Multifunctional finishing treatments applied on textiles for protection of emergency personnel

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REZUMAT – ABSTRACT

Tratamente de finisare multifuncțională aplicate materialelor textile pentru protecția personalului de intervenție în situații de urgență

Lucrarea prezintă rezultatele cercetărilor efectuate pentru obținerea de materiale textile multifuncționale cu efecte multiple, prin tehnici de finisare superioară, utilizând produse chimice funcționale sub formă de dispersii apoase. S-a studiat posibilitatea combinării tratamentului cu dispersii cu efecte fotocatalitice și antibacteriene cu un tratament de hidrofobizare/oleofobizare, care să ofere simultan atât efect fotocatalitic și antibacterian durabil, cât și efect hidrofob/oleofob, în limite satisfăcătoare pentru toate aceste efecte. Rezultatele evaluărilor de laborator, efectuate pe suportul textil țesut din 50% bumbac și 50% poliamidă HT funcționalizat, au demonstrat că tratamentul de hidrofobizare cu dispersii fluoropolimerice poate fi combinat cu un tratament cu dispersii fotocatalitice pe bază de dioxid de titan sau cu dispersii pe bază de clorură de argint și dioxid de titan pentru obținerea de efecte multiple fotocatalitice, antibacteriene și hidrofob/oleofobe fără a diminua efectele de funcționalizare care s-ar fi obținut prin tratamentele realizate individual.

Cuvinte-cheie: tratamente de funcționalizare, efect hidrofob, activitate fotocatalitică, activitate antibacteriană, efecte combinate

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The paper presents the results of the researches carried out for obtaining multifunctional textile materials with multiple effects, by means of superior finishing techniques, using functional chemicals in the form of aqueous dispersions. It has been studied the possibility of combining treatment with dispersions with photocatalytic and antibacterial effects with a hydrophobic/oleophobic treatment that simultaneously provides both sustainable photocatalytic and antibacterial effect as well as hydrophobic/oleophobic effect within satisfactory limits for all these effects. The results of the laboratory evaluations performed on 50% cotton and 50% functionalised HT polyamide textile fabrics showed that hydrophobization treatment with fluoropolymer dispersions can be combined with the treatment with titanium dioxide photocalatytic dispersions or silver chloride and titanium dioxide dispersions to obtain multiple photocatalytic, antibacterial and hydrophobic/ oleophobic effects without diminishing the functionalization effects that would have been achieved by individual treatments.

Keywords: functionalization treatments, hydrophobic effects, photocatalytic activity, antibacterial activity, combined effects

INTRODUCTION

Functional clothing can therefore be defined as a generic term that includes all such types of clothing or assemblies that are specifically engineered to deliver a pre-defined performance or functionality to the user, over and above its normal functions. Such clothing would normally be made from a mix of innovative materials, and functionality in this case would imply the added value or function that a garment is expected to perform. Functional clothing is a relatively new and exciting segment of the technical textiles group – one which is receptive to new product developments & technologies and abounding with niche applications. The emergence of performance clothing has been fuelled by recent breakthroughs and advances in technical fibres & fabrics and advances in garment manufacturing technologies. A lot of technologies originally developed for protective clothing applications have also become available in the public domain and form a major constituent of this field [1].

Textiles are considered to be the interface between the user and the environment, but besides this characteristic, they must also have an active role, adapting to major changes dictated by physiological needs, in line with changes in environmental conditions. The field of functional clothing is wide and diverse with each functionality having its own specifications, material requirements, consequent technologies and processes. End use applications are diverse and often quite complex, ranging from life saving and hostile environment responsive to those improving the quality of life [2].

Except the hydro- and oleophobic effects, multi-barrier properties (protection against heat and flame, heat stress and heat stroke protection, soil-release) and relevant physiological parameters (breathability, thermoregulating/insulating properties) and wearing comfort without the movement restriction are required for protective clothing. These properties achieved by customized yarn and fabric construction in combination with textile fibre selection, followed by special textile finishing and garment design (cut, multi-layered structures) [3].

