Statistic Modelling and Optimization of the Dyeing Process of Melana Fibres with Victoria Blue B Dye in the Presence of Anionic Retarders

CEZAR-DORU RADU[1], ION SANDU[2], RODICA DIACONESCU[3*], ELENA BERCU[4], HORIA- ADRIAN ALDEA[5]

[1],,Gheorghe Asachi,, Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Chemical Engineering, 71 D Mangeron Blvd., 700050, Iasi, Romania

[2] ,,Alexandru Ioan Cuza" University of Iasi, ARHEOINVEST Interdisciplinary Platform, 22 Carol I Blvd, 700506, Romania

[3],,Gheorghe Asachi,, Technical University Iasi, Faculty of Textiles-Leather and Industrial Management, 29 Mangeron Str., Iasi Romania

[4] Metropolitan Church of Moldavia and Bucovina (MMB), Department for restoration and preservation of the Christian art 'RESURRECTIO', 16 Stefan cel Mare si Sfant Av., Iasi, Romania

[5],,Gr.T.Popa" University of Medicine and Pharmacy, Faculty of Dental Medicine, 16 University Str., 700115, Iasi, Romania

The present study pursued the influence of polyelectrolytes based on maleic co-polymers with styrene (NaM-S) and vinylacetate (NaM-VA) under the form of natrium salt, in the tinctorial system consisting of Melana dyed with Victoria Blue B (VVB) - triarylmethane dye using the colour difference (ΔE), as a method to evaluate the interactions. Mathematical models of the studied dyeing processes have been developed and the necessary information on their significant factors is produced by means of experiment planning methods, known as Design of Experiment (DoE) or Experimental design. Optimal correlations between the application conditions and the colour differences obtained on Melana-type fibre have also been studied.

Keywords: Melana Fiber, Maleic Copolymers, Color Differences, Mathematical Models, Optimization Process

The large afinity of the cationic dyes for the acrylic fibers is the result of the electrostatic interactions and hydrophobic interactions between the fibre and the dye, which results in nonuniform dyeing for acrylic fibres. The dyeing of the polyacrylnitrile fibers with cationic dyes occurs in three stages [1-3]:

- absorption of dye cation on the external fiber surface;
- dye diffusion inside the fibre;
- formation of electrovalences between dye cations and fibre anions.

The first and the third stages occur at very high velocities, the velocity of the second stage being decisive for the entire dyeing process.

The factors governing the first stage are: temperature, dye liquor stirring and fibre electric potential. At the beginning of dyeing, when the dye concentration in the bath is high, the absorption rate is also high, but when the balance is reached, the dye concentration in the float is much smaller. This is true irrespective of the initial dye concentration in the float (small under 1%, or big over 1%). At initial large concentrations, the depletion rate is no longer influenced by the dye concentration in the float. The depletion rate changes depending on the dye concentration in the float similar to the variation of the concentration in the fibre in terms of the dye concentration in solution. The modification of the dye concentration at the fiber surface determines the variation in the same direction and of the same importance of the gradient concentration (dc/dx) responsible for dye raising rate on the fiber. The high dye sorption rate represents the main cause of the dyeing non-uniformities; this peculiarity, together with the impossibility of conventional dyes to migrate represent the real cause of the difficulty to obtain a uniform dyeing. In order to obtain uniform dyeing, it is necessary to control very carefully the temperature rising rate after exceeding the vitrifying temperature. When this is not possible, one must resort to the utilization of balancing and retarder agents [3, 4].

The present study pursues the influence of poly-electrolytes based on maleic copolymers with styrene (NaM-S) and vinyl acetate (NaM-VA) under the form of sodium salt, on the color difference (ΔE) of the Melana type polyacrylonitrile fibers dyeing with triamino-triarylmethane dye – Victoria Blue B (VBB). The partners used in this study were selected taking into account the medical and biomedical properties [5-13].

