ALTERNATIVE
Environment Friendly Functional Barrier Textiles Based on Photoactive Phthalocyanine Dyeings

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PHOTOACTIVE PTCs for dyeing with antimicrobial effect

PTCs: Blue-green-coloured aromatic macrocyclic compounds capable to form coordination complexes with different metals. CuPTCs as common dyes: E.g. Sumifix Turquois Blue G (N) conc and Indanthren Brill Blue B (Co²⁺).

Al, Zn PTCs are photoactive:
Absorbing a photon, excited photosenzitizer is capable to interact with a triplet oxygen present in the air creating a short-living singlet oxygen – a very reactive form of oxygen capable to kill majority of microorganisms. The lifetime of the $^1O_2$ is only several μs: the effect limited to max 20 nm from the surface of modified textile.

Mechanism of photosensitized reactions of $O_2$:

- Singlet oxygen
  - short living (μs)
  - antimicrobial
  - effect limited on the fabric surface (20 nm)

ecofriendly and washpermanent antimicrobial system
no leaching to the environment

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Centre for Organic Chemistry, Ltd.:

Synthesis of Al and Zn PTCs for textile finishing:

- reactive (VS, MCT, cyanal-type): cotton (10)
- direct: cotton (3)
- disperse: polyester (10)

INOTEX Ltd.: Textiles dyeing and fastnesses evaluation (accred. lab)

Example of dyeing processes:

Cotton

Polyester

Aftertreatment (soaping):
1g/l TANATERGE PURA 92°C 15 min,
water 60°C 10 min, water 20°C 10 min overflow

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Best results for Cotton: Vinyl Sulphone R group
p-amino phenyl sulphate ethyl suphone (PAFSES)

PTC No. Structure
1146/75 Zn$\text{PTC(SO}_2\text{NHC}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}_1(\text{SO}_3\text{H})_{2,1}}$
1134/231 AlOH$\text{PTC(SO}_2\text{NHC}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}}_{1,8}$

Shade after dyeing
washing 5 x 60°C
washing 10 x 60°C

Colourfastnesses (for healthcare sector accord. EN 14237 levels 4 required)

<table>
<thead>
<tr>
<th>Colourfastness</th>
<th>Standard</th>
<th>PTC 1164/75 – Zn/VS</th>
<th>PTC 1134/231 – Al/VS</th>
</tr>
</thead>
<tbody>
<tr>
<td>in water</td>
<td>EN ISO 105-E01</td>
<td>4-5/4/4</td>
<td>4-5/4/4</td>
</tr>
<tr>
<td>in alkaline perspiration</td>
<td>EN ISO 105-E04</td>
<td>4-5/3-4/3-4</td>
<td>4-5/3-4/4</td>
</tr>
<tr>
<td>in acid perspiration</td>
<td>EN ISO 105-E04</td>
<td>4/4-5/4-5</td>
<td>4-5/4/4</td>
</tr>
<tr>
<td>in washing 60°C (C1S)</td>
<td>EN ISO 105-C06</td>
<td>3-4/3/3-4</td>
<td>3/3-4/4</td>
</tr>
<tr>
<td>rubfasasness - wet</td>
<td>EN ISO 105-X12</td>
<td>4-5 warp</td>
<td>4-5 warp</td>
</tr>
<tr>
<td>rubfastness - dry</td>
<td>EN ISO 105-X12</td>
<td>4 warp</td>
<td>4-5 warp</td>
</tr>
<tr>
<td>lightfastness</td>
<td>Q-SUN XE1S*</td>
<td>3-4D</td>
<td>3-4D</td>
</tr>
</tbody>
</table>

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Evaluating photoactivity of PTC dyed fabrics

Testing of capability of fabrics to produce the singlet oxygen by an iodide method:

\[
^1\text{O}_2 + 2\text{I}^- + \text{H}^+ \rightarrow \text{I}_2
\]

\[
\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-
\]

Determination of the triiodide content growth rate:

- Fabric placed in a dish with the iodide solution and exposed to the light
- Red-light emitting diode (LED) light source (photocatalytic effect initiation)
  the red LED emitting spectrum corresponds with an absorption spectrum of blue PTCs
- Spectrophotometric determination \( A (\lambda = 351 \text{ nm}) \)
- \( \text{I}_3^- \) growth rate as a direction \( k_{poz} \) of the liear dependency

<table>
<thead>
<tr>
<th>Sample (3% PTC dyed cotton)</th>
<th>( k_{obs} \times 10^2 \text{ [min}^{-1}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>unwashed fabric</td>
</tr>
<tr>
<td>PTC 1164/75 - Zn/VS</td>
<td>3,23</td>
</tr>
<tr>
<td>PTC 1134/231 - Al/VS</td>
<td>14,00</td>
</tr>
</tbody>
</table>

**AI/VS PTC dyed cotton more photoactive than Zn/VS PTC dyed cotton**

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PHOTOSENSITIVE PTCs for dyeing with antimicrobial effect

Antimicrobial activity of Al/VS and Zn/VS PTC dyed cotton fabric

EN ISO 20743: Determination of antibacterial activity of textile products

Modified standard - illumination needed

Two different light sources selected:

• Energy Saving SPIRAX SP0318 MEGAMAN, E 27, 18 W, 1200 lm 2700 K (warm white): a lamp with a wavelength simulating light conditions in building interiors with a limited daylight access

• NARVA LT 36 W/D65, artificial daylight, COLOURLUX proof, and a lamp-tube simulating outdoor daylight environment.