Textile finishing plays an essential role in modifying the appearance, texture, touch and performance of all textiles so that the perception of the end user should be appropriate. Therefore, the use of functional finishing is particularly appreciated by textile manufacturers as it involves surface modification techniques that can be achieved in the final stages of the chemical finishing process. Functional finishing technologies allow manufacturers to continue using traditional raw materials, existing classical machinery and technologies while at the same time gaining added value, thereby enabling the potential buyers interested in functional or multifunctional fabrics to be stimulated and captured [4–5].

In order to obtain multifunctional textile materials with multiple photocatalytic, antibacterial and hydrophobic/oleophobic effects, this article presents laboratory technological experiments for the functionalization of traditional fiber textile materials by means of finishing techniques using functional chemical products as aqueous dispersions. In this regard, the possibility of combining treatment with dispersions with photocatalytic and antibacterial effects with a hydrophobic/oleophobic treatment has been studied, which simultaneously provides both a durable photocatalytic and antibacterial effect and a hydrophobic/oleophobic effect within satisfactory limits for all these effects.

EXPERIMENTAL

Materials

For technological functionalization experiments, a textile fabric was used which includes both in the warp and weft direction Nm 50/2 yarns made of 50% cotton/50% polyamide HT. To obtain textile materials with photocatalytic activity, commercial photocatalytic aqueous dispersion based on TiO_2 – AERODISP® W 740 X with 40% content of the active substance (Evonik Degussa, Germany) has been used. The product based on fluorocarbon polymer dispersions (C6) NUVA 2114 (ARCHROMA), has been used for hydrophobic/oleophobic treatment. Sanitized® T 27-22 Silver (Sanitized AG, Switzerland) has been used in order to obtain the antibacterial effect.

Preliminary preparation of the textile fabrics

In order to ensure a proper hydrophilicity of the textile material, which ensures the proper functioning of the textile backings, they have been subjected to conventional preliminary preparation by hot alkaline treatment, at a pH of medium alkalinity, on a laboratory jigger.

Dyeing of the textile fabrics

The dyeing of the textile fabrics was performed with the direct dye Sirius Light Turquoise Blau GL (DyStar) and with a dyes mixture: Solophenil direct dye and Nylosan ROT N 2RBL reactive dye.

The parameters of the preliminary preparation and dyeing are presented in table 1.

Functionalization treatments

The categories of chemicals selected to confer multifunctional effects were applied on the textile fabrics by padding method on the laboratoy padder (Roaches, UK). After impregnation, the samples were heat treated for drying/condensation on the specific laboratory equipment for these operations (Roaches, UK). The experimental variants are shown below.

Functionalization treatments for conferring the combined antibacterial-oleophobic/hydrophobic effect. To confer the antibacterial-hydrophobic/oleophobic combined effect, the textile fabrics were subjected to treatment in the concomitant phase with the

Table 1

PARAMETERS OF PRELIMINARY TREATMENT AND DYEING FOR THE FABRIC MADE OF 50% COTTON/50% PA

Composition of the treatment baths	Temperature	Duration of treatment	M:LR
Bath 1: Hot alkaline treatment 2 g/L Kemapon PC 3 g/L Na_2CO_3 3 g/L trisodium phosphate	95°C	60 min	1 : 10
Bath 2: Dyeing 2% Light Turquoise Blau GL 20 g/L NaCl	95°C	60 min	1 : 10
Bath 2: Dyeing 3% Solophenil 3% Nylosan ROT N 2RBL 20 g/L NaCl 1 mL/L CH_3COOH	98°C	60 min	1 : 10
After each technological operation, rinsing was performed under the following conditions: 80°C, 60°C, 40°C for 10 minutes each rinsing and a cold rinse for 10 minutes			

