MIDWOR - LIFE14 ENV/ES/000670

With the contribution of the LIFE financial
instrument of the European Commission

PROJECT MIDWOR Deliverable B1.1

Report on the pre-industrial applications and characterization of DWOR and alternatives

Project acronym:	MIDWOR-LIFE
Project full title:	Mitigation of environmental impact caused by DWOR textile finishing chemicals studying their nontoxic alternatives
Grant agreement no.:	LIFE14 ENV/ES/000670
Responsible partner for deliverable:	LEITAT
Contributing partners:	Haga clic aquí para escribir texto.
Author(s):	Marolda Brouta-Agnésa (MB) ; Jordi Mota (JM)
Nature[1]:	R
Dissemination level[2]:	CO
Total number of pages:	40
Version:	2.1
Contract delivery date:	31/03/2017
Actual delivery date:	31/03/2017

Version control

Number	Date	Description	Publisher	Reviewer
0.1	20/06/2016	Initial version	MB	
0.2	15/09/2016	Alternative products reviewed	MB	
0.2	30/12/2016	Alternative products reviewed	MB	
1.0	31/03/2017	Contract deliverable	MB	A. Detrell
2.0	10/05/2017	Inclusion of Sol-gel alternative	MB	A. Detrell
2.1	26/05/2017	Public version	MB	A. Detrell

[1] **Nature of Deliverable**: **P**= Prototype, **R**= Report, **S**= Specification, **T**= Tool, **O**= Other.

[2] **Dissemination level**: **PU** = Public, **RE** = Restricted to a group of the specified Consortium, **PP** = Restricted to other program participants (including Commission Services), **CO**= Confidential, only for members of the Consortium (including the Commission Services)

Contents

1. Introduction

In the previous preliminary action A2, a pre-screening of the technical performance (task A2.1) and of the environmental impact (task A2.2) of the selected DWORs has been done according to the information available on the state of the art, scientific databases and suppliers' information. At the end of this action A2, nine DWORs products (long chain fluorocarbons C8, short chain fluorocarbons C6, perfluorosilicones, silicones and sol-gel products) have been studied according to suppliers' information and the information available in the scientific and technical bibliography.

In this action B1 (task B1.1), those products have been studied more deeply by applying them on the selected fabrics and by characterizing their technical performance (task B1.3).

The results of the survey from the preliminary action A1 help to identify the textile application sectors more affected by the PFOA and PFOS contaminants issue. According to these sectors, five fabrics suitable for five different textile applications have been selected, which represent the main sectors affected by the long chain perfluorocarbon issue. Indeed, fabric number 3 (195 g/m2, 100% PES, sport - mountain) and fabric number 8 (175g/m2, 100% PES, work wear - polo) from deliverable A1.1 are similar and only fabric number 8 has been selected for both application sectors. The difference between these fabrics resides in their weaving structure, weight, density and composition. Then, the DOW specified that 9 repellent products should be tested but we finally studied 12 finishing products.

The present deliverable explains how the 12 DWOR repellents have been applied on the different fabrics and the results obtained (technical performance before and after ageing).

In the next deliverable "Report on the industrial applications and characterization of DWOR and alternatives", the most representative and effective alternatives of DWORs will be selected and analysed (performance, environmental impact and risk assessment).

The next figure presents briefly the work done in preliminary actions, how this work has been used for implementation actions (at pre industrial scale – Task B1.1) and how it will be transferred to the industrial scale (Task B1.2).

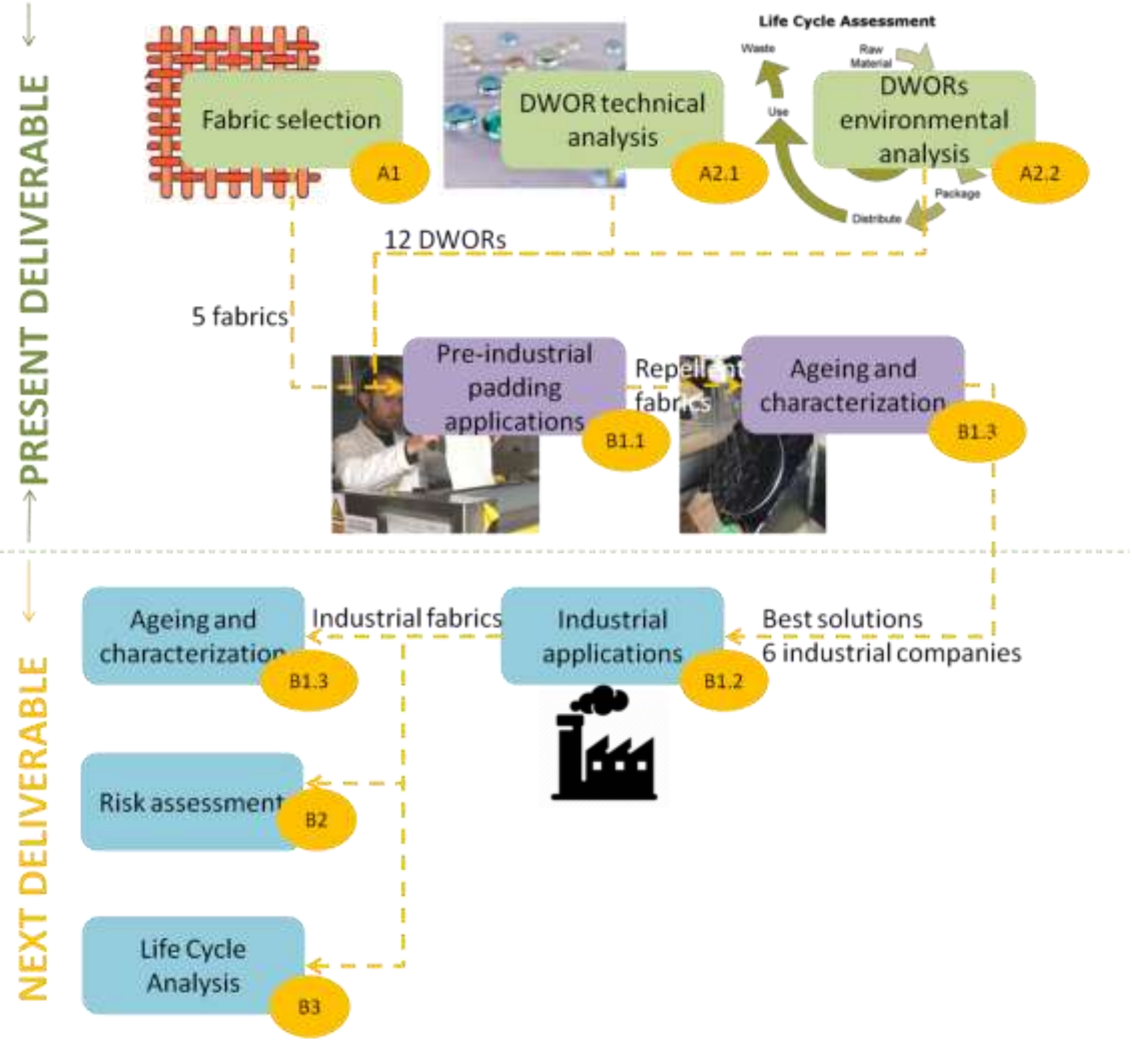


FIGURE 1 REPRESENTATION OF THE PROGRESS OF THE PROJECT.