Experimental part
Materials and methods
The dye: Victoria Blue B: VBB (Merk, Dearmstadt, Germany), were used as received. The dye structure is presented in figure 1.
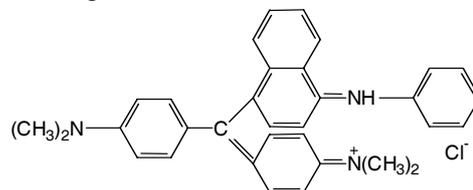

Fig. 1. Chemical structure of the VBB dye

Polyelectrolytes: The utilized polyelectrolytes are copolymers of the maleic acid with styrene (NaM-S), and the copolymer of the maleic acid with vinyl acetate (NaM-VA), both as sodium salts. The two polyelectrolytes were obtained from copolymers of the maleic anhydride with vinyl acetate or styrene, synthesized in laboratory according to our own method or methods described in literature with Mv = 70000 for NaM-VA and Mv = 95000 corresponded to NaM-S [14, 15]. The polyelectrolyte structures are illustrated in figure 2.
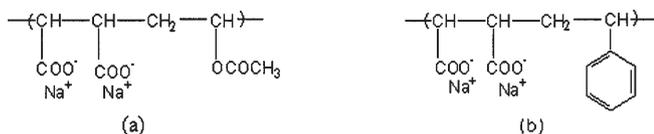
* email: rodicamdiaconescu@yahoo.com

Fig. 2. Chemical structures of the copolymers NaM-VA (a) and NaM-S (b)

Melana fibre: The Melana fibre is a polyacrylonitrile fibre based on a ternary polymer (acrylonitrile, vinyl acetate, α-methylstyrene) obtained through a radical polymerization reaction initiated in the redox system with potassium persulphate-natrium metabisulphite, its schematic structure being presented in figure 3 [1, 3, 4, 16].
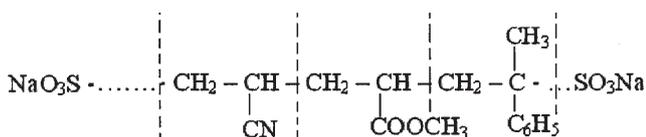

Fig. 3. Schematic structure of Melana fibre

Dyeing method: The dyeing was performed with a dyeing device Mesdan Lab with 6 dyeing positions. The dyeing (by six dyeing of one gram for each colour position) of Melana fibres was performed in aqueous solutions (distilled water), with VBB, in the presence of the polyelectrolytes NaM-VA or NaM-S at dye and polyelectrolyte concentrations of: 0.5; 1.0; 1.5; 2.0; 2.5%, the float having a pH of $5.5 \div 6.2$ adjusted with acetic acid 10% and a hydromodule of 1:50. Practically, to the aqueous solution of the dye, one adds polyelectrolyte in different concentrations and some drops of acetic acid to adjust the pH. The dyeing flask is magnetically stirred 5 min for homogenization, and then the solution stays still for 30 min, after which the Melana fibres (1g) are added. The solution is stirred again for 5 min, and then the dyeing flask follows a thermal regime. The dye liquor is heated up to 80°C, being then maintained at this temperature for about 10 min. The heating continues up to temperatures of 90, 95 or 100°C at a heating rate of 1°C/min, keeping this temperature constant for 75 min, after which the dyeing solution is cooled slowly. The dyed Melana is washed intensely for 5 min with cold water and 5 min with warm water and then dried at room temperature. Besides the dyeing performed in the presence of the two poly-electrolytes, witness (standard) dyeing of Melana was also performed with VBB, in the presence and absence respectively of the two polyelectrolytes at 90°C for 75 min.

Colour differences have been measured with a portable Datacolor 2002 spectrophotometer type Check Plus [3]. We resorted to the measurement of color differences ΔE and implicitly of the color intensity respectively by measuring the color components L*, a*, b*:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2},$$

where ΔL^* indicates any brightness difference and is marked with "+" if the sample that reproduces is lighter (brighter) than the witness, and with "–"if it is darker than the witness.

