

XXVth IFATCC
INTERNATIONAL CONGRESS

27-29

APRIL 2021
ENSAIT-FRANCE



Functional finishing of cotton fabric by water-based formulations of sol-gel premodified polysaccharides

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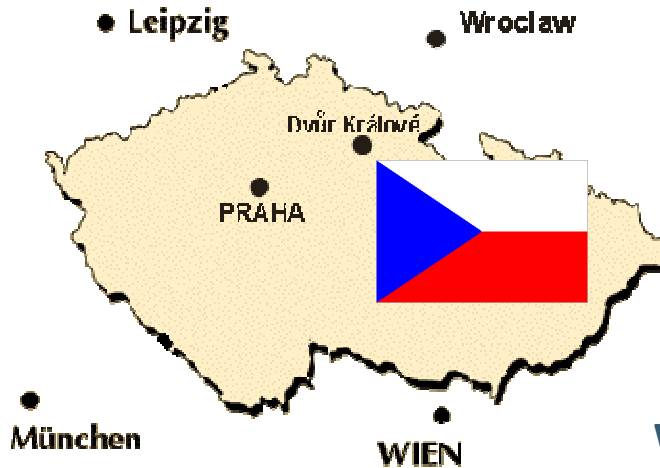
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Technology
Agency
of the Czech Republic

TH02020145 Hydrophobic UV-lacquers and nano-layers protecting substrates against bio-attack

Private small textile innovation company: R&D, textiles and auxiliaries production, technologies development, optimization and technology transfer

- Successor of former Textile Finishing Research Institute founded in 1949
- Privatized in 1996 (Ltd.)
- SME: 40 employees, turnover ca €3.2Mio



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Working in heart of European textile production

■ TEXTILE AUXILIARY AGENTS

customised R&D, production, sales and distribution

■ DYES, colouristic department

colour matching and calculation of dyeing recipes

■ SMALL-SCALE

finishing / coating capacity

short runs production



■ NEW TECHNOLOGIES

development and transfer,
flexible service, cleaner production,
sustainability, dematerialization



■ ACCREDITED TESTING LABORATORY ISO EN 17025

■ ECO SERVICES AND CONSULTANCY

■ SPECIAL MACHINERY equipment and devices production

Content

- Sol-gel finishing – principle and limitations

- Sol-gel premodification of polysaccharides for their application by water-based processes
 - Aim, Idea/Principle
 - Polysaccharides selection and sol-gel functionalization
 - Application of modified polysaccharides on textiles

- Functional (AMB/antifouling) and mech-fyz. properties evaluation

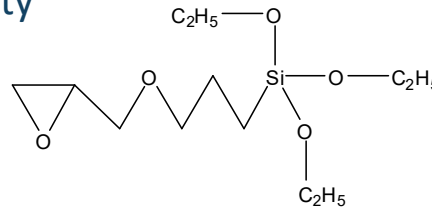
▪ Sol-gel finishing – principle and limitations

Sol-gel modification of textile surfaces

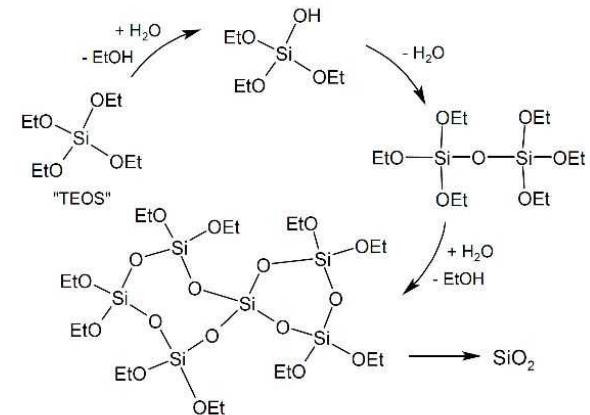
by organomodified alkoxysilanes as precursors:

innovative technology of textile finishing:

- Different functional properties according to alkoxysilanes modification (DWR, AMB, antiscratch,..)
- Applicability at acceptable temperatures (organomodified derivatives), flexibility
- Cross-linking with textile substrate
- Thin and durable functional layers



example



BUT

- **Limited to solvent-based systems** (isopropanol, BCS, ethanol): special machinery needed – impossible for common textile finishing mills with equipment for conventional water-based finishing

