The Synthesis of Some Food Dyes for Natural and Synthetic Fibres

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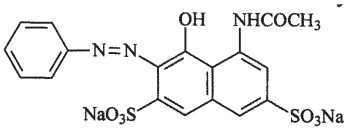
The paper presents the synthesis of 5 food dyes: G Red, 12 Red, Blue 1, Yellow 8, Orange 4 and their application on woollen fibres, polyamide and natural silk. Their structure, purity and affinity to wool, natural silk and polyamide were analyzed.

Keywords: dyes, natural and synthetic fibres

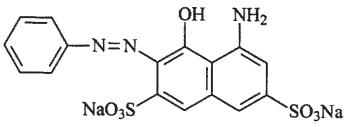
The food dyes with carotene are used in the manufacture of bread and pastry, butter, margarine, jellies, etc [1]. The pigments from plants are also used as dyes [2], alongside with pigments which were extracted from fruits or vegetables [3]. The fruit juice is turned into a starch paste which is more soluble at low temperatures.

Most of the synthesized food dyes are monoazo dyes. They result from the diazotization of amines which is followed by coupling with various coupling components. The water soluble dyes were analyzed in various ways. Their chemical properties were determined and, as a result, they were classified into basic, neutral, sulphonated and non-sulphonated.

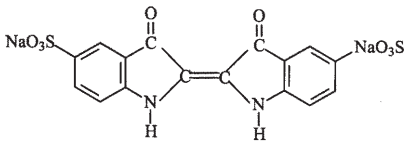
The following food dyes were obtained: 12 Red [4], 10 Red [5], Blue 1 [6], Yellow 8 [7], Orange 1 [8]. New methods were used. The chemical formulae of these dyes are the following:



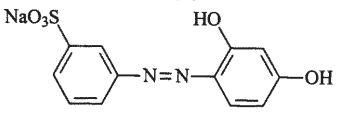
Red G



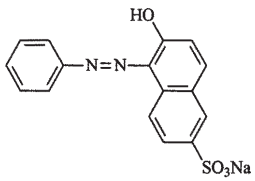
Red 12



Blue 1



Yellow 8



Orange 4

Experimental part

The solutions of the dyes have a concentration of 1-4% in water. The dye sample to be analyzed is spotted on the chromatographic plate. It is left for 30 min in the tub with the mobile phases to migrate on a distance of 8.5 cm from the layer margin. The dye spot is visualized in the daylight.

Solvents: normal butanol, ethyl alcohol, water, normal propanol, sodium bicarbonate.

Dyeing is on wool, polyamide and natural silk.

The synthesis of the dyes:

1. The preparation of Red 12 is performed via diazotization of aniline and acetification of N-sulphonic acid H, as in the literature [9].

The coupling of the diazotized aniline (0.05 moles) with acetified acid H (0.05 moles) is performed as follows: 20.25 g (0.05 moles) of N-acetyl acid H disodic salt are dissolved into water, the resulted solution having a *p*H= 6.5-7. It is then cooled at 0^0C by addition of 5.3 g (0.05 moles) of Na_2CO_3 and ice. The diazoderivative solution is pored over in the next 20 min, while stirring it continuously.

The reaction mass should always be weakly alkaline (it is tested with Brilliant Yellow paper). After two hours of continuous stirring, a test is performed in order to see if the diazoderivative has disappeared from the mixture. The reaction masses then heated at 60^0, it is salified with 100 g NaCl, stirred for one hour, cooled at 20^0C and filtered. The resulted precipitate is pressed and dried at 70^0C. In order to be coupled to acid H, a wet cake containing 15.95 g (0.05 moles) acid H monosodic salt is dissolved into 77 mL H_2O with $NaHCO_3$ added to it to get a weakly acid solution (*p*H~5).

The resulted solution is poured into the diazoderivative solution while stirring it, the temperature being lower than 10^0C. Stirring continues for 8-10 h and the final product is food dye Red 12.

The food dye Blue 1 is prepared by adding 10 g indigo to 50 mL H_2SO_4 with vigorous stirring.

The stirring continues for 15 min at approximately 30^0C. Then the solution is heated to 80^0C and it is stirred for 2 more hours. It is left until the next day, when an aqueous solution saturated with sodium chloride is prepared. Ice and then indigo are added to it and then the solution is filtered.

The filtrate is washed with sodium chloride saturated solution.

