



European Union European Regional Development Fund

ODOR REDUCTION THANKS TO TEXTILE MATERIALS

CETI Thierry LE BLAN IFTH Arnaud VATINEL

Technical Manager

thierry.leblan@ceti.com

Olfactive analysis laboratory Manager

avatinel@ifth.org

6th RESET Seminar on "New materials and new applications" Huddersfield, 31.01.2018

31/01/2018



Origin of odours from Textiles

Vapour Pressure Emitted compounds function of the product Individual compound Complex mixture



Emission of impurities and contaminants from the transport, storage and handling of the products (new material) OR after contact with the skin (using conditions) Substances contained in the product Emission of auxillary compounds impurities and contaminants from the process



Textile and skin interactions



- SKIN = not sterile surface : Ecosystem which plays an important role in the body balance
- Resident micro-organisms : various bacteria adapted to the physiological skin conditions : surface temperature between 30°C and 35°C, pH from 5 to 6,5, various nutritive substances (perspiration, sebum from the sebaceous glands, cellular fragments)
- Major skin microflora strains : Staphylococcus (*Staphylococcus aureus* and *epidermidis* Grampositive), micrococcus, aerobic and anaerobic corynebacteria, propionobacteria and, in case of lack of hygiene : Gram-negative bacteria
- Transient micro-organisms (Temporary colonization) : constituted of many micro-organisms from endogenous (from the body) or exogenous (environnement) sources.



Textile and Bacteria interactions



- Role of the textile in odour generation : Act as a barrier which block the water evaporation and increase its condensation. The consequent moisture combined with the presence of nutrients at the interface between the skin and the textile induce the growth of micro-organisms and the potential to generate malodour.
- Reinforced by the high specific surface of the textile products
- After 8H of « normal » wearing, the bacteria population reach 10^4 / cm²
- The body odour intensity is considered as a malodour from 10⁷ germs/cm². As the number of bacteria can double about every 30 minutes, a malodour can be perceptible after 12 hours of a « normal » wearing.



Interaction Textile / Odorous substances

- Relation between malodour and number of total specific bacteria Coryneforms (*James et al. 2004*)
- Other bacteria participate to the gobal sweat odour : Staphylococci and Micrococci
- Odorous compounds issued from the bacteria degradations :
 - ✓ 3-Methyl-2-hexenoic acid (axillary) H₂c CH₂ Lor
 - ✓ Isovaleric acid (feet)
 - ✓ 3-hydroxy-3-methylhexanoic acid
 - ✓ Thioalcohol

 \checkmark

. . .

- ✓ Androstenone





Textile – Bacteria interactions in the odour release

- First Observations :
 - ✓ Higher adhesion of bacteria on hydrophobic, non polar surfaces : Polyester vs. Cotton (*Fletcher, M., 1996. Bacterial adhesion*)
 - ✓ Lower growth of Staphylococcus on hydrophilic compared to hydrophobic fibers (*Teufel and Redl, 2006*)
- Complementary Studies :
 - Comparable microbial numbers on wool, cotton and polyester after 1 day use (*Teufel and Redl, 2006*)
 - ✓ Higher <u>survival rate</u> of bacteria on wool than on polyester or cotton
 - ✓ BUT : odour intensity is lower on wool



Source : Mc. Queen et al. (2007). Odour Intensity on apparel fabrics and the link with bacterial populations. Textile Research Journal, 77, 449-456



Odour retention on fabrics – Axillary odours



- The odour intensity is higher for hydrophobic fibers regardless of sweat composition (Polyester >> Cotton and Wool)
- Significant results were obtained in particular for Wool fabrics which are less odorous after wear than polyester (panel of 13 assessors)
- Short-chain carboxylic acids were detected as responsible of the polyester odour after wear (Otago University)
- An other study (New Zealand) found that wool fabrics retained about 66% less body odour intensity than polyester fabrics and 28% less than cotton fabrics (olfactory measurement)



Odour retention on fabrics – Feet odours

- Sensory Study on odours emissions from socks made with different fabrics
- From The Wool Research Organisation New Zealand Inc. (WRONZ), become Canesis Network Ltd and then AgResearch Ltd.



