MITIGATION OF ENVIRONMENTAL IMPACT CAUSED BY DURABLE WATER AND OIL REPELLENTS TEXTILE FINISHING CHEMICALS

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LIFE14 ENV/ES/000670

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CONTRIBUTORS: AEI TÈXTILS, LEITAT, CETIM, CS-POINTEX, CLUTEX, CSIC-IQAC

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CONTACT:
AEI TÈXTILS
INFO@MIDWOR-LIFE.EU
HTTPS://MIDWOR-LIFE.EU

THE PROBLEM

What are DWORs?

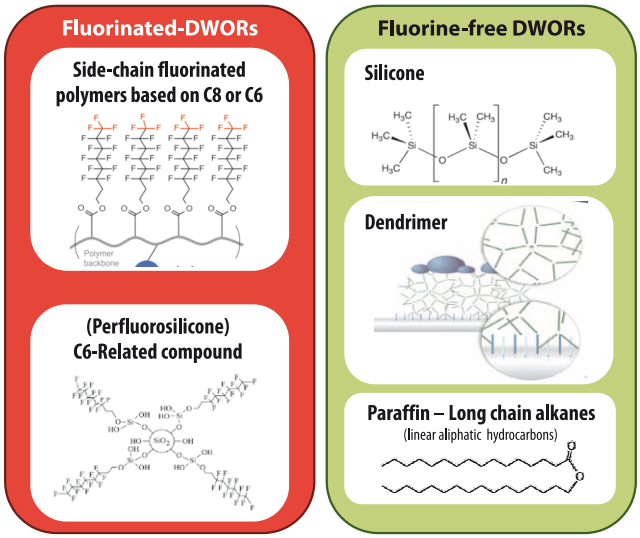
DWORs, Durable Water and Oil Repellents, are textile finishing products mainly made of long chain fluorocarbon polymers (perfluorochemicals) to provide fabrics with hydrophobic and/or oleophobic properties.

Which DWORs alternatives are available?

While a broad range of DWORs are available, those are mostly classified between fluorinated and fluorine-free.

Fluorinated DWORs are subdivided in perfluorocarbons (characterized by its side-chain length: C8, C6, C4…) and perfluorosilicons with similar properties. Most fluorinated DWOR present high performance and have oil repellency properties.

Fluorine-free products have aroused interest during the last decade as potential alternatives over fluorinated DWORs after the concerns express by policy-makers

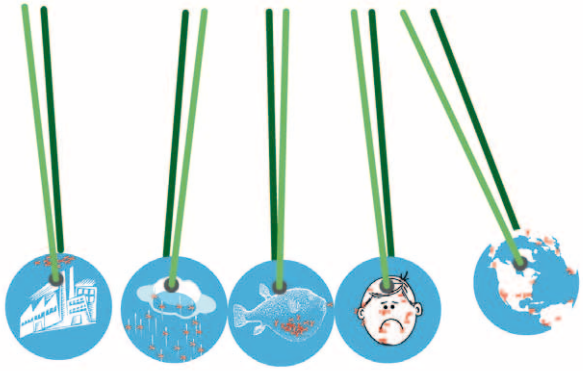


What are the problems?

Main **environmental concern** raised by fluorinated DWORs is that its **fluorinated chains** may be severed from the polymeric backbone, releasing perfluoroalkyl substances (PFAs) that degrade to perfluoroaklyl acids (PFAAs).

Among the different PFAAs, two compounds are the most concerning and studied: Perfluorooctanoic acid (PFOA) and Perfluorooctane sulfonic acid (PFOS) which are well known for its persistence and bioaccumulation after being detected around the world in the food chain, drinking water and human blood.

PFOAs and derived products (including polymers) were included in the restriction list (Annex XVII of REACH); production and placement into market **will be banned starting on July 4th 2020** except for personal protective textile applications where the ban is postponed until July 4th 2023.



Current substitutes in the market, mostly based on C6-fluorocarbons are also under the regulatory radar and some national authorities have started the produce to include them into the REACH restriction list.

Therefore, there is an imperative need to find adequate substitutes and update the relevant stakeholders and policy-makers on the best available technologies with mitigated environmental and health impact.

