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INFLUENCE OF DIFFERENT PARAMETERS ON DYEING OF KNITTING MATERIAL WITH REACTIVE DYES

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Abstract. *Our studies concern the effects of different parameters on dyeing process of knitting materials with reactive vinyl sulphonic dyes. Based on the corresponding parameters correlations, an estimation of ultrasound application validity in dyeing processes of cotton – type textile substrates has been established. Desired color hue may be attained with application of ultrasound reducing dye concentration or shortening dyeing time for 20 min with reduction of salt concentration even to 20 g/dm*^{3}.

Key words: *cellulose fibers, different parameters of dyeing process, reactive vinyl sulphonic dyes, ultrasound*

INTRODUCTION

The processes of textile improvement use huge water volume, electric energy and heat. The most of these processes use additives to accelerate or slow down the reactions. This permits a mass transport from a liquid medium to the textile surface in a reasonable time, without temperature increase. Analogously, in dyeing processes, transport of dyes from a solution to the fiber surface and further into its interior structure depends on time, temperature and various factors. Taking all this into consideration, a desirable quality of product may be achieved. Earlier studies suggested a possible ultrasound role in an improvement of some selected dyeing systems [1-7]. Until now, the mechanism of ultrasound influence on textile substrate, dye and the including processes taking place in a solution and inside the fibers, is not clear yet. An establishment of a universal model seems to be inappropriate, taking into consideration a variety of dyes and fibers, their chemical composition, structure and the application procedure [8-12].

An effect of different ultrasound frequency on each one reactant of reactive sulphonic dye – cellulose fiber system, the effect of addition of different salt quantity, different temperature and time of dyeing process has been studied in this paper.

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THEORETICAL PART

Numerous systems exist for the systematization - objective measurement of colours. The most important are: Commission International de l' Eclairage (CIE), Deutche Institut fur Normung - German Standard Institute (DIN), Natural Colour System (NCS), Ostwald's and Munssel's systems [13-16]. CIE and DIN chromatic systems are scientifically recognized as the bases for numerical evaluation of colours and the calculation of differences between them. Modern colorimetry is based on the Grassmann's laws of additive mixing.

Numerical evaluation of colour

The system of coordinates designated as L*, a* and b* was recommended by CIE in 1976. One colour is completely determined by three coordinates: L*, a* and b* or L*, C* and H* [13-16].

L* is the vertical coordinate of a three-dimensional system of colours, which has values from 0 (black) to 100 (for white);

a* is the horizontal coordinate the values of which range from –80 (green) to +80 (red);

b* is the horizontal coordinate the values of which range from –80 (blue) to +80 (yellow).

Colour is determined by three dimensions by David and Katz, owing to its interpretation in coloured space: H (the hue), L (the lightness) and C (the chroma) [13-16].

Multicoloured (yellow, red, green, blue) and non-multicoloured nuances are distinguished according to colour hue. The colour lightness presents a measure in which one colour is light or dark expressed in light degrees from white to black colour. The saturation describes the colour intensity and represents the distance from the black-white axis [13-16].

Colour coordinates are calculated by the following equations:

$$L^* = 116(Y/Yn)^{1/3} - 16 \quad (1)$$

$$a^* = 500[(X/Xn)^{1/3} - (Y/Yn)^{1/3}] \quad (2)$$

$$b^* = 200[(Y/Yn)^{1/3} - (Z/Zn)^{1/3}] \quad (3)$$

$$E^* = (L^{*2} + C^{*2})^{½} \quad (4)$$

Calculation of colour differences

The equations for the calculation of colour differences are defined on the basis of theoretical conclusions, experience and experimental results [13-16].

$$DE^* = [(DL^*)^2 + (Da^*)^2 + (Db^*)^2]^{½} \quad (5)$$

$$DE^* = [(DL^*)^2 + (DC^*)^2 + (DH^*)^2]^{½} \quad (6)$$

DE* - total colour difference

Da* - the difference on the red-green coordinate ($Da^* = a^*_{sample} - a^*_{standard}$)

+ Da* marks redder, - Da* marks greener;

Db* - the difference on the blue-yellow coordinate ($Db^* = b^*_{sample} - b^*_{standard}$)

+ Db* marks more yellow, - Db* marks bluer;

DL* - the difference in lightness ($DL^* = L^*_{sample} - L^*_{standard}$)

+ DL* marks lighter, - DL* marks darker;

DC* - the difference in chroma ($DC^* = C^*_{sample} - C^*_{standard}$)

+ DC* marks more brilliant, - DC* marks more opaque.

DH* – the difference in colour hue is calculated by equation:

$$DH^* = [(DE^*)^2 - (DL^*)^2 - (DC^*)^2]^{1/2} \quad (7)$$

EXPERIMENTAL PART

Knitting material "Interlock 100% ZW" (produced in Textile Industry "Nitex" – Nis) was dyed in an investigation. Basic characteristics of the non-dyed knitting material (100% viscose, micro-fibers) are presented in Table 1.

Table 1. Basic characteristics of non-dyed knitting material

Knitting material Interlock (100% viscose, micro-fiber)	
$Tt_{knitting}$	20 tex
Tt_{fiber}	1.0 dtex
Mass/m	308 g/m
308 g/m (denier)	220 g/m^2 (mass/s. m)
Illuminant – Whiteness criterion	
D65 - 10º - C.I.E.	70.07 %
C – 2º - Berger	85.70 %

Firstly, water was demineralized using ion-exchange resin (Levatit S-100).

Realized pretreatment of knitting material:

1. 1 g/dm^3 Nonionic (moistening solution),
2. 3 g/dm^3 Na_2CO_3,
3. rinsing,
4. cold washing,
5. neutralization (0.5 g/dm^3 CH_3COOH – 15 min),
6. cold washing.