- Confirm previous studies (Wool, far less odours compared to Polyester or Acrylic)



Synthesis : Influence of the type of fiber on bacteria and odour

	Polyester	Cotton	Visc ose	Acrylic	Polyami de	Wool
Odour	+++ (fatty acids, Ketones and aromatic comp.)	+ (Aldehydes)	+	+ +	+ +	- / + (Aldehyde s / Ketones)
Bacteria initial development	+ +	+	+	+	+	+
Bacteria persistancy	+ + (2, 4, 5)	+ (1, 2, 5)	 (1, 3, 4)	- (1, 2, 3, 4)	+ / - (1, 5) (2, 3)	+ + (1, 2, 4, 5)
Origin	Develop. of specific odour releasing strains					



Impact of washing on textile odours

- Fabric softeners seems to enhance the bad odour on Polyester (Laitala et al. 2012)
- Lipase in detergents may have an impact on odour formation (Munk et al. 2000)
- Volatile substances like carboxylic acids are faster removed in a washing process than micro-organisms (Chung and Seok, 2012)
- Volatils substances are easier removed on Cotton than on Polyester (McQueen et al., 2013)
- Volatiles from washing machine contribute to laundry malodour (Stapleton et al., 2013)



Source : Laitala et al. (2012). Troubles with the Solution : Fabric Softeners and Odour Properties. Tenside Surf. Det., 49 (5), 362-368.



Potentially odorant substances at the interface of human skin and textile





Testing

Olfactory Evaluation :

- External parameters control (French norms (sensory analysis) AFNOR V09 105, SSHA).

- Samples management

- Measurement of Detection, Intensity, type of Odours (+ deodorization efficiency, following ISO 17 299)

- Repeatability and reproducibility of the measurement

Microbiological testing :

- ISO 20743, ASTM2149, JIS L 1902 & AATCC100

Other Tests :

- Durability (Wash, Abrasion)
- VOC (GC/MS and HPLC/MS)
- Air or water permeability







- Sensory deodorization :

Textile : controled release (microcapsules, resines)

- Masking Agents (biology / biochemistry) : Hiding bad odours (essential oil) : Competitive chemical bonding with the olfactory receptor (« fragrance finishing ») : masquodor[®] (Protex)
- Neutralizing Agents (chemitry) : Based on a chemical reaction directly with the malodourous substance (air or liquid phase) : Decrease of the « bad » odour intensity or modification of the chemical structure (odour modification)
- Processes : Impregnation (crosslinking agent), Spraying, Coating, Incorporation in the fibre.
- Stage : Impregnation : thermal fixation (=at 130 to 170°C (drying and curing step)
- Release : Physical (dialytic : wall insoluble and product soluble in water and body fluids) / Biochemical (enzymatic degradation) / Chemical (dissolution by specific reactions)



Microencapsulation

Advantages : many manufacturing processes / Several types of textiles Disadvantages : Curing temperature decreased aroma retained inside the microcapsule / washing durability (< 25 home launderings) / Biocidal products regulation (BPR) 528/2012



- Chemical deodorization :

Textile : Addition of chemically active products to degrade odorous substances (ex : TiO2 for photocatalysis)

- Chemical reaction to transform substances with a bad odour in other substances without odour or with a better odour
 - Redox réactions (organic compounds),
 - Acido-basic (nitrogenous compounds with acidic reagent or sulfur compounds with basic reagent)
 - Ionic exchange (ammoniac or sulfure compounds neutralization by ferric salts or acétaldéhyde, H2S and amines by polyoxometalates)
 - Photocatalysis (Reaction between radical species from O2 and H20 and organic compounds)





- Biochemical deodorization: *Textile : biocides*
- Bactériostatic : Hinder proliferation of bacteria (without changing bacteria's skin flora).
- Bactericide : Eliminate microorganisms (lethal action)





- Biochemical deodorization:

Textile : biocides

- o Regulations (biocide directive N°98/8/CE : Biocide market regulation)
- Selection of the technology depending on the objective (fabric protection or deodorization) and on the manufacturing process (melting process : dissolution in the melting polymere (PES, PA et PP), Dry or Solvent process : dissolution in the solvent (cellulosic acetate, acrylic and chlorofibers) or wet process: dissolution in water (viscose)

Biocide	Ratio (%)	Price (\$/kg)
Silver	32,5	70* - 130
Silane Quats	13	30 - 50
Quats	4,5	50

Source : Report Biocides in Textiles, 2017

And... Triclosan, Zinc Pyrithione, Izothiazolinones (BIT, MIT, CMIT), formaldehyde releasers, phenolic derivates, paraben, copper, organic acids, alcohols