PROJECT OBJECTIVES

The main objective of **MIDWOR-LIFE** was the **mitigation of the environmental, health and safety impacts of current and alternative Durable Water and Oil Repellents (DWOR)** by analyzing their environmental impact and technical performances in order to assess textile manufacturers on the best available technologies for repellent finishing.

Specific objectives:

- To evaluate the environmental impact of current DWORs and their alternatives
- To evaluate the risks posed to human and environmental health of the current DWORs and their alternatives
- To compare the technical performance between current and alternative DWORs

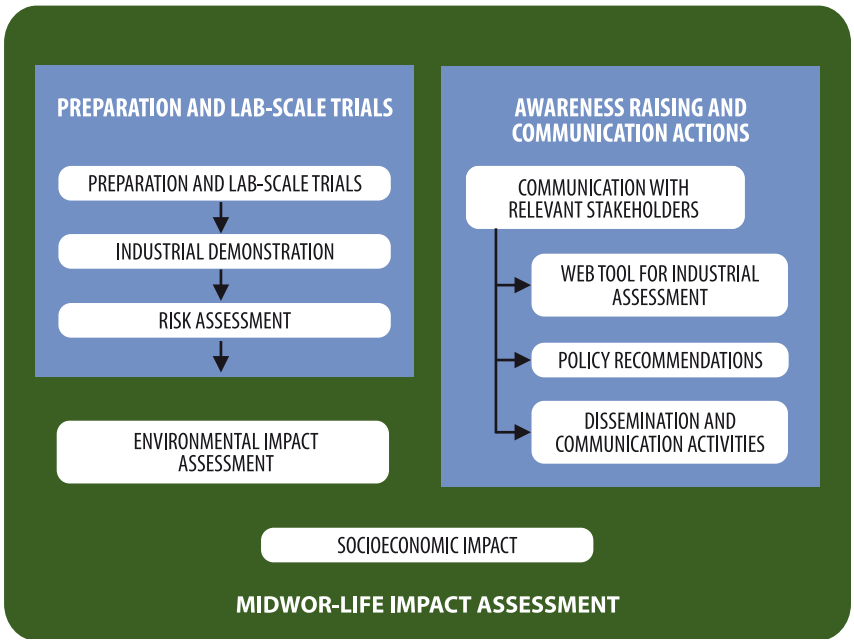
Let's make a more sustainable world

MIDWOR-LIFE PROJECT

The MIDWOR-LIFE project had two main pillars: experimental demonstration and awareness raising.

Experimental actions included the technical demonstration occurred, firstly at pre-industrial scale and later at industrial level in 6 industrial textile industries from 3 countries and the assessment of the risks and the environmental impact.

Awareness raising and communication actions included a series of industrial workshops, communication to general public for awareness raising, a set of policy recommendations for improving the competitiveness of the European textile companies and a dedicated web tool to facilitate textile companies in making self-assessments of the available DWORs.



MIDWOR-LIFE has studied how to mitigate the environmental impact caused by current DWORs (Durable Water and Oil Repellents) used in the textile finishing industry by analyzing their non-toxic alternatives

ACTION 01

PREPARATION
Market study to determine the most relevant fabrics and DWORs used in different applications

ACTION 02

DEMONSTRATION
DWOR products have been applied onto fabrics in the laboratory and then at industrial scale in 6 textile companies in Spain (2), Italy (2) and Czech Republic (2).

ACTION 03

ENVIRONMENTAL IMPACT
For each alternative DWOR an Environmental Life Cycle Analysis (E-LCA) has been carried out to evaluate its environmental performance

ACTION 04

SOCIOECONOMIC IMPACT
A Social Life Cycle Assessment (S-LCA) has been used to measure alternative DWORs´impact on workers, community consumers, value chain actors and society

ACTION 05

COST EFFICIENCY
Non-toxic DWORs has only been considered „substitues" if they have a positive environmental and socioeconomic impact AND they are cost-efficient

