Multifunktionale Ausrüstung von Textilien mit wasserbasierten nanoskaligen Beschichtungssolen

Multifunctional finish of textiles with water-based nano-scaled coating sols using one functional matrix

Vortragende:

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2) Yvette Dietzel: Sächsisches Textilforschungsinstitut e.V. (STFI); Germany
Outline

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2 Development of novel lacquers on the basis of hybrid polymers for fiber finish
   ➢ Inorganic-organic hybrid polymers
   ➢ Materials synthesis by wet chemical processing
   ➢ Basic properties of hybrid polymer coatings

3 Utilized substrates and functionalized water-based inorganic-organic hybrid polymers

4 Sol application by impregnation

5 Influence of the new hybrid polymers on the selected properties of the filter media
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   ➢ Antimicrobial properties
   ➢ Hydrophobic properties
   ➢ Electrostatic properties

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Motivation of the project work

➢ Textile finisher are often confronted with the task of combining different product features/chemistries such as hydrophobic/hydrophilic properties, easy-care, antistatic, flame-retardant and antimicrobial properties in one multi-functional finishing lacquer.

➢ Another challenge is the frequently different fiber chemistry in fiber blends within one textile, which makes it very difficult to find a suitable recipe for the finishing bath.

➢ Objective of the research project was the development of novel/innovative multifunctional and long-term-stable coating systems based on nano-scale inorganic-organic functional layers (ORMOCER®) for the finish of:
  ➢ a) textile fabrics and
  ➢ b) textile threads
for technical textiles, and metallized fabrics.

➢ Such nano-technological material syntheses permit the realization of combinations of properties such as water-/oil-repellency with flame resistance and antistatic and/or antimicrobial effects within one functional matrix.
Innovation - development of novel lacquers on the basis of hybrid polymers for fiber finish

ORMOCER®
adjustable material properties
generate new functions

Inorganic material
Hybrid material ORMOCER®
Organic polymer

ORMOCER®e: developed at Fraunhofer ISC, Trademark of Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e.V. in Germany

11. ThGOT - Thementage Grenz- und Oberflächentechnik, 15. 17. September 2015, Zeulenroda
Innovation - development of novel lacquers on the basis of hybrid polymers for fiber finish

Starting compounds for the synthesis - bifunctional silanes

```
RO          (CH₂)n          R'
RO—Si—RO   joining segment

network former

network modifier or network former

sol-gel-process

hydrolysis and condensation reactions for creating an inorganic network

photochemically or thermally induced curing for creating an organic network
```
Innovation - development of novel lacquers on the basis of hybrid polymers for fiber finish

Sol-gel process: creation of the inorganic network

1. hydrolysis

\[ \equiv Si-OR + H_2O \iff \equiv Si-OH + ROH \]

2. condensation

\[ \equiv Si-OH + HO-Si \iff \equiv Si-O-Si + H_2O \]
\[ \equiv Si-OH + RO-Si \iff \equiv Si-O-Si + ROH \]
ORMOCER® chemistry: speciality of Fraunhofer ISC

ORMOCER® chemistry: structural units and precursors

- precursor type 1
- precursor type 2
- precursor type 3
- precursor type 4

| inorganic network | modified inorganic network | organic crosslinking inorganic-organic network | organic network |

inorganic ↔ organic

11. ThGOT - Thementage Grenz- und Oberflächentechnik, 15. 17. September 2015, Zeulenroda
Flow chart: Production of coating materials via the sol-gel process

- silanes, alkoxides
- hydrolysis, condensation
- solvent exchange
- filtration, centrifugation
- conventional application techniques
- wet film
- curing: thermal, photochemical
- coating
- water, catalyst
- alcohol
- gel
- Sol
Research on sol-gel materials/ORMOCER®s at Fraunhofer ISC

P: Products based on ORMOCER® technology

- separation processes
- batteries (Li+)
- fuel cells
- medical technology
- biodegradable fibers P
- ceramic fibres (T)

- hardcoats PP PPPP
- barriers PP, decoration P
- corrosion protection
- antisoiling/-fogging
- antistatics
- antireflective P
- dielectrics, passivation
- optical waveguides P
- ion conductors
- optical filters P
- piezoelectric
- photocatalytic
- antibacterial
- electrochromic
- transparent conductive
- sensors

- fillers, pigments
- optics
- photonics
- electronics
- medical technol.
- diagnostics
- cosmetics P

