Azo Dyes for Colouring Leathers

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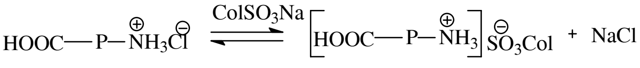
Some acid azo dyes were synthesized by coupling the 2,2'-benzydinesulphonic acid diazonium salt to ß-naphtol, phenyl-methyl-pyrazolone, G-salt, H-acid. The resulted dyes were analyzed via chromatography, IR and UV-Vis spectra and then were applied on sheep and pig skins. The dye was tested afterwards.

Key words: acid azo dyes, 2,2'-benzydinesulphonic acid, dyeing skins.

The synthesis azo dyes of different structures and shades are well-known for their capacity to dye and print textile materials and various types of leather, plastics, rubber, lacquers and paints.

In their form, the acid azo dyes colour the substrate they are applied on. The anion is coloured by forming the salt of the basic groups from their structure. The acid azo dyes have sulphonic groups in their molecules and, more rarely, carbonylic ones, which, as sodium salts, make the dyes water soluble. They have the property of dyeing various substrates like wool, natural silk, leather and polyamidic fibres in a bath which was weakly acidulated with H_2SO_4, CH_3COOH, HCOOH. These dyes have no affinity for cellulose fibres (cotton, flax, hemp).

When dyeing leathers with acid azo dyes, the procedures are similar to those applied in dyeing wool [1].



$$HOOC-P-\overset{\oplus}{N}H_3\overset{\ominus}{Cl} \xrightleftharpoons{ColSO_3Na} \left[HOOC-P-\overset{\oplus}{N}H_3\right]\overset{\ominus}{S}O_3Col + NaCl$$

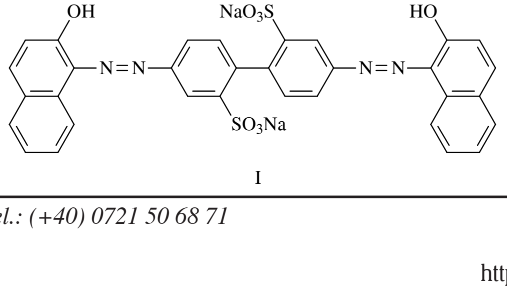
The acid dyes can be also differentiated by their covering power. They can be tested on substrates for which they have affinity. The main areas of use [2] for dyeing leathers are: leathers for clothes and footwear clothes made from synthetic fibres (untreated cellulose, cellulose acetate, nylon, polyester, artificial silk, etc.).

The acid azo dyes are extremely useful in the skin-dressing industry, due to their wide range of application and their good results in dyeing leathers, as they penetrate deeply into them and they have a wide variety of colours and shades.

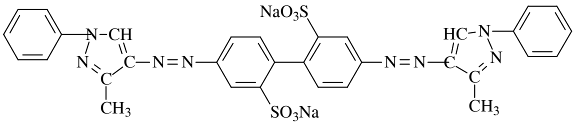
The present paper intends to synthesize an orange dye with a colouring capacity similar to Sellacht Orange GSN which is produced by CIBA GEIGY and also to observe the variation of the colour system formed by the same diazotizing component and different final coupling components.

In order to synthesize the dyes we used the data from the literature concerning the structure of acid azo dyes [3] and the procedures of obtaining them [4 - 7].

The paper describes the synthesis of the following dyes:



I



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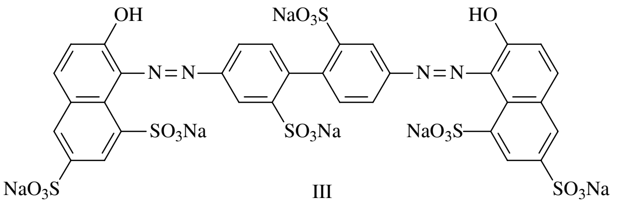

