Stefan Brzeziński[1)], Agnieszka Kaleta[1)], Dorota Kowalczyk[1)], Grażyna Malinowska[1)], Bogumił Gajdzicki[2), 3)]

[1)] **Textile Research Institute, Department of Unconventional Technologies and Textiles,**
ul. Gdańska 118, 90-520 Łódź, Poland

[2)]**Technical University of Lodz, Institute of Textile Architecture,**
ul. Żeromskiego 116, 90-543 Łódź, Poland

[3)]**Textile Research Institute, Department of Textile Chemistry and Products Modification,**
ul. Brzezińska 5/15, 92-103 Łódź, Poland

Effect of Changes in the Nanostructure of the Outer Layer of Synthetics Fibers on their Dyeing Properties

Abstract
*Numerous, often contradictory, literature reports concerning the influence of various types of atmospheric plasma on the dyeing properties of fibres inclined us to undertake investigations into the use of corona discharge for the preliminary modification of textiles. These discharges were generated and applied by means of original multi-segment electrodes installed in a generator specially constructed to operate continuously and to make it possible to carry out the modification process under conditions similar to those in industry. This paper presents findings concerning the effect of corona discharge on the dyeing properties of woven fabrics made of polyester (PET), polyamide (PA6) and polypropylene (PP) continuous filament yarns. Pretreated with corona discharge, these fabrics were dyed by the exhaustion (dye exhaustion from a dyebath at an elevated temperature/pressure) and continuous Thermosol processes using hot air to fix the dye. The differences in color, ΔE, between corona treated and untreated samples were determined on the basis of spectrophotometric measurements in the CIE L*a*b colour system. Although no improvement in the effectiveness of dyeing by exhaustion was found, the intensity of dyeing by the continuous Thermosol process was considerably increased, especially in the case of woven fabrics of PET and PP yarns. Based on the tests of the surface properties of modified fibres, reasons are presented for the effect of corona discharge modification on the dyeing results obtained.*

Key words: *corona discharge, synthetic filament woven fabrics, dyeing, continuous dyeing process, batch dyeing method, dyeing kinetics, wettability, dyebath absorption.*

Introduction

Despite the large number of papers presenting the results of studies on the effect of low-pressure plasma modification, especially various types of atmospheric plasma, on the surface properties of textiles, few of them concern changes in fibre dyeing properties, and the results of those differ very much. The major problem is a lack of specified process conditions for both plasma modification and the dyeing process itself, which makes it difficult to have a settled opinion on the real possibilities of improving dyeing properties resulting from the treatment of textiles with various types of plasma [1].

Information reported in published papers, including literature provided by the manufacturers of equipment for plasma modification, is most often limited to general statements about possible improvement in textile dyeability without details concerning the modifying treatment conditions, the type and characteristics of dyes applied, and the dyeing process itself. It should be mentioned that the capability of increasing the intensity of dyeing fibre/textiles as a result of using plasma pretreatment, primarily with low-pressure plasma, has been confirmed only in the case of wool. The action of plasma on wool damages the epicuticle layer, being a hydrophobic barrier hindering dye diffusion inside the fibre. However, an improvement in dyeability has been achieved only under conditions of dye bonding in steaming processes, e.g. in the case of printed fabrics, which is a relatively short-lasting process carried out in the presence of limited amounts of water (derived from condensing steam). There has been no improvement in the dyeability of wool textiles modified by plasma treatment, especially in dyeing by exhaustion, where dyes are exhausted from dyebath over a considerably longer time in an aqueous medium. Hence plasma pretreatment has been successfully introduced to prepare woollen woven or knitted fabrics for printing, but it has not yet been used to intensify the dyeing of wool fabrics [1, 2, 11]. As far as synthetic fibres are concerned, the papers reporting a positive effect of plasma treatment on their dyeability are rare and arouse some doubts [1, 3 - 5], which seems to be understandable if only taking into account the superficial character of plasma treatment without making changes in the fibre material, into which the dye diffuses [1, 6 - 8, 10, 11].

The aim of the present study was to assess the effect of corona discharge modification on the dyeing properties of polyester (PET), polyamide (PA6) and polypropylene (PP) woven fabrics. After plasma pretreatment these fabrics were dyed by the batch process (dye exhaustion from a dyebath) and continuous Thermosol method with dye fixation in hot air [11].

Table 1. *Characteristics of the materials investigated.*

No.	Type of fibre polymer	Warp		Weft		Surface weight of fabric, g/m^2	Preparation procedure for pretreatment
		Yarn charactristics	Number of threads /10 cm	Yarn characteristics	Number of threads /10 cm		
1	PET	84 dtex f48 twistless, spot tacked yarn	390	150 dtex f216 twistless yarn	320	89	Washing, thermal stabilisation for 20 s. at 190 °C
2	PA6	72 dtex f17	380	160 dtex f144	310	81	Washing, thermal stabilisation for 20s. at 185 °C
3	PP	84 dtex f33	460	84 dtex f33	330	72	Washing

Experimental

Materials

Woven fabrics

Woven fabrics of synthetic filament yarns with presented in ***Table 1*** characteristics were used in the investigations.

