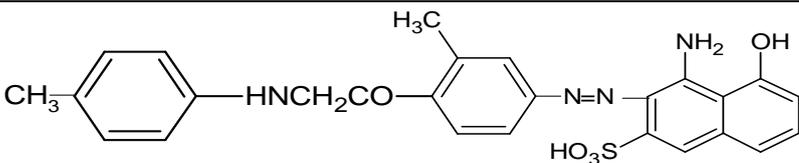
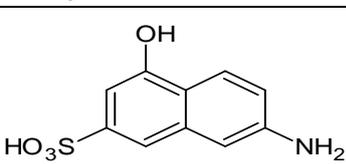
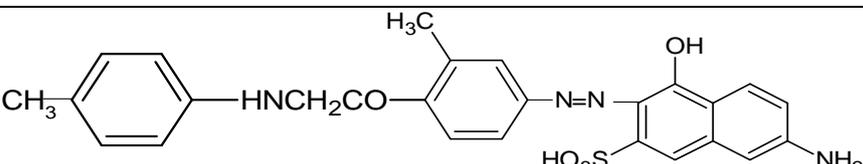
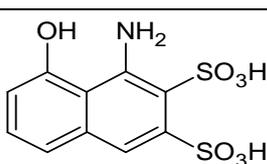
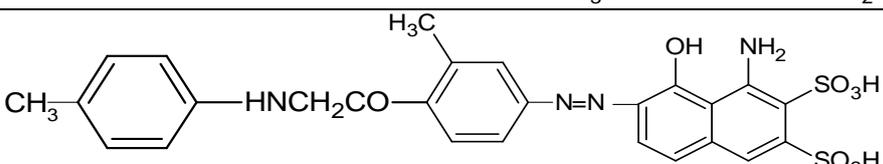
Dye No	Coupling component	Acid azo Dyes
2a		
2b		
2c		
2d		
2e		
2f		
2g		

Table: I Position selected Bands in IR Spectra of Aid azo dyes

Dye No	Primary amine cm^{-1}	C-H Stretching aromatic cm^{-1}	N=N Stretching aromatic cm^{-1}	Naphthelene Substituted cm^{-1}	1,4-di Substituted cm^{-1}	Primary Alcohol cm^{-1}	SO ₂ Stretching cm^{-1}	Tertiary Amine cm^{-1}	S=O Stretching vibration of Sulfonic acid cm^{-1}
R-1	3440	2920, 1615;1650	1590 1640	1560	1570,1155, 1040.	1030, 1100;1250	1150;1160 1300	1140 1350	1150;1040 660
R-2	3450	2940,2975, 1620,1425	1630	1575	1560, 1160.	1030, 1100; 1260.	1180;1100 1340	1150 1375	1150;1040 675
R-3	3430	2625,1620, 1475,1475	1640	1540	1570, 1165;1030	1030, 1240;1100	1175;1350 650	1160 1360;1350	1150 675
R-4	3450	2900,2950, 1510,1615	1575 1630	1550	1530, 1130;1040	1030, 1100;1230	1350;1180 1150;650	1140 1345;1370	1150;1060 660
R-5	3450	2950, 1620; 1610	1610	1550	1570, 1155;1040	1030, 1050;1100	1180 1375	1150 1360	1190;1040 670
R-6	3440	2915, 1570;1530	1630	1540	1510,3010, 1175,1040.	1050 1100	1175 1350	1140 1375	1180;1030 660
R-7	3430	2925, 1570;1515	1575,1630	1575	1610,1205, 1050.	1050, 1100;1275	1330;1120 650	1180 1350	1150;1030 675

All the spectra compared the bands around 2890 and 2950 cm^{-1} presented of $-\text{CH}_2$ of $-\text{COCH}_2$ group

Table: II. Characterization of novel Acid azo dyes.