- Sol-gel premodification of polysaccharides for their application by water-based processes

... as a way to transfer of solvent-based sol-gel process
from textile mill to TAA production facility

Aim: Textiles with Antimicrobial and Antifouling effect

Idea-Principle: The sol-gel process based on a patented sol-gel textiles modification in isopropanol (Patent CZ 303 861) was used for

- 1. Batchwise sol-gel premodification of selected suitable methyl-cellulose derivative(s)**
by polymerization of organic-inorganic hybride precursors:
- 3-(trialkoxysilyl)propylmethacrylates
 - Ag, Cu, Zn salts (exceeded microorganisms scope: bacteria, fungi, algae)



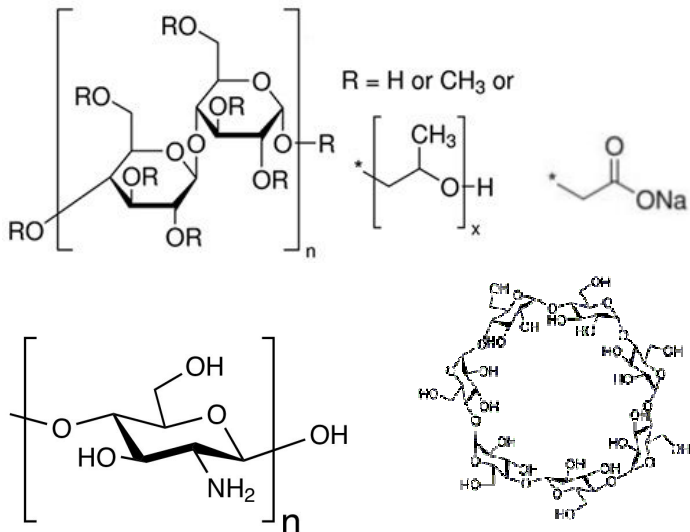
- 2. Application of sol-gel premodified polysaccharides by water-based finishing system on cellulosic-based fibers + cross-linking**

- Sol-gel premodification of polysaccharides for their application by water-based processes

Polysaccharides selection and sol-gel functionalization

Suitable polysaccharide (PS) properties:

- Insoluble in solvents (isopropanol) – batchwise sol-gel modification of PS in powder form
- Soluble or gel/colloid-forming in water – application on textiles after sol-gel premodification



Polysaccharides for sol-gel premodification trials:

- Chitosan (low viscose)
- β -cyclodextrine
- **Hydroxypropyl-methyl-cellulose (HPMC) - selected**
- Carboxymethylcellulose (CMC) – **alternative**
- Starch – partially hydrolysed, water-soluble
- Microcellulose (Arbocel) 8 μm

- Sol-gel premodification of polysaccharides for their application by water-based processes

Polysaccharides selection and sol-gel functionalization Technical University of LIBEREC

1. Antimicrobial hybride sol AD30 prepared by patented proces: CZ 303 861

- precursors: TMSPM (3-(trimethoxysilyl-propyl-methacrylate)
TEOS (tetraethoxysilan) } TMSPM:TEOS 2,5:1
- solvent: isopropanol
- Ag, Cu and Zn salts added in 2% w. per each metal

Sol AD 30 was prepared by acid hydrolysis/condenzation by addition of stoichiometric amount of water $k = 2$ ($k = [H_2O]/\text{alkoxysilane}$) and dibenzoylperoxide (catalysed by HNO_3)



2. AMB modification of polysaccharides: 12 g HPMC + 36 ml sol AD30(1:1), 55 min stirring – thickening, drying 45°C/90 min, polymerization completion 85°C/2 hrs



Only HPMC (and partially CMC) suitable, others deposit during processing

HPMC AD30: sol-gel premodified HPMC - greenish powder: (99,1% yield),
Ag, Cu, Zn content: 0,134% w. each



- Sol-gel premodification of polysaccharides for their application by water-based processes

Application of modified polysaccharides on textiles INOTEX

HPMC AD30: stable gel forming with water, suitable for coating (cotton 120 g/m² plain weave)