Dyes and auxiliary agents

For dyeing fabrics by exhaustion, the following were used:

- PET and PP woven fabrics
  Disperse dye: C.I. Disperse Blue 73 - Synten Blue P-BGL (Błękit syntenowy P-BGL from Boruta - Kolor, Poland)
  Dispersing agent: Dyspergator NNO, a nonionic dispersing agent from Organika-Rokita, Poland
- PA6 woven fabric
  Acid dye: C.I. Acid Red 154 - Lanasyn Red F-2B (Lanasyn Rot F-2B from Clariant, Switzerland)
  Leveling agent: Lanyl TLS, oxyethylated fatty alcohol from Olea, France
  Acid-forming agent: Nylacide TA conc., mixture of organic esters from Olea, France.

For dyeing PET, PA6 and PP woven fabrics by the Thermosol process, the following were used:

- Disperse dye: C.I. Disperse Blue 73 - Synten Blue P-BGL (Błękit syntenowy P-BGL) from Boruta-Kolor, Poland
- Disperse dye: C.I. Disperse Red 54 - Synten Scarlet P-3GL (Szkarłat syntenowy P-3GL) from Boruta-Kolor, Poland
- Dispersing agent: Dyspergator NNO from Organika-Rokita, Poland.

The structural formulae of the disperse dyes used are shown in ***Figure 1.***

Aparatus

Corona discharge generator for the modification of textiles

The corona discharge pretreatment of textiles was carried out by means of an original generator, designed and made in the course of our earlier studies [13, 14, 16]. Its construction makes it possible to carry out the modification by a continuous method. The generator is equipped with an original multi-segment electrode that allows one to obtain a high and uniform degree of modification without affecting the strength properties of the fabric. It should be mentioned that in the modification of textiles with corona discharge, there is a specific contradiction that considerably limits the industrial use of this type of atmospheric plasma. This contradiction is due to the fact that two inverse conditions should be fulfilled: the necessity of supplying a corona discharge of high activation energy to the fabric, and the energy of destructive streamers should be reduced to a level that eliminates the hazard of local thermal damage to textiles, providing the highest possible discharge. We solved this problem by developing an original system of dividing the energy dose of corona discharge required for the modification, whose quantified measure is E_j in J/cm^2, into series *n* lower doses, E_{jn}, whose total action on fibre/fabric provides the level of plasma modification expected ($E_j = n \times E_{jn}$). [13, 14, 16, 17]. At the same time, such 'component' energy doses are low enough to provide a high level of discharge uniformity and the elimination of streamers. To accomplish this, original sets of multi-segment electrodes were designed and made (***Figure 2***) [13, 14].

As shown by the investigation performed, the system developed turned out to be effective for the obtainment of the modification effect expected without deterioration in the strength properties of fibres [10 - 14, 16, 17].

'AHIBA NUANCE' Top Speed automatic laboratory dyeing machine from AHIBA (Switzerland), used for dyeing fabric samples in special metal pressure containers.

Two-roller laboratory padding machine with a horizontal setting of squeezing rollers for the application of working baths onto flat textiles of 35 cm width, from BENZ GmbH (Switzerland).

Laboratory unit for continuous dyeing with dye fixation in hot air - Thermosol from BENZ S.A. (Switzerland).

CM 2600d spectrophotometer from Konica Minolta, used for measuring colour in the CIE L*a*b system with the use of D65 light at an observation angle of 10°.

Spectronic GENESYS 5 spectrophotometer from Milton Roy (USA), used for the determination of the quantity of dye bonded with fibres by measuring the absorption of dyebath before and after dyeing.

Sigma 701 tensiometer (KSV Instruments Ltd., Finland), used for the determination of the contact angle of material by the dynamic method; values of the

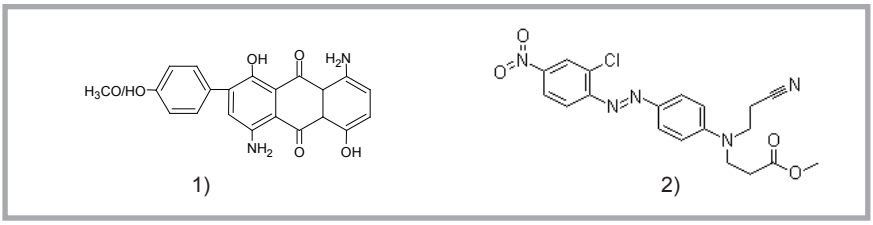

Figure 1. *Structural formulae of the disperse dyes; 1) C.I. Disperse Blue 73, 2) C.I. Disperse Red 54.*