The values of Δa^* and Δb^* indicate the sample positions on the chromatic diagram, namely "a" represents chromatic variation/deviation to red for positive values and to green for negative values. Similarly, for the "b" coordinate, the positive values indicate yellow colors and the negative ones- blue colors, the chromatic intensity being higher the higher is the numerical value [17-25].

In order to obtain the mathematical model of the studied processes and the necessary information on the significant factors, an experiment planning is carried out, known as *Experimental design or Design of Experiment* (*DoE*). The data collected according to the experimental program are used to estimate the model coefficients. These represent the relation between the response ye (ΔE) and the factors $x_1, x_2..x_n$. The principle of the estimation (approximation) method is represented by the multiple linear regressions (RLM) [3].

Experimental design is a branch of the mathematical statistics and includes the mathematical tools used to establish the number of experiments, the conditions of realization and the methods to estimate the experimental results. The adequate experimentation project is chosen in terms of the type of the necessary dependence.

The central rotable composed programs are the most indicated for the type of problem approached in this study. We mean to obtain minimum dispersions, equal in all the experimental points. The experimental points must be situated at approximately equal distances to the program centre, in order to realize equal dispersions. The central. rotable composed program for four independent variables contains 31 experiments [3, 26-29]:
- 16 experiments corresponding to the program 24;
- 7 experiments situated on the axes of coordinates at distances $\alpha = \pm 1$;
- 7 experiments in the program centre.

In the present case we performed 31 dyeings for each of the 2 systems.

Optimization Method: In this case the *Method of descending simplex* is used (initiated by Spendley, Hext and Himsworth [1962] and improved later by Nelder and Mead [1965]) [3].

This differs from other deterministic minimization methods because it does not explicitly need one dimensional optimization algorithms. The method presents the evaluation principles only for functions, not for the derivatives, being a 0th order method [30, 31].

Based on experimental results and theoretical appreciations concerning the Melana fibres dyeing process with cationic dye in the presence of anionic polyelectrolytes, the colour modifications *ye* (ΔE) were chosen as optimization criterion [32]. The factors (independent variables) with significant influence on the process have been established, namely x_1 – dye concentration (%), x_2 – polyelectrolyte concentration (%), x_3 – dyeing time (min) and x_4 – dyeing temperature (°C) [3].

Within the statistical modelling, the determination field of the experiment centre and the variation step have been established for each factor apart, taking into account the

Table 1
FIELDS AND STEPS OF VARIATION
FOR INDEPENDENT VARIABLE

Factor	UM	Coded factor	$x_{min} \rightarrow x_{max}$	x_{io}	-2	-1	0	1	2	Step
Dye conc.	%	x_1	0.5→2.5	1.5	0.5	1	1.5	2	2.5	0.5
Polyelec.conc.	%	x_2	0.5→2.5	1.5	0.5	1	1.5	2	2.5	0.5
Dyeing time	min	x_3	30→120	75	30	52.5	75	97.5	120	22.5
Dyeing temperature	°C	x_4	80→100	90	80	85	90	95	100	5

restrictions for the technological and technical realization of the process. The data are illustrated in table 1.

Results and discussions

The data collected according to the experimental program are used to estimate the model coefficients. This represents the relationship between the responses ye (ΔE) and the factors x_1, x_2, x_3 and x_4. The principle of the estimation (approximation) method is represented by the multiple linear regressions RLM.

Based on the results provided by the MODDE program, it has been considered that the equation which expresses the best ye (x_1, x_2, x_3, x_4) has the form:

$$ye = bo + b_1 x_1 + b_2 x_1 + b_3 x_3 + b_4 x_4 + b_{11} x_{12} + b_{22} x_{22} + b_{33} x_{32} + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{14} x_1 x_4 + b_{23} x_2 x_3 + b_{24} x_2 x_4 + b_{34} x_3 x_4$$

After this, a statistic model was elaborated through a *central rotable composed program for four independent variables*. Based on the experimental program and experimental results produced through automated processing on an IBM-PC computer, the response functions for VBB dye are presented bellow [3].