Dye No	Molecular Formula	Mol.Wt (gm/mole)	Melting Point $^{\circ}\text{C}$	% C		% H		% N	
				Found	Cal	Found	Cal	Found	Cal
2a	$\text{C}_{26}\text{H}_{24}\text{N}_4\text{O}_4\text{S}$	488	230	63.90	63.93	4.90	4.91	11.40	11.47
2b	$\text{C}_{26}\text{H}_{24}\text{N}_4\text{O}_4\text{S}$	488	337	63.90	63.93	4.90	4.91	11.40	11.47
2c	$\text{C}_{26}\text{H}_{24}\text{N}_4\text{O}_4\text{S}$	488	214	63.90	63.93	4.90	4.91	11.40	11.47
2d	$\text{C}_{26}\text{H}_{24}\text{N}_4\text{O}_8\text{S}_2$	584	233	53.40	53.42	4.00	4.10	9.50	9.58
2e	$\text{C}_{26}\text{H}_{24}\text{N}_4\text{O}_5\text{S}$	504	242	61.80	61.90	4.70	4.76	11.10	11.11
2f	$\text{C}_{26}\text{H}_{24}\text{N}_4\text{O}_5\text{S}$	504	223	61.80	61.90	4.70	4.76	11.10	11.11
2g	$\text{C}_{26}\text{H}_{24}\text{N}_4\text{O}_8\text{S}_2$	584	242	53.40	53.42	4.00	4.10	9.50	9.58

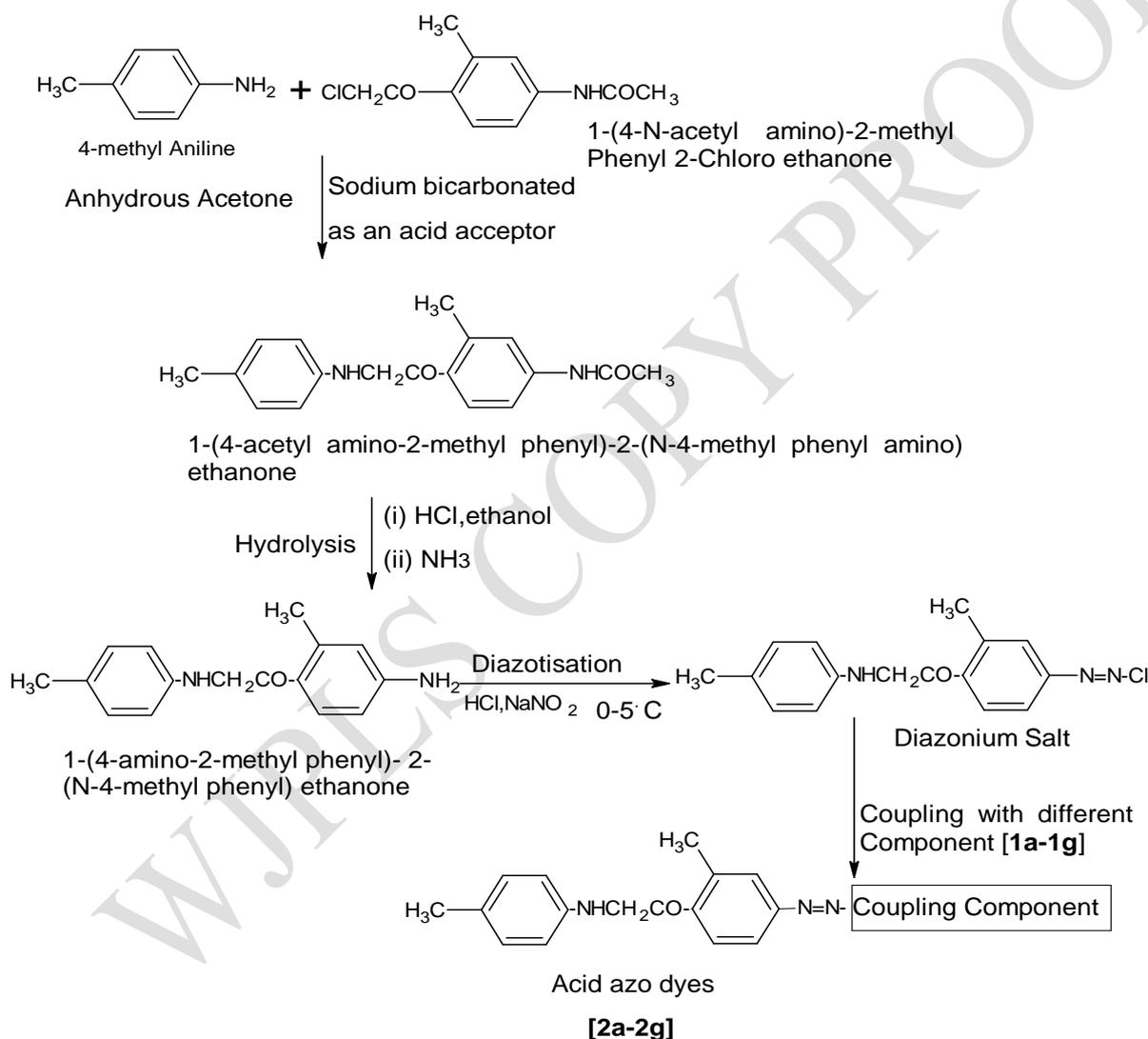
Table: III. Absorption maximum (λ_{\max}), Intensities ($\log \epsilon$), Acid azo dyes on Wool and Nylon fabrics.