2. Final selection of fabrics

The fabric selection has been made according to the results of the survey to the textile industries. This selection has been made as well after contacting different companies, suppliers and experts in the use of durable water and oil repellents in the textile industry. The most relevant textile sectors for the application of DWORs have been selected first (automotive, fashion, sportswear, work wear and upholstery). Then, the most representative fabrics for each sector have been defined.

The fabric selection has been updated from the initial selection (deliverable A1.1) with similar textiles (but different weight or slightly different composition). The fabric characteristics are more specific to their final application and have been suggested by the industrial companies working with fluorocarbon finishing products.

This part presents the importance of each sector in the use of long chain fluorocarbons for water and oil repellence. The fabric selected for each sector is also described.

2.1. Automotive

ar floor mats)

Textiles are found in high quantities in cars in woven type (seats cover or door panels) and in nonwoven type (carpets, interior facings, under-the hood fabrics, etc.). Some of the nonwovens employed in the automotive industry require a high level of water and oil repellency to achieve antistain properties. Most common compositions are 100% polyester (PES) fabric (mostly for the nonwovens parts) and sometimes blended with natural fibres.

The fabric selected for the automotive sector is presented in the next table.

Sector	Automotive
Application example	Fabric for carpets
Composition	100 % polyester
Structure	Punching nonwoven
Weaving structure	-
Weight	210 g/m^2
Colour	Light grey
Picture	

TABLE 1. AUTOMOTIVE FABRIC DATA SHEET

2.2. Fashion

ion textiles

The consumption of water repellent finishing in the fashion sector is highly present. Fashion is one of the textile branches where more restrictions of PFOAs and PFOSs contaminants are claimed due to social aspects. Many organizations such as Greenpeace [3], ECHA [4] and others regulatory bodies [5] are making pressure to avoid the use of long chain fluorocarbons in the clothing industry. Fashion industry is the most pointed sector concerning the perfluoroalkyl acids (PFAAs) by-products issue. The consumer demand of water and oil repellency on garments from the fashion industry has increased the last few years[6]. However, the performance requirements of this industry on the DWOR market is still less than the performance requirements of the technical textiles segment[7].

Polyester is highly used in the fashion industry, blended with cotton. As this fibre has been selected for the other application sectors of the project, another fibre nature (also important in the fashion industry) has been selected: wool. Also, wool is the main fabric

[3] PFC Revolution in the Outdoor Sector, Greenpeace, Feb 2017.
[4] ECHA Annex, RAC concludes on PFOA restriction. The Committee finalises two opinions for authorisation, and adopts six opinions on harmonised classification and labelling. September 2015.
[5] Directive 2006/122/EC, European REACH regulation
[6] C.N. Shivarama Krishnan, Water and oil repellent finishes. Fibre2Fashion.
[7] Durable Water and Soil repellent chemistry in the textile industry – a research report. P05 Water Repellency Project. 2012.

composition used by one of the supporting companies for the industrial application (Task B1.2). The selected fabric is presented in the next table.

Sector	Fashion
Application example	Fabric for suits
Composition	100 % wool
Structure	Woven
Weaving structure	Twill weave
Weight	180 g/m^2
Colour	Dark blue
Picture	

TABLE 2. FASHION FABRIC DATA SHEET

2.3. Sportswear

orts wear

Source: Flickr

The demand of multifunctional sportswear fabrics is expected to increase more over the coming years. Waterproof property can be applied in a wide range of textiles for outdoor sports in general such as tents, backpacks, jackets, etc.[8] For waterproof textiles, polyurethane dispersions are applied on sportswear to achieve this property. However, the surface tension required to achieve oil repellency is more difficult to achieve with silicones, dendrimers or very short chain fluorocarbon polymers. Oil repellency is required for example in products such as shirts, jackets, skirts, pants or luggage7. Many well-known sportswear brands (Adidas, Nike, Puma...) collaborate with Greenpeace under the Detox campaign to eliminate the use of toxic substances such as PFC (perfluorinated compounds) from their production chain by 2020[9,10,11].

[8] Market Research Report, Waterproof Breathable Textiles Market Size, 2016.
[9] Greenpeace. Detox My Fashion.
[10] Greenpeace. A Red Card for sportswear brands. May 2014.
[11] Greenpeace. Which fashion brands are going toxic-free? July 2016.

The fabric selected for the sportswear sector is presented in the next table.

Sector	Sportswear
Application example	Fabric for t-shirt
Composition	100 % polyester
Structure	Knitted
Weaving structure	Jersey piqué
Weight	175 g/m^2
Colour	Dark blue
Picture	

TABLE 3. SPORTSWEAR FABRIC DATA SHEET

2.4. Workwear

Source: Flickr

Vorkwear

Workwear is another textile sector where the necessity to achieve high water and oil repellency is high. In most cases, fabrics for workwear have to provide good water, oil and even petroleum repellency, which is up to date achieved with long chain fluorocarbon materials. Main workwear clothes include fabrics for industry workers, medical sector, uniforms, military clothes, corporate wear for hotel or restaurants. In the workwear branch, water and oil repellency can be combined with others functionalities such as flame retardancy for fire fighters or antimicrobial properties for medical clothes.

The fabric selected is the common used in polo shirts. It has the same characteristics than the fabric selected for sportswear t-shirt.

Sector	Workwear
Application example	Fabric for polo shirt
Composition	100 % polyester
Structure	Knitted
Weaving structure	Jersey piqué
Weight	175 g/m^2
Colour	Dark blue
Picture	

TABLE 4. WORKWEAR FABRIC DATA SHEET

2.5. Upholstery

Upholstery fabrics such as sofa fabrics, curtains or cushions present more difficulties than clothes to be washed. Also, their domestic washing and drying is complicated (such as sofas, for example). However, textiles for upholstery are exposed to water and oil-based stains and require high abrasion and wear resistance. Due to these reasons, these kinds of fabrics have to present good and durable water repellency or stain release.

Upholstery

The fabric selected for the upholstery sector is presented in the next table.

Sector	Upholstery
Application example	Fabric for sofas
Composition	100 % polyester
Structure	Woven
Weaving structure	Woven
Weight	250 g/m^2
Colour	Dark blue
Picture	

TABLE 5. UPHOLSTERY FABRIC DATA SHEET

Different fabrics representing five textile sectors (employing high quantities of DWORs) have been selected and are presented in the next figure.

FIGURE 2. FABRICS SELECTION AND APPLICATION ACCORDING TO THE TEXTILE SECTORS.

3. Final selection of DWOR products

Many DWOR products have been studied in the previous actions. Their theoretical analysis and comparison has been made according to surveys, scientific database research, review articles, auxiliary, finishing and end user companies' feedback. Different products have been selected taking into account their chemistry (long chain C8, short chain C6, hybrid silicones and perfluoropolymers, silicones and sol gel).

This part make a short description of each product selected. We studied two long chain fluorocarbon products (C8), seven short chain fluorocarbon products (C6), one hybrid fluorinated and silicone product, one silicone based product and one sol gel product. C8 are considered as the conventional product and the others as the alternatives which are actually proposed on the market. The next part (4. Application process) will indicate if these products can be considered as good alternatives to C8 from a technical point of view. Action B2 and B3 will consider risk assessment and environmental impact of those DWOR alternatives.