The tinctorial Melana fibers dyed with VBB in NaM-VA presence

Based on the results of the performed experiments, we have obtained for the tinctorial system (Melana VBB, NaM-VA) the following mathematical model:

$$y_e = 16.8057 + 4.98375\, x_1 + 2.94042\, x_2 + 2.09958\, x_3 +$$
$$+ 5.19542\, x_4 - 0.64195\, x_1^2 - 1.22445\, x_2^2 - 1.1282\, x_3^2$$
$$+ 1.3293\, x_4^2 - 0.873124\, x_1 x_2 + 1.09187\, x_1 x_3 -$$
$$- 0.72937\, x_1 x_4 + 0.995625\, x_2 x_4$$

After examining the coefficients of the mathematical model within the field of the established factors, the following information was obtained:
- colour difference ye (ΔE) increases with increasing concentration of the VBB dye (x_1), and the polyeletrolyte NaM-VA (x_2), and the dyeing time (x_3), and the dyeing temperature (x_4).
- ye increases with the increase of the values of $x_1 x_3$, $x_2 x_4$ and decreases with the increase of $x_1 x_2$ and $x_1 x_4$.

The tinctorial Melana fibres dyed with VBB in NaM-S presence

Based on the results of the performed experiments, we have obtained for the tinctorial system (Melana VBB, NaM-S) the following mathematical model:

$$Y_e = 13.96 + 6.81584\, x_1 + 2.8275\, x_2 + 3.30417\, x_4 + 1.30625\, x_3^2$$
$$- 2.085\, x_1 x_4 + 0.96875\, x_2 x_3 + 1.51813\, x_3 x_4$$

After examining the coefficients of the mathematical model within the field of the established factors, the following information was obtained:
- colour difference ye (ΔE) increases with increasing concentration of the dye VBB (x_1), and the polyeletrolyte NaM-S (x_2), and dyeing temperature (x_4).
- ye decreases with the increase of the values of $x_1 x_4$ and increases with the increase of the values of $x_2 x_3$, $x_3 x_4$.

The results of a previous study [33] concerning Melana fibres dyeing with MB in the presence of NaM-S have shown that the polyelectrolyte presents a retardation effect during the process of Melana dyeing with MB. The accelerating effect of Melana fibres dyeing process with MB in the presence of NaM-VA appears due to the easiness with which the dye cations are released from the metachromatic compound, and the real possibilities to react with anionic groups from the ends of Melana fibre chain. After examining the coefficients of the mathematical model within the field of the established factors, the following information or (Melana, MB, NaM-VA) system was obtained: colour difference ye (ΔE) increases with increasing concentration of the dye MB (x_1), and the polyeletrolyte NaM-VA (x_2), and the dyeing time (x_3) and it decreases with increasing dyeing temperature (x_4). For (Melana, MB, NaM-S) system, the following information was obtained: the colour difference ye (ΔE) increases mainly with the increase of the dye concentration (x_1), dyeing time (x_3) and temperature (x_4), and it decreases with the increase of the polyelectrolyte concentration (x_2). These results are in good agreement with the color difference to these systems in our early studies [34].

Polyelectrolytes NaM-S and NaM-VA present a retardation effect irrespective of the concentration at which they are found in the process of Melana sample dyeing with CV, due to the large volume of dye molecules and the hydrophobia of these systems. The steric hindrance phenomenon is more pronounced in the case of Melana samples dyed in the presence of NaM-S, due to the styrene radical. In addition the triaminotriphenylmethane dyes (for instance Crystal violet) present very marked remission phenomena, such that the colour (greenish) of their crystal is complementary to the colour of the solutions they make (red-violet) [11, 33].

