

# Influence of Maleic Polyelectrolytes on the Methylene Blue at Dyeing of Polyacrylonitrile Fibres

CEZAR-DORU RADU<sup>1</sup>, ELENA BERCU<sup>2\*</sup>, ION SANDU<sup>3,4</sup>, LILIANA-GEORGETA FOIA<sup>5</sup>

<sup>1</sup>, Gh. Asachi, Technical University Iasi, Faculty of Textiles-Leather and Industrial Management, 29 Mangeron Str., Iasi, Romania

<sup>2</sup> Metropolitan Church of Moldavia and Bucovina, Department for Restoration and Preservation of the Christian art 'RESURRECTIO', 16 Stefan cel Mare si Sfanta Avenue, Iasi, Romania

<sup>3</sup> Alexandru Ioan Cuza, University of Iasi, ARHEOINVEST Interdisciplinary Platform, 22 Carol I Blvd, 700506, Iasi, Romania

<sup>4</sup> Romanian Inventors Forum, 3 Sf. Petru Movila Str., 700089, Iasi, Romania

<sup>5</sup>, Gr.T. Popa<sup>7</sup> University of Medicine and Pharmacy, Faculty of Dental Medicine, 16 Piata Natiunii Str., 700115, Iasi, Romania

*The present study pursues the influence of polyelectrolytes based on maleic co-polymers with styrene and vinyl acetate under the form of sodium salt, on the colour parameters CIEL\*a\*b\* of the Melana type polyacrylonitrile fibers dyed with Methylene blue. The work is part of a study on the metachromacy of cationic dyestuffs at dyeing the polyacrylonitrile fibres in the presence of cationic polyelectrolytes. The colours attributes are analyzed in terms of the tinctorial conditions: polyelectrolyte character and concentration, dyeing temperature and during time.*

*Keywords: maleic polyelectrolytes, polyacrylonitrile fibres, colour differences, tinctorial parameters, methylene Blue*

Recent spectroscopy studies concerning the cationic dyestuffs interaction with maleic polyelectrolytes in aqueous solutions show that the metachromatic shift in the case of these systems can be hypsochromic or bathochromic, more or less intense, and it depends on the dyestuff and polyelectrolyte structure, as well as on the working conditions [1-4].

The studies of spectral remission carried out on Melana samples dyed with cationic dyestuff in the presence of maleic polyelectrolytes have shown the maleic copolymer with styrene determines a retarding effect in the dyeing process, while the maleic acid co-polymer with vinylacetate induces an acceleration of the dyeing process under given conditions [5].

The polyacrylonitrile fibers belong to the category of carbocatenary synthetic fibers, having in their composition the polymer obtained from acrylonitrile. Since the monomers come from a wide variety of vinylic derivatives, such as: vinylchloride, vinyl acetate, methylacrylate, vinylpyridine, vinylpyrazine, methacrylic acid, styrene-sulphonic acid, etc, the fibres structure reflects the nature and proportion of the utilized monomers [6, 7]. For instance, the anionic groups of Melana come either from the initiator used to obtain the basic polymer, either from a comonomer. In the first case, the anionic groups can originate, for example, from the redox system  $K_2S_2O_8$  and  $Na_2S_2O_5$ , from which the molecules preserve as terminal groups the sulphonic or sulphate groups (their sodium salts respectively). If the initiator was benzoyl peroxide, the terminal groups are  $-COOH$ , while in the case of hydrogen peroxide the terminal groups are  $-OH$ . In other conditions, the anionic groups can be due to a co-monomer, for example itaconic acid, from which the carboxyl groups remain among the fiber macromolecules [8].

The present study pursued the influence of polyelectrolytes based on maleic co-polymers with styrene and vinylacetate under the form of sodium salt, in the tinctorial system consisting of Melana dyed with Methylene

Blue (MB) using the colour difference,  $\Delta E$ , as a method to evaluate the interactions. The obtained values are attributed to the modifications appeared in the colour components  $L^*$ ,  $a^*$ ,  $b^*$ , in terms of polyelectrolytes concentration and character, and the dyeing temperature and during time.