Table 2

THE CODIFICATION OF EXPERIMENTAL VARIANTS, TECHNOLOGICAL PARAMETERS, COMPOSITION OF THE TREATMENT BATHS		
Code	**Composition of the treatment baths**	**Technological operations/technological parameters**
V1	7 g/L Sanitized T 27-22 Silver	**1. Padding:** 2 bar squeeze pressure **2. Drying:** 100°C, 2 minute
V2	1 mL/L acid CH_3COOH (60%) 50 g/L NUVA N 2114 liq.	**1. Padding:** 2 bar squeeze pressure **2. Drying:** 100°C, 2 minutes **3. Heat-setting:** 170°C, 40 sec.
V3	1 mL/L acid CH_3COOH (60%) 50 g/L NUVA N 2114 liq. 7 g/L Sanitized T 27-22 Silver	**1. Padding:** 2 bar squeeze pressure **2. Drying:** 100°C, 2 minutes **3. Heat-setting:** 170°C, 40 sec.
V4	1 mL/L acid CH_3COOH (60%) 50 g/L Nuva 4211 liq.	**1. Padding:** 2 bar squeeze pressure **2. Drying:** 120°C, 2 minute
	50 mL/L AERODISP W 740 X	**3. Padding:** 2 bar squeeze pressure **4. Drying:** 120°C, 2 minutes
	1 mL/L acetic acid 60% 50 g/L Nuva 2114 liq.	**5. Padding:** 2 bar squeeze pressure **6. Drying:** 100°C, 2 minute **7. Heat-setting:** 170°C, 1 minute

Sanitized® T 27-22 Silver and with the hydrophobization product NUVA 2114, the operations of technological flow being the following: preliminary preparation → dyeing → padding in single bath with Sanitized® T 27-22 Silver and NUVA 2114 liq → drying → condensation.

Functionalization treatments for conferring the combined photocatalytic-hydrophobic/oleophobic effect. In order to obtain the water/oil repellent effect in combination with the photocatalytic effect it was chosen to treat the textile fabrics in successive phases with the product based on fluorocarbon polymer dispersions (C_6) with a hydrophobic/oleophobic effect (NUVA 2114) and with commercial photocatalytic dispersion based on TiO_2 (AERODISP® W 740 X). The sequence of the constituent operations of technological flow being the following: preliminary preparation → dyeing → padding with NUVA 2114 → drying → padding with AERODISP® W 740 X → drying → re-treatment by padding with NUVA 2114 → drying → condensation.

The codification of the experimental variants, the operations, technological parameters and composition of the treatment baths for each treatment alternative selected in order to produce multifunctional textiles are shown in table 2.

Methods

Evaluation of the photocatalytic activity of functionalized fabrics. Photocatalytic activity of textile fabrics treated in succesive phases with comercial photocatalytic dispersion based on TiO_2 and with the water and oil repellent product base on fluorocarbon dispersion was evaluated by determining the photodegradation efficiency of methylene blue dye (MB), used as aqueous solution of 0.008 g/L. Functionalized textile material were immersed for 30 minutes in MB solution and subsequently has 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 λmax (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 DatacolorTM 650 spectrophotometer (Datacolor, Switzerland) and the light source was the illuminant D65/10. Values obtained for 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.

Physical-chemical and physical-mecanical characteristics. The finished fabrics were also characterized in terms of the main physical-chemical and physical-mechanical characteristics, respectively: mass (SR EN 12127-2003), tensile strength (SR EN ISO 13934-1/2013), tearing strength (SR EN ISO 13937-3: 2002), resistance to water vapor in stationary mode (SR EN 31092/ A1:2013 ISO 11092:1997), air permeability (SR EN ISO 9237: 1999), thermal resistance (SR EN 31092/ A1:2013 ISO 11092:1997).

Evaluation of hydrophobicity of functionalized textiles. In order to evaluate hydrophobicity, the samples treated in different experimental variants were tested for surface wetting resistance – Spraytest (SR EN ISO 4920: 2013).

