MITIGATION OF ENVIRONMENTAL IMPACT CAUSED BY DWOR TEXTILE FINISHING CHEMICALS STUDYING THEIR NONTOXIC ALTERNATIVES

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EXTENDED ABSTRACT

Key Words: Durable water and oil repellent (DWOR), textile industry, human and environmental health

1. INTRODUCTION

Durable water and oil repellents (DWORs) are finishing treatments normally applied to fabrics to provide protection against water, oil and dirt. In addition to providing protection against water, oil and soil, these finishes also extend the life of products and keep them looking newer longer. DWOR technology has historically been achieved with textile finishes that contain a polymer to which long-chain perfluoroalkyl groups have been attached. These long-chain fluorinated polymers often contain residual raw materials and trace levels of long-chain perfluoroalkyl acids (PFAAs) as impurities.

Since the 1950's, long-chain PFAAs as well as polymers and surfactants containing long-chain perfluoroalkyl functionality that may degrade to form long-chain PFAAs have been widely used in industries and commercial applications [1]. As a result of the widespread uses, long-chain PFAAs including **perfluorooctanoic acid (**PFOA) and **perfluorooctane sulfonate (**PFOS) have been detected globally in the environment, wildlife and humans. PFOA and PFOS, the most widely known and studied long-chain PFAAs [2, 3], have been shown to be persistent in the environment, have long elimination half-life in wildlife and humans, and have toxicological properties of concern. Due to these properties, regulatory actions have been put in place or are being considered in several countries to manage these substances. PFOAs and derived products (including polymers) were included in the restriction list (Annex XVII of REACH); production and placement into marked will be banned starting on July 4th 2020 except for personal protective textile applications where the ban is postponed until July 4th 2023. There is also a shift within industries towards DWOR chemistries containing shorter perfluoroalkyl chains as well as non-fluorinated chemistries.

Regarding DWOR alternative products, the tendency is to replace the C8 fluorocarbon chemistry by C6 or C4 fluorocarbon products or even fluorine-free water repellents. In fact, currently, new commercial DWOR finishes are coming onto the market based on short chain fluorocarbons, hybrid systems or some fluorine free products. Sol-Gel technology, perfluorosilicones and modified silicones.

2. PROJECT OBJECTIVES AND PARTICIPANTS

MIDWOR-LIFE was an European project, who grouped three textile clusters from Spain, Czech Republic and Italy (AEI Tèxtils, CLUTEX and CS-POINTEX) which represented the industrial textile sector of their countries and also, joined two technological Spanish centers (LEITAT and CETIM) and a Spanish research Centre (IQAC) that belongs to the Spanish National Research Council (CSIC) for the three years.

The main objective of this project was to mitigate the environmental, health and safety impacts of current and alternative DWOR alternatives, by analyzing their environmental impact and their technical performances, in order to help manufacturers to move on the best available technologies for repellent finishing:

- ✓ Evaluation of the environmental impact of DWOR and their available alternatives
- ✓ Evaluation of the risks posed by DWOR and their alternatives for human and environmental health
- ✓ Comparison the technical performance between current and alternative DWORs

3. MIDWOR-LIFE EXPERIMENTAL WORK

3.1.Preparation and Lab-scale trial

At lab scale, the padding process consisted of impregnating the fabric and then inserting it into foulard. The fabric was then dried and cured in a stenter frame. The characterization of the treated samples includes the spray test (UNE EN ISO 4920) and the oil test (UNE EN ISO 14419) in order to evaluate the water and oil repellency grade, respectively. These tests had been performed on original samples, after washing (UNE EN ISO 6330, 10 cycles at 30ºC) or dry cleaning (UNE EN ISO 3175-2), and ironing.

3.2.Industrial demonstration

The products that achieved better results at pilot scale were selected to be applied on industrial scale. Six textile manufacturing companies were responsible to apply by padding the selected products on the selected fabric: Inotex and Nanomembrane, from Czech Republic, Biella Manifatture Tessili and Tintoria Finissaggio 2000, from Italy, and E.Cima and Hidrocolor, from Spain.

3.3.Risk assessment

A comparative risk assessment of conventional and alternative DWOR active ingredients was performed based on exposure estimation using the life cycle map and mapping of uses to identify critical exposure scenarios, and industrial partners questionnaire to collect data.

3.4.Environmental impact assessment

Life Cycle Assessment (LCA) has been proposed as the best framework for assessing the potential environmental impacts of products (COM (2003)302) from a comprehensive approach, covering all the stages of its life (raw matters, transportation, production, use and disposal). As part of MIDWOR-LIFE Project, a LCA has been developed in order to evaluate the environmental impact of the three fluorinated DWORs (C8-PFC & C6-PFC chemistry and perfuorosilicone) and three fuorine-free alternatives (silicone, dendrimer and paraffin).

4. MIDWOR-LIFE RESULTS

First, DWOR products and fabrics were selected to work during the entire project (Table 1).
The industrial results are generally higher than those from pilot applications, and should also be more accurate and reliable.
Regarding the results, it can be found that if oil repellency is truly needed, a short-chain fluorinated product (C6) or a perfluorosilicone can be enough to fulfill this requirement, avoiding the use of long-chain fluorocarbons.
However, if only water repellent properties are needed, the non-fluorinated alternatives can achieve very good results, particularly on polyester with the tested products. **Therefore, non-**

fluorinated chemistries can substitute the fluorinated DWOR products for water repellency with similar performance than conventional C8.

Table 1: DWORs selected in the MIDWOR-LIFE project

Type DWOR / Chemical structure	Type of fabrics/application
C8 / Perfluorinated acrylate copolymer	Non-woven PES / car carpets
C6 / Perfluorinated acrylate copolymer	Woven PES / sofa
Fluorine-free / Silicone	Knitted PES / polo for work/sport
Fluorine-free / Dendrimer	Woven WO/ suits
Fluorine-free / Paraffin	
Fluorine-free /Alkyl urethane	
PFSi / Hybrid perfluorinated silicones	

The hazard profile of each active ingredient was estimated and some challenges are detected:

- In the commercial products evaluated, the chemical identity of the active substances was not reported in the safety data sheet. This is due to the lack of obligation to report ingredients that are not triggering the hazardous classification of the mixture.
- Most of the active substances are polymers and therefore are not subject to registration under REACH regulation.
- Textile finishing industry does not have the necessary information to take into consideration safety aspects associated to the active ingredients of DWOR formulations.

Impact of C6-DWORs is approximately 1/3 of its equivalent in C8 chemistry, due to the lower reported impact of SC-PFC derivatives over environment and human toxicity and similar to perfluorosilicone, due to the presence of C6-PFC on its composition.
Regarding the fluorine-free DWORs studied, dendrimer showed the smallest footprint among the DWORs studied, followed by silicon and paraffin with barely no difference between these three compounds, with a reduction of the global impact of 97-98% compared with C8-DWOR.

Acknowledgement: Authors wish to thank the LIFE Environmental Policy and Governance program from the European Union for its financial contribution to the MIDWOR-LIFE project (LIFE14 ENV/ES/000670). (www.midwor-life.eu)

Also, the authors thank all other MIDWOR Consortium partners for their work, especially to LEITAT for their lab treatments and characterization and CETIM for their LCA study.

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