3.1. Conventional DWORs based on long-chain fluorocarbon (C8)

The products identified as long-chain fluorocarbon (C8) and selected for the next activities are the following:

Product 2A is a permanent stain repellent finish for cellulosic, wool and silk and is specifically recommended for synthetic.

Product 2B is a permanent stain repellent finish for cellulosic, polyester, polyamide and wool fibres and their blends. Particularly good effects can be obtained on cellulosic fibres.

3.2. Alternative DWORs

After contacting with the chemical industries, the repellent finishing selection has been updated as following:

Products 3 is an oil, water and stain repellent finish of cotton, viscose, synthetic / cellulose and synthetics for special end uses.

Product 3A is a repellent finishing including oil, water and stain protection of cellulose, synthetic / cellulose and synthetic fabrics for protective clothing.

Products 3B is a durable water repellent treatment for fabrics, textiles, and nonwovens. It is manufactured with renewably sourced, non-fluorinated, plant-based material that can be replenished naturally over time.

Product 6A is a permanent water and oil and stain repellent finish on all kind of fabrics (native or man-made substrates).

Product 6B is a durable water and oil repellent treatment and coating of pure cotton, polyester or polyamide and their blends with cotton.

Product 6C is a permanent oil and water repellent finish on all kind of fabrics, especially for non-woven made of synthetics.

Product 6D is a durable water and oil repellent product made for pure cotton, polyester or their blends.

Product 8 provides excellent water and oil repellency to all types of fabric substrates. It is not based on C-8 fluoroalkyl compounds, resulting in a PFOA-free product. Its performance is durable through extended home laundering.

Product 9 is a permanent to washing and dry cleaning reactive silicone emulsion gives durable waterproof finish and softening properties to both cellulosic and polyester fabrics and their blends. On cellulosic fibres, it is generally used with thermosetting resins. It is both formaldehyde and fluorocarbon free and complies with the Öko Tex Standard 100.

Product 10 is a fluoroalkylfunctional water borne oligosiloxane which acts as a surface modification agent on hydroxyfunctional substrates like cotton (by covalent bonding). This product can form a three dimensional network on the substrate surface, then we will check if a physical (not covalent) linking can be made on polyester fabrics.

A model of its chemistry is deduced in the next figure:

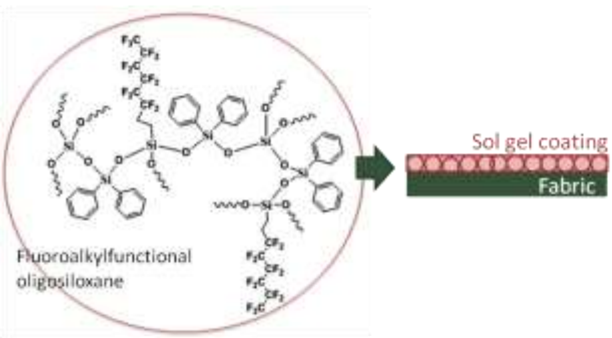


FIGURE 3. GENERAL REPRESENTATION OF THE WATER AND OIL REPELLENT SOL GEL SOLUTION[12]

3.3. Products summary table

A summary of the selected products is presented in the next table:

Num	Technology	Chemistry	Composition
2A	conventional	C8	Aqueous preparation of perfluoro acrylic copolymer
2B	conventional	C8	Acrylic- perfluoroalkyl-copolymer
3	alternative	C6	Dispersion of a fluoroacrylate copolymer
3A	alternative	C6	Dispersion of a fluoroacrylate copolymer
3B	alternative	C6	Alkyl urethane
6A	alternative	C6	Perfluoroalcylpolyacrylate and additives
6B	alternative	C6	Fluoralkyl acrylate copolymer
6C	alternative	C6	Perfluoroalcylpolyacrylate
6D	alternative	C6	perfluoro acrylic copolymer in water
8	alternative	Perfluorosilicones	Fluoralkyl acrylate copolymer
9	alternative	Silicones	Silicone emulsion
10	alternative	Sol gel	Fluoroalkylfunctional water borne oligosiloxane

TABLE 2. PRODUCTS SELECTED

4. Application process

4.1. Padding process description

Padding is a conventional technique in which the fabric is submerged in a textile auxiliary bath and then squeezed between two squeeze rollers by setting a certain pressure and speed. The amount of finishing solution or emulsion applied is referred as the wet pick-up of the fabric and is usually expressed as a weight percentage on the untreated fabric.

After the application of the chemical finish, the fabric is dried to eliminate the water and cured to fix the finishing on the fiber surface.

[12] S. Park et al. Synthesis and characterization of a fluorinated oligosiloxane-containing encapsulation material for organic field-effect transistors, prepared via a non-hydrolytic sol–gel process. Organic Electronics 13, 2786–2792. 2012.

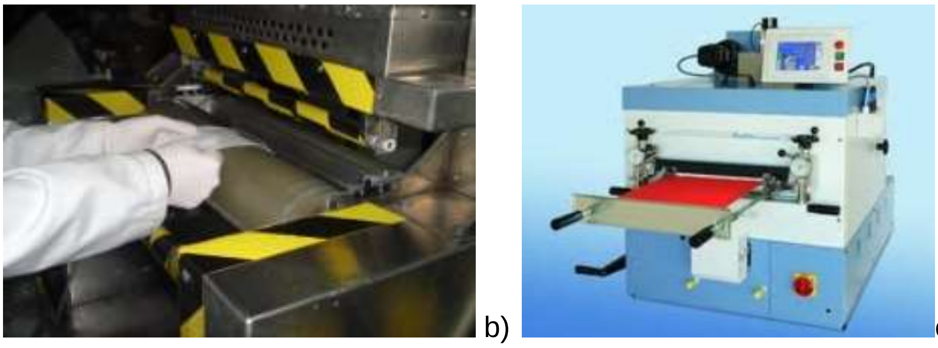
a)  b) ç

FIGURE 4. A) REPRESENTATION OF THE PADDING AND B) THE DRYING AND CURING PROCESS AT LABORATORY SCALE.

The process parameters have been varied taking into account the supplier recommendations in order to determine the best conditions to achieve the highest water and oil repellency. Parameters such as padding velocity, padding pressure, drying and curing temperatures, bath pH and product concentration has been studied (see Table 3). The fabric pick up value has been calculated in each case.

The optimum application conditions detected for each product type is detailed in the next part.

4.2. Application conditions by product type

Each product has different application conditions to achieve its best water and oil repellency. These conditions are presented in the next table, by product type:

Reference	Concentration. [g/L]	P (bar)	Drying	Curing
2A.1	20	3	120ºC-7min	160ºC-1,5 min
2A.2	30	3	120ºC-7min	160ºC-1,5 min
2B	35	3	110ºC-8min	160ºC-1,5 min
3.1	30	3	110ºC - 7 min	150ºC - 3 min
3.2	50	3	110ºC - 7 min	150ºC - 3 min
3A	70	3	120ºC-7min	160ºC-1,5 min
3B	45	3	120ºC-7min	160ºC-1,5 min
6A	40	3	110ºC-8min	150ºC-2 min
6B	33	3	110ºC-8min	160ºC-1,5 min

6C	30	3	110ºC-8min	150ºC-3 min
6D	37	3	110ºC-8min	160ºC-1,5 min
8.1	20	3	110ºC-8min	160ºC-1,5min
8.2	60	3	110ºC-8min	160ºC-1,5min
9.1	30	3	110ºC - 8 min	150ºC - 1,5 min
9.2	60	3	110ºC - 8 min	150ºC - 1,5 min
10	100	3	110ºC - 8 min	150ºC - 1,5 min

TABLE 3. APPLICATION CONDITIONS BY PRODUCT TYPE

4.3. Summary of treated samples

A summary of the samples treated in this action B1.1 is presented in the next table. In green, the samples which have been developed and in grey the samples which have been discarded due to low affinity with the substrate or low effectiveness at the defined concentration.

