STUDIES TOWARD THE SUBSTITUTION OF PERFLUOROCARBONS IN HYDROPHOBIC AND OLEOPHOBIC TEXTILE FINISHES

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2. PURPOSE OF THE STUDY

To devise hydrophobic and oleophobic textile finishes as an alternative to the use of perfluorocarbon-based (mainly C8 but also C6) substances.

3. METHODOLOGY

Three types of experiments have been carried out as part of this substitution study:

- Technical experiments, aimed at preparing textile samples making use of different alternative hydrophobic finishes.
- Quality measurements, to assess the hydrophobic and oleophobic properties and the resistance to washing of the textiles prepared.
- Toxicity measurements, to establish the level of toxicity of the proposed substitute substances with respect to PFCs.

4. TEAMS INVOLVED IN THE STUDY

Preparation of the textiles with hydrophobic finishes was carried out in cooperation with a team from Technical Advice, S. L. (Barcelona, Spain) led by Mr. Joan Roca and Mr. Lluís Ponsá of the Asociación Española de Químicos y Coloristas Textiles.

Characterization of the hydrophobicity, oleophobicity and stain resistance of the prepared textiles was carried out by a team from Technical Advice, S. L., with the assistance of Leitat Technological Center (Barcelona, Spain)

Toxicity measurements were carried out by a team from the Department of Genetics of the University of Santiago de Compostela, Spain (USC), led by Prof. Laura Sánchez Piñón, Prof. of Genetics at the Faculty of Veterinary (USC).

5. TECHNICAL EXPERIMENTS

5.1 Scientific and technological background[1]

a) Introduction

Hydrophobic and oleophobic finishes confer very desirable physical and chemical properties to fabrics, to realize higher value textile products. Finishes that repel

[1] a) Schindler, W. D.; Hauser, P. J. *Chemical Finishing of Textiles*. Woodhead Publishing Ltd. CRC Press, Boca Raton: 2004. Chapter 6; b) Holme, I. *Innovative technologies for high performance textiles*, Color. Technol. **2007**, *123*, 59-73; c) Mahltig, B. *Functional Finishes for Textiles*. Paul, R. (ed.), Woodhead Publishing-Elsevier Ltd., Cambridge: 2015.

water, oil and dry dirt are important in all parts of the textile market – for clothing, home and technical textiles. Water repellency is achieved by using different product groups, but oil repellency is attained at present only with fluorocarbon polymers.

b) Mechanisms of repellency

The repellency properties of a solid material are determined both by the chemical composition of the solid surface but also by the surface topography, which means the roughness of the surface.

Repellent finishes achieve their properties by reducing the free energy at fibre surfaces. If the adhesive interactions between a fibre and a drop of liquid placed on the fibre are greater than the internal cohesive interactions within the liquid, the drop will spread. If the adhesive interactions between the fibre and the liquid are less than the internal cohesive interactions within the liquid, the drop will not spread. Surfaces that exhibit low interactions with liquids are referred to as low energy surfaces.

5.2 Methodology

In this study we have compared the hydrophobic and oleophobic properties imparted to textile fabrics by different types of chemical finishes that could replace perfluorocarbon-derived treatments.

a) Selection of hydrophobic treatments and the textile substrates to study

The selection of the types of hydrophobic finishes was performed taking in to account the hydrophobic finishing techniques which have commercial application:

- PFCs-based repellent finishes (to serve as technological, quality and toxicity benchmarks)
- Paraffin-based repellent finishes
- Silicone-based repellent finishes
- Specific polymeric and polymeric-dendrimer repellent finishes

The textile substrates chosen for this study are representative of the fabrics most commonly used for apparel manufacturing.

The following table 1 shows the commertial hydrophobic finishing agents (formulations) used to prepare finishing textile samples and the textile substrates chosen for this study.

BRAND NAME (TYPE), CONCENTRATION	TEXTILE SUBSTRATES
OLEOPHOBOL CO (FLUOROCARBON C8), 60 g/l. **NUVA N2114 liq. (FLUOROCARBON C6), 60 g/l.** **ARKOPHOB FFR liq. (PARAFFIN-POLYMER), 130 g/l** **RUCO-DRY ECO (DENDRIMER-POLYMER), 130 g/l** **ROCO GUARD ECO-PLUS (DENDRIMER-POLYMER), 80 g/l** **PHOBOTONE WS conc. (SILICONE), 40 g/l** **ZELAN R3 (ALKYL-URETHANE), 80 g/l** **SMARTREPEL Hydro CMD liq. (MOD. FATTY POLYMER/PARAFFIN), 100 g/l** **SMARTREPEL HYDRO PM LIQ. (MOD. FATTY POLYMER/PARAFFIN), 100 g/l**	100% **COTTON** 50% **COTTON**/50% **POLYESTER** 100% **POLYESTER** 100% **POLYAMIDE** 100% **VISCOSE**

