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PHOTOCATALYTIC EFFECT OBTAINED ON TEXTILE BY FINISHING TECHNIQUES

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Abstract: *This study approached the experimentation of deposition by padding of commercial photocatalytic dispersion AERODISP® W 740 X with 40% solid content of TiO_2 on RIPSTOP fabric, made of 100% cotton yarns Nm 70/1 and a network of polyester filament yarns 330 dtex, both in warp and weft directions. The deposition of photocatalytic dispersions on the textile material have been realised by treatment in concomitent phase of textile support with photocatalytic dispersions and with chemical substances used in fixation of TiO_2 nanoparticles. As chemical substances used in fixation of TiO_2 nanoparticles different crosslinking agents have been used: Itobinder AG (acrylic copolymer), Itobinder U30 NEW (polycarbonate urethane polymer) and Itocoat LJ25 (urethane resin). Itocatalyst SCS and Itocatalyst A were used as catalysts. Photocatalytic activity of functionalized textile materials was evaluated by determining the photodegradation efficiency of methylene blue dye as pollutant, measuring the color difference of the irradiated samples compared with non-irradiated samples. Washing durability of the samples treated with photocatalytic dispersions was conducted qualitatively by determining the photocatalytic activity remaining on the textile fabrics after 1 washing cycle. Electron microscopy was used for viewing the distribution of TiO_2 particles on the surface of textile materials treated with the photocatalytic dispersions. Ti content existing on the surface of the textile materials was performed by energy dispersive X-ray spectroscopy.*

Key words: *photocatalytic textiles, TiO_2, photodegradation efficiency, washing durability*

1. INTRODUCTION

A very important segment of the application of TiO_2 in the textile industry is resolving the problem of binding nanoparticles to the fabric. The central problem is to assure tight binding of nanoparticles to the surface of textiles in order to increase the durability of the desired properties. The literature stated several methods used for this purpose, these are the following: methods that uses covalent linking agents, a layer by layer methods, and methods for the introduction of reactive functional groups onto textile surface [1-6]. In order to obtain textile supports with photocatalytic activity was experimented at the laboratory level the deposition on the textile materials in different variants experimental of a commercial photocatalytic dispersion.

2. EXPERIMENTAL

2.1 Materials

Deposition of photocatalytic dispersions was performed on RIPSTOP fabric, with fibre

composition of 83% cotton/17% filament polyester, made of 100% cotton yarns, Nm 70/1 and a network of polyester filament yarns 330 dtex, both in warp and weft directions. For functionalization treatment the commercial dispersion AERODISP® W 740 X with 40 wt% TiO_2 P25 nano titanium dioxide in water have beend used (Evonik Degussa Corporation). As chemical substances used in fixation process of TiO_2 nanoparticles were used different crosslinking agents, supplied from LJ Specialities (UK): Itobinder AG (acrylic copolymer), Itobinder U30 NEW (polycarbonate urethane polymer) and Itocoat LJ25 (urethane resin). Itocatalyst SCS and Itocatalyst A were used as catalysts (LJ Specialities, UK).

2.2. Preliminary preparation of textile materials

Prior to functionalization treatments the textile fabrics were subjected to preliminary preparation: enzymatic desizing, hot alkaline treatment and bleaching.

2.3. Treatment of textile materials with photocatalytic dispersions

The deposition of photocatalytic dispersions on the textile materials was realised through treatment in concomitant phase of textile support with photocatalytic dispersions and with chemical substances used in fixation process of TiO_2 nanoparticles. The treatment of textile materials with photocatalytic dispersions was performed by padding, on the laboratory padder, under the following conditions: 2 passes, 2 bar squeezing pressure. Drying and curing of textile materials was made on the drying/curing/heat-setting/vaporization**,** model TFO/S 500 mm (ROACHES, UK).