## Experimental part

### Materials

We have used the MB dyestuff, the Merck reagent used as such, without purification or other modifications. The dye structure is presented in figure 1.

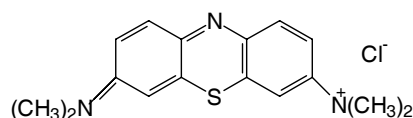


Fig. 1. Chemical structure of the MB dyestuff

The utilized polyelectrolytes are copolymers of the maleic acid with styrene, and the copolymer of the maleic acid with vinylacetate, both as sodium salts. The two polyelectrolytes were obtained from copolymers of the maleic anhydride with vinylacetate or styrene, synthesised in laboratory according to our own method or methods described in literature [9-13]. Chemical structures of the polyelectrolytes are presented in figure 2.

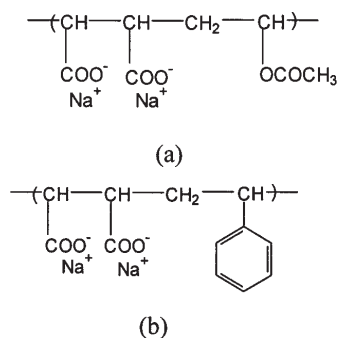


Fig. 2. Chemical structures of the polyelectrolytes: (a) Sodium maleate - vinylacetate (NaM-VA); (b) Sodium maleate - styrene (NaM-S).

\* email: e.bercu@yahoo.com

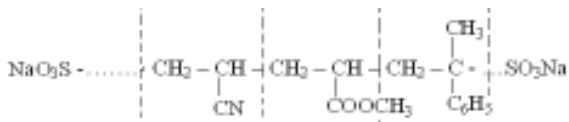


Fig. 3. Schematic structure of Melana fibre

The structure of the Melana fibre is schematically presented in figure 3.

### Dyeing Protocol

Dyeing was carried out with a Mesdan lab dyeing device with 6 dyeing positions.

Series of 6 dyeing operations of 1 gram for each coloristic position of Melana fibres were performed in aqueous solution (distilled water) with MB in the presence of the NaM-VA or NaM-S polyelectrolytes at dyestuff and polyelectrolyte concentrations of: 0.5; 1; 1.5; 2; 2.5%, the solution with pH = 5.5 - 6.0 adjusted with 10% acetic acid and a liquor ratio of 1:50. Practically, to the dyestuff aqueous solution of the dyestuff one adds polyelectrolyte in different concentrations and acetic acid - some drops to adjust the pH. The dyeing flask is magnetically stirred for 5 min for homogenization and then the solution stays still for 30 min, after which Melana fibres are added (1g). The solution is stirred again for 5 min and then the dyeing flask follows the thermal regime. The dyeing solution is heated up to 80°C and kept 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. This temperature is maintained for about 75 min, after which the dyeing solution is slowly cooled (1°C/min). The dyed Melana is intensely washed for 5 min with cold water and 5 min with warm water, manually squeezed and dried at room temperature.

Besides the dyeing operations performed in the presence of the two poly-electrolytes, witness (standard) operations of Melana dyeing were also carried out in the absence of the polyelectrolytes at 90°C for 75 min.

Colour differences were measured with a portable Datacolor 2002 Check Plus spectrophotometer [14].

In this way, the colour parameters  $L^*$ ,  $a^*$ ,  $b^*$ ,  $h^*$  and  $C^*$  respectively, as well as the colour differences  $\Delta E$  [15-27] were determined.

The colour difference was computed with the formula (1):

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

where:  $\Delta$  indicates the difference between the batch sample in the present case the tinctorial determinations

as compared and a witness sample specified in tables 1, 2 and 3, between batch and witness;  $\Delta L$  represents the lightness difference (%) between batch and witness. If  $\Delta L > 0$ , then the sample which reproduces (batch) is lighter than the witness; if  $\Delta L < 0$  the sample which reproduces (batch) is darker than the witness.