UV parts of spectra eliminated in both lamps

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PHOTOACTIVE PTCs for dyeing with antimicrobial effect

Antimicrobial activity of Al/VS and Zn/VS PTC dyed cotton fabric

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

- **Antibacterial activity – A (log)**

<table>
<thead>
<tr>
<th>Cotton fabric dyed with Zn/VS PTC 1146/75 (3% dyeing)</th>
<th>Light source</th>
<th>Light exposition (J/cm²)</th>
<th>S. aureus</th>
<th>E. coli</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unwashed</td>
<td>daylight indoor conditions SPIRAX</td>
<td>2,1</td>
<td>5,1</td>
<td>6,5</td>
</tr>
<tr>
<td>5 x washed at 60°C</td>
<td>daylight indoor conditions SPIRAX</td>
<td>5,0</td>
<td>5,1</td>
<td>4,6</td>
</tr>
<tr>
<td>10x washed at 60°C</td>
<td>daylight indoor conditions SPIRAX</td>
<td>2,1</td>
<td>2,9</td>
<td>1,9</td>
</tr>
<tr>
<td>5 x washed at 60°C</td>
<td>daylight outdoor conditions NARVA</td>
<td>2,1</td>
<td>2,3</td>
<td>1,2</td>
</tr>
<tr>
<td>10x washed at 60°C</td>
<td>daylight outdoor conditions NARVA</td>
<td>5,0</td>
<td>3,8</td>
<td>4,7</td>
</tr>
</tbody>
</table>

- **Antibacterial activity – A (log)**

<table>
<thead>
<tr>
<th>Cotton fabric dyed with Al VS/ PTC 1134/231 (3% dyeing)</th>
<th>Maintenance type</th>
<th>S. aureus</th>
<th>E. coli</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washing</td>
<td>Unwashed</td>
<td>5,5</td>
<td>4,9</td>
</tr>
<tr>
<td></td>
<td>5 x washed at 60°C</td>
<td>5,6</td>
<td>4,1</td>
</tr>
<tr>
<td></td>
<td>10x washed at 60°C</td>
<td>3,0</td>
<td>3,5</td>
</tr>
<tr>
<td>Washing + CHT (chemo-thermo-disinfection)</td>
<td>Unwashed</td>
<td>5,0</td>
<td>6,0</td>
</tr>
<tr>
<td></td>
<td>5 x washed at 60°C + CHT</td>
<td>5,0</td>
<td>5,5</td>
</tr>
<tr>
<td></td>
<td>10x washed at 60°C + CHT</td>
<td>5,0</td>
<td>5,4</td>
</tr>
</tbody>
</table>

- **EN ISO 20743**

- \( F = C_t - C_0 \)
  - Growth value on the control sample (untreated)

- \( G = T_t - T_0 \)
  - Growth value on the antibacterial sample (PTC finished)

- Cotton fabric dyed with photosensitive PTCs have the reliable antimicrobial effect against G+ and G- microorganism strains.

- The antimicrobial effect stable in repeated washing (60°C) + CHT disinfection cycles (health care sector).

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Phototoxicity

3T3 NRU in vitro phototoxicity test (Regulation 440/2008 Method B.41; OECD TG432) 432

• phototoxicity = excessive reaction to sunlight

• photoactive substance + light (UVA) → non-immunological acute skin reaction (erythema, oedema, pigmentation), e.g. fig, bergamot oil, tetracycline, ...

• tested substance applied on fibroblasts Balb/c 3T3, NR dye uptake - only living cells

• 8 concentrations on two plates: one irradiated 5 J/cm² UVA (+UVA), second in the dark (-UVA)

• PM1: Photoirritation Factor calculated: COLIPA/BGW software comparison of cytotoxic concentrations decreasing cell viability to 50% in presence and absence of UVA:

\[
\text{PIF} = \frac{\text{EC}_{50} (-UVA)}{\text{EC}_{50} (+UVA)}
\]

Phototoxic : PIF ≥ 5
Probably phototoxic : PIF ≥ 2

OECD: substances with PIF = 2 considered as phototoxic

PM2: Mean Photo Effect (MPE)
comparing dose-response curves +UV and -UV, cut-off value 0.100
Cotton fabric dyed with pthalocyanine 1134/231
COLIPA/BGVV software