Table 1: *Codification of experimental variants*

Code	Content of treatment bath	Technological parameters
AV_1	**1.** 50 mL/L AERODISP W 740 X **2.** 20g/L Itobinder AG	**1.** Padding; **2.** Drying: 120^{0}C, 120 s; **3.** Curing: 150^{0}C, 120 s
AV_2	**1.** 50 mL/L AERODISP W 740 X **2.** 30 g/L Itobinder U30 **3.** 1g/L Itocatalyst SCS	**1.** Padding; **2.** Drying: 120^{0}C, 120 s **3.** Curing: 150^{0}C, 240 s
AV_3	**1.** 50 mL/L AERODISP W 740 X **2.** 20 g/L Itocoat LJ 25 **3.** 1g/L Itocatalyst A	**1.** Padding **2.** Drying: 120^{0}C, 120 s **3.** Curing: 160^{0}C, 120 s
AV4	**1.** 50 mL/L AERODISP W 740 X	**1.** Padding; **2.** Drying: 120^{0}C, 120 s; **3.** Curing: 150^{0}C, 240 s
BV1	**1.** 12.5 mL/L AERODISP W 740 X **2.** 20g/L Itobinder AG	**1.** Padding; **2.** Drying: 120^{0}C, 120 s **3.** Curing: 150^{0}C, 240 s
BV2	**1.** 12.5 mL/L AERODISP W 740 X **2.** 30 g/L Itobinder U30 **3.** 1g/L Itocatalyst SCS	**1.** Padding; **2.** Drying: 120^{0}C, 120 s **3.** Curing: 150^{0}C, 240 s
BV3	**1.** 12.5 mL/L AERODISP W 740 X **2.** 20 g/L Itocoat LJ 25 **3.** 1g/L Itocatalyst A	**1.** Padding; **2.** Drying: 120^{0}C, 120 s **3.** Curing: 160^{0}C, 120 s
BV4	**1.** 12.5 mL/L AERODISP W 740 X	**1.** Padding; **2.** Drying: 120^{0}C, 120 s; **3.** Curing: 150^{0}C, 240 s
CV1	**1.** 5mL/L AERODISP W 740 X **2.** 20g/L Itobinder AG	**1.** Padding; **2.** Drying: 120^{0}C, 120 s **3.** Curing: 150^{0}C, 240 s
CV2	**1.** 5mL/L AERODISP W 740 X **2.** 30 g/L Itobinder U30 **3.** 1g/L Itocatalyst SCS	**1.** Padding; **2.** Drying: 120^{0}C, 120 s **3.** Curing: 150^{0}C, 240 s
CV3	**1.** 5mL/L AERODISP W 740 X **2.** 20 g/L Itocoat LJ 25 **3.** 1g/L Itocatalyst A	**1.** Padding; **2.** Drying 120^{0}C, 120 s **3.** Curing: 160^{0}C, 120 s
CV4	**1.** 5mL/L AERODISP W 740 X	**1.** Padding: **2.** Drying: 120^{0}C, 120 s; **3.** Curing: 150^{0}C, 240 s

The samples codification, technological parameters and the composition of treatment baths are found in the Table 1.

2.4. Methods

2.4.1. Evaluation of photocatalytic activity of functionalizaed textile materials

Photocatalytic activity of textile fabrics treated with synthesized dispersions was evaluated by determining the photodegradation efficiency of methylene blue dye (MB) used as aqueous solution of 0.008 g/L. Textile materials treated with each type of photocatalytic dispersion were immersed for 5 minutes in MB solution. Subsequently, the samples have been subjected to UV irradiation for 6 hours using the "dark room" type CN 15 LC (Vilber Lourmat, France). Incorporated lamps (2 x 15 W) were the sources of ultraviolet radiations and emitted radiation of λ_{max} (emission) = 365 nm and respectively 254 nm. Evaluation of the photocatalytic activity was performed by measuring the color difference of the irradiated samples compared with non-irradiated samples (reference). Color measurements were performed according to ISO 105 J03:2001, using the Spectroflash 650 spectrophotometer (Datacolor, Switzerland) and the light source was the illuminant D65/10. Values obtained for chromatic parameters and color difference are the average of 5 individual measurements carried out on the treated samples with photocatalytic dispersions and on the standard samples considered, treated only with photocatalytic activity (AV_4, BV_4, CV_4).

2.4.2. Durability to washing

The washing durability of the samples treated with photocatalytic dispersions was determined only for the samples which show the significant photocatalytic effects. The samples treated with photocatalytic dispersions have undergone a washing cycle using REDKROME equipment (Ugolini-Italia) under the following conditions: 2g/L detergent containing no phosphate and bleaching agent, at a temperature of 40^0C for 30 minutes. Samples were subsequently rinsed and freely dried horizontally. The washed and unwashed samples were immersed for 5 minutes in a solution of methylene blue (0.008 g/L) and then exposed for 6 hours to UV irradiation (λ_{max}=365 nm). Evaluation of treatment durability to washing was conducted qualitatively by determining the photocatalytic activity remaining on the textile fabrics after washing, by spectrophotometric measurement of color difference between the washed-irradiated sample and the washed-non-irradiated sample.

