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FUNCTIONALISATION OF TEXTILE FABRICS WITH STABILIZED TiO_2 DISPERSIONS

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Abstract: *This study approached the experimentation of deposition by padding of some TiO_2 P25 dispersed photocatalytic systems 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. As stabilizers for photocatalytic dispersions the following products have been used: dodecyltrimethylamonnium bromide (DTAB), 2-[2-(2-methoxyethoxy)ethoxy] acetic acid (TODA) and poly(ethylene)glycol (PEG). Prior to functionalisation treatment, preliminary preparation in three successive steps were applied on textile materials (enzymatic desizing, hot alkaline treatment and bleaching), being followed by cationisation with a polyethylene polyamine resin or a pre-treatment with different crosslinking agents based on acrylic copolymer, polycarbonate urethane polymer or urethane resin. The photocatalytic activity of the textile materials treated with synthesized dispersions was investigated using methylene blue as pollutant. The evaluation was made before and after one washing cycle, in order to determine the durability to washing of applied treatments. 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. The sample treated with photocatalytic dispersion stabilized with TODA showed the higher photocatalytic activity, for which the greatest degree of discoloration was achieved after six hours UV irradiation. Pre-treatment with crosslinking type urethane resin offers good durability to washing of photocatalytic dispersions stabilized with TODA and PEG, confirmed by obtaining a discoloration after washing comparable to that obtained for the unwashed sample.*

Key words: *TiO_2, photocatalytic activity, washing durability, SEM, EDX*

1. INTRODUCTION

Chemical contamination can be manifested through the use of chemical warfare agents in military actions, in case of accidents and also in terrorist attacks [1]. Nowadays, it it obvious that there are increasing risks of chemical contamination by pesticides, widely used toxic chemicals, simoultaneously with an increasing need for the development of more effective protective materials for these purposes, which will not only represent a barrier against toxic chemicals, but will also perform a decontamination (decomposition) of toxic chemicals. One way to achieve self-decontaminating properties of textiles is to employ nanotechnologies. Nanotechnology has been used to obtain of new advanced functionalities for textile materials. TiO_2 nanoparticles are non-toxic and chemically stable under exposure to high temperatures, with photocatalytic activity, self-cleaning, UV protection and antibacterial properties [2-5]. To obtain textiles with decontaminating

properties of chemical warfare agents, this study approached the experimentation of deposition by padding of some TiO_2 P25 dispersed photocatalytic systems.

2. EXPERIMENTAL PART

2.1 Materials

Nano titanium dioxide TiO_2 P25 was used as photocatalyst with the anatase crystalline structure and average particle size of 21nm from Degussa Evonik (Germany). As stabilizers for photocatalytic dispersions, the following reagents have been used: dodecyltrimethylamonnium bromide – DTAB (synthesis grade, Aldrich), 2-[2-(2-methoxyethoxy)ethoxy] acetic acid – TODA (98,4%, Aldrich) and poly(ethylene) glycol–PEG (PEG 400, 99%, Scharlau Chemie) [6]. Deposition of dispersed photocatalytic systems 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. Prior to functionalisation treatment, textile fabric has been treated with different cationisation or crosslinking agents, supplied from LJ Specialities (UK): Itofix EZF (polyethylene polyamine resin), Itobinder AG (acrylic copolymer), Itobinder U30 NEW (polycarbonate urethane polymer) and Itocoat LJ25 (urethane resin). The photocatalytic activity of the textile fabrics treated with dispersions was investigated using methylene blue as pollutant.

2.2. Synthesis of photocatalytic dispersions

Synthesis, characterization and evaluation of photocatalytic activity of dispersions is presented elsewhere [6]. The synthesized dispersions have been coded as following: TiO_2_DTAB, TiO_2_TODA and respectively TiO_2_PEG.

2.3. Preliminary preparation of textile materials

To ensure proper hydrophilicity of the textile fabrics, respectively for a smooth running of functionalization stage, three successive steps for preliminary preparation were applied: enzymatic desizing, hot alkaline treatment and bleaching.