- dental composites PP
- electronics
- (micro-)optics P
- ceramic composites
- adaptronic components

fibers, membranes coatings (nano-) particles bulk materials
Innovation - development of novel lacquers on the basis of hybrid polymers for fiber finish

The Challenge

- Development of refining coating system for high-tech materials
- Combination of seemingly incompatible functions and features in one single textile
- Waterbased system

six functions in one refining coating system

- abrasion resistant
- flame retardant
- hydrophobic
- washproof
- antimicrobial
- antistatic
Utilized functionalized water-based inorganic-organic hybrid polymers

- **ORMTEX106-a/m/h**: abrasion resistant, antistatic, antimicrobial, partially hydrophobic
- **ORMTEX127-1-m/h**: antimicrobial, slightly hydrophobic
- **ORMTEX128-h**: antimicrobial system with additional hydrophobic/oleophobic properties
- **ORMTEX129-a/m/f**: slightly antistatic, antimicrobial, reduced flammability, hydrophobic
- **ORMTEX130-a/m/f**: slightly antistatic, antimicrobial, reduced flammability, slightly hydrophobic
- **ORMTEX131-a/m/f**: slightly antistatic, antimicrobial, reduced, flammability, slightly hydrophobic
- **ORMTEX126-h/e**: hydrophobic, antimicrobial, abrasion resistant, improved filter properties for filter materials made of nonwoven
- **ORMTEX124-e**: improved filter properties for filter materials made of nonwoven, abrasion resistant

Legend:  
- **a**: antistatic effect  
- **m**: antimicrobial effect  
- **h**: hydrophobic effect  
- **e**: electret effect
Utilized substrates and functionalized water-based inorganic-organic hybrid polymers

Utilized substrates
- Luminex C2 woven fabric, Klopman GmbH, Ratingen (60 % cotton / 40 % polyester; 230 g/m²; twill)
- Polyester woven fabric (Schneider Textilveredlung GmbH)
- Different threats (ALTERFIL)

Finish of textile samples - process parameters
- Substrate pretreatment (plasma or corona pretreatment)
- Dilution of ORMOCER® systems with water
- Combination of ORMOCER® systems with other finishing chemicals
- Process parameters
  - Squeezing pressure (0.2 bar – 6.0 bar)
  - Drying temperature (100 °C - 160 °C)
  - Drying time (5 min. - 50 min.)
SEM micrographs of selected finished woven fabrics - STFI

Luminex, plasma pretreatment
ORMTEX106-a/m/h_TOP

Luminex, plasma pretreatment
ORMTEX106-a/m/h_TOP, 5 x washed

Luminex
ORMTEX106-a/m/h_TOP_cured

Luminex
ORMTEX106-a/m/h_TOP_cured, 5 x washed

Polyester
ORMTEX106-a/m/h_TOP_new

Polyester
ORMTEX129-a/m/f, vacuum extraction, 0.6 bar

Polyester
ORMTEX130-a/m/f, vacuum extraction, 0.5 bar

11. ThGOT - Thementage Grenz- und Oberflächentechnik, 15. 17. September 2015, Zeulenroda
Best results - Agar diffusion plate test (according to DIN EN ISO 20645)

- Bacteria used for microbial tests: *Escherichia coli* (DSM no. 613), concentration of $4.2 \times 10^8$

- Conditioning of the test pieces:
The sterilized test specimen were put in petri dishes for 24 hours (48 hours).

- The zone of inhibition generated around the test specimen was not evaluated because the active ingredient is not soluble.

- A test specimen was evaluated with “good” provided that test piece was not covered itself with bacteria; few bacteria colonies could be formed by drying-out and peeling off the agar.
Best results - Agar diffusion plate test
(according to DIN EN ISO 20645)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inhibitory effect</th>
<th>Picture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Luminex, ORMTEX106-a/m/h, (3.11 %)</td>
<td>No formation of an inhibition zone, good inhibitory effect, significantly reduced microbial growth (only very small germs under the specimen)</td>
<td><img src="image1" alt="Image" /></td>
</tr>
<tr>
<td>Luminex, ORMTEX106-a/m/h_TOP_cured, 5 x washed, (0.76 %)</td>
<td>No formation of an inhibition zone, very few and very tiny dead germs, 100 % inhibitory effect</td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td>Luminex, ORMTEX128-h, (3.19 %)</td>
<td>No formation of an inhibition zone, significantly reduced microbial growth (only very small germs under the specimen), good inhibitory effect</td>
<td><img src="image3" alt="Image" /></td>
</tr>
<tr>
<td>Luminex, ORMTEX129-a/m/f, vacuum -extraction: 0.5 bar, (6.6 %)</td>
<td>No formation of an inhibition zone, very few and very tiny dead germs, 100 % inhibitory effect</td>
<td><img src="image4" alt="Image" /></td>
</tr>
</tbody>
</table>
A good or very good inhibitory effect can be achieved with the following ORMOCER® systems:

- **Filter media:**
  - ORMTEX126-h/e and ORMTEX124-e with solid add-ons from 0.8 % to 3.5 %

- **Luminex:**
  - ORMTEX106-a/m/h, ORMTEX126-h/e and ORMTEX128-h with solid add-ons from 0.8 % to 5.5 %

- **Polyester:**
  - ORMTEX106-a/m/h with solid add-ons of 4 %
  - ORMTEX130-a/m/f with higher solid add-ons
  - ORMTEX127-1-m/h with higher solid add-ons

- The results for the different batches are reproducible.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Sol dilution with water</th>
<th>Solid add-ons [%]</th>
<th>Grade for oil</th>
<th>Picture</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORMTEX106-a/m/h_TOP_new + oil-repellent</td>
<td>1 : 0</td>
<td>6,79</td>
<td>6</td>
<td><img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>ORMTEX106-a/m/h_TOP_new + oil-repellent</td>
<td>1 : 2</td>
<td>3,38</td>
<td>5 - 6</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>ORMTEX129-a/m/f + oil-repellent</td>
<td>1 : 0</td>
<td>6,15</td>
<td>5 - 6</td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>Polyester</td>
<td>1 : 0</td>
<td>106,46</td>
<td>3</td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Best results - Oleophobic properties (according to DIN EN ISO 14419)

ORMOCER® systems and achieved grades for oil:

- **Luminex woven fabric:**
  - **ORMTEX128-h:** solid add-ons < 2 % ➔ grade for oil: 2 - 3, solid add-ons from 3.2 % ➔ grade for oil: 4
  - **ORMTEX106-a/m/h:** combination with oil-repellent, solid add-ons from 3.4 % ➔ grade for oil: 5 - 6
  - **ORMTEX129-a/m/f:** combination with oil-repellent, solid add-ons from 6 % ➔ grade for oil: 5 - 6

- **Polyester woven fabric:**
  - **ORMTEX128-h:** solid add-ons from 3 % ➔ grade for oil: 3
Results - Electrical properties (according to DIN EN 1149-1)

- **Untreated polyester fabric**: surface resistance of $1.3 \times 10^{14}$ ohms; volume resistance of $8.0 \times 10^{12}$ ohms

- **Antistatic functionalized ORMOCER® s (solid add-ons: 3.0 % - 30.3 %)**:
  - Surface resistances of $3.7 \times 10^9$ ohms $< R < 1.5 \times 10^{13}$ ohms
  - Volume resistances of $3.6 \times 10^9$ ohms $< R < 8.5 \times 10^{11}$ ohms
Summary and outlook

- Suitable ORMOCER® systems to achieve a triple combination of functional properties such as water/oil-repellency, improved antistatic and antimicrobial effects are:
  - ORMTEX106-a/m/h + oil-repellent
  - ORMTEX128-h
  - ORMTEX127-1-m/h
  - ORMTEX129-a/m/f
  - **Solid add-ons** of approximately 3 % - 4 %
  - Textile-physical properties are not influenced.
  - Suitable substrates are Luminex and Polyester woven fabric.

- Suitable ORMOCER® systems to achieve a combination of four functional properties including flame-retardant effects are (Luminex):
  - ORMTEX130-a/m/f
  - ORMTEX129-a/m/f
  - **Solid add-ons** of approximately 16 % - 30 %
  - Suitable substrate is Luminex.
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What we offer for our industry partners:

Consulting and concept development

- realization of customer specific material concepts
- functionalizing of surfaces

Implementation

- technology transfer and implementation in industrial processes
- development of methods for process control and quality assurance
- trouble-shooting for mass production processes
- sparring partner for continuous dialogue on topical issues and new ideas

Analytics

- characterization of materials and surfaces