Commercial reactive dyes – vinylsulphonic types, without refining, were used:

1. BEZAKTIV Brillantorange V-3R (BEZEMA AG), Colour Index assignation - Reactive Orange 16, C.I. 17757. Formula: $C_{20}H_{17}N_3Na_2O_{11}S_3$; M = 617.54 g/mol, azo dye.

2. CIBACRON Navy V-B (CIBA-GEGY), Colour Index assignation – Reactive Black 5, C.I. 20505. Formula: $C_{26}H_{22}N_5S_6O_{21}Na_4$; M = 1024.00 g/mol, bifunctional diazo dye.

3. BEZAKTIV Brillantblau V-R spec. (BEZEMA AG), Colour Index assignation – Reactive Blue 19, C.I. 61200. Formula: $C_{23}H_{23}NO_2$; M = 345.17 g/mol, antrachinone dye.

4. BEZAKTIV Tuerkisblau V-G conc. (BEZEMA AG), Colour Index assignation - Reactive Blue 21, phthalocyanine dye.

Dyeing of knitting material based on viscose micro-fibers was performed with vinylsulphonic dyes by on-line isothermal treatment at 40, 50 and 60 °C, respectively; while dyeing with dye BEZAKTIV Brillantorange V-3R was done at temperatures 30, 40 and 50 C°. Similarly, dyeing was done with addition of different quantities of salts 80, 60 and 40 g/l NaCl, respectively at pH = 10.5 (pH was adjusted with Na_2CO_3). Dyeing was realized by two methods: conventional method (without ultrasonic effect) and ultrasonic method (frequencies 40, 200 and 600 kHz). Time of dyeing was: 80 and 100 min.

Ultrasonic instruments were used:

• an ultrasonic bath – with ultrasonic inductors at the bottom; applied frequency was 40 kHz, power 150 W. Dimensions: a x b x h = 300 x 150 x 200 mm, V = 8 dm^3;

• an ultrasonic reactor (Allied Signal ELAC Nautik GmbH) consisted of a generator (frequencies from 0 to 1600 kHz), a transformator (200 and 600 kHz) and reaction chamber (V = 0.5 dm^3). Used power was 50 W.

RESULTS AND DISCUSSION

The effect of different ultrasound frequency on knitting material dyeing

The effect of ultrasound of different frequencies on dyeing process, when dye Reactive Orange 16 is applied, is presented in Fig. 1-3. Dyeing process was followed at different temperatures (30, 40 and 50°C).

Different dyed samples of knitting material were used in the experiment: a sample dyed by a conventional method was designed as A, a sample dyed using ultrasonic method by Reactive Orange 16 dye was designed as B. Values for DL, Da, Db, DE are absolute values, given in parentheses.

When the effect of different ultrasound frequency was studied, the comparisons between samples B and A (as standard) were done. Temperatures in the case of dyeing sample B varied from 30-50 °C, while the quantity of added NaCl was the same 60g/dm^3. Applied ultrasound frequencies were: 40 kHz, 40 kHz + addition of air-bubbles, 200 kHz and 600 kHz.

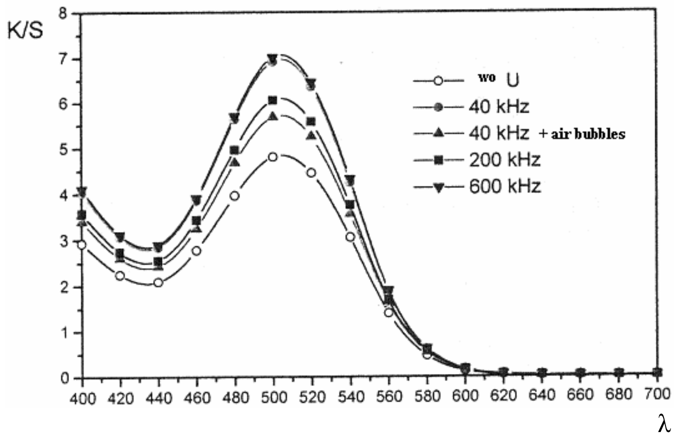

Fig. 1. K/S values (Reactive Orange 16 at 30 °C, with addition of 60 g/dm^3 NaCl) in dependence on wavelength (nm). Legend: wo U - without ultrasound effect

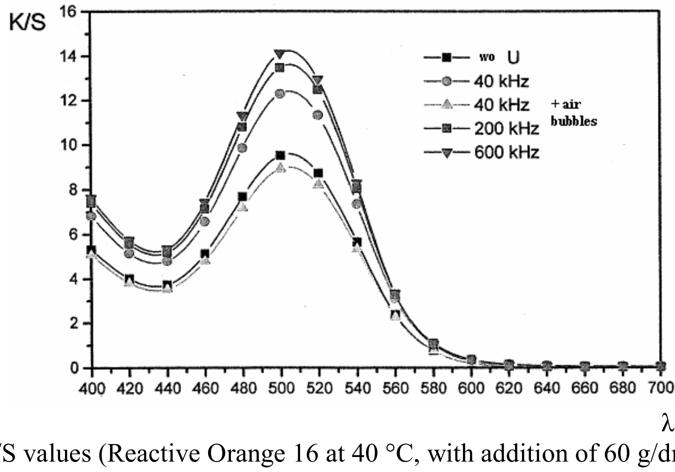

Fig. 2. K/S values (Reactive Orange 16 at 40 °C, with addition of 60 g/dm^3 NaCl) in dependence on wavelength (nm). Legend: wo U - without ultrasound effect