2.4. Pretreatments of textile materials

Pretreatment of textile materials with cationization agent

Cationization of textile material was performed in order to modify the surface electric charge of cellulose fibers, namely to introduce positively charged sites (cationic groups), able to attract the anionic groups through ionic attraction forces. This operation was conducted by impregnating the textile material on the laboratory padder with Itofix EZF. Impregnated textile material was subsequently subjected to drying operation.

Pretreatment of textile materials with various crosslinking agents

Pretreatment of textile material was performed by padding on the laboratory padder with three types of crosslinking agents, followed by drying of the impregnated material at a temperature of 120^0C for 2 minutes. Codification of all experimental variants as well as the componence of pretreatment baths are shown in Table 1.

2.5. Treatment of textile materials with photocatalytic dispersions

To deposit photocatalytic dispersions and to fix TiO_2 nanoparticles on the textile materials the following technological operations were successively carried out: impregnation→ drying → curing. Impregnation of pretreated textile materials with photocatalytic dispersions was performed by padding, on the laboratory padder, under the following conditions: 2 passes, 2 bar squeezing

pressure. Drying of the impregnated textile materials was carried out at a temperature of 120^0C for 2 minutes. Curing was performed differently, depending on the type of crosslinking agent used, as follows: Variant A – 0 minutes ; Variant B -170^0C, 1 minute ; Variant C - 150^0C, 4 minutes, Variant D - 150^0C, 4 minutes; Variant E - 160^0C, 2 minutes. Codification of the experimental variants in order to deposit and fix TiO_2 nanoparticles on the textile fabrics is shown in Table 1.

Table 1: *Codification of experimental variants in order to deposit and fix TiO_2 nanoparticles*

Content of pretreatment bath	Photocatalytic dispersion	Code of material treated with photocatalytic dispersion
-	TiO_2_DTAB	A_TiO_2_DTAB
10 g/L Itofix EZF		B_TiO_2_DTAB
20 g/L Itobinder AG		C_TiO_2_DTAB
30 g/L Itobinder U30, 1g/L Itocatalyst SCS		D_TiO_2_DTAB
20 g/L Itocoat LJ 25, 1g/L Itocatalyst A		E_TiO_2_DTAB
-	TiO_2_TODA	A_TiO_2_TODA
10 g/L Itofix EZF		B_TiO_2_TODA
20 g/L Itobinder AG		C_TiO_2_TODA
30 g/L Itobinder U30, 1g/L Itocatalyst SCS		D_TiO_2_TODA
20 g/L Itocoat LJ 25, 1g/L Itocatalyst A		E_TiO_2_TODA
-	TiO_2_PEG	A_TiO_2_PEG
10 g/L Itofix EZF		B_TiO_2_PEG
20g/L Itobinder AG		C_TiO_2_PEG
30 g/L Itobinder U30, 1g/L Itocatalyst SCS		D_TiO_2_PEG
20 g/L Itocoat LJ 25, 1g/L Itocatalyst A		E_TiO_2_PEG

2.6. Methods

2.6.1. 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 were stored in the dark for 1 h - for the adsorption-desorption equilibrium to be reached and 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. 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. For each textile material subject to a certain type of pre-treatment (series A, B, C, D, E), but not including treatment with photocatalytic dispersion, the degree of MB discolouration has been determined. These samples were immersed in the same conditions in MB solution, stored in the dark and exposed to UV irradiation for 6 hours.

2.6.2. Durability to washing

To test the durability to washing of applied treatments, the samples treated with photocatalytic dispersions have undergone a washing cycle using Scourotester equipment (Metrimpex, Hungary) 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), stored in the dark for 60 minutes 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. The results obtained, in terms of photocatalytic activity, were evaluated as compared to standard unwashed samples.

2.6.3. 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.

2.6.4. 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.