Based on the results of the performed experiments, we have obtained for the tinctorial system (Melana CV, NaM-VA) the following information: colour difference ye (ΔE) increases with increasing concentration of the CV (x_1), and the NaM-VA (x_2), and the dyeing temperature (x_4). For the tinctorial system (Melana CV, NaM-S) the following information was obtained: colour difference ye (ΔE) increases with increasing concentration of the CV (x_1), and the NaM-S (x_2), and the dyeing time (x_3) and it decreases with increasing dyeing temperature (x_4) [33, 35].

By heating the dye liquor, the dye - polyelectrolyte bonds break off, such that each VBB cation easily migrates toward charged sites from the ends of the macromolecular chain of the Melana fibres, interacting with them. In these cases, the retardation effect proves to be weaker as compared to that systems discussed above, due to the large volume of the VBB cations, which induces a pronounced steric hindrance, somehow braking the breaking off of the ionic bonds between the dye cations and polyelectrolyte cations, as well as the aggregate generation. In these cases, the retardation effect proves to be weaker due to the large volume of the VBB cations, which induces a pronounced steric hindrance, somehow braking the breaking off of the ionic bonds between the dye cations and polyelectrolyte cations, as well as the aggregate generation [33, 36, 37].

Mathematical models presented here were subsequently used to predict the studied processes and to determine the processing conditions necessary for optimal governing. In order to predict the influence of the independent variables on ye (ΔE) and their interactions, 222 response surfaces and 207 level curves were mapped out for the 2 studied systems [3]. Each time two factors were maintained constant (x_1, x_2 coded, equal to -1, 0 or 1), the other three being modified (figs. 4 and 5).
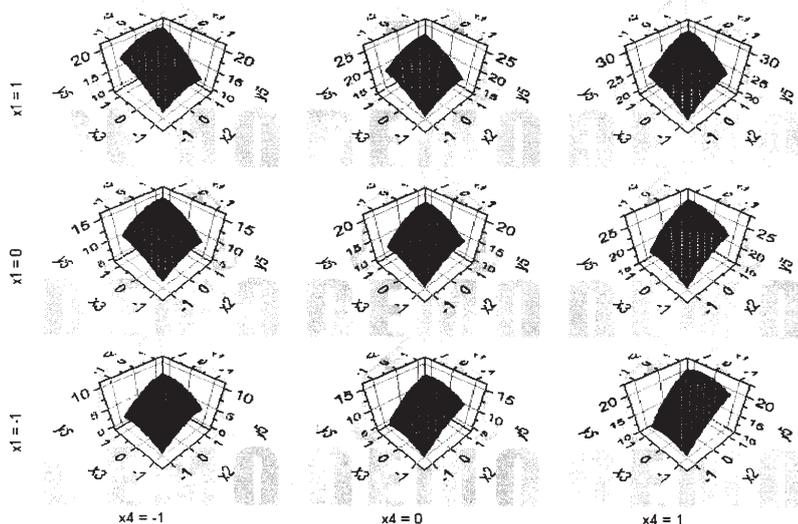
Fig. 4. Response surfaces for Melana fibre dyed with VBB in the presence of NaM-VA
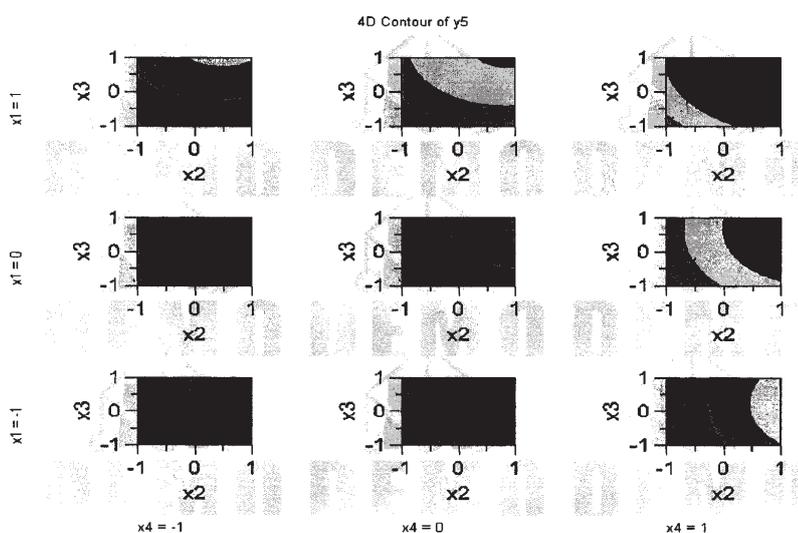
4D Contour of y5