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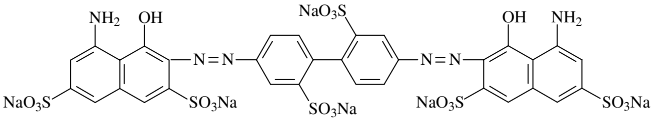

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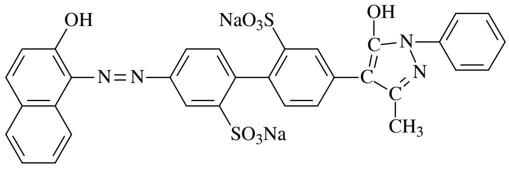
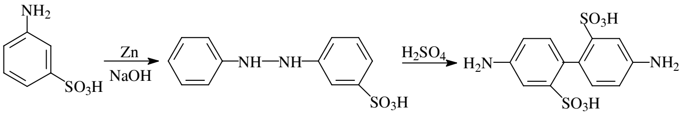


V

Experimental part

The benzydine-2,2-disulfonic acid is prepared by reduction of 3-nitrobenzene sulfonic acid with zinc in alkaline medium, followed by transposition in agreement with the following succession of reactions [2]:



As dye I is concerned, the reaction involves a coupling process with two moles of the same coupling component, the result being acid disazo dyes of the structure presented above. For the diazotization of 2,2'-benzydinesulphonic acid (BDS), in a BDS solution formed of 29.2 g BDS 59% in 150 mL water at 40^0C and 6g Na_2CO_3 up to pH=8-9 and 7.2g

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Dye	Dye Synthesis	Step	t^0C	pH	Time (h)	η (%)	Colour
I	β-naphthol ←BDS acid→ β-naphthol	Diazotization	8-10^{0}C	3-4	0.15-0.30		
		Coupling	8-10^{0}C	8-9	4	16.3	Red
II	F.M.P← BDS acid→ F.M.P	Diazotization	8-10^{0}C	3-4			
		Coupling	8-10^{0}C	8-9	3	88.7	Yellow
III	Salt G← BDS acid→Salt G	Diazotization	8-10^{0}C	3-4	0.50		
		Coupling	8-10^{0}C	8-9	4	74.5	Grey
IV	Acid H←BDS acid→Acid H	Diazotization	8-10^{0}C	3-4	0.50		
		Coupling	8-10^{0}C	8-9	3	78.3	Violet
V	β-naphthol ←BDS acid→ F.M.P	Diazotization	5^{0}C	8-9	1.5		
		Coupling	5^{0}C	8-9		85.7	Orange

Table 1
THE WORKING CONDITIONS FOR THE SYNTHESYS I-V

$NaNO_2$ 96% , 33mL HCl solution 32% and 5 g ice. The *p*H level is adjusted to 3-4. Then, 18 mL NaOH solution 35% is also added to it. The coupling is completed by introducing a β-naphthol solution over the solution of diazonium salt. The β-naphthol solution consists of 16g β-naphthol 99% with 150mL water, 12mL NaOH solution 35% heated to 80^{0}C and 1 mL NaOH 35% until *p*H gets to 8-9 and the dissolving process is completed. Then, it is diluted with water and ice until it gets to 250 mL and a temperature of 8-10^{0}C. After β-naphthol is introduced, the *p*H is maintained at 8-9 and the temperature is kept 8-10^{0}C.

After four hours, the dye suspension is heated to 80^{0}C and at this temperature it is neutralized with HCl diluted with water 1:10 up to *p*H=8-9. It is then precipitated with salt until the halo of a dye drop on the filter paper gets colorless. It is stirred for 15-30' and filtered on a Büchner funnel, the resulted paste being dried at 100-110^{0}C. An amount of 44.29g dry dye is thus obtained, η=76.3%.

Table 1 presents the working conditions for the synthesis of dyes I-V. The reaction conditions for the synthesis of dyes II – V are similar and are presented in table 1.