The values of  $\Delta a$  and  $\Delta b$  indicate the differences between the sample positions in the chromatic diagram [15-19]. Namely, "a" represents the chromatic shift toward red for positive values and toward green for negative values. Similarly, for the coordinate "b", the positive values indicate yellow colours and the negatives one indicate blue. They are both measured in Adams-Nickerson units (AN). The chromatic intensity, or saturation, estimated through the concept of chroma,  $C^* = (a^2 + b^2)^{1/2}$ , is higher, the higher are the absolute numerical values of the parameters  $a^*$  and  $b^*$ . The shade modification can be appraised by computing ( $h^* = \text{tg}(b^*/a^*)$ ).

### Results and discussions

Morphologically, the polyacrylonitrile fibres show an inhomogenic fibrillary structure with several discontinuities (pores, channels) and non-uniform cross section. The Melana fibres produced in Romania are polyacrylonitrilic based on a ternary polymer (85% acrylonitrile, 10% vinylacetate, 5%  $\alpha$ -methylstyrene), obtained through a radical polymerization reaction initiated in the redox system of potassium persulphate/natrium metabisulphite [8].

In order to interpret the colour modifications, considered as being due to the action of polyelectrolytes, dyeing temperature and during time on Melana dyed with MB, the CIE chromatic diagram  $L^*a^*b^*$  [14] was used. Table 1 presents the technological parameters and the values of the colour components in the case of dyeing the Melana fibres with MB in the presence of the NaM-S or NaM-VA polyelectrolytes at different concentrations.

The polyelectrolytes presence in the system of Melana dyeing with MB generates colour differences between the samples dyed in the presence of the two polyelectrolytes and the witness dyed sample. The colour difference is the highest,  $\Delta E = 9.42$  AN, in the case of Melana dyeing in the presence of NaM-S at a concentration of 1.5%, while in the presence of NaM-VA, the highest value of  $\Delta E = 11.6$  AN corresponds to the maximum polyelectrolyte concentration of 2.5%. One can notice that the highest saturation values ( $C^*$ ) were obtained in the case of Melana samples dyed at NaM-S or NaM-VA concentrations of 1.5%.

Recent studies on Melana dyeing with Crystal Violet [20] in the presence of NaM-S or NaM-VA have shown that the

**Table 1**  
DYEING PARAMETERS AND THE VALUES OF COLOUR COMPONENTS IN THE CASE OF DYEING THE MELANA FIBRES WITH MB IN THE PRESENCE OF THE NaM-S OR NaM-VA AT DIFFERENT POLYELECTROLYTE CONCENTRATIONS

No	MB concentration	Poly electrolyte concentration	Dyeing during time (min)	Temperature (°C)	Chrom C* (AN)	Hue h* (°)	$\Delta L^*$ (%)	$\Delta a^*$ (AN)	$\Delta b^*$ (AN)	$\Delta C^*$ (AN)	$\Delta h^*$ (°)	$\Delta E^*$ (AN)
	(%)	(%)										
	$C_{MB}$	$C_{NaM-S}$										
wit	1.5	0	75	90	36.97	243.0						
1	1.5	0.5	75	90	40.41	249.8	-4.75	2.84	-4.98	3.44	4.5	7.45
2	1.5	1.5	75	90	42.52	252.1	-4.25	3.73	-7.53	5.56	6.3	9.42
3	1.5	2.5	75	90	42.46	249.8	-2.86	2.13	-6.91	5.49	4.7	7.77
	$C_{MB}$	$C_{NaM-VA}$										
wit	1.5	0	75	90	36.97	243.0						
1	1.5	0.5	75	90	39.42	253.1	-8.77	5.32	-4.77	2.45	6.7	11.3
2	1.5	1.5	75	90	40.31	250.8	-8.71	5.1	-5.19	3.34	7.8	11.5
3	1.5	2.5	75	90	39.16	253.7	-8.97	5.82	-4.66	2.2	7.1	11.6