Fig. 5. Level curves for Melana fibre dyed with VBB in the presence of NaM-VA

No.	x_1	x_2	x_3	x_4	y_4	iter	log(D)
1	1.9991	1.2641	1.8099	2	41.411	324	-10
2	1.9999	-0.8576	1.1328	-1.9986	26.3583	227	0.7575
3	0.0978	1.9407	1.7029	2	36.6629	189	-10
4	2	2	0	2	38.469	0	-10
5	**1.9999**	**0.5514**	**1.907**	**1.9996**	**40.4751**	**203**	**-10**
6	1	1.4	-1	1.8	32.9952	16	-0.9068
7	1	1	1	1.8	37.3246	0	-10
8	0.8	0	0	2	34.9229	6	-10

In the present case, we expose for illustration the response surfaces and the level curves for Melana fibre dyed with VBB in the presence of NaM-VA when the concentration of the polyelectrolyte (x_2), as well as the dyeing duration (x_3) change, while the concentration of the dye (x_1) and dyeing temperature (x_4) are kept constant. The obtained response surfaces are of the types of ascending ridge, oblong saddle or, elliptic valley, while the level curves are constantly hyperbolas, ellipses or parabolas with saddle points for some systems, that can be displaced toward them (ΔE) maximum value, and maximum or minimum points in certain cases [3].

Optimization of the process of Melana dyeing with VBB in NaM-VA or NaM-S presence

The problem of optimization disscused here is a problem maximization of colour difference ye (ΔE), its solution being obtained in the MODDE application with descending simplex [3, 38-39].

Optimization of the process of Melana fibres dyeing with VBB in NaM-VA presence

The optimization of the process of Melana fibres dyeing with VBB in NaM-VA presence was performed without starting values, when these are implicitly generated by the MODDE application. The obtained results are presented in table 2.

Under these conditions, the optimum value of the colour difference is of $ye_1 = 40.4751$ and the optimum values of the deciding variables are: $x_1 = 2.49995$ g/L, $x_2 = 1.7757$ g/L, $x_3 = 117.9075$ min, $x_4 = 99.998$°C corresponding to the coded values 1.9999, 0.5514, 1.907 and 1.9996 respectively.

Finally, experimental verification of the found optimum values was performed. With this aim in view, the decisive variables were established at the obtained values. After

No.	x_1	x_2	x_3	x_4	y_4	iter	log(D)
1	1.9999	1.9999	-0.4017	-0.6291	38.8999	248	-10
2	1.9967	0.9025	-1.9833	-1.9987	42.4139	217	-10
3	1.9992	1.9999	-0.7313	-1.5975	41.7532	134	-10
4	2	2	0	2	34.08	0	-10
5	**1.9999**	**1.9996**	**0.7857**	**-1.9995**	**42.9448**	**211**	**-10**
6	1.8	1	1	-1	33.3763	0	-10
7	1.8	1	1	1	33.2856	0	-10
8	2	0.8	0	0	31.5575	6	-10

Table 3
MAXIMUM VALUES OF THE COLOUR DIFFERENCE

the experiment, the measured value of ye was 40.15, which confirm the estimated optimums.

Optimization of the process of Melana fibres dyeing with VBB in NaM-S presence

The optimization of the process of Melana fibres dyeing with VBB in NaM-S presence was performed without starting values, when these are implicitly generated by the MODDE application. The obtained results are presented in table 3.