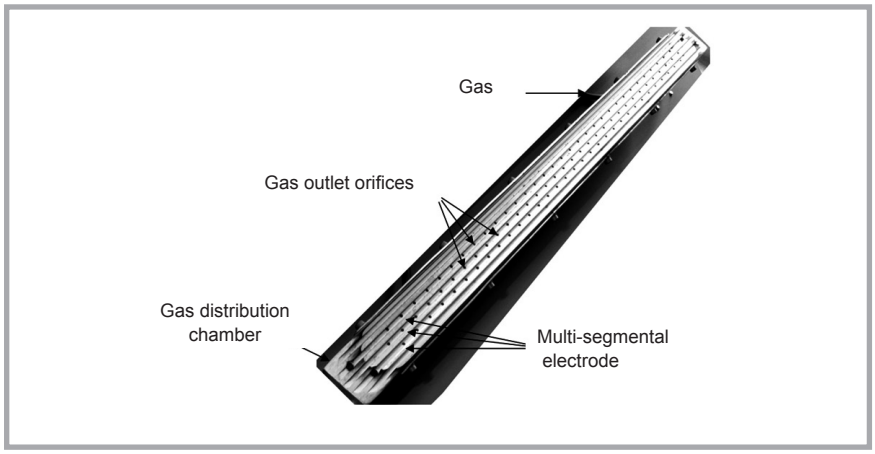

Figure 2. *Photo of the multi-segment electrode used in the experimental modifier.*

contact angle are used to calculate the free surface energy of the fabric tested.

System ISIS Link 300 EDX micro analyser (Oxford Instruments), used for the determination of the oxygen content in the fibre's outer layer.

Physical Electronics PHI 5000 Versa Probe Scanning Spectrometer (XPS), used for the determination of the oxidation degree of the fibre's outer layer.

Nanoscope IIIa (Digital Instruments, Santa Barbara, USA) atomic force microscope (AFM), used for the assessment of the topography of the fibre's outer layer in nanoscale dimensions and its changes resulting from the corona discharge modification.

Surface modification

The woven fabrics to be dyed were subjected to corona discharge pretreatment by means of the experimental generator, using the following unit activation energies (E_j) [12-17]: $E_j = 75.6$ J/cm^2 for PET fabric, $E_j = 18.9$ J/cm^2 for PA6 fabric and $E_j = 22.7$ J/cm^2 for PP fabric.

The unit activation energy, E_j, is the corona discharge energy per surface area unit of the fabric under activation, calculated from the following formula:

$$E_j = \frac{P_x B \times 60}{LA} \times 10^{-4} \text{ in J/cm}^2 \quad (3)$$

where:

P – maximum generator energy used (2100 W),

A – velocity of the fabric travelling through the interelectrode slot,

B – utilisation of the maximum power of discharge in %, and

L – electrode length in cm.

The process conditions of corona discharge modification have been established in the course of previous studies [12 - 17]. As a result of this plasma treatment we obtained the degree of physical and chemical modification of the fibre's outer layer expected, i.e. its nanostructuring and oxidation as confirmed by the results of AFM and EDX analyses [10, 12]. The changes in the surface properties of the modified woven fabrics expected are presented in ***Table 2***.

The use of AFM allowed the observation of the physical condition of the fibre's outer layer in a nanodimension scale both before and after corona discharge treat-

Table 2. *Surface properties of PET, PA6 and PP woven fabrics modified by corona discharge under optimised conditions.*

Type of fabric	Activation energy unit, J/cm^2	Selected surface properties of fabrics								
		Free surface energy, J/cm^2		Degree of wettability/ capillarity, cm		Contact angle with water, deg		Increase in the content of acid groups due to modification, 10^{-5} mol/g	O/C ratio EDX method	
		Before modification	After modification	Before modification	After modification	Before modification	After modification		Before modification	After modification
PET	75.6	38.45	48.16	5.45	10.65	63.35	51.03	1.70	0.7588	0.7915
PA6	18.9	41.79	45.02	5.05	8.7	60.00	56.92	2.81	0.3112	0.3440
PP	22.7	43.45	73.50	0.1	7.1	112.07	13.40	1.94	0.0808	0.1748