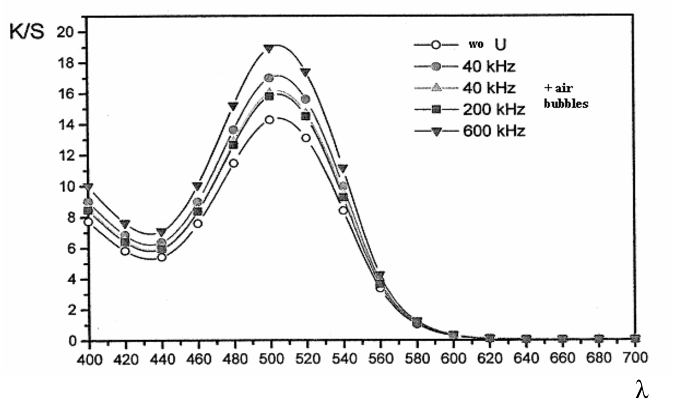

Fig. 3. K/S values (Reactive Orange 16 at 50 °C, with addition of 60 g/dm^3 NaCl) in dependence on wavelength (nm). Legend: wo U - without ultrasound effect

The results of colour differences between samples B dyed at 30 °C and A (Tab. 2) show that the sample B is darker (3.1, 1.6, 2.4, 3.2), redder (2.6, 1.1, 1.0, 2.9) and yellower (2.9, 1.2, 1.3, 3.1) for all applied frequencies. Total colour differences satisfy two allowed criteria, M&S (0.81, 1.4) and CMC (2:1) (0.95, 1.6), given by IS, for used ultrasound frequencies of 40 kHz with addition of air-bubbles and 200 kHz.

Table 2. The colour difference between the samples B (batch) and A (standard)

Standard Batch	A B			
Colour differences CIELAB Standard D65–10’ L 59.8 a 47.1 b 26.8				
Ultrasound (kHz)	DE	DL	Da	Db
40	5.0	3.1 darker	2.6 +a	2.9 +b
40 + air bubbles	2.3	1.6 darker	1.1 +a	1.2 +b
200	2.9	2.4 darker	1.0 +a	1.3 +b
600	5.3	3.2 darker	2.9 +a	3.1 +b

The results of colour differences between samples B dyed at 40 °C and A (Tab. 3) show that the sample B is darker (2.3, 4.2, 3.3) for applied ultrasound frequencies 40, 200 and 600 kHz, but lighter (0.1) when 40 kHz is used with addition of air-bubbles. Sample B is redder (1.3, 2.0) when frequencies of 40 and 600 kHz are used, but greener (0.8, 2.0) for applied frequencies of 40 kHz with addition of air-bubbles and 200 kHz. The same sample is more yellow (0.6, 3.0) for applied frequencies of 40 and 600 kHz, but bluer (1.1, 1.2) when dyeing method at 40 kHz with addition of air-bubbles is used and at 200 kHz. Total colour differences satisfy two allowed criteria, M&S (0.63) and CMC (0.59) for used ultrasound frequencies of 40 kHz with addition of air-bubbles.

Table 3. The colour difference between the samples B (batch) and A (standard)

Standard	A			
Batch	B			
Colour differences CIELAB Standard D65–10’	L 54.1	a 51.4	b 32.2	
Ultrasound (kHz)	DE	DL	Da	Db
40	4.3	2.3 darker	1.3 +a	0.6 +b
40 + air bubbles	1.4	0.1 lighter	0.8 -a	1.1 -b
200	4.8	4.2 darker	2.0 -a	1.2 -b
600	4.9	3.3 darker	2.0 +a	3.0 +b

The results of colour differences between samples B dyed at 50 °C and A (Tab. 4) show that the sample B is darker (1.2, 1.2, 0.9, 2.0), redder (1.0, 0.1, 0.2, 1.3) and more yellow (1.8, 0.5, 0.7, 2.7) for all applied frequencies. Total colour differences satisfy two allowed criteria, M&S (1.1, 0.65, 0.61) and CMC (1.0, 0.6, 0.55) for used ultrasound frequencies of 40 kHz, 40 kHz with addition of air-bubbles and 200 kHz.

Table 4. The colour difference between the samples B (batch) and A (standard)

Standard	A			
Batch	B			
Colour differences CIELAB Standard D65–10’	L 50.9	a 53.7	b 35.7	
Ultrasound (kHz)	DE	DL	Da	Db
40	2.3	1.2 darker	1.0 +a	1.8 +b
40 + air bubbles	1.3	1.2 darker	0.1 +a	0.5 +b
200	1.1	0.9 darker	0.2 +a	0.7 +b
600	3.6	2.0 darker	1.3 +a	2.7 +b

Other dyed samples of knitting material used in the experiment were designed: a sample dyed with Reactive Blue 19 dye as C, with Reactive Blue 21 as D, with Reactive Black 5 as E. For dyeing of samples designed as C, D and E, used temperature was 40 °C, the quantity of added NaCl 60g/dm^3. Applied ultrasound frequencies were: 40 kHz, 200 kHz and 600 kHz.

The results of colour differences between samples C and A (Tab. 5) show that the sample C is darker (2.7, 2.9, 2.2) and more yellow (1.3, 1.0, 1.1) for all applied frequencies, but redder (1.3, 1.2) for used frequencies of 40 and 200 kHz and greener (0.4) when frequency 600 kHz is applied. Total colour differences satisfy two allowed criteria, M&S (0.73) and CMC (0.52) for used ultrasound frequencies of 600 kHz.