Coating gel composition:

- **3% HPMC AD 30** - optimum concentration of in water for coating rheology
- 1% wetting agent (ERKANTOL NR)
- 1% defoamer (NOFOME AF)

+

Range of crosslinkers and binders – selection of the best combinations

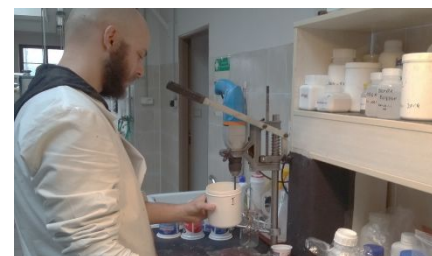
Comparison of

- Compatibility
- Colouration
- Rheology change
- Stability

Selection of the best formulation

200 ml samples of gel HPMC AD 30 prepared by mixing 15 min, 1000 rpm

Gel applied on cotton fabric by single coating: small samples – coating roller, gap 0,1 mm, drying: 110°C 2 min, curing 150°C 3 min, dry wet pick-up 6-8 g/m²



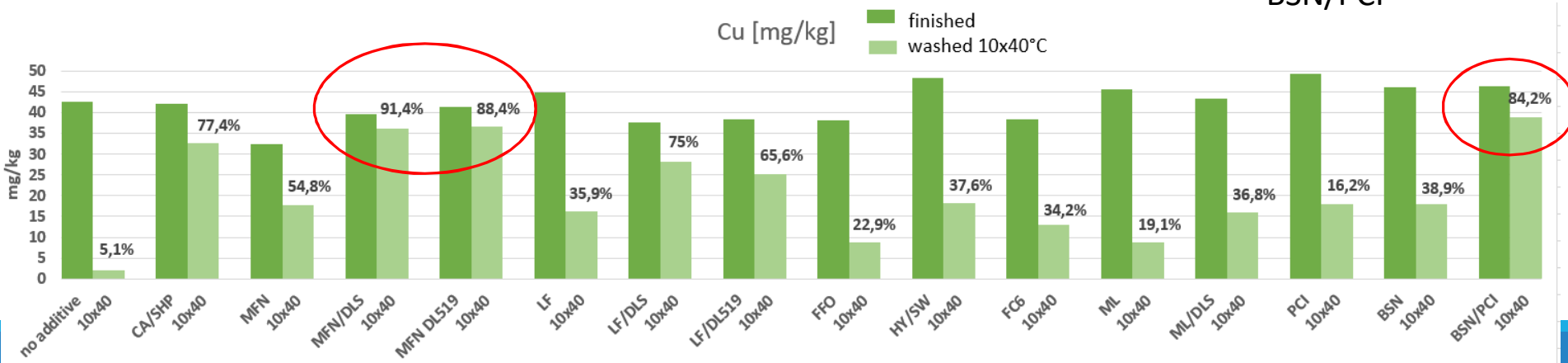
- Sol-gel premodification of polysaccharides for their application by water-based processes