Food dye Yellow 8 is prepared via diazotization of 8.05 g (0.05 moles) methanilic acid, similar to the data presented in the literature [10].

The coupling with resorcinol proceeds as follows:

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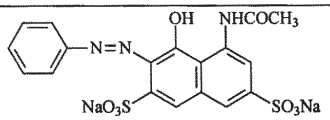
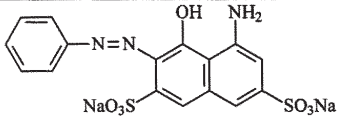
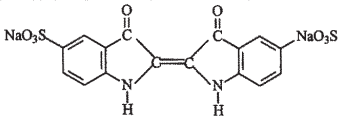
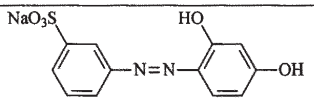
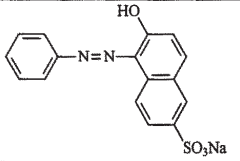
Nr.crt.	Dye formula	The resulted amount (g)	Yield (%)
1		17.35	85
2		12.9	80
3		9	90
4		4.8	80
5		16.5	85

Table 1
THE RESULTS OF THE SYNTHESIS OF DYES 1-5

5.5 g (0.05 moles) resorcinol are dissolved into 85 mL H_2O, then 8.2 g (0.097 moles) $NaHCO_3$ are added to the solution, together with 35 g ice for cooling at 0^0C. The diazoderivative suspension is added upon stirring at a temperature lower than 5^0C. The coupling process is very quick.

In order to prove that the diazoderivative is no longer present in the mixture the aureole of a salified sample placed on filter paper is touched with anthranilic acid alkaline solution. The *p*H level is adjusted to 7 by adding 10% HCl (with CO_2 release). The mixture is alkalinized again via addition of 6.9 g (0.065 moles) Na_2CO_3 and 8 g (0.135 moles) NaOH solution 30%.

The synthesis of Food Dye Orange 1 proceeds as follows: aniline is diazotized as before and it is coupled with salt G, which includes 15 g (0.005 moles) salt G which is dissolved into 10 mL H_2O with addition of 10.4 g NaOH solution 50%. Then, 100 g ice and 9.24 g (0.11 moles) $NaHCO_3$ are added to the solution. The whole mass is stirred continuously for 3 h in order to finalize the reaction (the disappearance of the diazoderivative from the mixture is verified by touching the aureole of a salified sample with aniline alkaline solution).

The product precipitates completely and it is filtered.

The application of these dyes on wool, polyamide and natural silk proceeds in the following way a wool sample is weighed, a float is prepared containing 1.2 g/L EDTA, 2g/L Acvafil and CH_3COOH 30% to get a *p*H = 4-4.5. The dye 0.1% is added and the float is heated to 10^0C. The wool is introduced in it now and the temperature is raised to 90-98^0C, being kept at this level for 90 min.

Then the wool sample is taken out and washed with water and EDTA. The application of these dyes on polyamide is performed in the same float. If the dye is too diluted, its concentration is raised. The float is kept at 90-98^0 for an hour. In the case of natural silk to the existing float, maybe a little more concentrated, 4 mL glycerol are added, while keeping the float temperature at 90-98^0.

Results and discussions

The data from table 1 present the results of the syntheses.

Dyes 1-5 were tested for purity. After the syntheses were performed, these tests were performed with thin layer chromatography. The ascending method on plastics foils of 10x20 cm [11]. The stationary phase is silicagel 60F254. The mobile phases which were worked in are:

1. – normal butanol 2 - butanol 1 - water
2. – normal propanol 2 - sodium bicarbonate 1

The R_f values which were determined in the chromatograms are:

	The R_f values (solvent 1)		The R_f values (solvent 2)
1	0.55	1	0.50
2	0.65	2	0.65
3	0.45	3	0.40
4	0.9	4	0.80
5	0.85	5	0.75

The presence of chromofore groups was made conspicuous with the help of VIS shorthand reports [12]. Dye 1 absorbs at wavelengths λ_{max} = 569.6 nm, dye 2 at λ_{max} =351.6 nm, dye 3 at λ_{max} = 605 nm, dye 4 at λ_{max} = 354.6 nm while dye 5 at λ_{max} =351.1 nm.

These food dyes were not applied on textile materials.

The present paper presents their application on wool, polyamide and natural silk. The dyeing were performed as in the diagram presented in figure 1.