Table 5. The colour difference between the samples B (batch) and A (standard)

Standard	A			
Batch	B			
Colour differences CIELAB Standard D65–10’ L 44.4 a -2.7 b -37.7				
Ultrasound (kHz)	DE	DL	Da	Db
40	2.7	2.7 darker	1.3 +a	1.3 +b
200	2.8	2.9 darker	1.2 +a	1.0 +b
600	4.0	2.2 darker	0.4 -a	1.1 +b

The results of colour differences between samples D and A (Tab. 6) show that the sample D is darker (1.2, 0.5, 2.4), greener (0.7, 0.3, 1.3) for all applied frequencies, but bluer (0.8, 0.8) for used frequencies of 40 and 600 kHz and more yellow (1.1) when frequency 200 kHz is applied. Total colour differences satisfy two allowed criteria M&S (0.79, 1.4, 1.0) and CMC (0.72, 0.71, 1.2) for all used ultrasound frequencies.

Table 6. The colour difference between the samples B (batch) and A (standard)

Standard	A			
Batch	B			
Colour differences CIELAB Standard D65–10’ L 71.9 a -26.4 b 18.6				
Ultrasound (kHz)	DE	DL	Da	Db
40	1.7	1.2 darker	0.7 -a	0.8 -b
200	1.2	0.5 darker	0.3 -a	1.1 +b
600	2.8	2.4 darker	1.3 -a	0.8 -b

The results of colour differences between samples E and A (Tab. 7) show that the sample E is darker (5.3, 5.5, 5.9), redder (1.0, 1.2, 1.1) and more yellow (0.8, 0.7, 0.8) for all applied frequencies. Total colour differences do not satisfy two allowed criteria M&S (3.1, 3.6, 3.8) and CMC (3.1, 3.4, 3.4) for used ultrasound frequencies.

Table 7. The colour difference between the samples B (batch) and A (standard)

Standard	A			
Batch	B			
Colour differences CIELAB Standard D65–10’ L 50.9 a 53.7 b 35.7				
Ultrasound (kHz)	DE	DL	Da	Db
40	4.2	5.3 darker	1.0 +a	0.8 +b
200	4.6	5.5 darker	1.2 +a	0.7 +b
600	4.9	5.9 darker	1.1 +a	0.8 +b

The results show that deepness of colour hue (K/S value on λ_{max}) is higher in ultrasonic method of dyeing than in a conventional one (C.I. Reactive Orange 16, λ_{max} = 500 nm). Ultrasound of frequencies 600 kHz causes the highest colour hue deepness, frequencies of

200 and 40 kHz smaller, respectively at 40°C; at temperatures 30 and 50°C, ultrasound of 40 kHz causes deeper hue than ultrasound of 200 kHz.

Specific method is air-bubbles involving with applied ultrasound (40 kHz). It was expected that this effect would intensify the cavitation effect and efficiency of dyeing process, as well. However, results show that total colour differences are $DE_{CIELAB76}$ = 2.3 and DE_{CMC} (2:1) = 0.95, smaller in comparison with conventional method and that one where only ultrasound (40 kHz) is used. Similar results are achieved at temperatures 40 and 50°C.

Figs. 4-6 show curves of spectral K/S values for Reactive Blue 19. Hue deepness for dyes: reactive blue19, reactive blue 21 and reactive black 5, become greater with an increase of applied ultrasound frequency (40, 200 and 600 kHz).

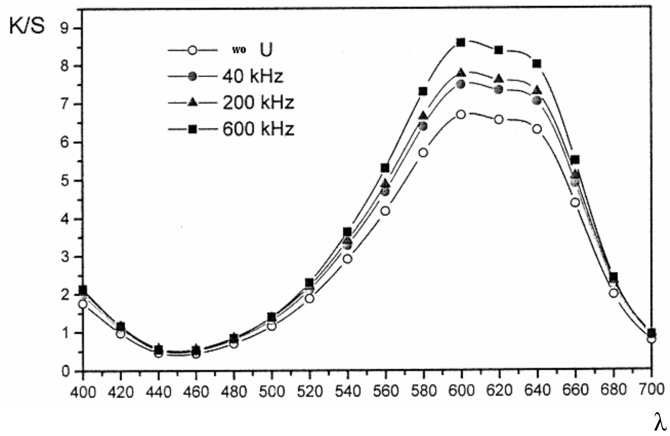

Fig. 4. K/S values (Reactive Blue 19 at 40 °C, with addition of 60 g/dm^3 NaCl) in dependence on wavelength (nm) Legend: wo U - without ultrasound effect

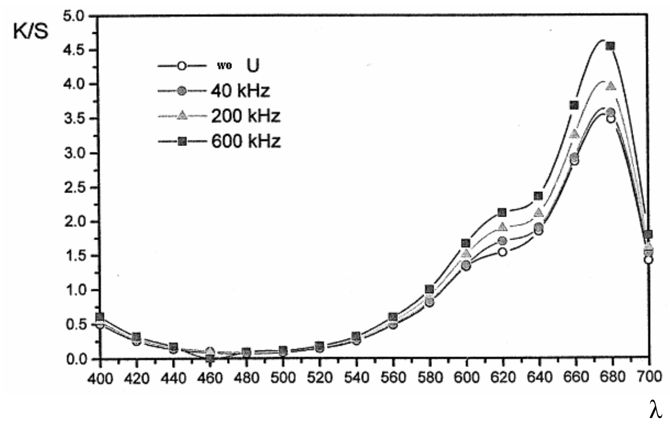

Fig. 5. K/S values (Reactive Blue 21 at 40 °C, with addition of 60 g/dm^3 NaCl) in dependence on wavelength (nm). Legend: wo U - without ultrasound effect