Application of modified polysaccharides on textiles

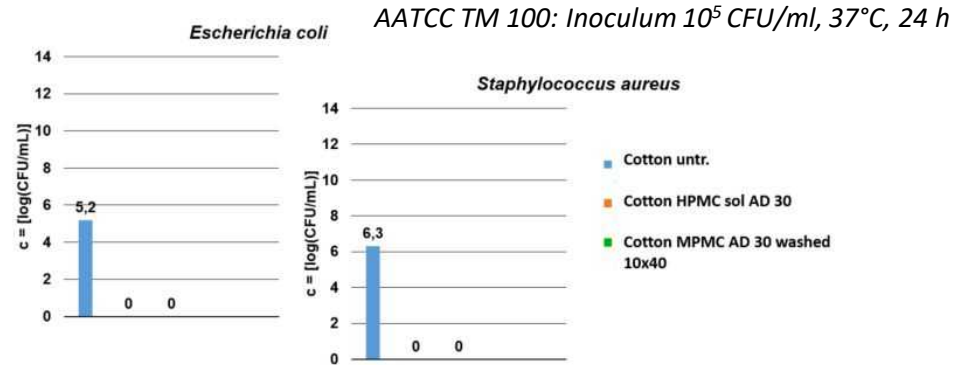
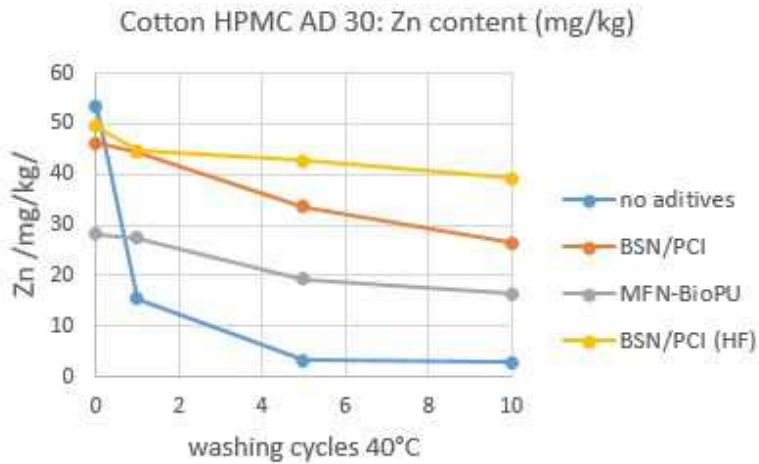
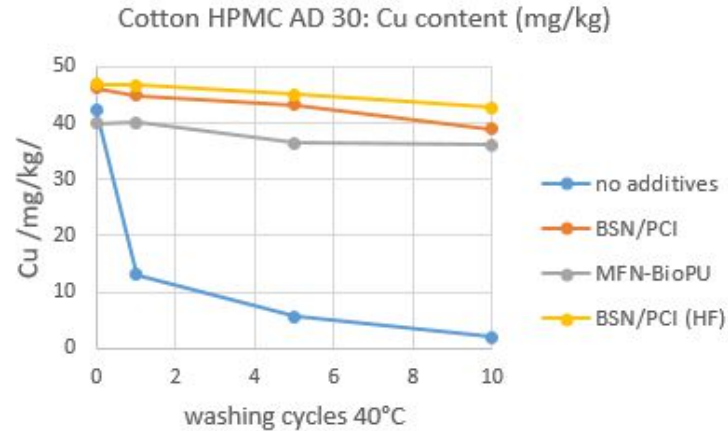
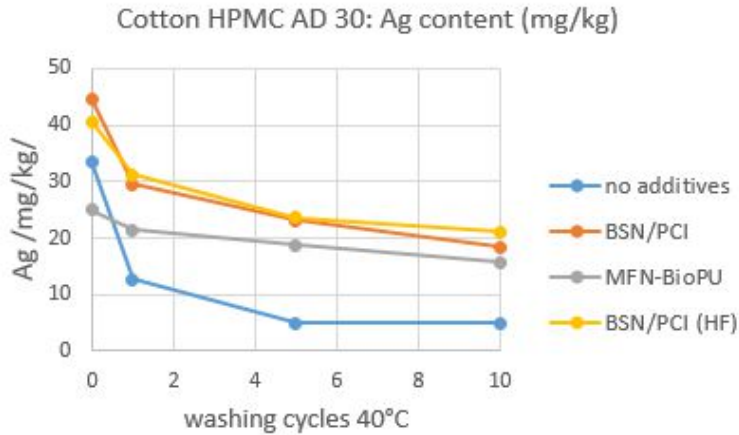
HPMS AD30 3% water gel + crosslinkers and binders