wit = witness

$\Delta E$  values in the case of the (CV, Melana, NaM-S) system are higher as compared to those of the (CV, Melana, NaM-VA) system. This difference is due to the structural characteristics of the dyestuff and the chemical character of the two polyelectrolytes: NaM-S which, besides the relative steric hindrance determined by the presence of the styrene radical in its structure, also increases the hydrophobia in the tinctorial system, while NaM-VA with a nucleophilic character, determines a decrease of the hydrophobia and implicitly a poorer dyeing of the Melana samples.

This does not happen when dyeing the Melana fibres in the presence of NaM-S or NaM-VA.

The MB ions with a thiazine structure (fig. 1) interact mainly by means of the electrostatic forces, with the anionic groups of the NaM-VA polyelectrolyte, in aqueous solution and get closer to each other, so that they can suffer a *multimerization*. This *multimerization* (polymerization) of the dyestuff along the polymer chain can be similar to the interaction that occurs in concentrates solutions of the dyestuff and involves two factors: the interaction of the  $\pi$  electrons of the adjacent cations and hydrophobic interaction. The last one is similar to the generation of mycelium in aqueous solutions of anionic detergents [21-28].

Some studies have shown that the configuration of the  $\pi$  electrons of the dye bond to the polyelectrolyte can influence mainly the distance between the positions of polyanion bonding [14, 29-32].

The values of the colour differences get modified with the addition of NaM-S to the dyeing solution. At small NaM-S concentrations, the MB aggregates break off, the dye ions interact with the charged positions of the polyelectrolyte, and other with the anionic positions from the ends of the Melana fibres chains, by means of ionic bonds.

The polyacrylonitrile fibres are hydrophobic; the water sorption under standard conditions being of 1-2%, and swelling in water is significantly reduced [8].

When the NaM-S concentration in the dyeing solution increases, the hydrophobia and the steric hindrance due to the styrene radicals increase, thus inducing a retardation or even a blockage of the migration of molecules or „light” dye aggregates toward the charged positions from Melana fiber ends. In these cases, the amount of dyestuff fixed on the Melana fibres is small, and the dyeing is nonuniform, a visually confirmed colouristic aspect. On the other side, given the high hydrophobia of these tinctorial systems consisting of Melana fibres, MB and NaM-S, physical interactions appear, of van der Waals type, hydrophobic and of hydrogen [8, 14, 17, 33].

Recent studies of spectral remission [5] show that, at small (0.5%) NaM-S concentrations in the dyeing solution, an acceleration of Melana fibres dyeing with MB occurs; also, with the increase of polyelectrolyte concentration in the dye solution (1.5÷2.5%), a retarding effect of Melana fibres dyeing takes place. The communications justify the above statements. The NaM-VA presence in the dye solution determines an acceleration of fibres dyeing irrespective of the polyelectrolyte concentration.

Figure 4 illustrates the variations of the colour parameters  $L^*$ ,  $a^*$ ,  $b^*$  corresponding to Melana samples dyed with MB, in terms of the concentration of NaM-S and NaM-VA polyelectrolytes.

The lightness values for Melana samples dyed with MB in the presence of NaM-S and NaM-VA (fig. 4a) are smaller than those of the witness sample and tend upward with increasing concentration of the two polyelectrolytes. In the