Dyes I – V were analysed by thin layer chromatography [8] after being purified by recrystallization from ethyl alchool [9]. Their purity was determined by chromatography on silica gel prop with N-N-dimethylformamide as eluent [8]. The UV-Vis spectra were performed with a UV-Vis-2-Carl Zeiss Jena apparatus. In order to test the structure of the dyes, the IR spectrum was performed (table 2) and the main frequencies are listed in table 2, being in agreement with the data in the literature [9]. Dyes I-V were applied on sheep skins, pig skins, ooze leathers and sheep skins with fur [10].

Tests were performed for dyeing, their fasteners values to light, wet and dry friction were compared.

The test results are presented in table 4. Their fastness to light was measured with a Xenotest device by exposing some testtubes coloured with these dyes, later comparing them after a limited period of time. Their fastness to wet and dry friction was measured with a lab-device with manual action, testing both the bather prop and the fabric on which the dye migrated.

Results and discussions

These attempts to use various coupling components resulted in the synthesis of a reddish orange dye, by using Acid G. As the coupling of 2,2'-benzydinesulphonic acid diazonium salt (BDS) with 2 moles β-naphthol gave a red dye and with 1-phenyl-3-methyl-pyrazolone (FMP) the dye which resulted was yellow, we came to the conclusion that an orange dye could be produced if we resorted to a successive coupling of 2,2'-benzydinesulphonic acid diazonium salt in the first coupling reaction with 1 mole of β-naphthol and then the monoazo would be coupled to 1 mole of 1-phenyl-3-methyl-pyrazolone (FMP), this dye II having structure V. An orange dye was thus synthesized.

Table 1 presents the preparation of dye I-V which occurs at 8-10^{0}C, while in the case of dye V a lower temperature level (5^{0}C) is necessary, to prevent the diazonium salt from breaking up into smaller parts during the coupling process which involves a successive addition of two coupling components.

The synthesis of dyes II and III require a longer period of time for the completion of their coupling because β-naphthol and Acid G are less reactive components. If we analyze the structure of the two coupling components, we notice that the absence of the NH_2 groups reduces the couplant reactivity (if they had these groups, their electron – rejecting property would make them react more easily with the diazonium ion).

In second coupling occurred in alkaline medium in all the five situations, the result being dyes as sodium salts which could be dissolved in water.

The preparation of the orange dye V has a better yield than in the case of dye III.

The thin layer chromatographic analysis [8] shows that yellow dye II (first position in the chromatogram) has a high purity level. Dye V which is orange (IIIrd position) presents a visible, unitary spot. Dye IV (violet) is less pure and its spot is very small.

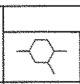
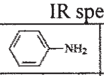
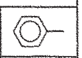
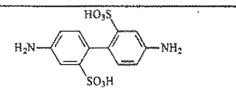
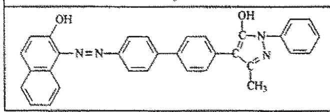
<table>
<tr><th rowspan="2">The analysed substance</th><th colspan="7">IR spectrum ν (cm^{-1})</th></tr>
<tr><th></th><th>—CH_3</th><th></th><th>—SO_3H</th><th>=C—OH</th><th>—CH</th><th></th></tr>
<tr><td></td><td>800</td><td>-</td><td>1520
1600</td><td>1010</td><td>-</td><td>2900</td><td>-</td></tr>
<tr><td></td><td>790</td><td>1530</td><td>-</td><td>1020</td><td>1200
1420
3420</td><td>-</td><td>490</td></tr>
</table>

Table 2
IR SPECTRA

Dye	λmax (nm)	ε
I	518.4	23885.3
II	409.2	21381.5
III	514.4	23963.1
IV	521.9	14197.5
V	426.2	29010.2

Table 3
UV-Vis SPECTRA

Table 4
THE FASTNESS VALUES OF DYEING SHEEP LEATHER

Sample	Colour	Light Fastness	Fastness to friction with marks 1-5	
			dry	wet
1	Yellow	3-4	4-5/2	2/1-2
2	Pale red	3	4/2-3	2-3/1
3	Red	3	4-5/2	2/1-2
4	Red	2	2/3	1-2/1-2
5	Red	2-3	2-3/3-4	2/1-2
6	Blue	1-2	2/2-3	1-2/1-2

The solubility tests for the new dyes in different solvents: methyl-alcohol, ethyl-alcohol, chloroform and water have proved that they are soluble in all these solvents.