- No crosslinker, pH: 5,1
- PCA: Citric acid/SHP, 70/32 g/kg, pH: 3,1
- TEXAPRET MFN: polymethoxymelamine resin (INOTEX), 60 g/kg, pH: 6,0
- IMPRANIL DLS: bio-PU/polyester binder (COVESTRO), 50 g/kg, pH: 6,5
- IMPRANIL DLS19: bio-PU/polyester binder (COVESTRO), 50 g/kg, pH: 6,3
- TEXAPRET LF (DMDHEU)/MgCl₂.6H₂O (INOTEX), 50/8 g/kg, pH: 5,0
- PROTOREZ FFO/CURITE 5184N (formaldehyde-free, TANATEX Chemicals), 80/16 g/kg, pH: 4,9
- TEXAFIX HY: acrylic binder, (INOTEX), 20 g/kg, pH: 6,2
- TEXAFIX SW: PU-resin based binder, (INOTEX), 20 g/kg, pH: 6,2
- ACRAFIX ML: melamine resin, (TANATEX Chemicals), 30 g/kg, pH: 5,8
- ACRAFIX PCI: blocked aliphatic polyisocyanate (TANATEX Chemicals), 30 g/kg, pH: 5,0
- ACRAMIN BSN/urea/EMULSIFIER WN: BSR copolymer, (TANATEX Chemicals), 75/3,5/3 g/kg, pH: 5,0
- BAYGARD BCS-01/TP-10: FC6/extender (TANATEX, Chemicals), 60/8 g/kg, pH: 5,2

- Application on cotton by coating (small samples)
- ↓
- Metals content (AAS) after finishing and washing 10x40°C (EN ISO 6330, 4N)
- ↓
- Best formulations:
 - MFN/Bio-PU
 - BSN/PCI



Cotton coating – selected HPMC AD30 formulations, stability in washing, AMB effect



- Sol-gel premodified cell-derivative crosslinked with cotton fiber
- High and stable AMB effect (TU Liberec)

AATCC TM 100:2006 Quantitative	<i>Escherichia coli</i> (G-) CCM 2024 (ATCC 9637) % inhibition	<i>Staphylococcus aureus</i> (G+) CCM 2260 (ATCC 1260) % inhibition
Cotton standard (Carlton) untreated	0%	0%
Cotton HPMC AD30 (MFN)	100%	100%
Cotton HPMC AD30 (MFN) washing 10x40	100%	100%
AATCC TM 147:2012 Qualitative Parallel Streak method Cotton HPMC AD30 (MFN)	No Halo zone	Halo zone ø 1 mm

▪ Application of modified polysaccharides on textiles – R2R upscale

HPMC AD 30 – 100% cotton coating/crosslinking: 2 gel formulations selected

I. Gel formulation

30 g/kg HPMC AD30
 40 g/kg bio-PU DSL (binder)
 50 g/kg MFN (crosslinker)
 8 g/kg MgCl₂·6H₂O
 10 g/kg NOFOME AF
 10 g/kg ERKANTOL NR
 852 g/kg water

.....
 Dry content: 9,5 %
 Viscosity: 52 dPa.s
 pH: 5,6
 Ag: 28,1; Cu: 35,1; Zn: 33,3 mg/kg

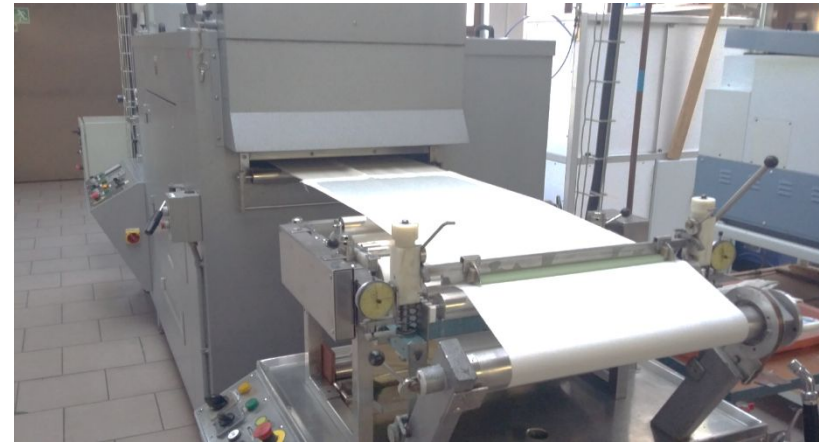
II. Gel formulation

30 g/kg HPMC AD30
 50 g/kg Acr. BSN (binder)
 60 g/kg Acr. PCI (crosslinker)
 10 g/kg NOFOME AF
 10 g/kg EMULSIFIER WN
 5 g/kg urea
 855 g/kg water