	Chemistry	AUTO FABRIC	FASHION FABRIC	UPHOLSTERY	SPORTSWEAR / WORKWEAR
2A.1	C8				
2A.2	C8				
2B	C6				
3.1	C6				
3.2	C6				
3A	C6				
3B	C6				
6A	C6				
6B	C6				
6C	C6				
6D	C6				
8.1	Perfluorosilicone				
8.2	Perfluorosilicone				
9.1	Silicone				
9.2	Silicone				
10	Sol gel				

TABLE 4. SAMPLES DEVELOPED AT INDUSTRIAL SCALE AND BEFORE AGEING

Once these samples have been obtained, they have been characterized by spray test, oil test and contact angle analysis. Then, they have been subjected to different ageing tests. Ageing has been taken into account since it can affect the technical performance of the products. Also, ageing could identify clearly which solution is the most effective under real conditions of use.

5. Characterization

This part presents the characterization tests done in the MIDWOR project, the ageing test of the treated samples and the results obtained before and after ageing, at pre-industrial scale.

5.1. Characterization tests description

AATCC 22 and UNE EN ISO 4920: Water repellency – Spray test

This standard measures the resistance of fabrics to wetting by water or the water repellency of fibres. In Figure 5 the Spray Test Ratings are presented:

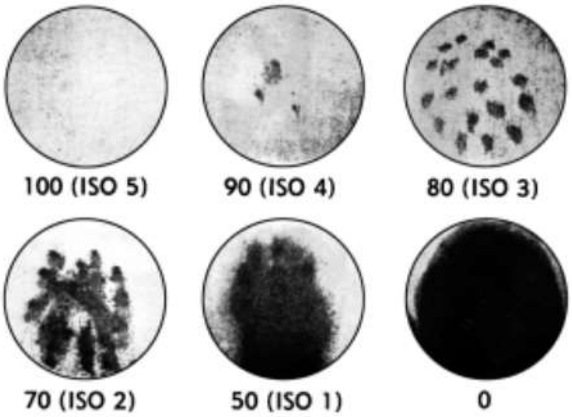


FIGURE 5. STANDARD SPRAY TEST RATINGS

- 100 (ISO 5): No wetting of the specimen face
- 90 (ISO 4): Slight random wetting of the specimen face
- 80 (ISO 3): Wetting of specimen face at spray points
- 70 (ISO 2): Partial wetting of the specimen face beyond the spray points
- 50 (ISO 1): Complete wetting of the entire specimen face beyond the spray points
- 0: Complete wetting of the entire face of the specimen

FIGURA 1. SPRAY TEST EXEMPLE

AATCC 118 and UNE EN ISO 14419: Oil repellency – Hydrocarbon Resistance Test

The AATCC Oil Repellency Grade is the numerical value of the highest-numbered test liquid which will not wet the fabric within a period of 30 sec. A grade of 0 is assigned when the fabric fails the Kaydol test liquid.

AATCC Oil Repellency Grade Number	Composition
0	None (Fails Kaydol)
1	Kaydol
2	65:35 Kaydol: n-hexadecane by volume
3	n-hexadecane
4	n-tetradecane
5	n-codecane
6	n- cecane
7	n-octane
8	n-heptane

TABLE 5. STANDARD TEST LIQUIDS – AATCC 118

In Figure 5 can be seen an example of the rating criteria:

- A: Passes – clear, well-rounded drop
- B: Borderline pass – rounding drop with partial darkening
- C: Fails – wicking apparent and/or complete wetting
- D: Fails – complete wetting

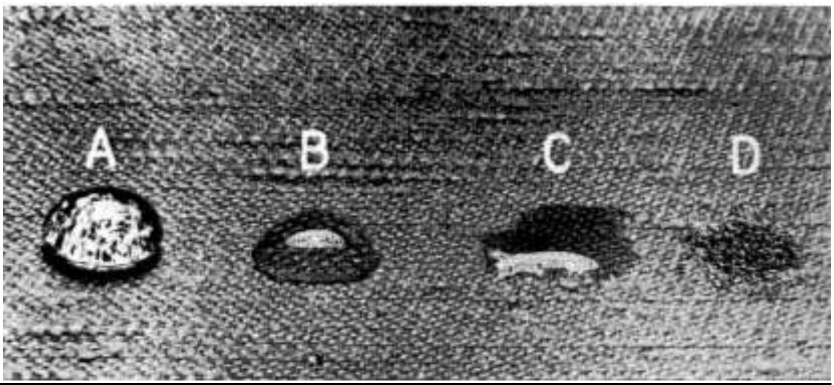


FIGURE 6. AATCC 118 GRADING EXAMPLE

Contact angle

The dynamic contact angle measurements are performed using a Krüss K100 tensiometer by immersion / emission of sample in deionized water. The advancing angle is determined during the immersion process and the movement back angle during the emersion process.

We previously measured the wetted perimeter of the sample (WL) using n-hexane, a liquid with low surface tension (σ_{hexane} = 18.4 mN / m at 20 ° C) and high movement capacity (perfect wetting assumption: contact angle = 0 °). The WL depends on the geometry of the sample and this value is the one used for the calculation of the contact angles. Knowing the value of WL and the surface tension of the liquid (in this case: σ_{water} = 72.8 mN / m, at 20 ° C), the value of the contact angle θ is calculated through the Wilhelmy equation using the advancing and receding wetting force (F) detected by the tensiometer:

$$\theta = arccos\left(\frac{F}{WL \cdot \sigma}\right)$$

5.2. Ageing tests description

The objective of ageing the treated samples is to determine the durability of the water and oil repellency under real use conditions. The ageing tests which have been done include: washing (excepted for wool), dry-cleaning (for wool) and ironing. The ageing tests conditions are detailed next:

Washing

Domestic washing has been performed using the standard UNE EN ISO 6330. Washing temperature was 30ºC. 10 cycles have applied in order to observe differences after and before washing but without exceeding the washing fastness of the finishing. The samples have been dried in a flat way after washing and conditioned 24 hours at 20ºC±2ºC and 65%±5% r.h[13] before the next evaluation (spray test, oil test and contact angle).

Dry cleaning

Dry cleaning has been performed under the standard UNE EN ISO 3175-2. Only 1 cycle have been made as dry-cleaning is a very aggressive treatment and the fabric is destined to suits application. The samples have been dried in a flat way after washing and conditioned 24 hours at 20ºC±2ºC and 65%±5% r.h before the next evaluation (spray test, oil test and contact angle).

Ironing

Hand ironing has been performed after domestic washing or dry cleaning, at 150ºC. Then, the samples have been conditioned 24 hours at 20ºC±2ºC and 65%±5% r.h before the next evaluation (spray test, oil test and contact angle).