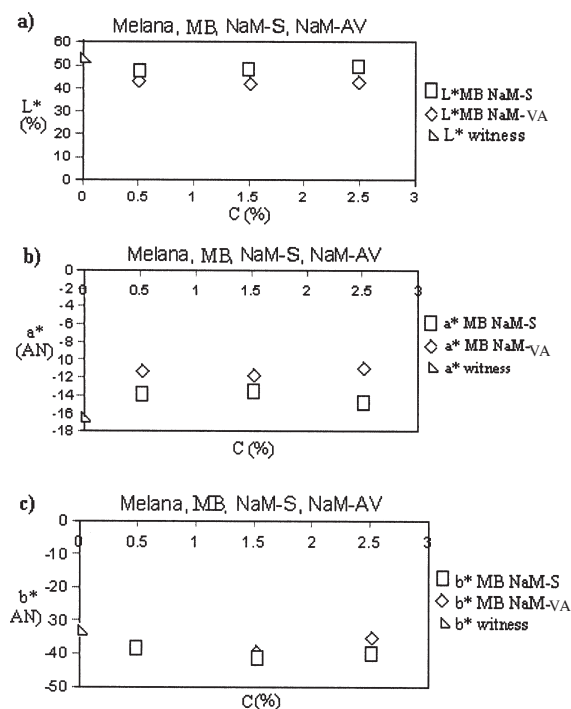


Fig. 4. The influence of the concentration of NaM-S and NaM-VA polyelectrolytes on the colour parameters in the tinctorial system Melana fibres-MB.

case of Melana samples dyed with MB in the presence of the NaM-S polyelectrolyte, the lightness values are sensibly bigger than those of Melana samples dyed with MB in the presence of NaM-VA.

The variations of the chromatic components of the colour,  $a^*$  and  $b^*$  render evident an alteration of hue ( $g/b/a$ ) and saturation ( $C = (a^2 + b^2)^{1/2}$ ) respectively, as illustrated in figure 4b and 4c. The Melana samples dyed with MB in the presence of the two polyelectrolytes (fig. 4b) are less green than the Melana samples dyed with MB in the absence of polyelectrolyte (witness sample); the Melana samples dyed with MB in the presence of NaM-VA polyelectrolyte have smaller values of  $a^*$  as compared to Melana samples dyed with MB in the presence of NaM-S polyelectrolyte. By analyzing the values of the  $b^*$  parameter (fig. 4c), which are negative (corresponding to blue), one can notice that the colour saturation increases, the Melana samples dyed with MB being more blue than the witness.

From the illustrated data, one estimates that dyeing the Melana samples with MB in the presence of polyelectrolytes induces colour modifications whose intensity depends on the concentration and the character of the two polyelectrolytes. One can not exclude the possibility that these modification are only of metachromatic nature. Table 2 presents the technological parameters and the values of the colour components in the case of dyeing the Melana fibres with MB in the presence of NaM-S or NaM-VA at different dyeing during times.

It can be noticed from table 2 that for the (Melana, MB, NaM-S) system,  $\Delta E$  decreases with the increase of the dyeing during time, the highest value being of 10.22 AN at  $t = 30$  min, while in the case of (Melana, MB, NaM-VA) system,  $\Delta E$  increases with the increase of dyeing during time, the highest value being of 13.24 AN corresponding to  $t = 120$  min. Significant modifications of the hue appear for the (Melana, MB, NaM-S) tinctorial system at the duration  $t = 30 \div 75$  min; in the case of the (Melana, MB, NaM-VA) tinctorial system, significant modifications appear during time  $t = 120$  min, while the saturation values are

No.	MB concentration	Poly electrolyte concentration	Dyeing during time	Temperature	Chroma C*	Hue h*	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	$\Delta C^*$	$\Delta h^*$	$\Delta E^*$
	(%)	(%)	(min)	(°C)	(AN)	(°)	(%)	(AN)	(AN)	(AN)	(°)	(AN)
	$C_{MB}$	$C_{NaM-S}$										
wit	1.5	0	75	90	36.97	243.0						
1	1.5	1.5	30	90	41.73	252.8	-6.07	4.44	-6.92	4.76	6.7	10.2
2	1.5	1.5	75	90	42.52	252.1	-4.25	3.73	-7.53	5.56	6.3	9.4
3	1.5	1.5	120	90	42.02	248.8	-1.81	1.57	-6.23	5.05	3.9	6.6
	$C_{MB}$	$C_{NaM-VA}$										
wit	1.5	0	75	90	36.97	243.0						
1	1.5	1.5	30	90	38.71	251.7	-8.8	4.6	-3.82	1.7	5.7	10.7
2	1.5	1.5	75	90	40.31	250.8	-8.71	5.1	-5.19	3.3	7.8	11.5
3	1.5	1.5	120	90	38.83	253.9	-10.9	6.0	-4.3	1.8	7.1	13.2