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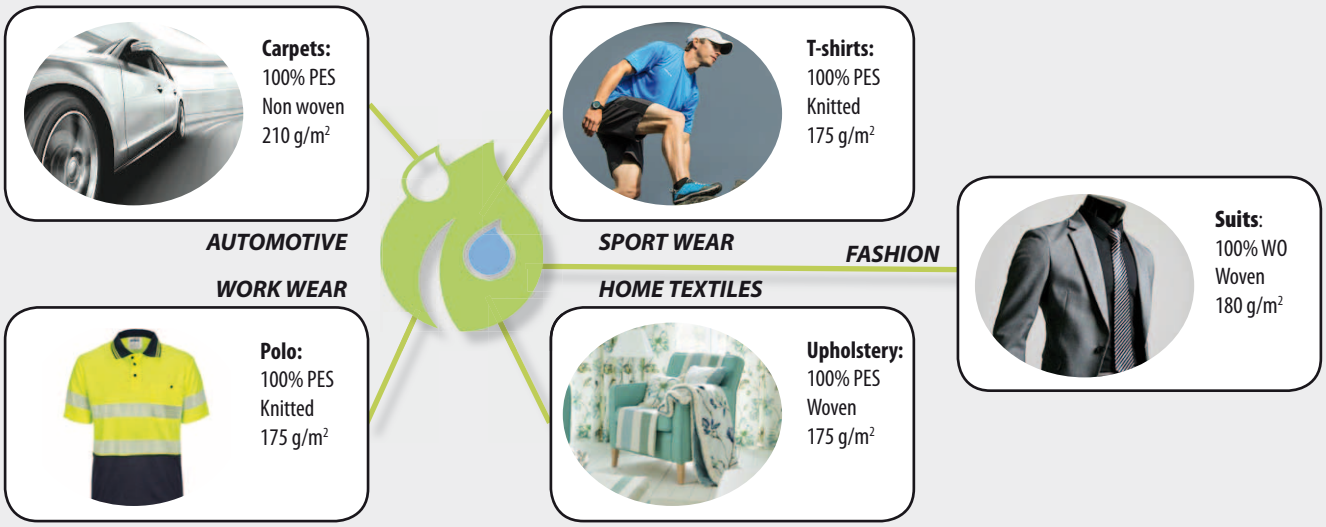
AEI TÈXTILS, a non-profit organization representing the Catalan technical textiles cluster is the coordinator of the project. The consortium is completed by another 5 partners: 3 research institutes/technological centers from Spain: LEITAT Technological Center, CETIM and the Institute of Advanced Chemistry of Catalonia from CSIC plus 2 technical textile clusters, CS-POINTEX from Italy and CLUTEX from the Czech Republic.

MIDWOR-LIFE project is an example of collaboration between clusters, with the aim to improve competitiveness of their members, SMEs in the technical textiles sector.

PREPARATION AND LAB-SCALE TRIALS

A selection of the different textile materials and finishing products was performed based on the results of a survey with textile companies from participating clusters on their needs in regard to the durable water and oil finishing properties.

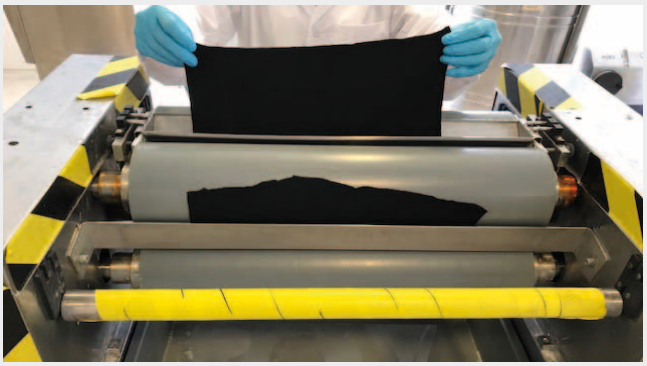
The fabric selection consists of four fabrics representing five different sectors of the textile industry: work wear, automotive, home textiles, fashion and sport wear.