Table 2: *Color difference parameter values obtained for functionaslized samples*

Variant code	Colour difference parameters				Variant code	Colour difference parameters			
	DL*	DC*	DH*	DE*		DL*	DC*	DH*	DE*
A_ TiO_2_DTAB	3.08	-8.77	-2.75	9.71	**A_TiO_2_TODA**	4.98	-11.52	-2.98	12.90
B_ TiO_2_DTAB	3.83	-11.35	-5.87	13.34	**B_TiO_2_TODA**	2.59	-8.61	-4.20	9.92
C_ TiO_2_DTAB	6.88	-15.28	-4.12	17.26	**C_TiO_2_TODA**	5.05	-12.15	-2.10	13.32
D_ TiO_2_DTAB	4.46	-10.70	-2.49	11.86	**D_TiO_2_TODA**	5.85	-13.39	-2.55	14.84
E_ TiO_2_DTAB	3.34	-9.55	-1.32	10.20	**E_TiO_2_TODA**	4.84	-10,97	-2.11	12.18
A_ TiO_2_PEG	3.08	-9.22	-2.54	10.05	**A_MB**	-0.85	-0.39	0.01	0.94
B_ TiO_2_PEG	3.67	-9.84	-5.20	11.72	**B_MB**	-0.60	-0.75	-0.52	1.09
C_ TiO_2_PEG	0.70	-5.64	-2.83	6.35	**C_MB**	-0.87	-0.35	0.50	1.06
D_ TiO_2_PEG	1.91	-7.96	-4.04	9.13	**D_MB**	0.72	-2.51	0.11	2.61
E_ TiO_2_PEG	4.23	-10.18	-3.94	11.70	**E_MB**	0.01	-1.81	0.55	1.89

Analyzing the values of color differences it can be found that discolouration of MB dye, without the contribution of TiO_2 nanoparticles is low, the difference in lightness between the non-irradiated control samples and the irradiated ones having negative subunitary values (darker than the non-irradiated reference) in samples A, B and C, or positive in samples D and E. Textile materials treated with photocatalytic dispersions without the addition of chemicals for fixing (code A) shows the photocatalytic efficiency, the difference in lightness obtained between the irradiated and non-irradiated samples having positive values, 3-4 absolute units higher as compared to non-irradiated reference. The biggest difference in lightness (DL*=4,98) has been obtained for dispersion stabilized with TODA, followed by DTAB and PEG with equal values obtained for DL* (DL*=3,08). Preliminary treatments performed with different crosslinking agents (series B, C, D and E) for fixing the TiO_2 P 25 Degusa on the textile materials do not decrease the photocatalytic effect.

3.2. Durability to washing

The washing durability of the samples treated with synthesized dispersions was determined by assessing the photocatalytic effect after 1 washing cycle by color measurement, the results being shown in Table 3. By analyzing the values of color measurement performed it can be seen that the difference in lightness of the samples pre-treated with resins (series B, D, C and E) decreases after the washing process, generally indicating a degree of semi-permanent fixation of performed treatments. Among the performed pretreatments series, it can be noted ITOCOAT LJ25 treatment, for which the value of difference in lightness after washing has been comparable to that obtained for the unwashed sample (samples E_TiO_2_TODA and E_TiO_2_PEG). The product ITOBINDER AG also provides a good fixation degree for the photocatalytic dispersion D_TiO_2_DTAB.

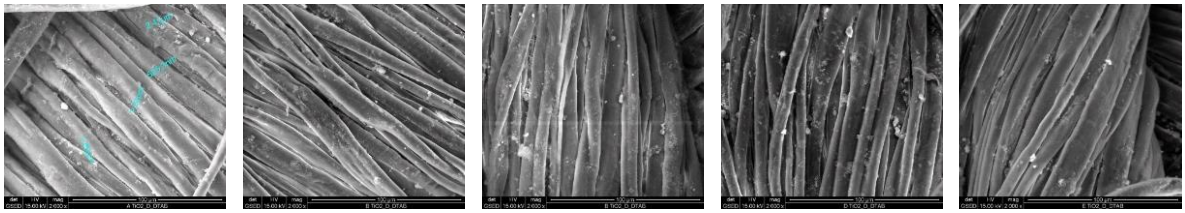
Table 3: *Color difference parameter values obtained for treated samples with photocatalytic dispersions before and after washing*