Under these conditions, the optimum value of the colour difference is of $ye_1 = 42.9448$ and the optimum values of the deciding variables are: $x_1 = 2.49995$ g/L, $x_2 = 2.4998$ g/L, $x_3 = 92.67825$ min, $x_4 = 80.49975°C$ corresponding to the coded values 1.9999, 1.9996, 0.7857 and 1.9995 respectively.

Finally, experimental verification of the found optimum values was performed. With this aim in view, the decisive variables were established at the obtained values. After the experiment, the measured value of ye was 41.18, which confirms the estimated optimums.

Conclusions

By examining the coefficients of the mathematical model in the value range of the considered factors for the two systems, one can notice that for the (Melana, VBB, NaM-VA) system ΔE increases mainly with the increase of the dye and polyelectrolyte concentrations, dyeing temperature and dyeing time, until for the (Melana, VBB, NaM-S) system ΔE increases mainly with the increase of the dye and polyelectrolyte concentrations and dyeing temperature.

The response surfaces are of ascending ridge, oblong saddle or elliptical valley types, while the level curves are hyperbolas, parabolas or ellipses, with the saddle point for some systems which can be displaced toward the maximum value of ye (ΔE), as well as maximum or minimum points in certain cases. There are also situations where straight lines appear which indicates the insignificant influence of some parameters on the target function.

The optimization of the processes of Melana fibres dyeing with VBB in the presence of NaM-VA or NaM-S was performed without starting values, when these are implicitly generated by the MODDE application. It was found out that the ΔE values measured during the experiments performed for the two systems are close to the ΔE optimum estimated values.

References
1. STOICHITESCU L. I., Theoretical and practical bases of dyeing and printing textile materials, Ed.Performantica, Iaşi, 2002, p.57.
2. VONCINA B., VIVOD V., JAUSOVEC D., Dyes Pigm., **74**, 2007, p.642.
3. BERCU E., Interaction of cationic dyes with anionic polyelectrolytes in aqueous solutions, PhD Thesis, " Gh.Asachi" Technical University Iasi, 2011, p.77.
4. GRIGORIU A., COMAN D., Dyeing and printing bases of textile materials, Ed. Tehnopress, Iaşi, 2001, p.93.
5. POPESCU I., SUFLET D. M., PELIN I. M., CHITANU G. C., Rev. Roum. Chim., **56**, (3), 2011, p. 173.
6. CHITANU G. C., POPESCU I., CARPOV A., Rev. Roum. Chim., 50, 2005, p.589.
7. CHITANU G.C., ZAHARIA L. I., CARPOV A., Int. J. Polym.Anal. Charact., 4, 1997, p. 1.
8. BARANOWSKA I., MASLINSKA-SOLICH J., SWIEREKCZ S., J. Planar Chromatogr., 5, 1992, p. 458.
9. BRESLOW D. S., EDWARDS E.I., NEWBURG N. R., Nature, 246, 1973, p.160.
10. HODNETT E. M., Polymer News, 8, 1983, p.323.
11. FLORU L., URSEANU F., TARABASANU C., PALEA R., Chemistry and Technology Aromatics and Organic Dyes Intermediates, Ed. Did. şi Ped., Buc.,1980, p.432.
12. ELDEM Y., OMER I., Dyes and Pigments, **60**, 2004, p.49.
13. ALEF. El-SAYED A., EL GABRY L. K., ALLAN O. G., J. Mater Sci: Mater Med, **21**, 2010, p.507.
14. CHITANU G. C., CARPOV A., ASAFTEI T., Patent No.106745, (ROM) 1993.
15. CHITANU G.C., Study of physical-chemical properties of maleic anhydride copolymers, PhDThesis, 'Al. I. Cuza' University, Iaşi, 1995, p. 57.
16. POPESCU V., Research on improving the quality of PAN fibers, finished knitted fabrics for industry , PhDThesis," Gh.Asachi" Technical University Iaşi, 1998, p.87.
17. RADU C. D., Measurement of color , Ed. Rotaprint, Iasi, 2004, p.61.
18. POPESCU, V., MANEA, L.R., SANDU, I.G., CHIRCULESCU, A.I., SANDU, I., Rev. Chim. (Bucharest), **64**, no. 3, 2013, p. 281.
19. SANDU, I.C.A., LUCA, C., SANDU, I., Rev. Chim, (Bucharest), **51**, 2000, p. 532.
20. ATODIRESEI G.V., SANDU, I.G., TULBURE, E.A., VASILACHE, V., BUTNARU, R., Rev. Chim. (Bucharest), **64**, no. 2, 2013, p. 165.
21. SANDU I., LUCA C., SANDU I.C.A., CIOCAN, A., SULITANU, N., Rev. Chim., (Bucharest), **52**, 2001, p. 485.
22. SAVIUC-PAVAL, A.M., SANDU, A.V., POPA, I.M., SANDU, I.C.A., BERTEA, A.P., SANDU, I., Microscopy Research and Technique, **76**, (6), 2013, p. 564.
23. SANDU, I.C.A., LUCA, C., SANDU, I., POHONTU, M., Rev. Chim., (Bucharest), **52**, no. 7-8, 2001, p.409.
24. POPESCU, V., MANEA, L.R., SANDU, I.G., CHIRCULESCU, A.I., SANDU, I., Rev. Chim., (Bucharest), **64**, no. 3, 2013, p. 281.
25. SAVIUC-PAVAL, A.M., SANDU, I., POPA, I.M., SANDU, I.C.A., VASILACHE, V., SANDU, I.G., Rev. Chim., (Bucharest), **63**, no. 2, 2012, p. 170.
26. CLOCOTICI V. , Introducere în statistica multivariată, Univ. Al.I.Cuza, Iasi, 2007, p.96.
27. MONTGOMERY D., RUNGER G., Applied statistics and probability for engineers, Third Edition, John Wiley & Sons, Inc., USA, 2003, p.84.
28. TOMA V., DIACONESCU R-M., SANDU I., VASILACHE V., BERCU E., Mat. Plast., **50**, no. 4, 2013, p.264.