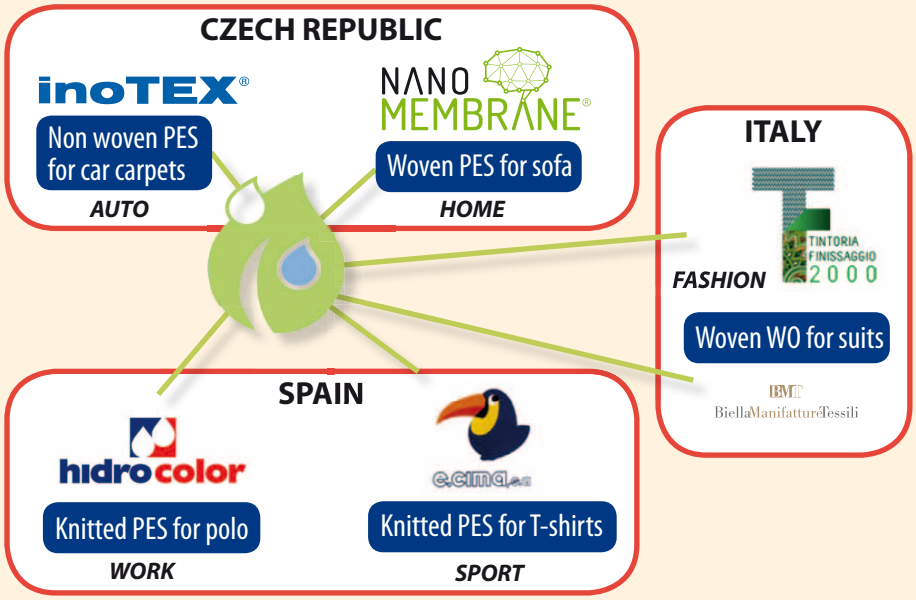
Fourteen repellent finishing products available on the market were selected including fluorinated and fluorine-free products:

First of all, the selected repellent finishing products were applied on the different selected fabrics by padding, at pilot scale. The process consists of impregnating the fabric and then inserting it into two squeezing rolls, were the excess of water is eliminated. The fabric is then dried and cured in a stenter machine.

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 have 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.

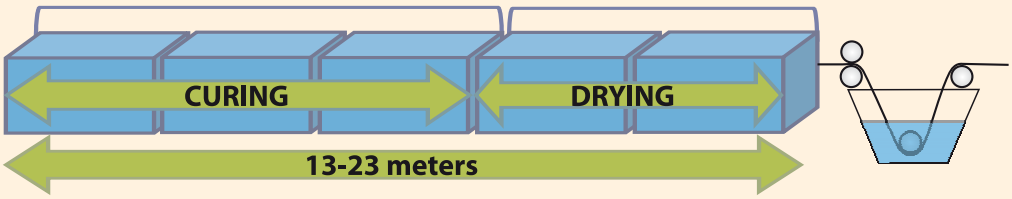


INDUSTRIAL DEMONSTRATION



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.

The companies that collaborated with MIDWOR-LIFE project in performing the industrial demonstrations are: Inotex and Nanomembrane, from Czech Republic, Biella Manifatture Tessili and Tintoria Finissaggio 2000, from Italy, and E.Cima and Hidrocolor, from Spain.



			AUTO	SPORT / WORK	HOME	FASHION
AATCC 22, UNE EN ISO 4920			Polyester nonwoven	Polyester knitted	Polyester woven	Wool woven
Water repellency	PFCs	C8	**3,5**	**4,5**	**5**	3
		C6	**5**	**4,5**	3	**3**
		PFSi	2,5	**4,5**	**4,5**	*not tested*
	F-free	Silicone	**3**	2	*not tested*	*not tested*
		Dendrimer	2,5	**4,5**	2,5	**2**
		Paraffin	2	0,5	2,5	2,5
		Alkyl urethane	2	2	4,5	*not tested*

			Polyester nonwoven	Polyester knitted	Polyester woven	Wool woven
AATCC 118, UNE EN ISO 14419						
Oil repellency	PFCs	C8	**8**	**5,5**	**6,5**	0
		C6	**6,5**	**5,5**	2	**2,5**
		PFSi	6,5	**5**	**6**	*not tested*
	F-free	Silicone	**0**	0	*not tested*	*not tested*
		Dendrimer	0	**0**	0	**0**
		Paraffin	0	0	0	0
		Alkyl urethane	0	0	0	*not tested*
			Unwashed	10 washing cycles + ironing	10 washing cycles + ironing *	1 dry cleaning cycle + ironing