Antimicrobial tests. The antibacterial activity of the functionalized materials in different variants was qualitatively determined in accordance with ISO 20645: 2004 (E) standard method, by using of cultures in liquid medium replicated at 24 hours of ATCC 6538 *Staphylococcus aureus* (Gram-positive) and *Pseudo - monas aeruginosa* (Gram-negative) strains. For determination, the samples were cut in circular shape with a diameter of 2 cm and subsequently disposed in the middle of Petri plates. The culture medium was poured into two layers in Petri plates, lower layer consists of culture medium free from bacteria and the upper layer being inoculated with the test bacteria, then incubated at 37°C and analyzed after 48 hours. Antifungal efficiency testing was carried out against *Candida albicans* (ATCC 90028) strain, according to ISO 20743:2007 standard, by absorption method of microbial inoculum on the functionalized fabrics. Textile materials were cut in samples with 1 cm^2 surface area, and placed in sterile tubes. Afterwards, 50 μL of microbial inoculum was pipetted on the surface of the material, with microbial concentration of 6×10^3 UFC/mL, followed by 24 h incubation at 36°C. After incubation period, samples were each washed with 3 mL of sterile deionized water, and each tube was vortexed for 20–30 seconds, followed by sampling of 100 μL from each tube and plated on Petri dishes with agarized Sabouraud media, with a Drigalski spatula. Plates were held at room temperature for 30 minutes, and then incubated, with the lid facing down (to avoid formation of condensation on the lid), for 24 h at 36°C.

RESULTS AND DISCUTIONS

Photocatalytic effect

Colour differences atributes were determined considering as reference the samples treated both with the photocatalitic dispersion and the water/oil repellent product, before UV irradiation, the obtained values being shown in table 3.

Table 3

COLOUR DIFFERENCES ATRIBUTES BEFORE AND AFTER UV IRRADIATION

Sample code	Observation	Colour difference DL*	Colour difference DE*	Sample color
V4	Before UV irradiation	Reference		
	UV irradiation 254 nm	–0.31	4.26	
	UV irradiation 365 nm	1.17	2.59	
M*	Before UV irradiation	Reference		
	UV irradiation 254 nm	0.27	2.17	
	UV irradiation 365 nm	0.40	1.21	

** Sample is preliminary treated and dyed without any of the functional treatments*

From the analysis of the values obtained for the difference in lightness DL* it is found that the most obvious photocatalytic effect is registered in the case of the fabric treated with commercial photocatalytic dispersion (AERODISP W 740 X) and with the hydrophobic/oleophobic product (NUVA 2114) after irradiation at 365 nm, in this case, the highest value for this parameter (DL* = 1.17) has been obtained.
The relatively low value obtained for this parameter does not reveal a less efficient photocatalytic effect, this behavior can be attributed to the fact that the hydrophobic textile material absorbs a much diminished amount of MB, which can be degraded by UV discoloration. In the case of the witness sample, which was not subjected to the functionalization treatment, a difference in lightness between the non-irradiated samples and those irradiated at the two wavelengths, with positive subunit values (lighter than the non-irradiated sample), is due to the sensitivity to UV radiation of dyes used for dyeing textile samples and less to the decoloration of the MB dye used to assess the photodegradation effect.

Physical-mecanical characteristics

The main physical-mechanical characteristics are present in the table 4.

Table 4

PHYSICAL-MECANICAL CHARACTERISTICS

Characteristic		Code V1	V2	V3	V4
PHYSICAL-MECANICAL CHARACTERISTICS					
Mass [g/m²]		269	265	236	238
Tensile strength, [N]	Warp	1423	1421	1411	1401
	Weft	1067	1087	880	942
Tear strength, [N]	Warp	49,8	57,8	53,30	54,9
	Weft	36,1	42,9	41,00	39,6

The tensile characteristics such us tensile strength and tear strength of finished samples are given in table 4. The comparative analysis of tensile strength and tear strength values obtained for all the treated samples shows that:

- tensile strength, for the samples treated according to the V3 experimental variant (hydrophobic/oleophobic/antibacterial combined treatment) decreases in the warp direction by 0,84% compared to V1 variant (antimicrobial treatment) and by 0,70% compared to V2 (hydrophobic/oleophobic treatment) and decreases in the weft direction by 17,52% compared to V1 variant, and by 19,04% respectively, compared to V2 variant;
- tear strength for the V3 variant records an increase in the warp direction compared to V1, by 6,5% in the warp direction and by 11,9%, respectively, in the weft direction and a decrease in the warp direction compared to V2 by 7,78% and, 4,42%, respectively, in the weft direction;
- tensile strength of the samples treated according to the V4 variant (photocatalytic/hydrophobic/oleophobic combined treatment) decreases by 1,4% in the warp direction and by 13,3% in the weft direction compared to the V2 variant (hydrophobic/oleophobic treatment);
- tear strength for V4 variant decreases by 5,01% in the warp direction and by 7,69% in the weft direction compared to the variant with V2 (hydrophobic/oleophobic treatment).

Table 5 shows the fabric comfort related characteristics, such as surface wetting resistance, air permeability, water vapour resistance and thermal resistance.

Table 5

FABRIC COMFORT CHARACTERISTICS			
Characteristic	**V2**	**V3**	**V4**
Wetting resistance			
ISO scale	5	5	5
AATCC photographic scale	100	100	100
Air permeability, [l/m^2 s] (100Pa)	31.65	38,48	44,11
Water vapour resistance under steady-state conditions, R_{et}, [m^2 Pa/W]	-	7,05	7,47
Thermal resistance, R_{ct}, [m^2 K/W]	-	0,0189	0,0180

All the finished fabrics show similar level of air permeability, water vapour resistance under steady-state conditions and thermal resistance. The multifunctional treated samples in different experimental variants and tested from the point of view of the hydrophobic effect by superficial wetting test (Spraytest), have shown maximum values of 100 on the AATCC photographic scale, regardless of the variant of finishing applied, thus indicating a very good hydrophobic effect. It has thus been demonstrated that hydrophobic treatment can be combined with photocatalytic effect treatment or with the treatment to obtain the antimicrobial effect, without diminishing the hydrophobic effect.

Antimicrobial tests

Antibacterial activity. Images of Petri plates after 48 h incubation are shown in figure 1. The evaluation of antimicrobial activity consisted in highlighting the presence or absence of the inhibition zone around the samples, the size of the inhibition zone being calculated by the formula:

$$H = D - \frac{d}{2} \quad (1)$$

where:

H is the inhibition zone (mm);

D – the total diameter of the sample and the inhibition zone (mm);

d – sample diameter (mm).

The results obtained from the evaluation of antimicrobial activity for the treated samples in different experimental variants are shown in table 6. For antibacterial activity testing it was considered as the witness sample (M) the dyed fabric without the functionalization treatment.

From the analysis of the data obtained by testing the antibacterial activity, it was found that for the samples tested with *Staphylococcus aureus* there were increases on the contact surface as observed on the entire culture medium area on all samples, except for the V1 sample having a 1.5 cm inhibition area. For samples tested with *Pseudomonas aeruginosa*, the only sample that totally inhibited growth was V2. The V3 sample has no antibacterial activity, both for Gram