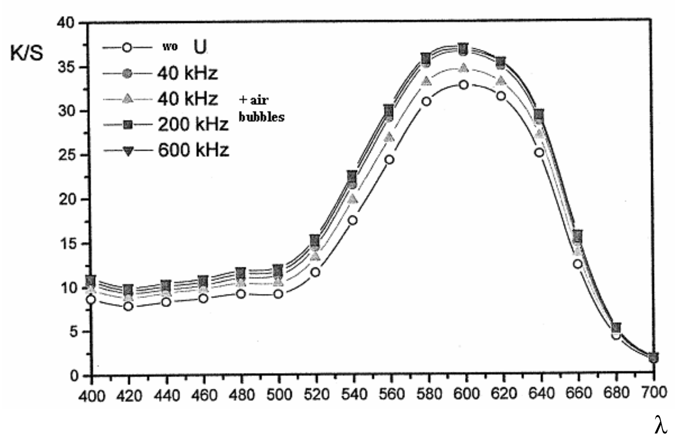

Fig. 6. K/S values (Reactive Black 5 at 40 °C, with addition of 60 g/dm^3 NaCl) in dependence on wavelength (nm) Legend: wo U - without ultrasound effect

The effect of addition of different NaCl quantity on knitting material dyeing

When the effect of addition of different NaCl quantity was studied, the comparison between samples B and A (as standard) was done. Temperatures in the case of dyeing sample B varied from 30-50 °C, applied ultrasound frequency was 40 kHz, while the quantity of added NaCl varied from 40-80 g/dm^3.

It appears from the results of colour differences between samples B dyed at 30 °C and A (not shown) that the sample B is darker (3.2, 3.0, 1.4), redder (2.3, 2.0, 0.7) and yellower (2.7, 2.3, 0.9) when quantities 80, 60 and 40 g/dm^3 of NaCl are added. Total colour differences satisfy two allowed criteria M&S (0.62) and CMC (0.72) in case of dyeing with addition of 40 g/dm^3.

It is evident from the results of colour differences between samples B dyed at 40 °C and A (not shown) that the sample B is darker (2.5, 2.0), redder (1.9, 0.3) and more yellow (1.9, 0.3) when quantities 80 and 60 g/dm^3 of NaCl are added. Total colour differences satisfy two allowed criteria M&S (1.3, 0.84) and CMC (1.5, 0.87) when dyeing is performed with addition of 80 or 60 NaCl g/dm^3.

Regarding the results of colour differences, it is obvious between samples B dyed at 50 °C and A (not shown) that the sample B is darker (0.8) when 80 g/dm^3 of NaCl is added, but lighter (0.9, 1.8) when 60 g/dm^3 or 40 g/dm^3 of NaCl is added. The same sample is greener (0.4, 1.3, 1.7) and bluer (0.8, 2.0, 2.9) when quantities 80 - 40 g/dm^3 of NaCl are added. Total colour differences satisfy two allowed criteria M&S (0.55, 1.1) and CMC (0.52, 1.1) when dyeing is performed with addition of 80 or 60 NaCl g/dm^3.

The effect of salt concentration (80, 60 and 40 g/dm^3) was regarded on example of C.I. Reactive Orange 16 at temperatures 30, 40 and 50 °C without and with ultrasound (40 kHz). Results (Figs. 7-9) express that ultrasonic method of dyeing with smaller concentration of salt (60 g/dm^3, and in some cases 40 g/dm^3) gives deeper hue in comparison with that achieved by conventional method with addition of 80 g/dm^3 salt. These results are registered during dyeing at 30 and 40 °C, while at 50 °C ultrasonic dyeing with addition of 60 g/dm^3 gives somewhat lighter dye, but registered colours differences are in allowed limits, $DE_{(M\&S)}$ = 1.1 (allowed limit DE = 1.4) and $DE_{(CMC\,(2:1))}$ = 1.1 (allowed limits of tolerance DE from 1.2 to 1.4).

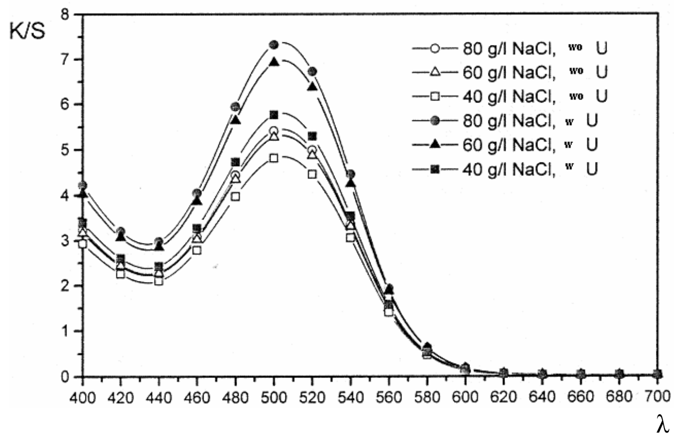

Fig. 7. K/S values (Reactive Orange 16 at 30 °C, with addition of different g/dm^3 NaCl) in dependence on wavelength (nm). Legend: wo U - without ultrasound effect w U - with ultrasound effect

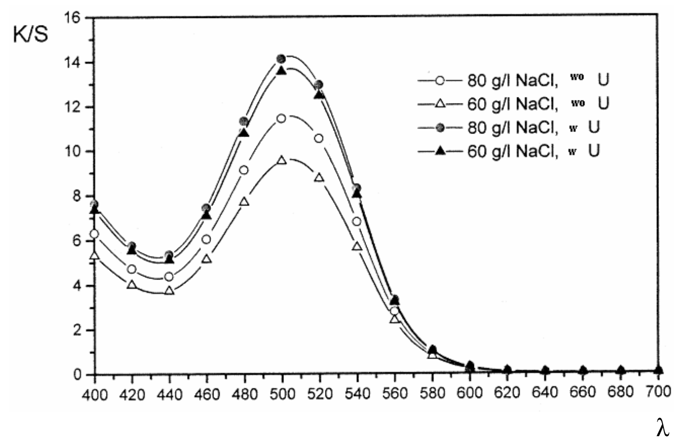

Fig. 8. K/S values (Reactive Orange 16 at 40 °C, with addition of different g/dm^3 NaCl) in dependence on wavelength (nm). Legend: wo U - without ultrasound effect w U - with ultrasound effect