** Only the industrial samples have been ironed - Bold indicates results from tests performed on the industrial demonstration*

The industrial results on water and oil repellency are generally higher than those from pilot applications, and should also be more accurate and reliable.
Regarding the results, it can be seen that if oil repellency is truly needed, a short-chain fluorinated product (C6) or a perfluorosilicone can be enough to fulfil 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-based products.**

RISK ASSESSMENT

Alternative finishing additives available on the market were selected for laboratory validation of technical performance and industrial demonstration and for assessment of occupational risks.

A comparative risk assessment of conventional and alternative DWOR active ingredients was performed based on:

Toxicological assessment

Identification of the active ingredient: For some products, the active ingredient was not reported in the Safety Data Sheet or in other technical documents, and was not provided by the supplier.

Assumptions were based on public reports or literature, taking into consideration the most frequent active substances of the corresponding chemical family used in textile applications.

Compilation of the hazard profile: Based on harmonized classifications and, if not available, CLP (Classification, Labelling and Packaging of substances and mixtures) notifications. In the case of polymers, based on the properties of the monomers (present as unreacted precursors or degradation products).

Derivation of Stoffenmanager Hazard Class for eyes and inhalation

In red: parameters with no information
In blue: reasonable estimations are possible

Exposure estimation

Life cycle map (system boundaries) and **mapping of uses** to identify critical exposure scenarios.

Questionnaire to collect data on operational conditions and risk mitigation measures to collect exposure determinants for each of the industrial partners.

Characteristics determining exposure

Chemical Substance	Chemical entity of the substance and its concentration	Process	Process type (energy involved)
	Product form (Physical state of the product and vapour pressure)		Containment and degree of engineering control measures (Local Exhaust Ventilation)
	Impurities (unreacted monomers) and degradation products	Operational Conditions	Temperature
	Chemical changes: hazards associated to the chemical reaction and the reactants and by/products of the textile finishing process		In-use concentration (Dilutions)
			Duration of the process
			Frequency of events
			Risk Management Measures (PPE)

Derivation of Stoffenmanager Hazard Class for eyes and inhalation

Qualitative evaluation of risks associated to each

Determination of the hazard profile of each active ingredient, stoffenmanager hazard class per product and process, stoffenmanager exposure class and risk class:

** Assuming that 2% of PFOA/POFS and PFHxA/PFHxS could remain unbound in the C8- or C6- based polymers, respectively [Russel et al., 2008. Environ Sci Technol 42:800] and such polymers are present in the product in a maximum concentration of 30% (according to the upper limit range disclosed in the safety data sheets).*

PFOA: Perfluorooctanoic acid
PFOS: Perfluorooctane sulfonic acid
PFHxA: Perfluorohexanoic acid
PFHxS: Perfluorohexane sulfonic acid
PDMS: Polydimethylsiloxane

Chemical family of the DWOR active ingredient		Substance for the hazard assessment	Risk Class		
			Inhalation	Skin (L)	Skin (UPT)
Fluorinated	Polymer based on C8	PFOA	II-Moderate	III - Low	II -Moderate
		PFOS			
	Polymer based on C6	PFHxA	III - Low		
		PFHxS			
	PFSi (C6 related compound)				
Fluorine-free	Silicone	PDMS	III - Low		
	Dendrimer	Dendrimer	III - Low	II-Moderate	III - Low

Challenges in the comparative risk assessment process:

- 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.
- The potential human health and environmental impacts of these substances are related to their content of unreacted substances and/or possible release of monomers and other degradation products. Given no quantitative information is available on these aspects; equal assumptions were taken for all polymeric alternatives. However, these aspects could indeed be determining the differences in terms of human or environmental health impact.