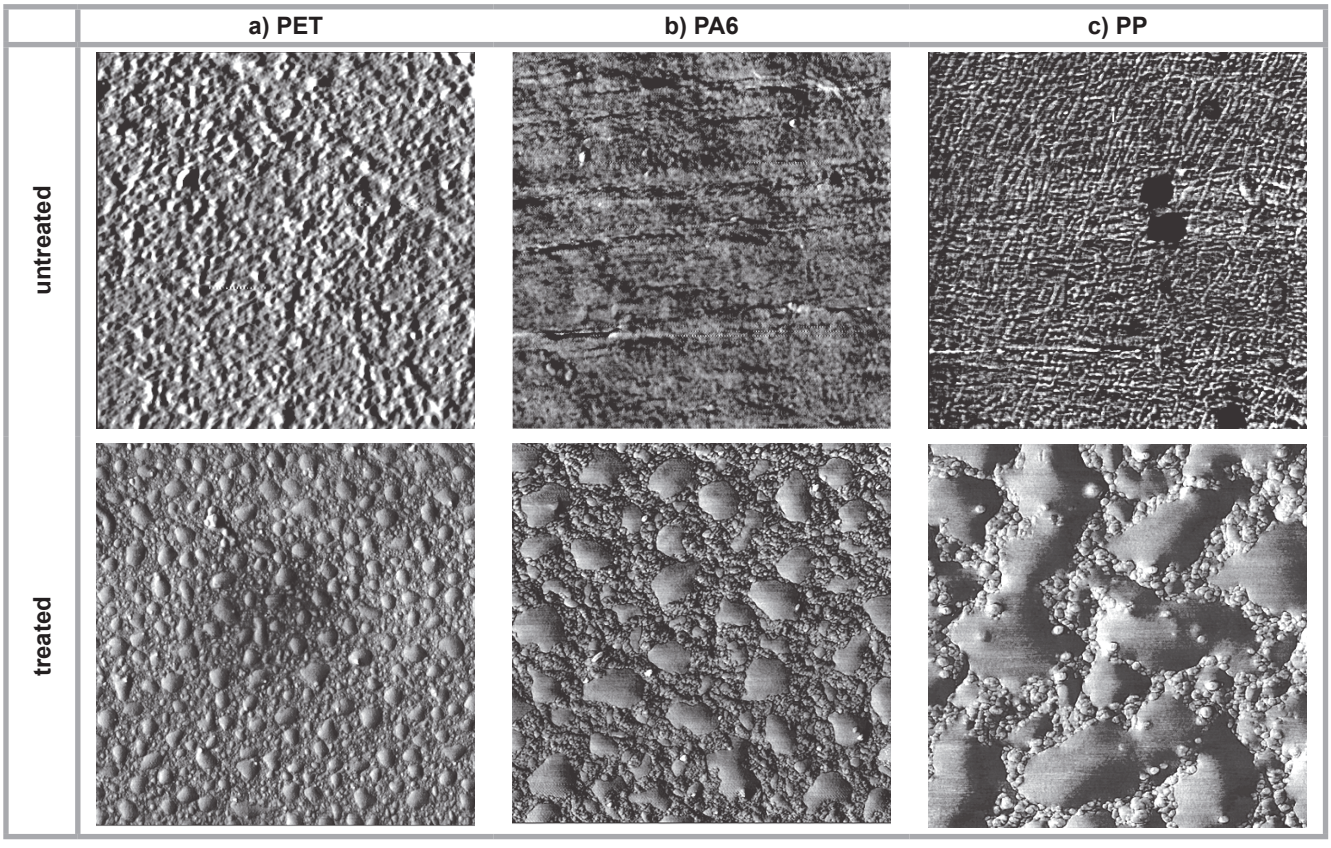

Figure 3. *Nanostructuring of the outer layer of fibres in woven fabrics subjected to corona discharge treatment under optimised conditions: a) PET (E_j = 75.6 J/cm^2), b) PA6 (E_j =18.9 J/cm^2), c) PP (E_j = 22.7 J/cm^2). (The AFM photos were taken by Professor Adam Tracz of the Center of Molecular and Supermolecular Research, PAN Łódź).*

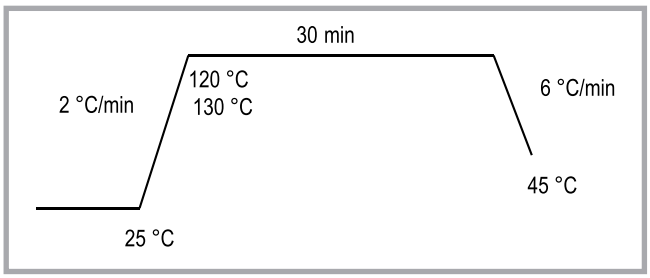

Figure 4. *Conditions of dyeing PET fabric by exhaustion with C.I. Disperse Blue 73 (Błękit syntenowy P-BGL).*