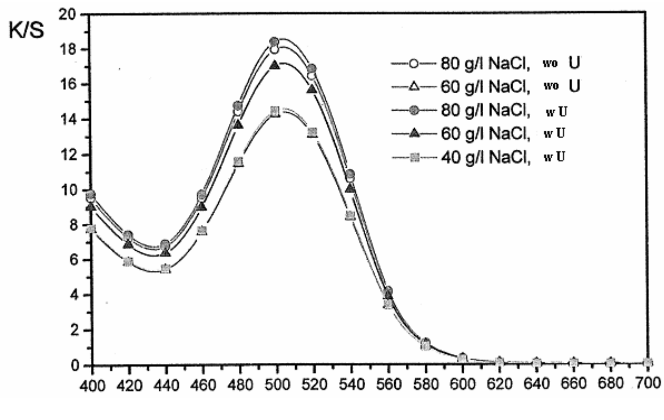

Fig. 9. K/S values (Reactive Orange 16 at 50 °C, with addition of different g/dm^3 NaCl) in dependence on wavelength (nm). Legend: wo U - without ultrasound effect w U - with ultrasound effect

The effect of temperature on knitting material dyeing

When the effect of dyeing temperature was studied, the comparisons between samples B and A (as standard) were done. Temperatures varied 50-30 °C, applied ultrasound frequency was 40 kHz, while the quantity of added NaCl was 60 g/dm^3.

The results of colour differences between samples B and A (not shown) present that the sample B is darker (1.2, 0.1, 9.0) at temperatures of dyeing from 50 °C to 30 °C; redder (1.0) and more yellow (1.8) at dyeing temperature 50 °C. The same sample is greener (0.3, 6.7) and bluer (0.5, 8.9) when the temperatures of dyeing are 40 °C and 30 °C. Total colour differences satisfy two allowed criteria M&S (1.1, 0.3) and CMC (1.0, 0.2) for applied temperatures 50 °C and 40 °C.

When the effect of dyeing temperature was studied, the comparisons between samples D and A (as standard) were done. Temperatures varied from 60 to 40 °C, applied ultrasound frequency was 40 kHz, while the quantity of added NaCl was 60 g/dm^3.

Regarding the results of colour differences between samples D and A (not shown), it appears that the sample D is darker (3.2, 1.8, 2.4) at temperatures of dyeing from 60 °C to 40 °C; redder (1.6) and more yellow (0.8) at dyeing temperature 40 °C. The same sample is greener (1.2, 1.3) and bluer (1.3, 1.1) when the temperatures of dyeing are 60 °C and 50 °C. Total colour differences satisfy two allowed criteria M&S (1.2) and CMC (1.4) for applied temperature 50 °C.

Investigating ultrasonic dyeing with Reactive Orange 16 at temperatures 30, 40 and 50 °C (Fig. 10.) and with Reactive Blue 21, at 40, 50 and 60 °C (Fig. 11) in comparison with conventional method at the same temperatures, it is observed that they showed different behavior. Reactive Orange 16 is more reactive one, ultrasonic method gives approximately the same dye deepness at 40 °C as in conventional method at 50 °C ($DE_{(CIE)} = 0.66$; $DE_{(M\&S)} = 0.31$; $DE_{(CMC\ (2:1))} = 0.28$). Beside that, system heating is need only at beginning, somewhat later temperature maintains due to thermal energy generated by decay of the cavitation bubbles.

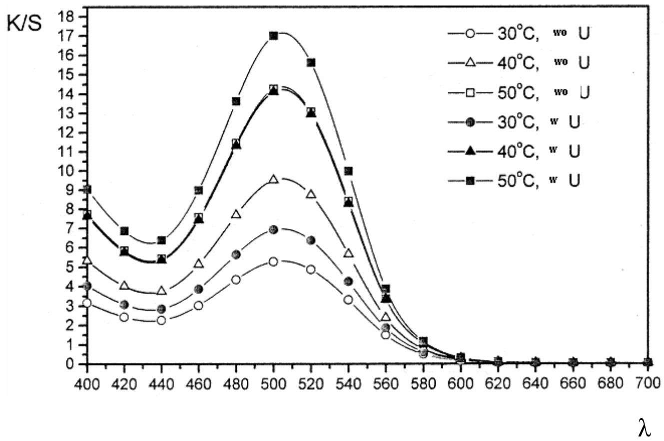

Fig. 10. K/S values (Reactive Orange 16) at different temperatures (conventional and ultrasonic method, 40 kHz) in dependence on wavelength (nm) Legend: wo U - without ultrasound effect w U - with ultrasound effect

