FUNCTIONAL REACTIVE DYEING OF COTTON BASED ON PHOTOACTIVE PHTHALOCYANINES

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Abstract: *An innovative photoactive phthalocyanine based antimicrobial system used for textile barrier finishing was studied and optimized as a new tool for photo-initiated antimicrobial functionality of textiles. A range of photoactive phthalocyanines containing Zn or Al and reactive groups capable to create a covalent bind with cellulosic fibres was synthesised and applied on the cotton fabric by the reactive dyeing process. The antimicrobial efficiency of the finished fabrics was determined according to a modified standard relevant for health-care textiles evaluation during repeated washing and chemo-thermo-disinfection maintenance cycles. The unique properties of textiles dyed with photoactive phthalocyanine derivatives were confirmed. This type of textile finishing can be used for simultaneous dyeing and preparation of antimicrobial/self-cleaning textile materials with a long-lasting wash-permanent barrier effect as an effective, safe and less environmentally risky alternative of conventional antimicrobial systems. A range of PTCs containing Zn or Al in their structure and reactive groups capable to create a covalent bond with the cellulosic fibre was synthesised in Centre for Organic Chemistry, Pardubice. These derivatives were applied on cotton fabric in INOTEX, Dvůr Králové n. L. as reactive dyestuffs under optimized conditions. Resulting colour-fastnesses were evaluated according to relevant standards. Testing of photoactivity of the finished textiles was conducted in Centre for Organic Chemistry by means of an iodide method. Antimicrobial activity of the finished textiles was evaluated in the National Institute of Public Health, Prague according to the modified standard EN ISO 20743 after dyeing and repeated maintenance cycles prescribed for health care sector: washing at 60 °C (EN ISO 6330, Wascator, 6N, EEC - standard phosphate-free detergent, conducted in INOTEX) and chemo-thermo-disinfection prescribed for health care sector (washing 60-65 °C followed by rinsing with solution of Persteril - peracetic acid 36%, conc. 0,2 ml/l conducted in the Commercial Laundry & Dry Cleaning Company, Náchod, Czech Republic).*

Keywords:

1 INTRODUCTION

Photoactivity of PTC compounds containing certain metals as a central atom is based on production of singlet oxygen $^1O_2$ when exposed to light. This highly reactive form of oxygen is able to kill majority of microorganisms and to destroy some pollutants. The lifetime of the singlet oxygen is only several microseconds and therefore the field of its effect is 20 nm from a surface modified by chosen PTC derivatives. These unique properties of photoactive PTCs systems were used for preparation of antimicrobial/self-cleaning textile materials with long-lasting wash-permanent barrier effect as an effective, safe and less environmentally risky alternative of conventional antimicrobial systems [1, 2].

2 EXPERIMENTAL

2.1 Dyeing

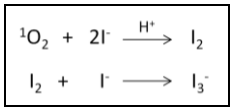
PTC derivatices containing Zn or Al in their structure and reactive groups (VS: vinylsulphone and MCT: monochlorotriazine) creating a covalent bond with cellulosic fibre were synthesised in Centre for Organic Chemistry, Pardubice. These green-bluish dyestuffs were applied on cotton fabric (120 g/m^2, plain weave shirting, desized and scoured) in INOTEX, Dvůr Králové n. L. under optimized conditions by exhaustion process of reactive dyeing (LR 1:20, 60°C). Resulting colour-fastnesses were evaluated according to relevant standards (Table 1).

Table 1 Colourfastnesses of PTS dyed cotton fabric

Colourfastness	Standard	Results
water	EN ISO 105-E01	4/4/4-5
washing 60°C	EN ISO 105-C06	3-4/4/4-5
perspiration alkaline	EN ISO 105-E04	4/3-4/4-5
perspiration acid	EN ISO 105-E04	4/4/4-5
rubbing dry	EN ISO 105-X12	4-5
rubbing wet	EN ISO 105-X12	4
light Q-SUN	EN ISO 105-B02	3D

2.2 Testing of photoactivity

Testing of photoactivity of the finished textiles was conducted in Centre for Organic Chemistry by means of an iodide method with a spectrophotometric determination of the triiodide production (Equation 1).



Equation 1 Triiodide forming at single oxygen presence

A red-light emitting diode (LED) light source was used for the photocatalytic effect initiation. The rate of the singlet oxygen production was determined as a growth rate of I_3^- expressed as a direction k_{obs} of the linear dependency. The results after the dyeing and after repeated maintenance cycles were compared (Table 2).

Table 2 Colouration and singlet oxygen production of PTC dyed cotton in dependence on maintenance cycles No.

Maintenance cycles for health care sector : washing 60°C+ chemothermodisinfection		
No. of cycle	Relative depth of shade /%/	Singlet oxygen production $k_{obs}.10^2$ [min^{-1}]
0	100	0.1051
1	108.30	0.1064
5	100.81	0.1032
10	103.94	0.0960
25	89.99	0.1114

2.3 Testing of antimicrobial efficiency

Antimicrobial activity of the finished textiles was evaluated in the National Institute of Public Health, Prague according to the modified quantitative standard EN ISO 20743. The antimicrobial effect and its permanency were evaluated after dyeing and after repeated washing (60 °C) and chemo-thermo-disinfection cycles as a prescribed maintenance procedure for fabric used in health-care sector. For the antimicrobial efficiency testing following bacteria strains were used: G-negative *Escherichia coli,* CCM 4517 and G-positive *Staphylococcus aureus,* CCM 4516).
The evaluation of antimicrobial activity of textiles according to the standard EN ISO 20743 were performed using the standardized Absorption method (an evaluation method in which the test bacterial suspension is inoculated directly onto samples) in Petri dishes (contact time 18 – 24 h, temperature 37° C). Antibacterial activity (A) was calculated according to Eq. 2:

$$A = (\log C_t - \log C_0) - (\log T_t - \log T_0) = F - G$$

Equation 2 Calculation of antimicrobial efficiency

where $F(C_t - C_0)$ = Growth value on the control sample (untreated)
$G(T_t - T_0)$ = Growth value on the antibacterial sample (PTC finished)

The microbiological tests were conducted using selected light sources necessary for photocatalytic effect initiation under intensity of light radiation 2.1 and 5 J/cm^{-2}. The light sources simulation indoor and outdoor conditions were used.

Results of antimicrobial activity of PTC dyed cotton fabric after finishing and repeated washing at 60°C and chemothermodisinfection cycles are summarised in Table 3 (light source simulating daylight indoor conditions).

Table 3 Antimicrobial activity of PTC dyed cotton

Antimictobial activity – A (log)			
Maintenance cycles	**PTC dyed cotton (3% dyeing)**	***S. aureus***	***E. coli***
Washing	Unwashed	5.5	4.9
	5 x washed at 60 °C	5.6	4.1
	10x washed at 60 °C	3.0	3.5
Washing + Chemo-thermo-disinfection	Unwashed	5.0	6.0
	5 x washed at 60 °C + CHT	5.0	5.5
	10x washed at 60 °C +CHT	5.0	5.4

3 CONCLUSIONS

From the results of antibacterial activity it can be concluded that cotton fabric dyed with a photosensitive PTC derivative has a high antimicrobial effect against both G+ and G- bacteria strains. This effect is stable in repeated washings at 60° C. Moreover the stability of the effect in repeated washing followed by a chemo-thermo-disinfection used in health care sector has been proved This type of barrier finishing/dyeing represents an effective non-toxic and eco-friendly alternative of antimicrobial finishing systems and is suitable for apparel textiles and bed-linens.

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