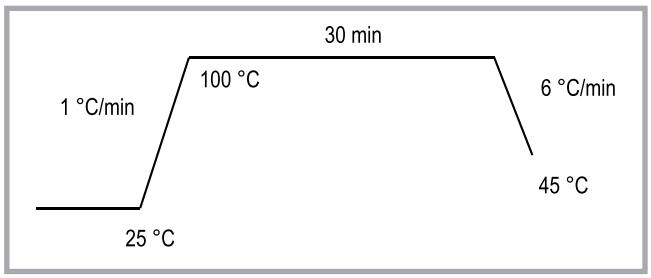

Figure 5. *Conditions of dyeing PA6 fabric by exhaustion with C.I. Acid Red 154 (Lanasyn Rot F-2B).*

ment. As shown in ***Figure 3***, the fibres of PET, PA6 and PP woven fabrics subjected to the modification show characteristic changes in their surface nanotopography, i.e. a considerable increase in their specific surface [15, 16, 18].

The dynamometric measurements of the strength properties (tensile strength) of the woven fabrics performed before and after the modification show no adverse changes as a result of the corona discharge pretreatment [16]. This statement concerns the fabrics of all the three types of filament yarns under investigation; however, as shown in ***Table 2***, the optimised unit activation energies established are of various levels [16]. It was the optimised modification conditions that were used in the pretreatment of the woven fabrics before the dyeing process.

Assessment of the effect of plasma pretreatment on the dyeing properties of fibres/fabrics

Examinations were carried out with both untreated and plasma pretreated woven fabrics under optimised conditions. Dyeing was performed by two basic methods:

- ***exhaustion*** *under increased pressure and temperature* through dye exhaustion from a dyebath
- ***Thermosol continuous method*** with dye fixation in hot air.

Dyeing by exhaustion

The dyeing of fabrics was carried out in a laboratory dyeing machine (AHIBA NUANCE Top Speed) with a liquor ration of 1:60, and the initial dye content in the dyebath in relation to the sample being dyed was as follows:

- acid dye (dyeing PA6 fabric): C.I. Acid Red 154 (Lanasyn Rot F-2B) – 0.8% by wt.;
- disperse dye (dyeing PET and PP fabrics): C.I. Disperse Blue 73 (Błękit syntenowy P-BGL) – 2% by wt.

The process conditions of dyeing PET and PA6 fabrics are shown in ***Figures 4*** and ***5***.

The examinations included the fibre dyeing rate in a real dyeing process as well as changes in the final colour intensity determined in spectrophotometric measurements of the colour difference ΔE.

Considering the negative results of the preliminary dyeing of PP fabrics with disperse dyes, these fabrics were excluded from further examinations.

Dyeing by the Thermosol continuous method

PET, PA6 and PP woven fabrics that were both untreated and modified with corona discharge under optimised conditions were dyed with the following disperse dyes: C.I. Disperse Blue 73 (20 g/dm^3) and C.I. Disperse Red 54 (20 g/dm^3) using the laboratory dyeing unit in the Thermosol method. The dyeing consisted in padding the fabric in a bath containing a dye and nonionic leveling agent, followed by drying and final heating. The padding process was carried out in a two-roller paddler with a horizontal roller system. The pressure of the squeezing rollers was 20 kG/cm and the padding rate - 1 m/min. The bath absorption (imbibition) by PET unmodified/modified woven fabric was at a level of 62/68%, PA6 unmodified/modified fabric - 78/83% and PP unmodified/modified fabric - 32/55%. The fabrics after padding were dried at 100 - 120 °C and heated, depending on the type of fibre, at 200 °C (PET), 170 °C (PA6) or 120 °C (PP). The heating time was 40 s (PET), 60 s (PA6) and 10 min (PP). To remove uncombined dyes, the fabrics were washed at a temperature of 60 °C for 15 min in a washing bath and then rinsed in water at temperatures of 60 °C, 40 °C and 20 °C, followed by drying at 100 °C.

All the untreated and modified woven fabrics dyed by both the batch and continuous processes were tested for colour fastness to perspiration and wet and dry abrasion. These tests were carried out according to the following obligatory European standards: PN-EN ISO 105-E04:1999 'Textiles. Testing the fastness of dyeings. Fastness of colour to perspiration', and PN-EN ISO 105- X12:2005 'Textiles. Testing the fastness of dyeings. Part X12: Fastness of colour to abrasion'.

Results and discussion

Dyeing by exhaustion

Effect of corona discharge pretreatment on changes in fabric dyeing intensity – difference in colour ΔE

The reemission of colour was measured by means of a CM 2600d spectrophotometer with geometry d/8. Calculations were performed by means of the CIE L*a*b system, using light D65 at an observation angle of 10°. The colour difference, Δ*E*, between the plasma pretreated and untreated samples was determined according to the following formula:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \qquad (4)$$

where:

Δ*L* – difference in brightness between plasma pretreated and untreated samples,

Δ*a* – difference in colour from green to red between plasma pretreated and untreated samples,

Δ*b* – difference in colour from blue to yellow between plasma pretreated and untreated samples.