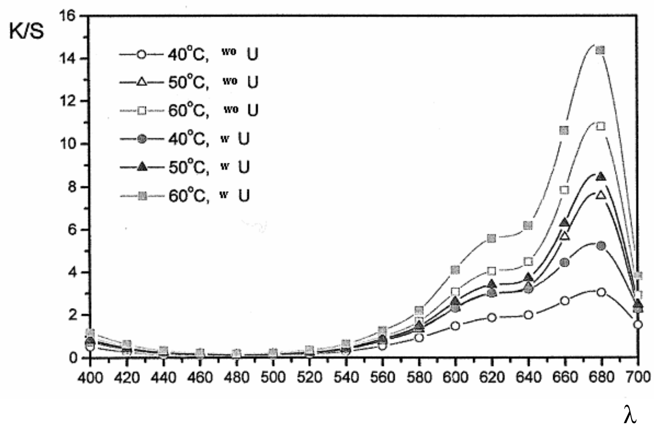

Fig. 11. K/S values (Reactive Blue 21) at different temperatures (conventional and ultrasonic method, 40 kHz) in dependence on wavelength (nm) Legend: wo U - without ultrasound effect w U - with ultrasound effect

In the case of Reactive Blue 21, less reactive dye, temperature is very important factor that ultrasound can not compensate. Namely, ultrasonic dyeing gives deeper dye in comparison with conventional at the same temperature, but the obtained dye is lighter with important differences in chromacity than the dye obtained by conventional method at higher temperature for 10 °C.

The effect of time on knitting material dyeing

When the effect of dyeing time was studied, the comparisons between samples B and A (as standard) were done. Time varied from 100 to 80 min, applied ultrasound frequency was 40 kHz and the quantity of added NaCl was 60 g/dm^3, while temperature was 40 °C.

The results of colour differences between samples B and A (not shown) present that the sample B is darker (3.3, 1.3) redder (2.0, 1.3) and more yellow (3.0, 1.7) regardless the time of dyeing process (100 or 80 min). Total colour differences satisfy two allowed criteria M&S (0.9) and CMC (1.1) when dyeing process lasted 80 min.

The results of colour differences between samples C and A (not shown) show that the sample C is darker (2.7, 0.1) and more yellow (1.3, 0.5) regardless the time of dyeing process (100 or 80 min). The same sample is redder (0.08) when time of dyeing process is 80 min, but greener (1.3) when time of applied dyeing is 100 min. Total colour differences satisfy two allowed criteria M&S (0.6) and CMC (0.4) when dyeing process lasted 80 min.

The results of colour differences between samples D and A (not shown) present that the sample D is darker (1.2), greener (0.7) and bluer (0.8) when the time of dyeing process is 100 min. The same sample is lighter (0.8), redder (0.8) and more yellow (0.7) when time of dyeing process is 80 min. Total colour differences satisfy two allowed criteria M&S (0.7, 0.6) and CMC (0.7, 0.6) regardless the time of dyeing process (100 or 80 min).

The results of colour differences between samples E and A (not shown) show that the sample E is darker (5.3, 0.1) and more yellow (0.8, 0.5) regardless the time of dyeing process (100 or 80 min). The same sample is greener (0.08) when the time of dyeing process is 80 min and redder (1.0) when the time of dyeing process is 100 min. Total colour differences satisfy two allowed criteria M&S (0.6) and CMC (0.4) when the time of dyeing process is 80 min.

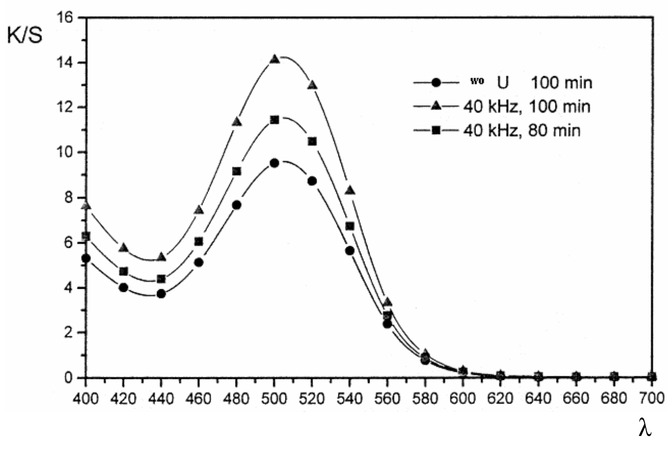

Fig. 12. K/S values (Reactive Orange 16) with different time of dyeing (conventional and ultrasonic method, 40 kHz) in dependence on wavelength (nm)
Legend: wo U - without ultrasound effect

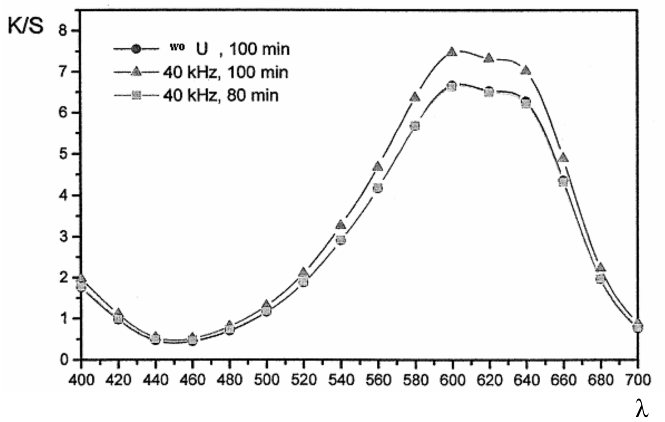

Fig. 13. K/S values (Reactive Blue 19) with different time of dyeing (conventional and ultrasonic method, 40 kHz) in dependence on wavelength (nm) Legend: wo U - without ultrasound effect

