2016

VALENTINO SPA

PFCs SUBSTITUTION CASE STUDY

INDEX

Commitment Overview

Within Detox Solution Commitment of February 6th 2013 and in line with the precautionary principle, VALENTINO SPA (VSPA) presents a substitution case study on a safer alternative to Poly and Per-Fluorinated Chemicals (PFCs) in order to minimizing the environmental impacts of manufacturing processes.

1. Introduction

Poly and Per- Fluorinated Chemicals (PFCs) are a large group of chemicals that have been used since many years by the apparel industry as main components of Durable Water Repellent (DWR) finishes to provide products with water repellent properties. Several PFCs have been recognized as highly persistent, potentially bio-accumulative and toxic. In addition, many PFCs have been detected globally in the environment, biota, humans and food items.

This study reports the results of tests performed on a PFCs-free water-repellent alternative applied on leather and textile substrates.

2. Substituted substances

PFCs (PERFLUORINATED/POLYFLUORINATED COMPOUNDS)		ABBREVIATION	CAS
1	Perfluorooctane sulfonates	PFOS	1763-23-1; Various
2	Perfluorooctanic acid	PFOA	335-67-1
3	Henicosafluoroundecanoic acid	PFUnA	2058-94-8
4	Heptacosafluorotetradecanoic acid	PFTeA	376-06-7
5	Pentacosafluorotridecanoic acid	PFTrA	72629-94-8
6	Tricosafluorododecanoic acid	PFDoA	307-55-1
7	Perfluorononanoic acid	PFNA	375-95-1
8	Perfluorodecanoic acid	PFDA	335-76-2
9	Perfluoro-3,7-dimethyloctanoic acid	PF-3,7-DMOA	172155-07-6
10	Perfluorodecane sulfonic acid	PFDS	335-77-3
11	2H,2H,3H,3H-perfluoroundecanoic acid	H4PFUnA	34598-33-9
12	2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	N-Me-FOSE	24448-09-7
13	2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	N-Et-FOSE	1691-99-2
14	N-methylperfluoro-1-octansulfonamide	N-Me-FOSA	31506-32-8
15	N-ethylperfluoro-1-octanesulfonamide	N-Et-FOSA	4151-20-2
16	Perfluorooctane sulphonamide	PFOSA	754-91-6
17	1H,1H,2H,2H-perfluoroctylacrylate	6:2 FTA	17527-29-6
18	1H,1H,2H,2H-perfluorodecylacrylate	8:2 FTA	27905-45-9
19	1H,1H,2H,2H-perfluorododecylacrylate	10:2 FTA	17741-60-5
20	1H,1H,2H,2H-perfluoro-1-hexanol	4:2 FTOH	2043-47-2
21	1H,1H,2H,2H-perfluoro-1-octanol	6:2 FTOH	647-42-7
22	1H,1H,2H,2H-perfluoro-1-decanol	8:2 FTOH	678-39-7
23	1H,1H,2H,2H-perfluoro-1-dodecanol	10:2 FTOH	865-86-1

24	Perfluoroheptanoic acid	PFHpA	375-85-9
25	7H-dodecafluoroheptanoic acid	HPFHpA	1546-95-8
26	Perfluoroheptane sulfonatic acid	PFHpS	375-92-8
27	Perfluorobutanoic acid	PFBA	375-22-4
28	Perfluorobutane sulfonic acid	PFBS	59933-66-3;749861-23-2;375-73-5
29	Perfluoropentanoic acid	PFPeA	2706-90-3
30	Perfluorohexanoic acid	PFHxA	307-24-4
31	Perfluorohexane sulfonic acid	PFHxS	355-46-4
32	Perfluorobutanesulfonate K-salt	PFBS-K	29420-49-3
33	Perfluorohexanesulfonate Na-salt	PFHxS-Na	82382-12-15
34	Perfluordecanesulfonate Na-salt	PFDS-Na	2806-15-7
35	1H,1H,2H,2H-Perfluorooctanesulphonic acid	1H,1H,2H,2H-PFOS	27619-97-2
36	2H,2H-Perfluorodecanoic acid	H2PFDA	27854-31-5
37	Perfluoroheptanesulfonate Na-salt	PFHpS-Na	68555-66-8
38	Perfluorodecanesulfonate K-salt	PFDS-K	2806-16-8
39	Perfluorodecanesulfonate NH4-salt	PFDS-NH4	67906-42-7
40	Perfluoro-1-octanesulfonyl fluoride	POSF	307-35-7
41	1H,1H,2H,2H-perfluorodecane sulfonate	8:2 FTS	39108-34-4