2.4.3. Electron microscopy

Vizualization of distribution of TiO_2 particles on the surface of textile materials was conducted using Quanta 200 (FEI, Netherlands) electron microscope with X-EDS module integrated.

2.4.4. Energy-dispersive X-ray spectroscopy

Highlighting the Ti content existing on the surface of the textile materials treated with the photocatalytic dispersions was performed by energy dispersive X-ray spectroscopy (EDX).

3. RESULTS AND DISCUSSIONS

3.1. Evaluation of photocatalytic activity of the functionalized textile materials

Color difference parameters were determined considering as reference the non-irradiated samples treated with photocatalytic dispersions, their values being given in Table 2. Analyzing the values of the colour difference parameter measured for the treated samples with commericals

photocatalytic dispersions is found that photocatalytic activity diminushes gradually way with the decreasing of TiO_2 content from treatment bath, the smallest values for the difference of lightness (DL*) obtaining for the samples of C batch, with a content of 5 mL/L AERODISP W 740 X. The textile materials treated with photocatalytic dispersions, without addition of crosslinking agents (AV_4, BV_4 and respectivly CV_4 samples) presents photocatalytic efficiency, the values obtained for DL* having positive values higher with 8 absolute units (AV_4, λ = 365 nm), 5 absolute units (BV_4, λ = 365 nm) and respectivly 3 absolute units (CV_4, λ = 254 nm) in comparison with the sample of non-irradiated refference. The addition in the treatment bath of binders diminishes in lesser or bigger way the photocatalytic efficiency of treated samples with photocatalytic dispersion, the biggest reduction of the photocatalytic activity obtaining in the case of sample with high content of photocatalytic dispersion (50 g/L AERODISP W 740 X) and the binder based on acrylic copolymer (sample AV_1), the smallest reduction being observed in the case of sample which containing binder based on polycarbonate urethane (sample AV_2). In the case of samples treated with a low content of photocatalytic dispersion (5 g/L AERODISP W 740 X (Code C) the reduction effect of photocatalytic efficiency in the presence of the binders is not observed.

Table 2: *Color difference parameter values obtained for samples treated with photocatalytic dispersions*

Sample code	Irradiation	Colour difference parameters			
		DL*	DC*	DH*	DE*
AV_1	365 nm	4.66	-11.06	-1.56	12.11
	254 nm	4.28	-9.23	-1.71	10.32
AV_2	365 nm	6.17	-14.42	-1.52	15.76
	254 nm	5.20	-11.10	-1.70	12.38
AV_3	365 nm	5.66	-12.08	-1.40	13.41
	254 nm	5.23	-9.91	-1.42	11.29
AV_4	365 nm	8.51	-18.20	-2.78	20.29
	254 nm	3.71	-8.13	-0.51	8.95
BV_1	365 nm	4.00	-10.75	-0.74	11.49
	254 nm	3.20	-8.93	-1.04	9.54
BV_2	365 nm	3.49	-10.84	-0.01	11.39
	254 nm	5.41	-13.21	-1.36	14.34
BV_3	365 nm	3.60	-9.86	-0.30	10.50
	254 nm	2.87	-8.79	-0.75	9.27
BV_4	365 nm	5.41	-12.03	-1.34	13.25
	254 nm	4.14	-8.09	-1.87	9.27
CV_1	365 nm	4.51	-12.18	-0.50	12.99
	254 nm	4.18	-10.04	-1.35	10.96
CV_2	365 nm	2.07	-6.96	0.52	7.27
	254 nm	3.30	-9.20	-0.83	9.81
CV_3	365 nm	0.95	-6.09	0.41	6.18
	254 nm	3.65	-9.10	-1.28	9.89
CV_4	365 nm	0.34	-3.91	1.07	4.07
	254 nm	3.85	-9.02	-1.15	9.88

3.2. Washing durability

The washing durability of the samples treated with photocatalytic dispersions was determined by assessing the photocatalytic effect after 1 washing cycle by color measurement the results being shown in Table 3.