[13] Relative Humidity

The treated samples presented in the previous Table 4 have been washed or dry cleaned and ironed. Spray test, oil test and contact angle have been performed after each ageing test. However, not all ageing tests have been performed on all fabrics since it depends on their final application (for example, the automotive fabric has not been washed and the upholstery fabric has not been ironed). The next table presents the tests performed on each fabric depending on their final application.

		AUTO FABRIC	FASHION FABRIC			UPHOLSTERY		SPORTSWEAR / WORKWEAR		
	Chemistry	Original	Original	Dry cleaned	Ironed	Original	Washed	Original	Washed	Ironed
2A.1	C8									
2A.2	C8									
2B	C6									
3.1	C6									
3.2	C6									
3A	C6									
3B	C6									
6A	C6									
6B	C6									
6C	C6									
6D	C6									
8.1	Perfluorosilicone									
8.2	Perfluorosilicone									
9.1	Silicone									
9.2	Silicone									
10	Sol gel									

TABLE 6. FABRICS CHARACTERIZED BEFORE AND AFTER AGEING

5.3. Results

In order to analyze the results, the water and oil repellency results are presented for each fabric. The different chemistries are compared and the influence of ageing (washing fastness and ironing) has been identified. All parameters are presented in the next figure:

4 fabrics
Automotive fabric
Suit fabric

5
C8
C6
Perfluorosilicone
Silicone
Sol gel

2
Water repellency
Oil repellency

2 ageing
Original
Washing
Ironing

FIGURE 7. PARAMETERS OF THE PRE-INDUSTRIAL STUDY

Water and oil repellency has been determined for all the fabrics.

Due to low affinity with the substrate (product not recommended by the supplier for certain textile compositions), not all the products have been applied on all the fabrics.

Ageing has been done according to the fabric final application.

The parameters studied for each fabric is presented in the tables at the beginning of each part.

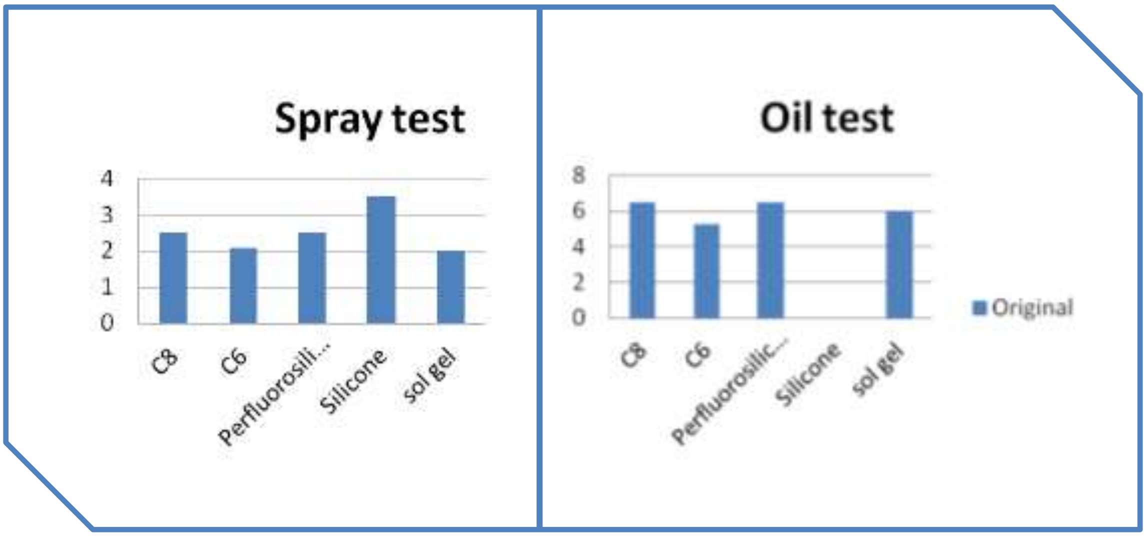
AUTOMOTIVE FABRIC (CARPETS)

The next table presents the parameters tested on the automotive fabric (nonwoven for carpets).

	AUTOMOTIVE FABRIC	Comments
Analysis	All (Water and oil repellency)	
Chemistries	All (C8, C6, Perfluorosilicone, silicone, sol gel)	
Ageing	No ageing	No washing and ironing is required for nonwoven carpets

TABLE 7. PARAMETERS STUDIED FOR AUTOMOTIVE FABRICS

The next graphs compare the oil and water repellency of the different chemistries on the original (unwashed, not ironed) fabric. An average value of each chemistry is given (two C8 products, seven C6 products, one perfluorosilicone, one silicone and one sol gel).



GRAPH 1. AUTOMOTIVE FABRICS RESULTS

Discussion:

The grade number value is indicated on the ordinate axis for the spray test (according to UNE EN ISO 4920 standard) and the oil test (according to the AATCC 118 or UNE EN ISO 14419 standards). Maximum grade number according to the standard for Spray test and Oil test is 5 and 8, respectively.

The variability of the method is of 1 or 2 points approx. depending on the test area, the type of fabric and the type of finish.

Water repellency:

According to the graph, silicone chemistry is more effective for water repellency on polyester nonwovens than others chemistries (C8, C6, perfluorosilicone and sol gel). This is due to the fact that the fluorocarbon polymers need to form a comb-like structure on the substrate (after curing) to provide optimum water and oil repellency (see next picture).

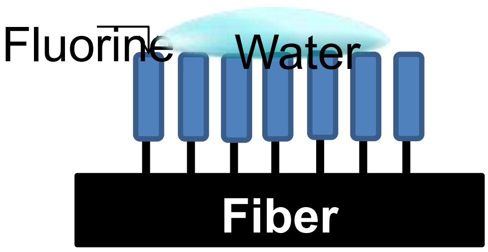


FIGURE 8. FLUOROCARBON POLYMERS COMB-LIKE STRUCTURE

This structure is more difficult to achieve on hairy and irregular surfaces[15] such as nonwovens. Water and oil repellency is easier to achieve when a uniform distribution of the finishing is made. Uniform coating is more difficult to achieve on nonwovens due to the protruding fibers. Moreover, singeing (burn the protruding fibers) or shearing (cut the protruding fibers) processes are advised before treatment in order to improve the water or oil repellency[15]. Both surface chemistry and roughness are important factors to achieve good water and oil repellency[14].

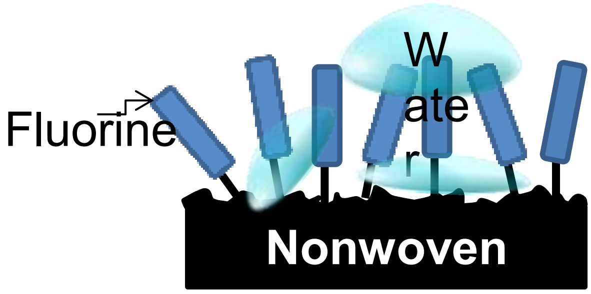


FIGURE 9. FLUOROCARBON POLYMERS STRUCTURE ON IRREGULAR NONWOVENS

Oil repellency:

Silicone product does not present oil repellency. The surface energy of a substrate must be lower than the surface energy of the liquid it wants to repel. Water, oil and silicone surface energy are 72 mN/m, 20 - 35 mN/m and 20 - 30 mN/m, respectively (see next table).