Sample code	DL*		Sample code	DL*		Sample code	DL*	
	U	W		U	W		U	W
A_TiO_2_DTAB	4.39	1.70	**A_TiO_2_TODA**	7.23	4.37	**A_TiO_2_PEG**	7.91	5.46
B_TiO_2_DTAB	2.96	1.10	**B_TiO_2_TODA**	3.85	2.03	**B_TiO_2_PEG**	5.06	3.94
C_TiO_2_DTAB	5.05	3.79	**C_TiO_2_TODA**	4.57	2.54	**C_TiO_2_PEG**	6.27	3.81
D_TiO_2_DTAB	7.20	5.45	**D_TiO_2_TODA**	4.27	3.51	**D_TiO_2_PEG**	3.93	2.86
E_TiO_2_DTAB	5.97	1.42	**E_TiO_2_TODA**	5.86	5.93	**E_TiO_2_PEG**	3.74	4.87

Legend: U = unwashed samples, W = washed samples

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. e.

Fig. 1: Electronic images recorded at a magnification X 2000 obtained for: a. - A_ TiO_2_DTAB, b. - B_TiO_2_DTAB, c. - C_TiO_2_DTAB, d. - D_TiO_2_DTAB, e. - E_TiO_2_DTAB

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. By analyzing the electronic images recorded for textile materials treated with photocatalytic dispersions, it can not be made a clear delimitation between the applied pre-treatment variants (A, B, C, D, E) and which is the most efficient solution in terms of TiO_2 particles immobilization on the surface of the textile material.

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. The highest quantity of Ti was obtained for samples treated with PEG-stabilized dispersions (code A and E, respectively). However, there can not be made a correlation between the degree of discoloration (photocatalytic effect) and the quantity of Ti found on the surface of each treated textile material.

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

Variant code	Ti content		Variant code	Ti content		Variant code	Ti content	
	Wt (%)	At (%)		Wt (%)	At (%)		Wt (%)	At (%)
A_TiO_2_DTAB	5.74	1.76	**A_TiO_2_TODA**	3.22	0.96	**A_TiO_2_PEG**	5.95	1.81
B_TiO_2_DTAB	2.58	0.77	**B_TiO_2_TODA**	4.21	1.27	**B_TiO_2_PEG**	2.75	0.82
C_TiO_2_DTAB	3.75	1.12	**C_TiO_2_TODA**	3.37	1.00	**C_TiO_2_PEG**	3.11	0.92
D_TiO_2_DTAB	4.72	1.42	**D_TiO_2_TODA**	2.47	0.73	**D_TiO_2_PEG**	4.37	1.32
E_TiO_2_DTAB	3.06	0.91	**E_TiO_2_TODA**	4.17	1.26	**E_TiO_2_PEG**	5.85	1.78

5. CONCLUSIONS

Textile materials treated with TiO_2 P25 dispersions showed photocatalytic efficiency, the colour intensity of irradiated samples being much lighter than that of non-irradiated samples. The sample treated with photocatalytic dispersion stabilized with TODA showed the best photocatalytic efficiency. Preliminary treatments performed with different crosslinking agents do not decrease the photocatalytic effect. Pre-treatment with Itocoat LJ25 offers good durability to washing of photocatalytic dispersions stabilized with TODA and PEG, confirmed by obtaining a discolouration grade after washing comparable to that obtained for the unwashed sample. Electron microscopy revealed the presence of microparticles deposited on the surface of the textile material in a relatively uniform layer of particles with different shapes and sizes. Functionalized textile material show a Ti content ranging between 2.47 - 5.95 %, the highest quantity of Ti being obtained for samples treated with PEG-stabilized dispersions. However, there can not be made a correlation between the degree of discoloration and the quantity of Ti found on the surface of each treated textile material.

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