Conclusions

- Textile finishing industry does not have the necessary information to take into consideration safety aspects associated to the active ingredients of DWOR formulations. In most cases, the identity of the active ingredients and their concentration in the commercial formulations is not disclosed.
- Most DWORs are based on polymers, which are considered not hazardous to the lack of bioavailability (lack of classification, lack of obligation to include them in SDS of the commercial products), but precursors and degradation products may be hazardous (as in the case of C8).
- The concentration of the unreacted monomers in the commercial products should be reported. In addition, information is also needed on the degradation of active DWOR ingredients during the drying and curing steps after the padding impregnation treatment, and the hazard properties of such degradation products.
- Due to the large number of assumptions made during the risk assessment process, a large uncertainty is associated to this analysis.

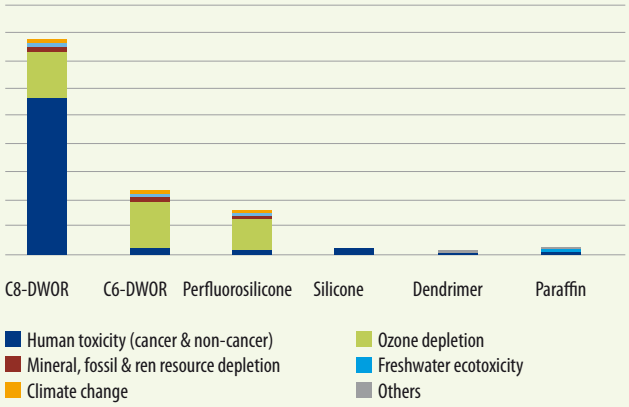
ENVIRONMENTAL IMPACT ASSESSMENT

Since 2000's, many alternatives have been proposed to replace perfluorochemical based DWORS, based mainly in short-chain perfluorochemicals (SC-PFC) (C6 or C4) and other PFC-free substances (waxes, silicones, dendrimers, etc.). However, both textile performance and environmental impact must be assessed for a successful substitution process.

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 different DWORs studied. This LCA includes six scenarios** to compare the environmental footprint of three fluorinated DWORs (C8-PFC & C6-PFC chemistry and perfluorosilicone) and three fluorine-free alternatives (silicone, dendrimer and paraffin).

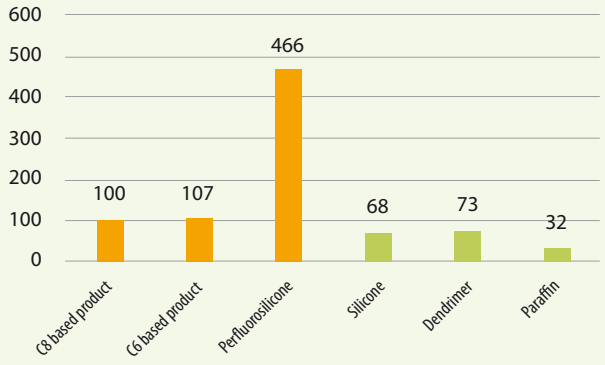
Results shows that C8-DWOR has the highest environmental impact, with a great effect over human toxicity caused by the release of PFC related compounds such PFOA, and PFOS. Impact of C6-DWORs is significantly lower, approximately 1/3 of its equivalent in C8 chemistry, due to the lower reported impact 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. The lack of information regarding its precise composition does not allow a reliable comparison between these three compounds.



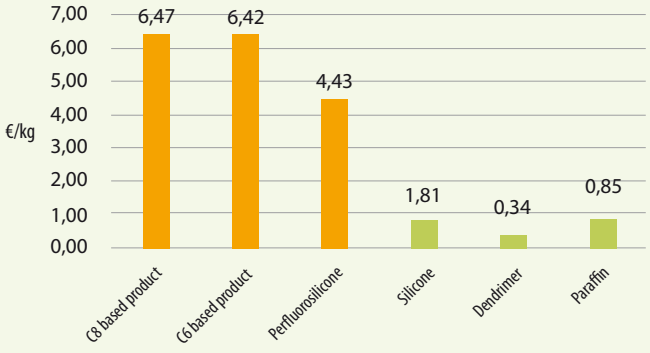
Environmental Cost

The price of fluorine-free alternatives (products shown in green) are lower than fluorinated treatments (see products marked in orange). Silicon-based repellents price is approximately the same than dendrimer-based repellents. Paraffin-based repellents are much cheaper compared to the fluorinated treatments, but require a higher dosage. The price of the perfluorosilicone assessed in the project is significantly higher than C8 and C6-based products.