Then silicone finishing repel water but does not repel oil.

Material	Surface energy (mN/m)
Water	72
Oil	20 - 35
Silicone	20 - 30
Fluorocarbons	10 -20

TABLE 8. SURFACE ENERGY OF DIFFERENT MATERIALS[15]

Fluorocarbon based chemistries have lower surface energy than oil, then provide good oil repellency to the substrates they are treated with (see next figure).

[14] J. Song and O. J. Rojas. Approaching super-hydrophobicity from cellulosic materials: A Review. Nordic Pulp & Paper Research Journal Vol 28 no. 2/2013.
[15] Tanveer Ahmed. Repellent finishes. From Textile Finishing Book.

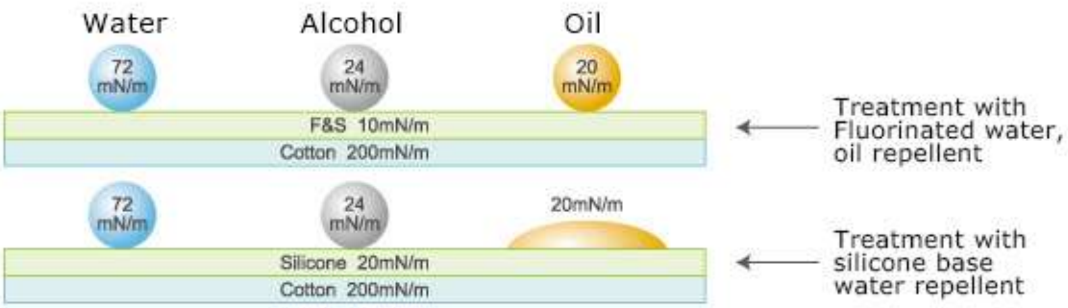


FIGURE 10. WATER AND OIL REPELLENCY MECHANISMS ACCORDING TO THE FINISHING CHEMISTRY (SILICONE OR FLUORINATED)

(SOURCE: TAIWANFLUORO TECHNOLOGY. FLUORINE-BASED WATER REPELLENT, OIL REPELLENT PRODUCT CHARACTERISTICS)

On the other hand, sol gel and perfluorosilicone alternatives present good oil repellency compared to conventional C8 chemistry. These products can be considered good alternatives to C8 chemistry. The sol gel reaction between dodecyl(trimethoxy)silane (DTMS) and tetraethyl orthosilicate (TEOS) precursors and fixation on cellulosic substrates (on polyester substrates, a physical fixation is obtained, not chemical) is presented next:

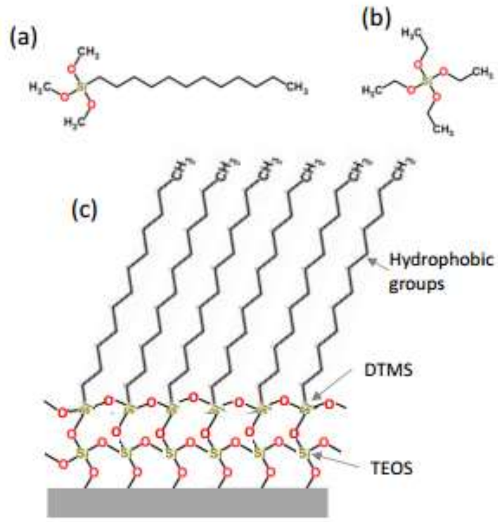


FIGURE 11. CHEMICAL STRUCTURE OF DTMS (A) AND TEOS (B) AND A SCHEMATIC DIAGRAM OF SOL GEL FILMS FORMATION ON CELLULOSIC FABRICS (C).[14]

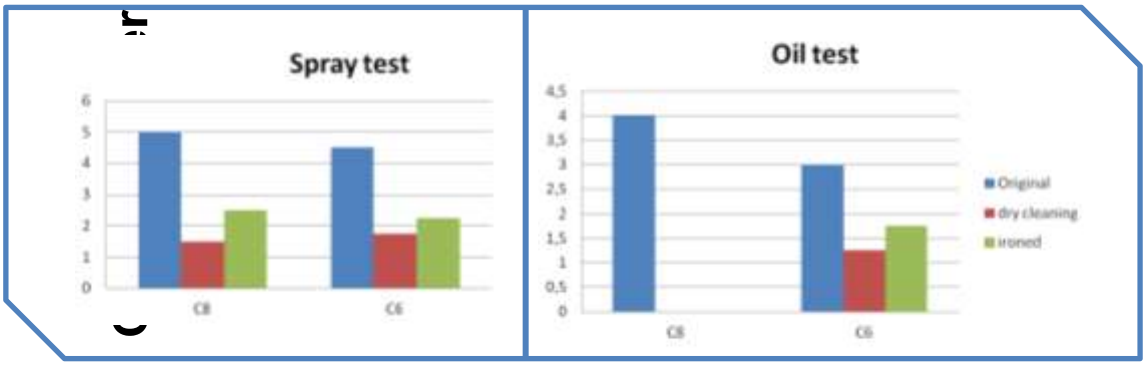
SUIT FABRIC

The next table presents the parameters tested on the suit fabric.

	SUIT FABRIC	Comments
Analysis	All (Water and oil repellency)	
Chemistries	C8 and C6	Perfluorosilicone, silicone and sol gel chemistries are not indicated for woolen fabrics by the supplier
Ageing	Dry cleaning Ironing	Domestic washing is not indicated for woollen fabrics

TABLE 9. PARAMETERS STUDIED FOR SUIT FABRICS

The next graphs compare the oil and water repellency of the different chemistries on the original, dry cleaned and ironed fabric. An average value of each chemistry is given (two C8 products and two C6 products).



GRAPH 2. SUIT FABRICS RESULTS

Discussion:

The grade number value is indicated on the ordinate axis for the spray test (according to UNE EN ISO 4920 standard) and the oil test (according to the AATCC 118 or UNE EN ISO 14419 standards). Highest grade number for Spray test and Oil test is 5 and 8, respectively.

The variability of the method is of 1 or 2 points approx. depending on the test area, the type of fabric and the type of finish.

Water repellency:

On wool fabric, water repellency of the alternatives C6 is close to water repellency of C8 chemistry. However, both chemistries present low washing fastness on wool. Cellulosic substrates have more affinity (permanent bonding) with fluorinated polymers than wool fabrics due to the presence of hydroxyl groups which can easily react with fluorocarbon polymers or silicone (see next picture).

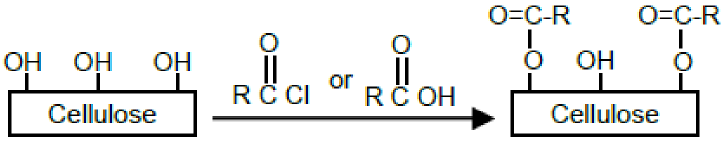


FIGURE 12. ESTERIFICATION REACTION OF CELLULOSE WITH ACID OR ANHYDRIDE AND A LONG CHAIN FLUOROCARBON POLYMER (R)[14].

On the other hand, ironing has restored (but not fully) the water repellency performance. Indeed, heat is responsible of orienting the fluorinated chain in a vertical position providing high hydrophobicity (see Figure 8. Fluorocarbon polymers Comb-like structure).