**Table 2**  
THE DYEING PARAMETERS AND THE VALUES OF COLOUR COMPONENTS IN THE CASE OF MELANA FIBRES DYEING WITH MB IN THE PRESENCE OF NaM-S OR NaM-VA AT DIFFERENT DYEING DURING TIMES

maximum at dyeing duration of 75 min, irrespective of the polyelectrolyte nature.

Figure 5 presents the variations of the  $L^*$ ,  $a^*$ ,  $b^*$  parameters corresponding to Melana samples dyed with MB, in the presence of NaM-S and NaM-VA polyelectrolytes in terms of the dyeing during times.

The lightness of the witness sample is higher than of Melana samples dyed with MB in the presence of NaM-S or NaM-VA (fig. 5a). The lightness increases with increasing dyeing time in the case of Melana samples dyed in the presence of NaM-S polyelectrolyte and diminishes with the increase of the dyeing during time in case of the Melana fibers dyed in the presence of the NaM-VA polyelectrolyte.

The values of  $a^*$  in the case of Melana samples dyed in the presence of NaM-S and NaM-VA polyelectrolytes are negative, smaller than those corresponding to the witness sample: with increasing dyeing during time, one can notice an upward tendency in the presence of the NaM-VA polyelectrolyte, while in the presence of NaM-S the tendency is downward (fig. 5b). With increasing dyeing during times the Melana samples are less green than the dyed witness samples.

One can notice in figure 5c that the values of  $b^*$  are negative, corresponding to blue for all the Melana samples dyed in the presence of the NaM-S and NaM-VA polyelectrolytes and are smaller than those corresponding to witness sample. With the increase of the dyeing during time from 30 min to 75 min, the values of  $b^*$  decrease, and within the interval 75 - 120 min the tendency is upward. The difference in the tinctorial behaviour of the two polyelectrolytes is not significant.

Table 3 presents the technological parameters and the values of the colour components in the case of dyeing the Melana fibres with MB in the presence of NaM-S or NaM-VA at different dyeing temperatures.

From table 3 data, the increase of the dyeing temperature determines colour modifications in the Melana samples dyed with MB in the presence of the two polyelectrolytes, rendered evident through the values of colour difference  $\Delta E$ . For instance, at the maximum dyeing temperature of 100°C, the colour differences are minimum (8.05 AN) in the case of the (Melana, MB, NaM-S) system. With the decrease of the dyeing temperature down to the minimum value of 80°C, the value of the colour difference  $\Delta E$  reaches its maximum (14.68 AN). In the case of the (Melana, MB, NaM-VA) system, the maximum colour difference is obtained at the temperature of 90°C. Based on the obtained chromatic values, the temperature is the main factor within this tinctorial system.

Maximum modification of hue and the maximum value of the saturation respectively in the case of the (Melana, MB, NaM-S) tinctorial system appear at 90°C, while for the (Melana, MB, NaM-VA) system, the saturation value ( $C^*$ ) increases with increasing dyeing temperature and reaches