Analysis of the values of Δ*E* allowed to determine the effectiveness of the corona discharge pretreatment of PET and PA6 woven fabrics with respect to their dyeing properties. The values of L, a, b and Δ*E* obtained are listed in ***Table 3***.

The difference in the colour of PP fabric was not tested due to the negative results of preliminary examinations.

Effect of corona discharge pretreatment on changes in the fabric dyeing rate

The kinetics of dyeing is defined by the rate at which the dye passes from the dyebath to the fibre. The dyeing rate can be characterised by means of kinetic dyeing isotherms (absorption curves) or the degree of dyebath exhaustion after a lapse of time during dyeing at a specified constant temperature. In our investigations, the dyeing rate was determined by the degree of dye exhaustion from the dyebath at various dyeing temperatures. The quantity of dye combined with fibre was determined by means of spectrophotometric measurements of the dyebath absorbance before and after dyeing. Based on the absorbance values obtained, the degree of dye exhaustion from the dyebath, W in %, was calculated from the following formula:

$$W = (A_p - A_k)/A_k \times 100 \text{ in } \% \quad (5)$$

where:

W – degree of dye exhaustion from the dyebath,

A_p – absorbance value at a wavelength characteristic of the given dye, measured before dyeing,

A_k – absorbance value at a wavelength characteristic of the given dye, measured after dyeing.

The degree of dye exhaustion from the dyebath, W in %, depending on the time and temperature of dyeing, was determined by dyebath sampling during the dyeing process. The values of W obtained for PET and PA6 woven fabrics are presented in ***Tables 4*** and ***5***.

The results of testing the dyeing fastness of PET and PA6 woven fabrics are listed in ***Table 6***.

Summary of the results of dyeing by exhaustion

The results of dyeing both PET and PA6 fabrics by exhaustion did not significantly change due to the use of plasma pretreatment. The modification process neither altered the dyeing kinetics and degree of fibre dyeing nor improved the dyeing fastness to perspiration and dry and wet abrasion. It should be added that the same results were obtained with the use of other dyes, such as disperse, acid and cationic dyes (PP), which indicates that the results of dyeing by exhaustion are at a similar level regardless of the type of dye used. It is known [1, 6, 9, 13] that plasma treatment, including both low-pressure plasma and atmospheric plasma, i.e. corona discharge, of fibres results in the modification of the thin outer layer only, interacting to a depth of 100 nm (according to other sources - up to 200 nm), while most of the fibre material in which the dye diffuses remains unchanged. This is just 0.7% to 1.5% in relation to the fibre thickness (diameter), amounting to 6500 nm in the case of even the thinnest fibre of the 'micro' type (the diameter of standard fibres is about twice as high). Taking into account the fibre mass, this would mean that over 99% of the fibre material remains beyond the

Table 3. *Values of L, a, b and ΔE obtained for PET woven fabric dyed at 120 °C and 130 °C for 30 min and PA6 woven fabric dyed at 100 °C for 30 min. 1)dyed at 120 °C, 2)dyed at 130 °C.*

Woven fabric		Dye	L	a	b	ΔE
PET[1)]	Unmodified	C.I. Disperse Blue 73 (Błękit syntenowy P-BGL)	47.30	-4.18	-37.55	-
	Modified		47.16	-4.57	-36.98	0.71
PET[2)]	Unmodified	C.I. Disperse Blue 73 (Błękit syntenowy P-BGL)	46.04	-3.49	-37.84	-
	Modified		45.63	-3.90	-37.31	0.79
PA6	Unmodified	C.I. Acid Red 154 (Lanasyn Rot F-2B)	40.08	52.93	5.09	-
	Modified		41.17	53.64	4.70	0.45

Table 4. *Degrees of dye exhaustion, W in %, for PET fabric dyed with C.I. Disperse Blue 73 at 120 °C and 130 °C.*

120 °C				130 °C			
Temperature, °C	Time, min	W, %		Temperature, °C	Time, min	W, %	
		Unmodified sample	Modified sample			Unmodified sample	Modified sample
40	10	4.0	2.6	40	10	4.0	2.6
60	20	4.9	3.3	60	20	4.9	3.3
80	30	5.3	3.7	80	30	5.3	3.4
100	40	12.6	13.4	100	40	12.6	11.9
120	50	70.9	70.9	130	55	77.9	71.0
120	55	77.9	77.4	130	60	83.5	82.1
120	65	84.6	82.1	130	70	84.1	84.9
120	80	85.3	84.9	130	85	84.8	84.8
120	110	86.1	86.1	130	115	85.3	85.1

Table 5. *Degrees of dye exhaustion, W in %, for PA6 fabric dyed with C.I. Acid Red 154 (Lanasyn Rot F-2B) at 100 °C.*