Biochemical deodorization: formulation and application processes

- o Biocide coated finishes (90% production in volume of pure product)
 - Aegis, Aglon, Purista (Lonza), Irguard (BASF), Foamfresh (Piedmont), Sanitized, Ultrafresh (Thomson), Silvadur (Dow), Pure TF (HeiQ)
 - Processes : Exhaustion, Padding, Spraying
 - Stage : Pre-spinning (on thread), Finishing (on raw textile), Spraying



- o Biocide Inherent fibres (10% production)
 - Allerban (Advansa), Coolmax (Asota), Saniguard (Miroglio), Rhovyl, Bactershield (Sinterama), Mushon (Toray), Bioactive (Trevira), Radilon (Radici), XT2 and X-static Fibers (Silverescent products, Noble), Newlife (Polygiene / Sinterama)
 - Processes : Synthetic fibre production
 - Stage : Spinning solution, mixed at the melt polymer

Limits :

- Some studies did not prove the efficiency of antibacterial treatments on odour reduction (*Mc Queen et al. (2013), Journal of the textile institute, 104 (1), p. 108*) and the durability is still called into question (Swedish Chemicals Agency, KEMI, PM 8/15, 2015)
- High cost of treatment



Entrapment deodorization :

Textile : Trapping charges (physical and chemical interactions : cyclodextrines, activated carbons, silica gel, argiles, zeolites)

ACTIVATED CARBON

- Odorous substances are chemically or physically fixed on active sites at the surface of the material Hydrogen, Van der Waals or ionic bonds (+ chemical functionalisation to increase reactivity)
- Chemical selectivity depending on :
 - The pore size (macropores : from 50 to 2000 nm, mesopores : from 2 to 50 nm, micropores : < 2 nm)</p>

Activated

Carbon

✓ The polarity (hydrophilic characteristics)



NEW DEVELOPMENTS

- Activated carbon fibers (in comparion with standard activated carbon functionalisation : larger specific surface, better adsorption capacity, better accessibility to micropores, faster adsorption kinetics)
- Porous polymers: Control of the specific surface and hydrophilic parameters, purity

Products : HeiQ Fresh NKU (zeolithes), Scentry (Microban, activated carbons),



- Entrapment deodorization - CYCLODEXTRINES

Torus-shaped molecules with hydrophobic cavities between 0,5 and 0,85 nm (trapping of



Advantage :

Cyclodextrines

- Do not interact with dying products (colour and odour efficiency)
- Efficiency proved on real samples (cigarette smoke: *Setthayanond, J et al. (2017). Cellulose, vol.24, issue 11, pp.5233-5250*)

Table	1.	Feasible	interactions	between	β-CD	and	some	textile	fibres
[14].									

Parameter	Cotton	Wool	PES	PA	PAN	PP
lonic interactions	16.0	+	-	+	+	9
Covalent bonds	+	+		+		-
Van der Waal forces	÷	-	+	+	+	C.
Crosslinking agents	+	+	+	τ.	i.	÷
Graft polymerisation	+	+	+	+	+	+

+=possible,-=not possible, PES-polyester, PA-polyamide, PAN-polyacrylonitrile, PP-polypropylene.

AOBCI. AUTEX Research Journal, vol.11, N°4; Dec 2011



Anti-odour fabrics – Market Study

Entrapment technology

- Carbon based (Activated carbon, activated carbon fibers...)
 - Zorflex (Calgon)
 - Cocona (replaced by 37,5)
 - Scafé
 - Bamboo charcoal (Acelon Chemical)
 - Saratech (Blücher)
- Minerals (zeolites, clays, nanomaterials...)
 - LAVA XL (Sciessent)
- Polyméric (Synthetics polymers...)
- Molecular (Cyclodextrines)





- Activated Carbon Fibers





- Cyclodextrine solutions
- Pulcra Chemicals GmbH : Anti-odour treatment Cyclofresh® (+ silver : cyclofresh plus®)
 - o Liquid application
 - Body odours absorption + Fragrance release
 - o Suit with many types of fabrics
 - o Regenerated by washing or spraying
 - Sanitized AG : Traitement ACTIFRESH®
 - Liquid / Solid applications (liquid, paste, masterbatch, powder), for extrusion, padding, extraction, spray, coatings









-



Source : Welch, K.T.; Lan, T. & Aylward, B. Scentry (2016). Scentry® and ZPTech® : A bifunctional, Effective, and Durable Odor Solution for Polyester Activewear





European Union European Regional Development Fund

Thank you!