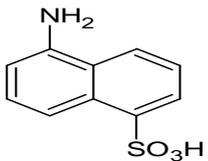
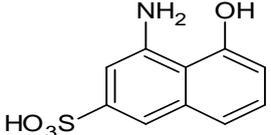
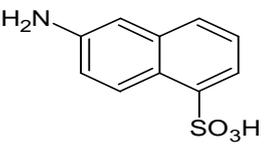
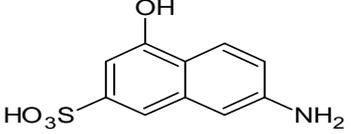
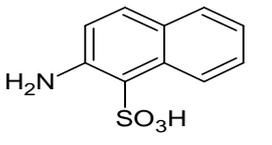
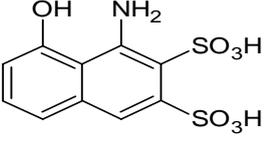
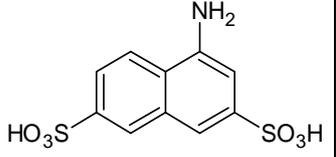
Dye	λ_{\max} (nm)	Log ϵ	Shade	Dyeing properties			
				Dyeing on wool		Dyeing on nylon	
				L	W	L	W
2a	471	3.895	Light red	5	4	5	4
2b	479	4.097	Light red	5	3	5	3
2c	487	4.023	Rose like	4 to 5	4	4 to 5	4
2d	407	4.450	Brown	4 to 5	4	4 to 5	4
2e	458	3.645	Dark Brown	4	3	4	3
2f	407	3.700	Brown	5	5	5	5
2g	480	4.783	Rose like	5	4	5	4

Light fastness: 1-poor, 2-slight, 3-moderate, 4-fair, 5-good, 6-very good.

Wash fastness: 1-poor, 2-fair, 3-good, 4-very good, 5-excellent.

Reaction scheme-I



1a	Laurent's acid		1e	Gamma acid	
1b	Bronner's acid		1f	J-acid	
1c	Tobias acid		1g	Chicago acid	
1d	H-acid				

CONCLUSION

The azo disperse dyes have been prepared using based on 1-(4-N-acetyl amino) 2-methyl phenyl, 2-chloro ethanone. The present study prepared acid azo dyes showed wide range of shades Light red, Light red, Rose like, Brown, Dark brown, Brown, Rose like. They showed good dyeing performance on wool and nylon fiber and The light fastness values of the acid azo dyes are more consistent. The dyeing showed an fair and good fastness to light, 2f acid azo dyes was excellent fastness to washing and other dyes were with good to very good fastness to washing.

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