Temperature, °C	Time, min	W, %	
		Unmodified sample	Modified sample
40	10	15.4	15.6
60	20	45.6	42.0
80	30	86.5	84.7
100	40	99.2	98.7
100	45	99.3	99.1
100	55	99.3	99.3
100	70	99.7	99.6
100	100	99.8	99.6

Table 6. *Dyeing fastness of PET and PA6 woven fabrics dyed by exhaustion.*

Woven fabric		Fastness to acidic perspiration			Fastness to alkaline perspiration			Fastness to abrasion	
		Colour change	White fabric staining		Colour change	White fabric staining		Longitudinal direction (along warp)	
			PET	CO		PET	CO	dry	wet
PET	Unmodified	5	5	4-5	5	5	4-5	4-5	5
	Modified	5	5	4-5	5	5	4-5	4-5	5
			PA	CO		PA	CO		
PA6	Unmodified	5	4-5	4-5	5	4	4	5	5
	Modified	5	4-5	4-5	5	4	4	5	5

Table 7. *Values of L, a, b and ΔE obtained for PET, PA6 and PP woven fabrics dyed by the Thermosol process.*

Woven fabric		Dye	L	A	b	ΔE
PET	Unmodified	C.I. Disperse Blue 73 (Błękit syntenowy P-BGL)	56,34	-4,83	-37,64	-
	Modified		51,31	-5,42	-32,51	7,20
PA6	Unmodified		45,60	-5,66	-39,91	-
	Modified		45,32	-6,34	-38,07	1,98
PP	Unmodified		84,47	-0,81	-16,05	-
	Modified		75,62	-2,96	-22,48	11,20
PET	Unmodified	C.I. Disperse Red 54 (Szkarłat syntenowy P-3GL)	56,96	49,88	45,28	-
	Modified		54,5	52,52	47,81	4,38
PA6	Unmodified		51,08	50,46	34,31	-
	Modified		51,30	50,51	34,74	0,49
PP	Unmodified		85,86	10,66	1,78	-
	Modified		82,41	14,88	3,88	5,85

Table 8. *Dyeing fastness of PET, PA6 and PP woven fabrics dyed with C.I. Disperse Blue 73 by the continuous process.*

Woven fabric		Fastness to acidic perspiration			Fastness to alkaline perspiration			Fastness to abrasion	
		Color change	White fabric staining		Color change	White fabric staining		Longitudinal direction	
			PET	CO		PET	CO	dry	wet
PET	Unmodified	5	5	5	5	5	5	5	5
	Modified	5	5	5	5	5	5	5	5
			PA	CO		PA	CO		
PA6	Unmodified	5	4	5	5	4	5	4-5	4-5
	Modified	5	4	5	5	4	5	4-5	4-5
			PP	CO		PP	CO		
PP	Unmodified	5	5	4-5	5	5	4-5	5	5
	Modified	5	5	4-5	5	5	4-5	5	5

Table 9. *Dyeing fastness of PET, PA6 and PP woven fabrics dyed with C. I. Disperse Red 54 by the continuous process.*

Woven fabric		Fastness to acidic perspiration			Fastness to alkaline perspiration			Fastness to abrasion	
		Color change	White fabric staining		Color change	White fabric staining		Longitudinal direction	
			PET	CO		PET	CO	dry	wet
PET	Unmodified	5	4-5	4-5	5	4-5	4-5	5	5
	Modified	5	4-5	4-5	5	4-5	4-5	5	5
			PA	CO		PA	CO		
PA6	Unmodified	5	2	3-4	5	2	3-4	4-5	4-5
	Modified	5	2	3-4	5	2	3-4	4-5	4-5
			PP	CO		PP	CO		
PP	Unmodified	5	5	4	5	5	4	4-5	4-5
	Modified	5	5	4	5	5	4	4-5	4-5

range of modification. Hence, even considerable changes in the supermolecular structure of the fibre's outer layer modified by plasma cannot significantly affect the dyeing properties of the fibre, as confirmed by the tests performed.

Dyeing by the Thermosol continuous method

Totally different results were obtained in the case of dyeing PET, PA6 and PP woven fabrics by the Thermosol method, where the dyeing process proceeds within a considerably shorter time than that of the batch process. In this case, the dye (in a dyebath) is first mechanically applied to the fibre/fabric surface, and then during fixation under hot air it diffuses inside the fibre and combines with the fibre material. The tests performed confirm a clear effect of the plasma modification on the colour intensity of woven fabrics dyed with disperse dyes. The differences in colour of individual synthetic woven fabrics expressed as ΔE are given in ***Table 7***.

The woven fabrics dyed by the continuous process were also tested for dyeing fastness to perspiration and dry and wet abrasion. The results obtained are listed in ***Tables 8*** and ***9***.