DWOR purchasing costs relative to the C8-based product

In addition to purchasing costs, complementary information on the evaluation of environmental externalities (indirect costs) has been determined. Indirect costs have been estimated by converting the environmental impacts into monetary terms. The life cycle impact assessment method used for calculating the impacts of externalities is ReCiPe, which is a valid and reliable method (EC, 2010). The estimated indirect costs of producing 1 kg of DWOR products are shown in the figure below. Fluorinated products (C8, C6 and perfluorosilicone) have higher indirect costs than fluorine-free products due to the higher impact caused on the environment and human health.

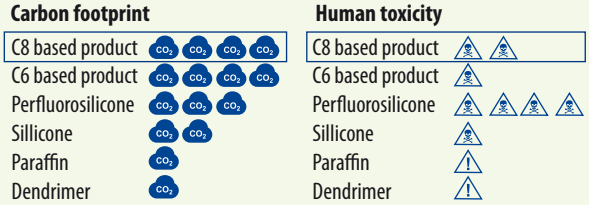


Estimated indirect costs of the production of 1 kg of DWOR product

WEB TOOL FOR INDUSTRIAL ASSESSMENT

The MIDWOR-LIFE web tool is aimed to raise awareness to the textile industry about the environmental and human health impacts of different DWOR used in textile finishing processes.
The tool provides the data visualization with pictograms to facilitate the understanding of non-experts in life-cycle assesment in addition to an extensive user guide for professionals interested to learn more about this methodology and dig deeper in the numerical values obtained.

Calculation of environmental & human health indicators



Available at: https://www.midwor-life.eu/

Results for the amount of textile treated

Qualntity of textile produced	Carbon footprimt	Water depletion	Energy consumption	Resource depletion	Human toxicity	Fresh water ecotocity
100.00	1461.16	117.84	0.00	0.05	0.00	797.06
(m^2)	(g CO2 eq)	(L)	(MJ)	(kg Sb eq)	(CTU)	(CTU)

POLICY RECOMMENDATIONS

The objective of the policy recommendations presented is to provide useful insights on how to improve and adapt the current environmentally-related policies based on the outcomes identified during the MIDWOR-LIFE project.

RECOMMENDATION FOR UPDATING THE BREF FOR THE TEXTILE INDUSTRY (TXT BREF)

TXT BREF is the document on Best Available Techniques (BAT) for the Textile Industry and it covers the industrial activities namely "Plants for pre-treatment (operations such as washing, bleaching, and mercerization) or dyeing of fibres or textiles where the treatment capacity exceeds 10 tons per day".

TXT BREF section	Recommendation
Chapter 2.9.2 Chemical finishing treatments	Proposal to include an additional point with information related to oil repellency.
Chapter 4: Techniques to consider in the determination of BAT	DWOR alternative is proposed to be added as BAT candidate for emerging technique, the hyper branched polymers (e.g. dendrimers). A new subchapter addressing DWOR products is proposed to be included.
Chapter 7.4 Recommendations for future work	To continue the work with the paraffin products: - to test the paraffin used with other type of fabrics; - to test other paraffin products.
Chapter 8: Annex I. Textile auxiliaries 8.8.5 Hydrophobic/ Oleophobic agents	A new category for dendrimers and hyperbranched polymers is proposed to be added.

RECOMMENDATION FOR UPDATING REACH ANNEXES

All selected DWOR products are **polymers** and therefore **are not subject to registration under current REACH regulation**. The potential human health and environmental impacts of DWORs are related to their content of unreacted substances and/or possible release of monomers and other degradation products. No quantitative information is available on these aspects; however, they could indeed be determining the differences in terms of human or environmental health impact.

The proposed recommendations for updating REACH make compulsory the registration of certain polymers including details of:

- Human health and environmental hazards
- Average molecular weight and oligomer content
- Presence of functional reactive groups
- Starting monomers
- Impurities
- Residual monomer content
- Degradation products

Polymers of low concern (as defined by the OECD, i.e. polymers posing low hazard to human health) should still benefit from a reduced/waived registration system.