Before dyeing, the dyes solubility in acid medium was tested. The results of these tests can be seen in table 2.

The dyeings were performed uniformly, the resulted colours ranging from red and ochre to blue and yellow.

Food dye Red 12 gives a cyclamen red colours on wool, cyclamen on polyamide and ochre-pink on natural silk. Food dye Yellow 8 gives the following colours: chromium-yellow on wool, yellow on polyamide and light ochre-yellow on natural silk.

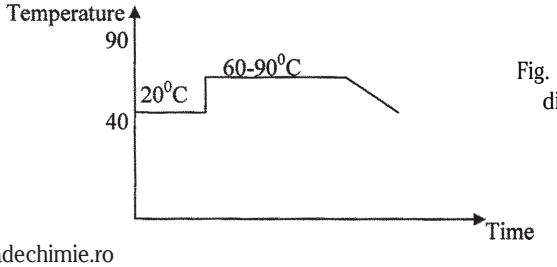


Fig. 1. Dyeing diagram

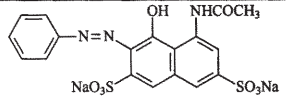
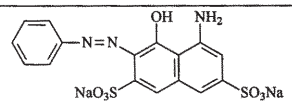
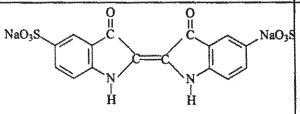
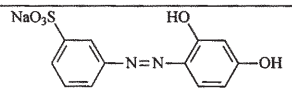
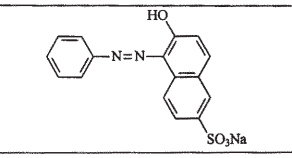
Nr. crt.	Dye formula	pH=6		pH=5		pH=4.5 -3.5	Colour
		20^0C	60^0C	20^0C	60^0C		
1		inso luble	insolu ble	partially soluble	solu ble	no change of colour	cycla men
2		parti ally solu ble	parti ally solu ble	partially soluble	solu ble	no change of colour	brick red
3		insolu ble	insolu ble	partially soluble	solu ble	no change of colour	blue
4		insolu ble	insolu ble	soluble	-	no change of colour	yellow
5		insolu ble	insolu ble	partially soluble	solu ble	no change of colour	brown

Table 2
SOLUBILITY OF DYES 1-5

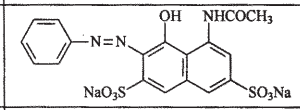
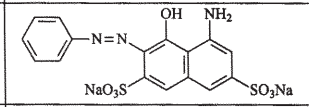
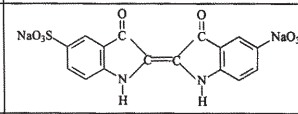
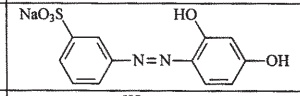
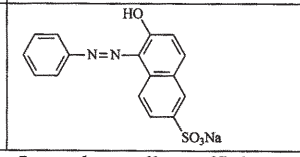
Nr. crt.	Dye Structure	Colour	Affinity		
			Wool	Natural Silk	Polyamide
1		cyclamen	xxxxx	xx	xxx
2		brick red	xxxx	xx	xxx
3		blue	xxxx	xx	xxx
4		yellow	xxxx	xx	xxx
5		brown	xxxx	xx	xxx

Table 3
THE AFFINITIES OF DYES 1-5 FOR THE FIBERS

Legend: excellent affinity = xxxxx; very good affinity = xxxx; good affinity = xxx; average affinity = xx; reduced affinity = x; no affinity = -.

The sample which was dyed with food dye Red 12 has the following colours: brown-orange, ochre-orange and light ochre. Food dye Blue 1 has the following colours: ultramarine, cobalt blue and medium blue.

Food dye Orange 4 can give the following colours: ochre-orange, yellow and ochre-yellow.

Table 3 presents the affinities of these dyes for the fibers. As it can be noticed, there is a very good affinity on wool, a good one on polyamide and an average one for silk.

Conclusions

Five food dyes were prepared and were used to dye not food products but textile materials.

The synthesized dyes were tested chromatographically and their solubility in acid medium was measured before being used in the dyeing process at temperatures ranging from 20^0C to 60^0C.

The synthesized dyes were applied on wool, polyamide and natural silk and their affinity for these fibers was tested.

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3. *** Colour Index, Ed.2, vol.2 p. 2783.
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