Table 1. Commercial hydrophobic finishing agents and textile substrates used in this study

b) Preparation of the textile samples

For the preparation of the hydrophobic finishing textile samples, the previous hydrophobic formulations were applied to the textile substrates at the concentrations shown in table 1 by following the same normalized procedure:

- Padding baths were adjusted to pH 5 to 6 with acetic acid and loaded with the appropriate booster agent.
- Application of each hydrophobic finish to the fabrics was performed by padding, with adsorption rates between 74-80%.
- Drying of the padded fabrics was carried out at 110 to 120 °C for 90 seconds.
- Curing of the dried fabrics was carried out at 170 °C for 60 seconds.

6. QUALITY MEASUREMENTS

6.1 Evaluation of textiles treated with repellent finishes

The following test methods were selected to evaluate the performance of the repellent finishes:

- Water repellency:
  - Resistance to water solutions (AATCC 193)
  - Spray test (ISO 4920: 2012)
- Oil repellency:
  - Resistance to hydrocarbons (UNE-EN ISO 14419: 2000)

For fabrics that require durable repellency performance, the usual test methods can be applied to fabrics that have been laundered or dry cleaned by standard methods (as AATCC TM 124 and TM 86).

6.2 Summary of performance results and relative cost of the repellent finishes

The following table 2 summarizes the results obtained for the parameters analyzed for each repellent compound used in the study and the estimated costs of the different treatments. The costs are relative to the PFC C8-based repellent treatment.

Parameters/Compounds	FL-C8	FL-C6	Dendrimer	Paraffin	Silicone	Polyurethane	New generation without FL
Compliance PFCs elimination	NO	NO	YES	YES	YES	YES	YES
Compliance CTW	NO	NO	YES	YES	YES	YES	YES
Repellency to Water	YES	YES	YES	YES	YES	YES	YES
Repellency to Oil & dirt	YES	Acceptable	NO	NO	NO	NO	NO
Repellency to Water & stain	YES	YES	YES	YES	YES	YES	YES
Resistance to washing (1-30 ºC)	Acceptable	Acceptable	Acceptable	Acceptable	Acceptable	Acceptable	Acceptable
Resistance to washing (5-30 ºC)	Acceptable	Acceptable	Acceptable	Acceptable	Acceptable	Acceptable	Acceptable
Resistance to dry cleaning	Acceptable	Acceptable	NO	NO	Moderate	---	NO
Estimated cost	100	100/140	86	160	90	---	180

Table 2. Performance results of the repellent finishes

6.3 Conclusions of the technical studies

The results obtained in this study show that:

a) All the chemical finishes tested are suitable to impart adequate repellency to water and water-based liquids to different types of commonly used fabrics.
b) In stark contrast with these positive results, only PFC-based finishes are suitable to impart oil repellency to the tested fabrics.
c) All of the finishes tested showed good resistance to washing.

d) Some of the non PFC-based finishes don't have resistance to dry cleaning.

7. TOXICITY MEASUREMENTS

Toxicity studies of the employed finishing agents were performed employing zebrafish embryos as model organism.[2]

- Scientific name: *Danio rerio*
- Line: wild-type.
- Source: Embryos used in this toxicity study were obtained from a zebrafish broodstock maintained in our laboratory.

7.1 Test conditions

Water temperature for broodstock aquaria is maintained at 28 °C and levels of the relevant physico-chemical parameters are measured weekly, especially those parameters affecting the embryos' wellbeing, such as: ammonium, concentration of nitrites and nitrates, concentration of chloride, water hardness, and pH. Egg fertilization rate was almost 100%. This value is above OECD recommendations (> 70%).

7.2 Methodology

The embryos were subjected to five increasing concentrations of the corresponding substance in 24-well plates. Four of these wells did not contain the chemical in solution, and acted as an internal negative control. Furthermore, an additional external negative control plate (without the specific substance under investigation), as well as a positive control with a solution of a reference substance (2,4-dichloroaniline 4 mg/L (CAS Number 95-76-1)), the toxicity of which had been demonstrated previously in the model organism used, were run in parallel to the experiment.