RECOMMENDATIONS FOR UPDATING VOLUNTARY SCHEMES

EU Ecolabel

Current EU Ecolabel criteria for textile products (2014)

MIDWOR-LIFE related criteria	Key outcomes
o Criterion 13. "Restricted Substance List (RSL)" o Criterion 14. "Substitution of hazardous substances and mixtures used in dyeing, printing and finishing" o Criterion 25. "Durability of function"	Only FC-free products would meet the criteria 13 and 14, but biodegradability and bioaccumulation potential still need to be tested (not available data in SDS). One FC-free chemical has been found which would meet the durability criterion for the textile applications of sportswear/ work wear (knitted polyester).

Green Public Procurement (GPP) criteria

Current GPP criteria related to textiles (2017)

MIDWOR-LIFE related criteria	Key outcomes
o Selection criteria o Chemical restrictions o Durability and lifespan extension	Textiles manufactured with DWOR products could be purchased by public authorities; specificities are outlined to reduce their environmental impacts.

SOCIOECONOMIC IMPACT

The socioeconomic impact on the local economy and community by the implementation of the proposed alternatives and the related environmental and risk management measures into EU textile industry have been key points for MIDWOR-LIFE project.

The main actors involved in the project are:

- Textile and chemical companies
- Research centers and Universities
- Platforms/Associations
- NGO's and public/government bodies

The work has been performed in order to:

- Increase awareness and knowledge about environmental impact concerning DWOR chemicals
- Increase health safety related to the high toxicity of Perfluorinated compounds both to humans and animals
- Increase the number of jobs in the DWOR sector
- Increase the quality of and quantity of DWOR information both performance and associated health and environmental impact
- Increase the search for innovative finishing products improving the quality of the textile industry
- Optimize the domestic economy by means of more sustainable products that allow increasing textile and clothing durability.

Indicator	Value achieved	Details
Stakeholders reached	More than 200	24 Universities and Research Centers 6 Policy / Government bodies / Organisations / NGO's 15 Associations More than 200 Companies
Workshop organised	9	More than 150 participants of which more than 100 companies
International events attended	More than 20	Presenting the project in international conferences and business conventions.
Panel/Notice boards	More than 30	Displayed in events with more than 15.000 people
Individual surveyed	More than 50	Through DWOR needs survey and individual follow ups
Professional reached	More than 300	Across different networking and disseminating activities

PROJECT DISSEMINATION AND COMMUNICATION

XXIV International Congress IFATCC 2016

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

M. Martí and A. M. Manich

IQAC-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain
meritxell.marti@iqac.csic.es

Abstract: *DWOR (Durable Water and Oil Repellents) are textile finishing products made of long chain fluorocarbon polymers to give repellency to water, oil and dirt to fabrics. These chemicals are persistent and bioaccumulative. Many perfluorochemicals have already been listed in different European regulations to put emphasis on their risk for humans and the environment.*

These products have been used in the textile industry since many years ago and tentative to replace them has been done since 2000. Alternative products are currently being proposed by different chemical companies for textile applications, however, the toxicity and environmental impact of these new alternatives is still unknown. The substitution of toxic and persistent perfluorochemicals is of high importance as they occupy a high place in the market and almost all alternatives are perfluorocarbons based products (fluorocarbons polymers with shorter chain length).

The main objective of the project is to mitigate the environmental, health and safety impacts of current and future Durable Water and Oil Repellents (DWOR) alternatives by analyzing their environmental impact and technical performances, in order to assess manufacturers on the best available technologies for repellent finishing. Moreover, the risks of the DWOR alternatives will be evaluated for human and environmental health in the textile finishing industry. In this perspective, policy recommendations will be set in order to promote the widespread implementation of the less toxic and most effective DWOR alternatives to fulfill REACH Regulation.

Key Words: *Durable Water and Oil Repellents*

CONTACT:
INFO@MIDWOR-LIFE.EU
HTTPS://WWW.MIDWOR-LIFE.EU
@MIDWOR-LIFE-PROJECT

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