29. RADU, C-D., BERCU, E., SANDU I., FOIA, L-G., Mat. Plast. **51**, no. 1, 2014, p.104

30. TALOI D., Optimizarea proceselor tehnologice. Aplicatii in metalurgie, Ed. Academiei, Bucuresti, 1987, p.105.

31. AZZOUZ A., Concepte de modelare si Elemente de Strategie in Design-ul industrial, Ed. Tehnica-Info, Chisinau,**147**, 2001, p.150.

32. ZAHARIA C., DIACONESCU R., SURPATEANU M., Central Eur. J. of Chem., **5**(1), 2007, p. 239.

33. BERCU E., DIACONESCU R.-M., RADU C. D., POPESCU V., European J. of Sci. and Theol., **8**(4), 2012, p.235.

34. BERCU E., SANDU I., RADU C-D, VASILACHE V., TOMA V., ALDEA H-A, Mat. Plast., **49**, no. 4, 2012, p.270.

35. BERCU E., DIACONESCU, R-M., BALAN, A , SANDU, I., POPESCU, V., CIOLOCA D-P., TOMA V., Mat. Plast., **51**, no. 1, 2014, p. 22

36. BALABAN, A.T., BACIU, M., POGANY I., Applications of the physical methods in organic chemistry, Ed. Stiinţifică şi Enciclopedică, Bucharest, 1983,

37. SILVERSTEIN, B.M., Spectrometric identification of organic compounds, Fifth edn., John Wiley & Sons, Inc., New York, 1991, p. 289.

38. CIUPRINA G., IOAN D., MUNTEANU I., REBICAN M., POPA R., „Optimizarea numerică a dispozitivelor electromagnetice", Printech, Bucureşti, 2002, p. 85.

39.***GAMSHomePage.GAMSDevelopmentCorp, http://www.gams.com/solvers/solvers.html, 2000

Manuscript received: 19.12.2013