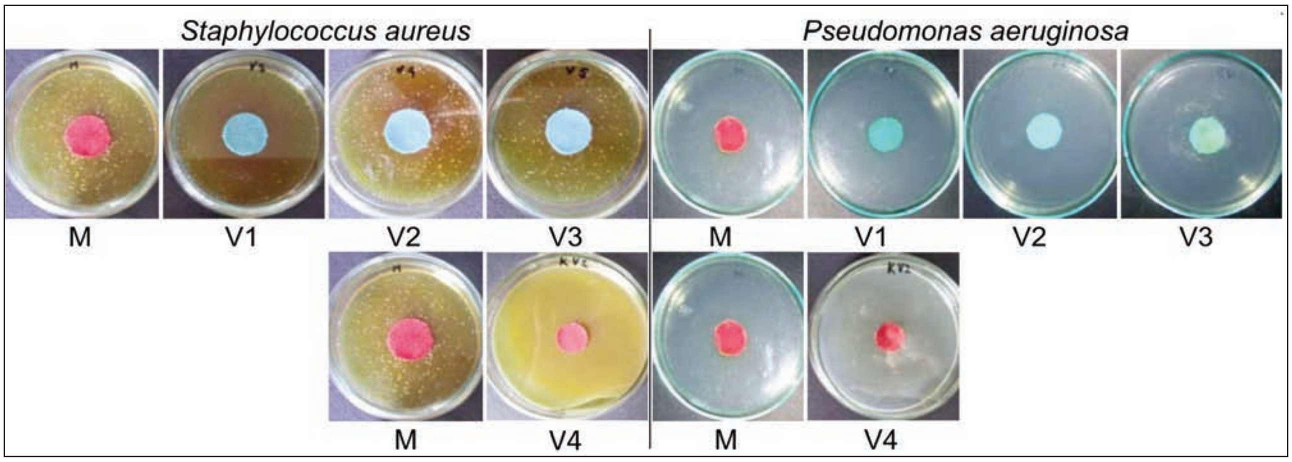

Fig. 1. Images of Petri plates after 48 h incubation

Table 6

EVALUATION OF THE ANTIBACTERIAL EFFECT				
	Staphylococcus aureus		***Pseudomonas aeruginosa***	
Code	**Inhibition zone** [cm]	**Evaluation**	**Inhibition zone** [cm]	**Evaluation**
V1	1.5	Satisfactory effect	-	Unsatisfactory effect
V2	-	Unsatisfactory effect	-	Satisfactory effect
V3	-	Unsatisfactory effect	-	Unsatisfactory effect
V4	-	Unsatisfactory effect	-	Satisfactory effect
M	-	Unsatisfactory effect	-	Unsatisfactory effect

positive and Gram negative microorganisms. The V4 sample has no antibacterial effect against the *Staphylococcus aureus* test strain but has completely inhibited the growth of *Pseudomonas aeruginosa*.

Antifungic activity. For antifungal efficiency quantification, the percentage and logarithmic reduction rate of each sample was calculated, related to untreated material (control). Testing of the antimicrobial activity of functionalized textile materials highlighted different rates of microbial reduction (table 7), dependent on the type of treatment performed.

Table 7

QUANTITATIVE ANTIFUNGAL EFFICIENCY TESTING			
Sample	**C_{24h} (CFU/mL)**	**R%**	**Log_{10} red.**
Control*	5.4×10^3 CFU/mL (C_0)	13.34	0.06
V1	0 CFU/mL	100	3.80
V2	5.4×10^3 CFU/mL	10	0.04
V3	0 CFU/mL	100	3.80

**Preliminary treated fabric, dyed and non-functionalized*

Antifungal tests results show maximum efficiencies of fabrics treated to confer multifunctional antimicrobial character (code V1) and multifunctional antibacterial/ oleophobic/hydrophobic (code V3), for which percentage reduction rates of 100%, against *Candida albicans* population, were obtained. The fabric treated with fluorocarbon (C_6) polymeric dispersions, for oleophobic/hydrophobic treatment, according to V2 variant, shows weak antimicrobial activity, with only 10% percentage reduction rate. The result may be due to pronounced hydrophobic character of the textile material (compared to V1 and V3), which allowed the pearling of microbial inoculum on the material (or inoculum leakage on the walls of the test tube), thus not allowing an optimal contact surface. The non-functionalized fabric (code M), showed a poor inhibition activity on growth and development of *Candida albicans* population, with a microbial reduction rate of 13.34%, most likely due to mechanical retention of microbial cells on the surface of the material.

CONCLUSIONS

Laboratory experiments performed on fabrics made of 50% cotton and 50% polyamide HT have demonstrated that hydrophobization treatment with fluoropolymer dispersions can be combined with treatment with titanium dioxide-based photocatalytic dispersions or dispersions based on silver chloride and titanium dioxide to obtain multiple photocatalytic, antibacterial and hydrophobic/oleophobic effects without diminishing the functionalization effects that would have been obtained by the individual treatments.

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