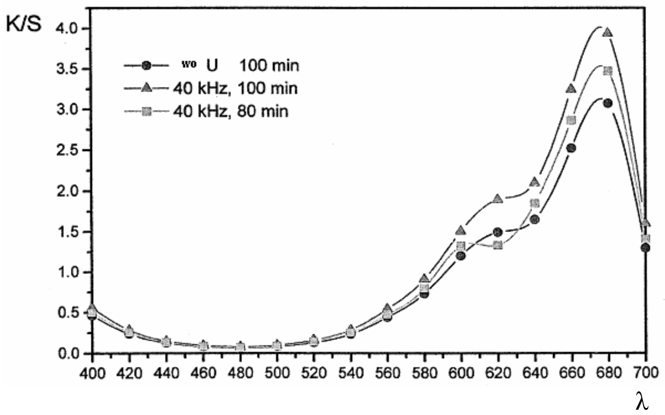

Fig. 14. K/S values (Reactive Blue 21) with different time of dyeing (conventional and ultrasonic method, 40 kHz) in dependence on wavelength (nm) Legend: wo U - without ultrasound effect

Similarly, systems with shorter dyeing time were investigated (Figs. 12-15). With shortening of dyeing time for 20 min, with the ultrasonic effect, dyes with deeper or the same hue are achieved in comparison with dyed material obtained by conventional method for 100 min. In this sense, the desired hue may be achieved with shortening of dyeing time and/or decreasing salt concentration and/or decreasing dye concentration.

Cellulose fibers (natural, as well as, produced ones) have been undergone on super molecular level under an ultrasonic effect. Namely, ultrasound has caused a decreasing of crystallinity amount.

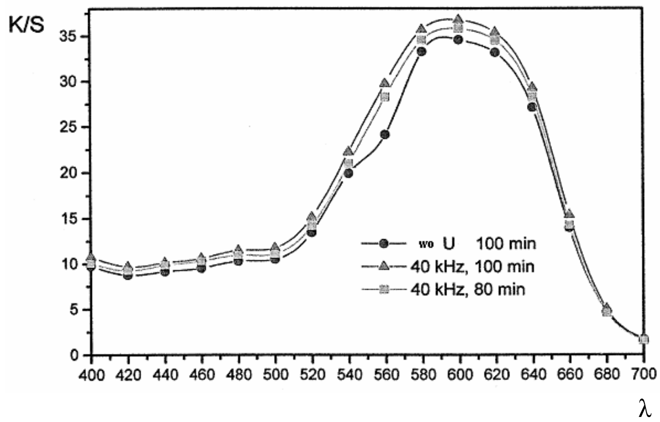

Fig. 15. K/S values (Reactive Black 5) with different time of dyeing (conventional and ultrasonic method, 40 kHz) in dependence on wavelength (nm). Legend: wo U - without ultrasound effect

In this experiment, four reactive vinyl-sulphonic dyes were investigated. In all cases, ultrasonic method causes an increase of dye exhaustion, but it varies in dependence on the concrete dye. Ultrasound waves accelerate diffusion processes, dye movement from solution to a fiber, contributing to reaction rate acceleration between water molecules and cellulose OH groups. In an ultrasonic method of dyeing an amount of fixed dye in comparison to absorbed one is much higher than without use of ultrasound. The efficiency of dyeing is higher with higher frequency of used ultrasound, what comprises higher exhaustion of dye, reduction of salt consumption and a deeper hue of realized due on a textile material. A heating of a medium during the dyeing process is unnecessary, regarding that an amount of ultrasonic energy being converted into thermal one in a heterogeneous system of textile dyeing. Moreover, a cooling is necessary in some moments of dyeing.

When higher frequencies of ultrasound are used, important factor is intensity of waves. With an increase of ultrasound frequency applied, higher dye exhaustion and deeper colour hue are obtained. Further investigations have to be directed to variation of applied ultrasound frequencies in aim to estimate optimal parameters on the final dyeing effects.

Dyeing in a presence of ultrasound during shorter time, 20 min (usually, 80 min) provides colours similar to conventional ones with an addition of salts (conditions – 80g/dm^3 and 100 min).

In all cases, the achieved colours of dyed materials present good to excellent resistance.

Dyeing process with use of ultrasound (40 kHz) and air-bubbles does not give the expected results. Use of combination ultrasound-bubbles-NaCl produces abundant foam in amount as much higher as concentration of salt is higher. Bubbles and arisen foam have blocked a diffusion of dye to a fiber surface. Consequently, the dye exhaustion was worse as well as a dye fixation to a textile substrate in comparison with a method when only ultrasound (40 kHz) was applied.

CONCLUSIONS

- Desired colour hue may be attained with application of ultrasound reducing dye concentration or shortening dyeing time for 20 min with reduction of salt concentration even to 20 g/dm^3. Taking into consideration that ultrasound contributes to heating of a medium, additional heating of process surround is completely unnecessary.
- Involving of air-bubbles during the ultrasound method of dyeing does not give satisfied results. Abundant foam appearing in combination ultrasound-air bubbles-salt represents particular unsuitability for control of process.
- This technological dyeing process is interesting in the sense of environmental protection because of better dye exhaustion and reduction of salts contents. Therefore, wastewaters contain fewer pollutants.
- Dyes obtained by ultrasound method have the same quality of resistance as those attained with conventional method.

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UTICAJ RAZLIČITIH PARAMETARA NA BOJENJE PLETENINE REAKTIVNIM BOJAMA

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Naša ispitivanja se odnose na efekte različitih parametara na proces bojenja pletenog materijala reaktivnim vinil-sulfonskim bojama. Na osnovu odgovarajućih korelacija parametara, data je ocena valjanosti primene ultrazvuka u procesu bojenja tekstilnih supstrata od pamuka. Željeni ton boje može se postići primenom ultrazvuka uz smanjenje koncentracije boje ili skraćivanje vremena bojenja za 20 min sa istovremenim smanjenjem koncentracije soli čak do 20 g/dm^3.

Ključne reči: *celulozna vlakna, različiti parametri procesa bojenja, reaktivne vinil-sulfonske boje, ultrazvuk*