Fabric extracted: 3 cm²/ml PBS buffer, 24 h, 37°C

unwashed

5 x washed at 60°C

Pthalocyanine 1134/231 (dye)

<table>
<thead>
<tr>
<th></th>
<th>+ light</th>
<th>- light</th>
<th>CutOff</th>
<th>Mean</th>
<th>Phototoxic Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>ED 50 (mg/l)</td>
<td>8.588</td>
<td>-</td>
<td>PIF</td>
<td>2.000</td>
<td>116.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.000</td>
</tr>
</tbody>
</table>

yellow point = + UVA
blue point = - UVA

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Cotton + pthalocyanine 1157/95 (1134/231)
COLIPA/BGVV software

Fabric extracted: 3 cm²/ml PBS buffer, 24 h, 37°C

unwashed

5x washed at 60°C + CHT

Living cells [%]

extract conc. 10

Living cells [%]

extract conc. 10

yellow point = + UVA
blue point = - UVA

After washing (+ CHT) no viability observed – all unfixed PTC removed

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Phototoxicity - RhE model EpiDerm™
(INVITTOX Protocol 121)

• „real skin“ model - normal human epidermal keratinocytes (epidermis, stratum corneum); dyed cotton in direct contact with cells more relevant than against more sensitive single cells

• 5 concentrations + blank on 4 tissues: 2 tissues irradiated (6 J/cm², + UVA), 2 tissues in the dark (-UVA). Viability MTT test (yellow colour + viable tissues → 3 h dark blue colour formazan), absorbance 570 nm

• prediction model: one or more test concentrations of the (+UVA) part of the experiment induces a decrease in viability exceeding 30% compared with identical concentrations (-UVA) Substances decreasing (+UV) viability of cells more than by 30% are considered to be phototoxic

• pilot study - application cotton with PTC 1134/231 unwashed 24 h, removal of cotton, rinse, ½ tissues irradiated - the decrease in viability cca 25%
PHOTOACTIVE PTCs for dyeing with antimicrobial effect

Reactive Al/VS PTCs up-scale:
cotton: lab. jig trials
- exahustion dyeing of ready made face-masks
- ready for mill-scale trial (ind. jigger)

Co/PES 50/50 blend dyeing trials running
(prolonged service life in long-term laundry)

Disperse Al, Zn/ PTCs with hydrophobic chain polyester: HT dying
dyeing trials and aftertreatment optimization
aimed to colorfastnesses improvement

<table>
<thead>
<tr>
<th></th>
<th>redukční čištění</th>
<th>termofixace</th>
<th>termofixace + redukční čištění</th>
</tr>
</thead>
<tbody>
<tr>
<td>1152/174</td>
<td>3%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stálobarvenost</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- v prání 60°C C15</td>
<td>3-4/3-4/3-4</td>
<td>4/3-4/2-3</td>
<td>4/3-4/3-4</td>
</tr>
<tr>
<td>- v potu kys.</td>
<td>3-4/4-5/4-5</td>
<td>4/4-5/4-5</td>
<td>4/4-5/4-5</td>
</tr>
<tr>
<td>- v potu alk.</td>
<td>4-5/4-5/4-5</td>
<td>4-5/4-5/4-5</td>
<td>4-5/4-5/4-5</td>
</tr>
<tr>
<td>- suchý otěr</td>
<td>2-3</td>
<td>3-4</td>
<td>3-4</td>
</tr>
<tr>
<td>- mokrý otěr</td>
<td>3-4</td>
<td>3-4</td>
<td>3-4</td>
</tr>
<tr>
<td>- na světle</td>
<td>2-3</td>
<td>3-4</td>
<td>2-3</td>
</tr>
</tbody>
</table>

100% cotton face mask

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**Conclusions:**

- **Photoactive Al, Zn PTC derivatives synthesised (> 20)**
  - reactive and direct PTCs for cotton and cotton/PES blends dyeing
  - disperse PTCs for polyester dyeing
  - PTC by coating under testing as well

- **Sample dyeing and dyed fabrics evaluation**
  - colourfastnesses
  - photoactivity: singlet oxygen production

- **The best alternatives** with high colourfastnesses & wash-stable photoactivity
  - cotton: PTC 1164/75–Zn/VS and PTC 1134/231–Al/VS

- **High and reliable washpermanent antimicrobial efficiency** of dyed textiles confirmed using modified EN 20743 (light source selection, G+ and G- strains)
  - stable in repeated washing and chemothermodisinfection

- The dyed fabrics are to be well aftertreated to remove properly unfixed dyes to prevent the risk of phototoxicity

**Functional cotton dyeing with stable antimicrobial effect have been developed and prepared for industrial transfer**
THANKS FOR YOUR ATTENTION

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