.....
 Dry content: 8,5 %
 Viscosity: 65 dPa.s
 pH: 5,9
 Ag: 38,5; Cu: 45,2; Zn: 46,2 mg/kg

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Continuous pilot line Werner-Mathis



Material: 100% cotton 116 g/m², pretreated, mercerized, 1,6 m, width 45 cm



Application: single coating, knife against roller, gap 0,2 mm

- Drying 120°C, 2 min (speed 0,5 m/min)
- Curing 150°C, 3 min (speed 0,37 m/min)

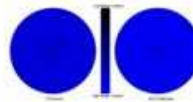


Dry pick up: approx 15 g/m²



▪ **Functional (AMB/antifouling) and mech-phys. properties evaluation**

100% cotton CARLTON	Standard	Cotton untreated		Coating HPMC AD30 – MFN/Bio-PU		
Sq weight /g/m ² /	ČSN EN 12127	115,8		132,2		
Dry pick-up /%/	-	-		16,4		
Metals content /mg/kg/ coated washed 1x40 washed 5x40 washed 10x40	AES	-	Ag	Cu	Zn	
			29,8	25,8	30,4	
			19,5	20,6	26,4	
			15,6	18,5	26,1	
15,2	17,5	25,4				
Tensile strength warp/weft /N/	ČSN EN ISO 13934-1	860/576		845/612		
Absorptivity /%/	ČSN 80 0831	97		89		
Rising height weft/mm/	ČSN 80 0828 (DIN 53924)	1 min: 36; 10 min: 57		1 min: 42; 10min: 54		
Stiffness warp/weft /mN/	ČSN 80 0835	8,4/8,5		27,5/20,4		
Air permeability /mm/s/	ČSN EN ISO 9237	455		95,6		
Breatheability /g/m ² .Pa.h/	ČSN EN ISO 15496	0,962		0,470		
Liquid transport (MMT)	AATCC 195 (SLD Atlas)	 OWTI: 4,5 OMM: 4,5		 OWTI: 4,5 OMM: 4		
Antimicrobial efficiency	AATCC TM 100:2006 finished	E. coli 0%	S. aureus 0%	E. coli 99,9%	S. aureus 99,9%	
	washed 10x40°C (EN ISO 6330)	-	-	99,9%	99,9%	
	AATCC TM 147:2012	No Halo zone	No Halo zone	No Halo zone	No Halo zone	

▪ **Functional (AMB/antifouling) and mech-phys. properties evaluation**

100% cotton CARLTON	Standard	Cotton untreated	Coating			Coating – DWOR +		
			HPMC AD30 – MFN/Bio-PU			HPMC AD30 – MFN/Bio-PU		
Sq weight /g/m ² /	ČSN EN 12127	115,8	129,3			132,8		
Dry pick-up /%/	-	-	13,5			16,6		
Metals content /mg/kg/ coated washed 1x40 washed 5x40 washed 10x40	AES	-	Ag	Cu	Zn	Ag	Cu	Zn
			75,7	79,5	82,7	60,2	65,3	65,2
			28,4	22,1	34,3	47,3	43,2	45,5
			16,3	19,1	25,0	31,5	36,8	33,7
			13,7	14,7	24,2	25,8	34,5	30,6
Tensile strength warp/weft /N/	ČSN EN ISO 13934-1	860/576	784/654			769/660		
Absorptivity /%/	ČSN 80 0831	97	78,1			9,3		
Rising height weft/mm/	ČSN 80 0828 (DIN 53924)	1 min: 36; 10 min: 57	1 min: 20; 10 min: 36			1 min: 0; 10 min: 2		
Hydrostatic head (cm)	ČSN EN ISO 20811	-	< 15			38,5		
Stiffness warp/weft /mN/	ČSN 80 0835	8,4/8,5	50,6/20,7			16,1/12,7		
Air permeability /mm/s/	ČSN EN ISO 9237	455	133,4			100,5		
Breatheability /g/m ² .Pa.h/	ČSN EN ISO 15496	0,962	0,231			0,108		
Liquid transport (MMT)	AATCC 195 (SLD Atlas)	 OWTI: 4,5 OMM: 4,5	 OWTI: 3 OMM: 2	 OWTI: 1 OMM: 1				
Antimicrobial efficiency	AATCC TM 100:2006 finished washed 10x40°C (EN ISO 6330)	E. coli 0%	S. aureus 0%	E. coli 100% 97%	S. aureus 98% 96%	E. coli 100% 98%	S. aureus 96% 94%	
	AATCC TM 147:2012	No Halo zone	No Halo zone	No Halo zone	No Halo zone	No Halo zone	No Halo zone	