Oil repellency:

C8 chemistry obtained better oil repellency than C6 chemistry, but lower washing fastness than C6 products.

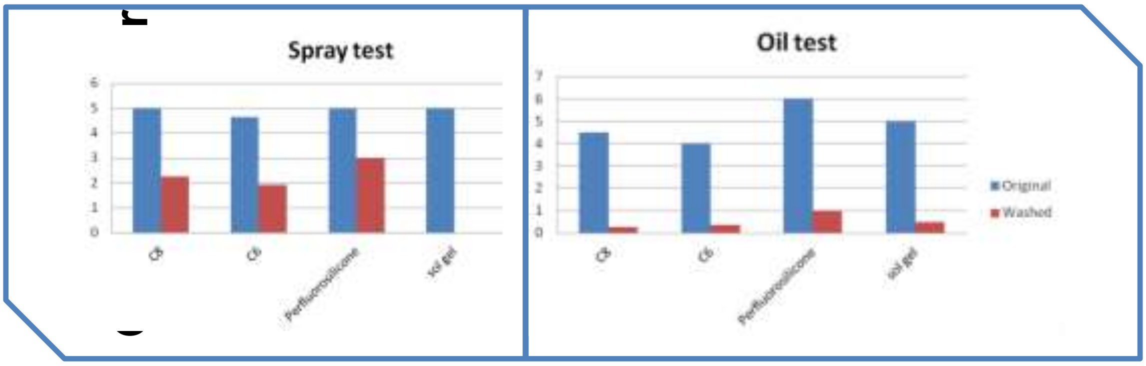
UPHOLSTERY FABRIC

The next table presents the parameters tested on the upholstery fabric.

	UPHOLSTERY FABRIC	Comments
Analysis	All (Water and oil repellency)	
Chemistries	C8, C6, Perfluorosilicone and sol gel	
Ageing	Washing	Ironing was considered not necessary for upholstery fabrics

TABLE 10. PARAMETERS STUDIED FOR UPHOLSTERY FABRICS

The next graphs compare the oil and water repellency of the different chemistries on the original and washed (not ironed) fabric. An average value of each chemistry is given (two C8 products, seven C6 products, one perfluorosilicone and one sol gel).



GRAPH 3. UPHOLSTERY FABRICS RESULTS

<u>Discussion:</u>

The grade number value is indicated on the ordinate axis for the spray test (according to UNE EN ISO 4920 standard) and the oil test (according to the AATCC 118 or UNE EN ISO 14419 standards). Maximum grade number for Spray test and Oil test is 5 and 8, respectively.

The variability of the method is of 1 or 2 points approx. depending on the test area, the type of fabric and the type of finish.

Water repellency:

The alternatives C6, perfluorosilicone and sol gel products showed very good water repellency (similar to C8 products).

Regarding washing fastness, sol gel product is not resistant to washing as the silanol groups of the finishing don't have reactive groups to react with on the surface. On polyester substrates, a physical adhesion of the coating layer take place giving good hydrophobicity (and oleophobicity). However, this layer is mechanically washed off during laundry implying that the fabric loose effectiveness. A better wash fastness is required for sol-gel finishing on polyester as DWOR alternative product.

Regarding the perfluorosilicone finishing, we can see that it achieved better washing fastness than the C8 products. This result is important meaning that the new chemistry is very effective in replacing long chain fluorocarbon polymers. This result has been observed on automotive, upholstery, sportswear and work wear fabrics.

This new hybrid technology also firmly anchors fluorine chains for superior repellency. This difference may be responsible of the highest oil repellency of perfluorosilicone compared to C8, showed in the Graph 3.

Oil repellency:

Perfluorosilicone and sol gel products present both better oil repellency than C8 products.

For the same reasons explained before, the new hybrid technology of perfluorosilicone (dual chemistry and strong anchors) seems to be more effective than C8.

Sol gel product obtained good results for oil repellency as it combines the fluorocarbon chemistry with the formation of a nanolayer on the fabric surface. Moreover, the sol gel product employed is a FAS 13, which is has 6 carbons linked to fluorine. But his ability to avoid PFOA and PFOS to the environment should be determined since the chemistry is different.

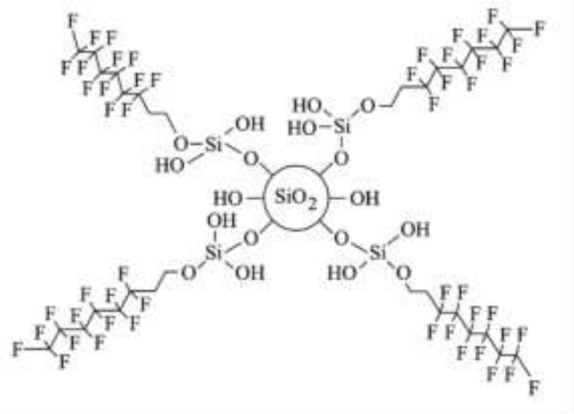


FIGURE 13. REPRESENTATION OF A FLUOROALKYL SILANE COMPONENT[16].

All the products present very low washing fastness, including the C8 products. This is due to the irregular surface of the fabric (hairy and velvet surface). The coating with the repellent products were not uniform and the comb-like structure were more difficult to achieve on such fabric[15]. For sol gel product, this low washing fastness is also due to the fact that the fixation of the coating layer is physical (not chemically bonded).

[16] Hydrophobic coating material and method for manufacturing the same. Patent number US 20130089670 A1. 2013.

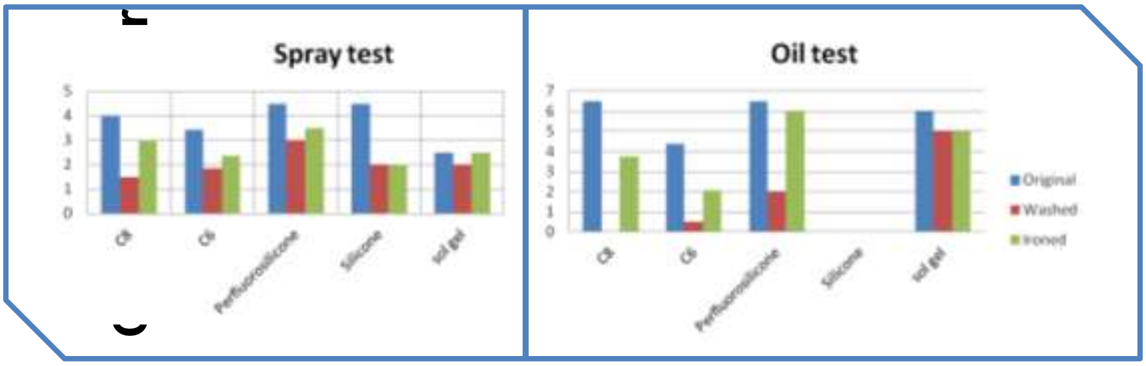
SPORTSWEAR / WORKWEAR FABRIC

The next table presents the parameters tested on the sportswear / work wear fabric.