Summary of the test results of dyeing by the continuous method

From the results obtained it follows that the intensity of colour of all the dyed fabrics was considerably increased depending on the type of fibre and surface properties of the woven fabric being dyed. Particularly big increments in Δ*E* were obtained in the case of PP and PET woven fabrics, while those for PA6 fabric were relatively small. These results also show that the increase in color intensity depends on the structure and properties of the dyes used. Considerably bigger differences in colour intensity were obtained in the case of C.I. Disperse Blue 73 than in that of C.I. Disperse Red 54. Considerably bigger differences in colour intensity were obtained in the case of C.I. Disperse Blue 73 than in that of C.I. Disperse Red 54. The differences observed in the intensity of the dyeings can be explained in terms of the smaller dimensions of dye particles in the dispersion (padding bath) - their hydrodynamic diameter - and the absence of steric hindrances in the molecular structure of C.I. Disperse Blue 73 dye. These features facilitate dye adsorption on the fibre surface, developed due to modification with corona discharge and its subsequent diffusion into the fibre. Modification with corona discharge brings about no changes in the colour fastness to perspiration and dry and wet abrasion of woven fabrics dyed by the continuous method.

The considerable increases in color intensity obtained by modification with corona discharge should be undoubtedly ascribed to the polarity increase in the fibre's outer surface and the significant change in its nanotopography. In view of the very short time of contact between the fabric and dyebath during the padding operation, the absorption of dyebath by the fabric depends significantly on its wettability, which, as shown in ***Table 2***, is considerably increased as a result of the modification. Hence one should also expect the woven fabrics modified to show an increased absorption of dyebath compared to unmodified fabrics. Considering the fact that the dyes used in the continuous dyeing process have a low substantivity, an increase in the absorption of dyebath by fibres is accompanied by a proportional increase in the quantity of dye applied on the fabric and then fixed in the thermal operation. To confirm the

Table 10. *Effect of modification with corona discharge on the absorption of aqueous bath during the padding process.*

Woven fabric		Bath absorption, %
PET	Unmodified	61.8
	Modified	67.5
PA6	Unmodified	78.5
	Modified	82,3
PP	Unmodified	31,5
	Modified	54,2

soundness of this reasoning, we examined the absorption of aqueous baths by woven fabrics of various types of synthetic fibres before and after their modification with corona discharge. These tests were carried out by padding previously washed, dried and conditioned fabrics by means of a laboratory two-roller padding machine (horizontally roller setting) using an aqueous bath at a temperature of 25 °C, a roller pressure of 15 kG/cm and a fabric travel rate of 5 m/min. The padded fabrics were then weighed to determine the content of absorbed water. The tests included both unmodified and modified woven fabrics (see section **Surface modification**). The results obtained are given in ***Table 10***.

As shown by both the previous results concerning the effect of the modification on fabric wettability and those given in ***Table 10***, the biggest changes in bath absorption take place in the case of PP woven fabric, then in PET fabric and the smallest in PA6 fabric. This corresponds somewhat to the results of colour intensity changes in woven fabrics dyed by the Thermosol process, given in ***Table 7***.

Conclusion

1. Based on the results obtained, one can state that the nanostructuring of a fibre's outer layer by corona discharge pretreatment neither makes significant changes in the color intensity (ΔE) of woven fabrics dyed by exhaustion nor affects the degrees of dye exhaustion - W in % of the dyeing, and the color fastness to perspiration and dry and wet abrasion.
2. This lack of the influence of fibre surface modification on dyeing synthetic fabrics by exhaustion is due to the fact that only a small portion of the fibre material (outer layer of fibres) is changed by the corona discharge pretreatment.
3. In the case of dyeing PET, PA6 and PP woven fabrics by the Thermosol process with dye fixation in hot air, a clear positive effect of the nanostructuring and chemical activation of the fibre's outer layer by corona discharge pretreatment on the intensity of its coloring was found.
4. As shown by the tests of fabric surface properties, modification with corona discharge considerably increases the wettability and, consequently, the absorption properties of the woven fabrics investigated, which makes it possible to increase the quantity of dye deposited and then fixed in the subsequent thermal operation. The dependence of the colour difference obtained on the type of dye results from the fact that the dyes used have different structures and properties.
5. The results obtained have not confirmed some literature data concerning the possibilities of a considerable increase in the dyeing intensity of textiles of synthetic fibres as a result of their modification with various types of atmospheric plasma. This statement concerns the results of dyeing by exhaustion under commonly used conditions.
6. The use of corona discharge pretreatment under the optimised process conditions developed and with an appropriate selection of dyes makes it possible to considerably increase the colour intensity of woven fabric, especially PP and PET fabrics, dyed by the continuous Thermosol process, which is of paramount practical importance.

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