In order to test the structure of dye V and that of its intermediate 2,2'-benzydinesulphonic acid, a comparative IR spectrum was performed [9]. The analysis of dye V spectrum stated the presence of vibrations characteristic for the intermediate groups. Also, their structure contained groups from the coupling components (table 2).

UV-Vis absorption spectra were made with a SPECORD UV-Vis apparatus, the solution of the dyes dissolved in distilled water being tested [6]. The extinction molar value was calculated and the results are presented in table 3.

The value of the wavelength where the maximum absorption occurs is in agreement with the data from the literature for the respective colours [8]. At the same time, the dye which has the lightest colour absorbs at the lowest wavelength (dye II violet, at 409.2 nm), whereas the dye with the darkest shade absorbs at the highest wavelength – 521.9 nm.

As for as the two orange dyes are concerned, only dye V is closer to the wavelength values which are specified in the literature [9] for maximum absorption of the orange shade.

Dye III has an absorption maximum shifted to red.

Dye IV, which resulted from coupling with acid H, has a spectrum with a stronger batochrome effect than the dye which was prepared via coupling with β-naphthol (I). Dye IV has an absorption maximum which is shifted towards higher wavelength than dye I.

The dye which was prepared by coupling with 2 moles of FMP (II) presents a bigger hypsochrome effect than the dye which resulted from coupling 1 mole FMP and 1 mole β-naphthol, whose absorption maximum is shifted towards lower wavelengths. The extinction molar coefficient value is at its highest for dye V, followed by III and II, which corresponds to an intensification of the colour due to a hypsochrome effect, similar to the one which can be noticed with the naked eye.

Dyes I-IV were used to colour sheep, pig, cow, leathers, velvet leather and fur sheep leathers.

The results of the colorings are similar to the data from the literature [10] starting from the lightest to the darkest shades.

The resulted dyes and dye Orange GSN have low affinity to these types of leathers.

Dye V is the closest to an orange shade. Their fastness to light, wet and dry friction was tested in parallel with the comparable dye.

The results of all these tests are presented in table 4.

The light fastness was tested with a Xenitest device by exposing some test tubes coloured with the dyes in question for a well-defined period of time and then comparing the contrast between the exposed sample and the witness sample, each of them being given a mark, comparative to the blue standards scale.

The results are pretty good for light fastness when dyeing sheep leather for all the dyes excepting dye IV. Dyes III and V gave good results the sample which was coloured with V had better fastness properties. Their fastness to wet and dry friction was tested with a manually activat lab device. Both the leather substrate which was subject to friction and the textile material where the dye migrated were analyzed.

Marking is done with the help of a scale of grey, with marks as ratios from 1 to 5.

For dry friction, the best values are obtained by the sample which was colored with dyes II and IV and also the comparative dye. For wet friction, the samples which were dyed with II, IV, V and with the comparative dye had the best results.

Conclusions

The present paper describes the synthesis of some acid disazo dyes, by coupling the benzydine-2,2'-disulfonic acid diazonium salt to â-naphthol, phenyl-methyl-pyrazolone, salt G and acid H. The resulted dyes were analysed - their shades, their ability to dye different types of leather and their fastness, in order to find a possible substitute for Sellacht Orange GSN.

The study of IR, UV-Vis spectro and of tinctorial analyses leads to the conclusion that the dye which was prepared by coupling the diazonium salt of benzydine-2,2'-disulfonic acid with β-naphthol and phenyl-methyl-pyrazolone can be used to replace Sellacht Orange GSN, produced by CIBA GEIGY.

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