Functional (AMB/antifouling) and mech-phys. properties evaluation

50/50 Co/PES GOLEM plain weave	Standard	Co/PES untreated		Coating HPMC AD30 – MFN/Bio-PU			Coating – DWOR + HPMC AD30 – MFN/Bio-PU		
Sq weight /g/m ² /	ČSN EN 12127	134,20		148,72			150,96		
Dry pick-up /%/	-	-		14,52			16,76		
Metals content /mg/kg/ coated washed 1x40 washed 5x40 washed 10x40	AES	-		Ag	Cu	Zn	Ag	Cu	Zn
				56,7	61,2	68,1	55,4	61,3	59,0
				47,5	54,2	50,7	44,2	56,0	55,3
				37,2	50,2	49,4	31,0	45,6	39,3
				30,4	45,1	47,0	23,4	38,8	31,7
Tensile strength warp/weft /N/	ČSN EN ISO 13934-1	662/569		647/576			558/583		
Absorptivity /%/	ČSN 80 0831	113,0		90,0			6,0		
Rising height weft/mm/	ČSN 80 0828 (DIN 53924)	1 min: 21; 10 min: 66		1 min: 8; 10 min: 25			1 min: 0; 10 min: 1		
Hydrostatic head (cm)	ČSN EN ISO 20811	-		< 15			35,7		
Stiffness warp/weft /mN/	ČSN 80 0835	3,63/2,21		35,6/30,4			125/115		
Air permeability /mm/s/	ČSN EN ISO 9237	759		268			195		
Breatheability /g/m ² .Pa.h/	ČSN EN ISO 15496	0,767		0,512			0,150		
Liquid transport (MMT)	AATCC 195 (SLD Atlas)	<p>OWTI: 4,5 OMM: 4,5</p>		<p>OWTI: 3,5 OMM: 3,5</p>			<p>OWTI: 1 OMM: 1</p>		
Antimicrobial efficiency	AATCC TM 100:2006 finished washed 10x40°C (EN ISO 6330)	E. coli 0%	S. aureus 0%	E. coli 99,8% 97,8%	S. aureus 99,9% 98,0%	E. coli 100% 98%	S. aureus 100% 99%		
	AATCC TM 147:2012	No Halo zone	No Halo zone	No Halo zone	No Halo zone	No Halo zone	No Halo zone		

Functional (AMB/antifouling) and mech-phys. properties evaluation

Antifouling effect - Orientation testing of algae growth

Textile (cotton) samples impregnated by a nutrient solution (peptone 1 g/l)



Immersed in water bath

- with content of P/N nutrients: (ammonium phosphate 0,05 g/l, urea 0,02 g/l)
- inoculated with pond water (10 ml/l)
- transparent closed container



1 month: lab temperature, daylight/sunlight



Reduced algae colonies growth observed

HPMC AD30 BSN/PCI

HPMC AD30 BSN/PCI/HF

HPMC AD30 MFN



■ Conclusion

- Sol-gel premodified cell-derivatives were prepared in a powder form
- Premodified cell-derivatives were applied on cotton and Co/PES blend by water-based gel formulations in combination with selected crosslinkers and binders by coating
- Good physiological parameters of finished textiles (hydrophilicity, moisture management, breathability, air permeability. Possible combination with DW(O)R for watertightness
- AMB properties stable in repeated washing (AATCC TM 100 and 147) determined, anti-fouling effect verified

Utility sample: CZ34433 :



Methylcellulose derivative mainly for antimicrobial treatment of textile and similar materials, especially materials containing cellulose, preparation for antimicrobial modification of textiles and similar materials and an antimicrobial textile and similar material

TH02020145 Hydrophobic UV-lacquers and nano-layers protecting substrates against bio-attack

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Thanks for your attention

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