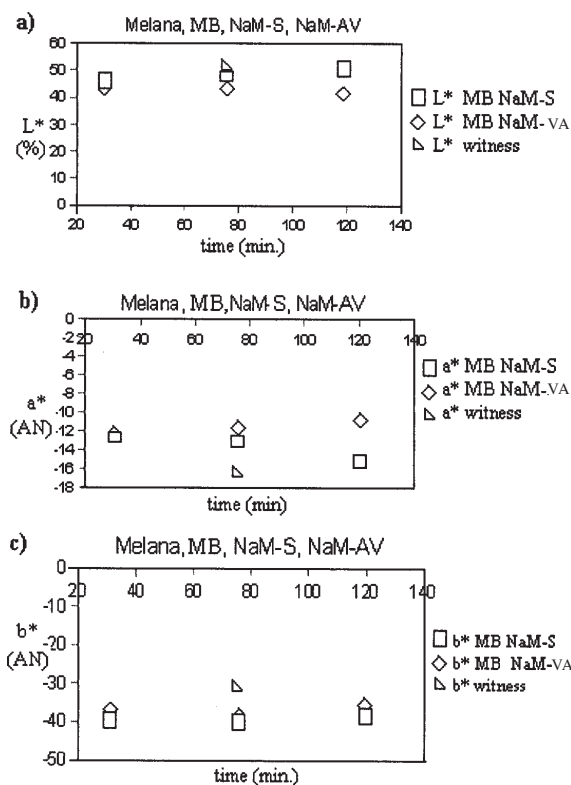


Fig. 5. The influence of dyeing during time on the colour parameters in the Melana fibres - MB tinctorial system

its maximum at 100°C. Maximum modification of hue is obtained at the temperature of 90°C.

Figure 6 illustrates the values of the parameters  $L^*$ ,  $a^*$ ,  $b^*$  corresponding to Melana samples dyed with MB in the presence of NaM-S and NaM-VA polyelectrolytes in terms of the value of dyeing temperature.

In figure 6a one can notice the lightness of Melana samples dyed with MB in the presence of the NaM-S polyelectrolyte tends downward with the increase of the temperature from 80 to 100°C. The lightness values for the witness samples are close to those of Melana samples dyed with MB in the presence of the NaM-S or NaM-VA polyelectrolyte and some of these values are overlapped.

The values of  $a^*$  for the same tinctorial system (fig. 6b) are negative (corresponding to green colour), higher than those of the witness sample at 80°C, and they increase with temperature increase from 80°C to 90°C. At 90°C the values of  $a^*$  for Melana samples dyed in the presence of NaM-S or NaM-VA polyelectrolyte are smaller than those of witness sample at 100°C. In other words, at a temperature of 100°C, Melana samples dyed with MB in the presence of NaM-VA are greener than those of Melana samples dyed in the presence of NaM-S.

**Table 3**  
DYEING PARAMETERS AND THE VALUES OF THE COLOUR COMPONENTS IN THE CASE OF DYEING THE MELANA FIBRES WITH MB IN THE PRESENCE OF NaM-S OR NaM-VA AT DIFFERENT DYEING TEMPERATURES

No.	MB Concntration (%)	Poly electrolyte concntration (%)	Dyeing during time (min)	Tempe rature (°C)	Chroma C*	Hue h*	$\Delta L^*$ (%)	$\Delta a^*$ (AN)	$\Delta b^*$ (AN)	$\Delta C^*$ (AN)	$\Delta h^*$ (°)	$\Delta E^*$ (AN)
	$C_{MB}$	$C_{NaM-S}$										
wit	1.5	0	75	90	36.97	243.0						
1	1.5	1.5	75	80	37.11	236.4	14.0	-3.7	2.0	0.14	-4.2	14.68
2	1.5	1.5	75	90	42.52	252.1	-4.2	3.7	-7.5	5.56	6.3	9.42
3	1.5	1.5	75	100	38.83	248.1	-6.0	2.3	-2.0	1.86	3.3	8.05
	$C_{MB}$	$C_{NaM-VA}$										
wit	1.5	0	75	90	36.97	243.0						
1	1.5	1.5	75	80	34.34	240.6	6.54	-0.05	3.0	-2.6	-1.4	7.2
2	1.5	1.5	75	90	40.31	250.8	-8.71	5.1	-5.1	3.3	7.8	11.5
3	1.5	1.5	75	100	40.81	243.6	1.73	-1.3	-3.6	3.8	0.4	4.2