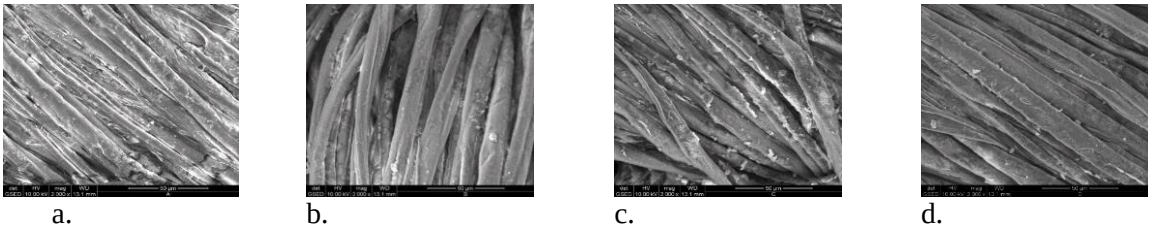
Table 3: *Color difference parameter values obtained for samples treated with photocatalytic dispersions*

Sample code	Colour difference parameters			
	Unwashed samples		Washed samples	
	DL*	DE*	DL*	DE*
AV_1	4.66	12.11	3.46	11.44
AV_2	6.17	15.76	5.59	14.74
AV_3	5.66	13.41	3.95	10.85
AV_4	8.51	20.29	4.59	12.77

From the analyzed batch is distinguished the treatment performed in concomitant phase with AERODISP W 740 X commercial dispersion and with the binder based on urethane polycarbonate (ITOBINDER U30 NEW), followed by the binder based on acrylic copolymer (ITOBINDER AG), the last from the batch in terms of fixation degree being the binder based on crosslinking urethane resin (ITOCOAT LJ25). The standard sample of the (code AV4) batch, realized without fixation binder, confirms the contribution to the chemical substances to the fixation of TiO_2 nanoparticles on the textile material, in this case the reduction of DL* between the unwashed and the washed sample being bigger, respectively a reduction with 4 units in absolte value, comparative with the realized samples in the presence of binders, for which the reduction of DL* value between the washed and unwashed sample is included between 1-2 absolute units.

3.3. Electron microscopy

Electronic images obtained at a magnification of x 2000 for textile materials treated with photocatalytic dispersions are shown in Figure 1.



a. b. c. d.

Fig. 1: *Electronic images recorded at a magnification X 2000 obtained for: a. –AV_1, b. – AV_2, c. –AV_3, d. – AV_4*

The electron microscopy has allowed only the evaluation of the grade distribution of TiO_2 particles on the fibers surface from the component of textile materials. Electronic images recorded for textile materials treated with TiO_2 based dispersions reveal that they are covered with a relatively uniform layer of particles, which are less agglomerated, of different shapes and sizes.

3.4. Energy-dispersive X-ray spectroscopy - EDX

Cuantification of the Ti content existing on the surface of textile materials treated with synthesized photocatalytic dispersions is shown in Table 4. In the case of textile materials treated with photocatalytic dispersion AERODISP W 740 X according to variant I (A batch) the bigger quantity of Ti was found for the sample which was considered standard for this batch, without addition of binders (code AV_4), correlating with the most pronounced photocatalytic effect found to this sample. The smallest content of Ti was found at the treated sample with acrylic copolymer ITOBINDER AG, for which were measured the smallest photocatalytic efficiency, materialized into the smallest value for DL* parameter.

Table 4: *Ti content existing on the surface of textile materials treated with photocatalytic dispersions*

Variant code	Ti content	
	Wt (%)	At (%)
AV_1	14.09	4.56
AV_2	26.19	9.36
AV_3	26.64	9.57
AV_4	27.05	9.82

5. CONCLUSIONS

Textile materials treated with AERODISP W 740 X dispersion in different experimental variants showed photocatalytic efficiency, this decrease's gradually with the diminution of the TiO_2 content from the liquor bath. The addition in the treatment bath of the chemical substances used in fixation of TiO_2 nanoparticles diminushes lesser or greater the photocatalytic efficiency of the treated samples with the photocatalytic dispersion, the biggest diminution of the photocatalytic effect obtaining in the case of variant with high content of photocatalytic dispersion (50 g/L AERODISP W 740 X) and the binder based on acrylic copolymer (sample AV_1). Electron microscopy revealed the presence of microparticles deposited on the surface of the textile material, in a relatively uniform layer of particles, which are less agglomerated, of different shapes and sizes. Samples treated with dispersions show a Ti content ranging between 14.09- 27.05%, the highest quantity of Ti being obtained for samples treated with the biggest content of TiO_2 without adding of binders (AV_4).

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