	SPORTSWEAR / WORK WEAR FABRIC
Analysis	All (Water and oil repellency)
Chemistries	All (C8, C6, Perfluorosilicone, silicone, sol gel)
Ageing	Washing and ironing

TABLE 11. PARAMETERS STUDIED FOR SPORTSWEAR AND WORK WEAR FABRICS

The next graphs compare the oil and water repellency of the different chemistries on the original, washed and ironed fabric. An average value of each chemistry is given (two C8 products, seven C6 products, one perfluorosilicone, one silicone and one sol gel).



GRAPH 4. SPORTSWEAR / WORK WEAR FABRICS RESULTS

Discussion:

The grade number value is indicated on the ordinate axis for the spray test (according to UNE EN ISO 4920 standard) and the oil test (according to the AATCC 118 or UNE EN ISO 14419 standards). Maximum grade number for Spray test and Oil test is 5 and 8, respectively.

The variability of the method is of 1 or 2 points approx. depending on the test area, the type of fabric and the type of finish.

Water repellency:

For sportswear and work wear fabrics, the perfluorosilicone and silicone products present very good water repellency. Washing fastness of silicone product is low. Ironing restored (not fully) the water repellent property of all chemistries except silicones. Indeed, silicones do not have better liquid repellent properties after a potential reordering of their polymeric chains under the action of heat.

Oil repellency:

For oil repellency as well, the perfluorosilicone product obtained best results (before and after washing, even if washing fastness is very low). Sol gel product obtained good results and present a very good washing fastness. This result can be due to the fact that the adhesion of the nanolayer is better on flat and regular substrates (sportswear / work wear fabric) than on irregular automotive nonwoven or upholstery velvet fabric.

Contact angle

Contact angle measurements are still running. This result is expected for beginning of June 2017.

6. Conclusions

Nine finishing products were planed to be analyzed according to the proposal but finally 12 products have been studied, thanks to the collaboration of textile auxiliary companies.

6.1. Chemistry

The most interesting result is the very good water and oil repellency demonstrated by **perfluorosilicone** product, before and after ageing, and with highest values than C8 chemistry. Perfluorosilicone combines a soil release and water and oil repellence property. Moreover, this technology includes the anchorage of the fluorocarbon chains to the substrate to improve the orientation of the fluorocarbon chains.

Silicone product is highly effective on nonwovens but do not present oil repellency since its surface energy is higher than the surface energy of oil. Fluorocarbon based chemistries have good oil repellency since their surface energy is lower than oil's one.

Sol gel product is highly effective on uniform surfaces but not resistant to washing, as polyester fibers does not have hydroxyl groups to react with silanol reactive groups of sol gel. However, on flat and uniforms surface, washing fastness has been maintained.

All fabrics lose part of their water and oil repellency property after washing but this property is restored after ironing. **Heat** (curing and ironing) restores the comb like structure of perfluoropolymers, necessary to achieve water and oil repellency. This indicates that not only the chemical structure (chemical composition and chemical bonds) is important to achieve good repellency but also the physical structure (fluorocarbon chains organization) as represented in the next picture.

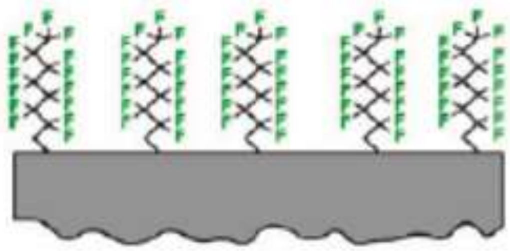


FIGURE 14. EXEMPLE OF COMB LIKE STRUCTURE ON THE FABRIC SURFACE[17].

C8 chemistry not always presented the best results, but **C6** chemistry always present results similar or lower than C8.

[17] Shaping Mesoporous Films Using Dewetting on X-ray Pre-patterned Hydrophilic/Hydrophobic Layers and Pinning Effects at the Pattern Edge, 2011.

6.2. Application sector

The fabric's characteristics also have an importance in the effectiveness of the repellent finishing.

Automotive nonwovens

For water repellency, silicone chemistry is more effective on automotive nonwovens than fluorocarbon based chemistries (C8, C6, perfluorosilicone and sol gel). Indeed, fluorocarbon chemistry need a uniform surface to achieve a comb like organization of its fluorinated carbon chains.

Fashion - woolen suits

C8 and C6 chemistries present low washing fastness on wool as chemical bonding is more difficult on this kind of substrate than on cellulosic fibers. In the absence of chemical bonds, during washing, heavier long chain fluorocarbons C8 could be easier to wash off than short chain C6.

Upholstery velvet fabrics

As automotive nonwovens, the upholstery fabric employed in this study has a velvet surface reducing the uniformity of the coating layer deposition. This induce difficulties for the organization of the fluorinated chains and then water and oil repellency is less than it could be.

Sportswear / work wear knitted fabric

Sol gel product is effective on flat knitted surface (mostly for oil repellency), before and after washing and ironing. The adhesion of the nanolayer is increased on flat and regular substrates such as this fabric. Sol gel is a best option for this kind of fabric than for nonwovens or velvet fabrics.

7. Next steps

The next step will consist in selecting the best finishing products according to the final application (taking into account the conclusions made in this deliverable). Then, these finishing will be applied on the different textile substrates in the industry. The product selection for each application sector will be defined in the next deliverable. Measurements and data will be collected in the companies during the application in order to perform the risk assessment (B2) and the LCA (B3).

The next figure presents the different companies which agreed to collaborate in the MIDWOR project. One fabric has been attributed to each company.

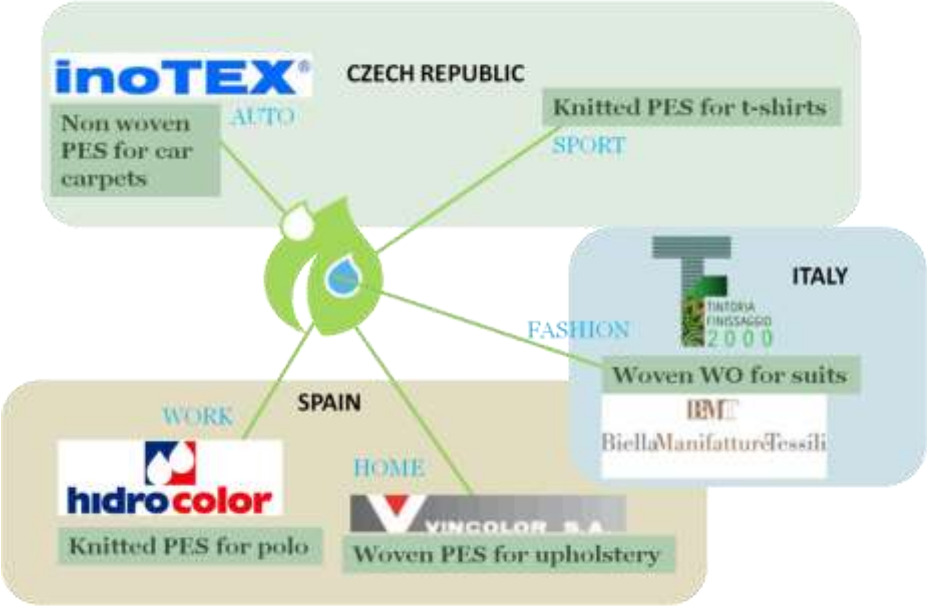


FIGURE 15.COLLABORATING COMPANIES AND FABRIC ATTRIBUTION TO EACH COMPANY