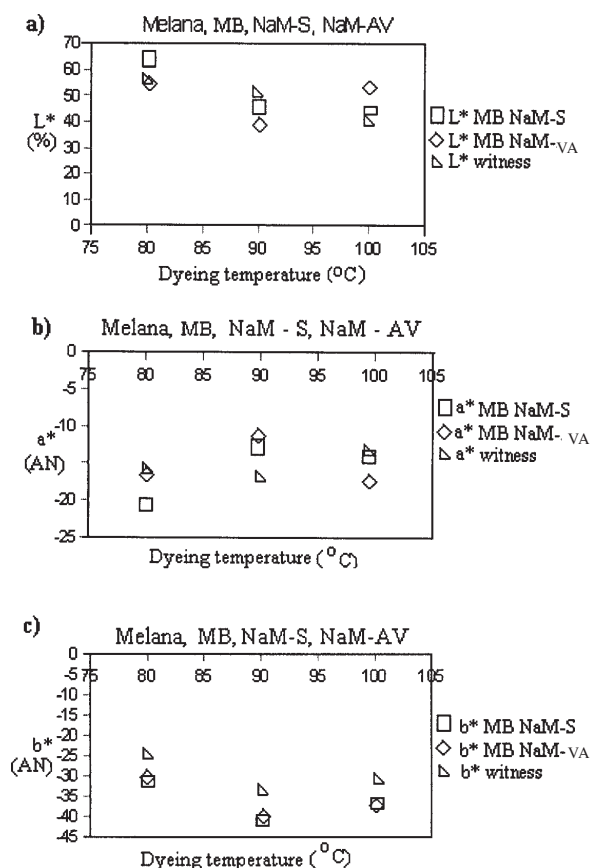


Fig. 6. The influence of dyeing temperature on colour parameters in the Melana fibres-MB tinctorial system

The values of  $b^*$  are negative (corresponding to blue colour) in the case of Melana samples dyed with MB in the presence of NaM-S and NaM-VA polyelectrolytes (fig. 6c), higher than those of witness sample at 80, 90 or 100°C, so that Melana samples dyed with MB in the presence of NaM-S or NaM-VA polyelectrolytes are more blue than the witness samples.

Among the two chromatic components of the MB dyestuff, the blue component is predominant over the green component for all the studied parameters: the variations of polyelectrolyte concentration, dyeing during time and temperature.

The interactions existing in the dyeing solution determine the formation of a complex system, difficult to detect through known investigation means, and this in the situation that the highest weight belongs to electrostatic interactions in the tinctorial system. The presence of

polyelectrolytes in function of thermal level, partners concentration can determine either the acceleration or the retardation of dyeing process. That is why the saturation, through the value of chrome  $C^*$ , and the colour difference represent the general effect of cationic dye fixation at the anionic dye centres of the polyacrylonitrile fibres. The details of the interactions that take place can be considered as a consequence of metachromasy.

### Conclusions

The polyelectrolyte presence in the tinctorial system favours an electrostatic synergy, determining the attraction of a larger amount of dyestuff around the textile substrate, manifested in lightness diminution.

The lightness values of the Melana samples dyed in the presence of NaM-S or NaM-VA are smaller than those of the witness sample; therefore the samples dyed in the presence of polyelectrolyte are darker than the witness dyed Melana samples.

At Melana dyeing with MB in the presence of the two polyelectrolytes, the colour modifications depend on the character and concentration of the two polyelectrolytes; the presence of small concentration of NaM-S in the dyestuff liquor determines an acceleration of Melana fibres dyeing with MB; yet, the increase of the polyelectrolyte concentration results in a retardation of Melana fibres dyeing; the presence of NaM-VA in the dyeing solution determines an acceleration of fibres dyeing irrespective of the polyelectrolyte concentration.

Despite the studied tinctorial system, which is very complex, one can not exclude the possibility that these colour modifications are only of metachromatic nature.

The increase of dyeing temperature or duration generates differences in the colour of the Melana samples dyed with MB, compared with the witness sample.

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