[2] For environmental toxicology studies employing zebrafish embryos as model organism, see: a) Lele, Z.; Krone, P.H. *The zebrafish as a model system in developmental, toxicological and transgenic research*. Biotechnol Adv. **1996**, *14*, 57–72; b) Yang, L., Ho, NY, Alshut, R., Legradi, J., Weiss, C., Reischl, M., Mikut, R., Liebel, U., Muller, F., Strahle, U., *Zebrafish embryos as models for embryotoxic and teratological effects of chemicals*, Reprod. Toxicol. **2009**, *28*, 245–253; c) Sipes, N.S., Padilla, S.; Knudsen, T.B., *Zebrafish as an integrative model for twenty-first century toxicity testing*. Birth Defects Res C. Embryo Today, **2011**, *93*, 256–267.

Measured control mortality rates were in accordance with OECD. It was under 10 % in the negative control, over 30 % in the positive control, and there was not more than one dead individual in the internal negative control. Besides, the mortality rate of the samples was corrected through an Abbott correction, taking into account the mortality rate of the negative control.
After the start of each test run, observations were made every 24 hours until the end of the test, which takes place after 96 hours, looking for lethal characteristics.

7.3 Toxicity studies of the commercial formulations used for textile finishes

The formulations described in table 1 (p. 5) were submitted to toxicity analyses as received from the corresponding chemical manufacturers, following the previously described procedure.

For each substance (commercial textile finishing mixture) a ZFET (Zebrafish Embryo Toxicity Test) was conducted at the following theoretical concentrations: 0.1, 1, 10, 100 and 1000 mg/L. Each experiment consisted of 12 zebrafish embryos assessed for each concentration.

The data measured allowed the determination of the toxicity rates LC_{50}, NOEC and LOEC for each substance, the results are summarized in the following table 3:

ENTRIES	SUBSTANCE (TYPE)	LC_{50}[1] (mg/L)	LOEC[2] (mg/L)	NOEC[3] (mg/L)
1	**RUCO DRY ECO-PLUS** (DENDRIMER-POLYMER)	313,7	1000	100
2	**SMARTREPEL Hydro CMD liq** (MOD. FATTY POLYMER/PARAFFIN)	162,5	1000	100
3	**ARKOPHOB FFR** (PARAFFIN-POLYMER)	156,9	100	10
4	**SMARTREPEL Hydro PM liq** (MOD. FATTY POLYMER/PARAFFIN)	29,9	100	10
5	**RUCO DRY ECO** (DENDRIMER-POLYMER)	21,3	100	10
6	**ZELAN R3** (ALKYL-URETHANE)	18,6	100	10
7	**PHOBOTONE WS con.** (SILICONE)	15,8	100	10

ENTRIES	SUBSTANCE (TYPE)	LC_{50}[1] (mg/L)	LOEC[2] (mg/L)	NOEC[3] (mg/L)
8	**NUVA N2114 liq** (FLUOROCARBON C6)	12,6	100	10
9	**OLEOPHOBOL CO** (FLUOROCARBON C8)	2,8	10	1

[1]LC_{50}: concentration at which death of 50% of individuals occurs. [2]LOEC: lowest concentration with lethal effects on embryos. [3]NOEC: No observed effect concentration.

Table 3. Toxicity studies of the commercial textile finishing mixtures

The results obtained in this study show that:

a) Fluorocarbon-derived finishing mixtures studied were the most toxic substances (entries 8 and 9).
b) Moderate toxicities were obtained for ARKOPHOB FFR, SMARTREPEL Hydro PM liq, RUCO DRY ECO and ZELAN R3 (entries 4-7) , between 5 and 10 times lower than the obtained for fluorocarbon C8-derived finishing mixture.
c) Lower toxicities were obtained for RUCO DRY ECO-PLUS SMARTREPEL Hydro CMD liq and ARKOPHOB FFR (entries 1-3), between 50 and 100 times lower than the obtained for fluorocarbon C8-derived finishing mixture.

8. CONCLUSIONS OF THE TECHNICAL AND TOXICITY STUDIES

According to the performed technical and toxicity studies, the following commercial textile finishing mixtures can be considered adequate replacements for the perfluorocarbon-derived treatments (table 3): RUCO DRY ECO-PLUS, SMARTREPEL Hydro CMD liq and ARKOPHOB FFR.

These commercial textile finishing mixtures are DENDRIMER-POLYMER, MOD. FATTY POLYMER/PARAFFIN and PARAFFIN-POLYMER based formulations respectively. These compounds have shown good repellency to water and stain in the technical studies performed and also good resistance to washing (table 2).
Taking into account these evidences and the estimated relative price of the selected treatments (table 2), these textile finishing agents are currently being used for the substitution of the perfluorocarbon-based agents as hydrophobic finishes to textile garments produced for Inditex.