Table 1: List of substituted PFCs

3. Alternative substance

The chemical nature of the PFCs-free alternative is a mixture consisting of the following components:

-Synergistic dispersion of various waxes;
-Polyester polyurethane-dispersion.

4. Case description

Poly and Per-Fluorinated chemicals (PFCs) have been used since many years by the apparel industry in order to provide products with water repellency.
Recent studies showed that several PFCs can be found in all environmental compartments (water, glacials, etc.) as well as food chain, animals and human blood, posing risk to human health and to the environment.
In this research, chemical and performance tests were performed on different leather and textile substrates, finished with a PFC-free alternative product (Ecoperl Active) supplied by CHT-Bezema to provide them with a water repellent functionality. Tests carried out on Ecoperl Active and on textiles and leathers treated with the same, resulted free of PFCs, APEOs, Phthalates and other investigated substances.
Samples details and chemical test results, methods, detection limits and investigated substances lists are shown in table 2 and 4.

Different performance tests (spray test, spray test after dry and water cleaning, water resistance of flexible leather, etc.) were performed, depending on the involved substrate, on 3 woven fabrics, 2 different kinds of leather and a split-leather treated with Ecoperl Active on two different finishing procedures.

Details and results are shown in table 3 (the characteristics of different substrates may influence performance results).

This case study involved two important leather and one strategic textile suppliers. All findings have been shared afterward with the relevant supply chain, encouraging the use of the PFCs-free alternative. Furthermore all third party test results and SDS of Ecoperl Active are available for our suppliers.
The present substitution case study has been compared against Subsport criteria and has been submitted to Subsport for publication on the related website.

5. Chemical Tests

CHEMICAL TESTS								
INVESTIGATED SUBSTANCES*	**TEST METHOD (DL)**	**ECOPERL ACTIVE**	**TEXTILE 1**	**TEXTILE 2**	**TEXTILE 3**	**SPLIT-LEATHER**	**LEATHER 1**	**LEATHER 2**
Azo dyes	EN 14362-1; UNI ISO 17234-1-2 (DL: 5 mg/Kg)	-	ND	ND	ND	ND	ND	-
Alkylphenols / Alkylphenol ethoxylates	ISO/DIS 18254; LC-MS analysis (DL:1 mg/Kg)	ND	ND	ND	ND	ND	ND	-
Chlorinated Phenols	ISO17070 (DL:0,05 mg/Kg)	-	ND	-	-	ND	ND	-
Cr(VI)	ISO 17075 (DL:3 mg/Kg)	-	-	-	-	ND	ND	-
Formaldehyde	GB18401 + GB/T2912.1 (DL:20mg/Kg); EN ISO 14184-1; EN ISO17226-2 (DL:10mg/Kg)	ND	ND	ND	ND	ND	ND	-
PFCs	CEN/TS 15968; (DL:20µg/Kg; 1 µg/m^2)	ND	ND	ND	ND	ND	ND	ND
Phthalates	CPSC-CH-C1001- 09.3 (DL:DIDP, DINP:10mg/Kg; OTHERS: 5mg/Kg)	ND	-	ND	-	-	ND	-
Lead	CPSC-CH-E1002-08 (DL:20mg/Kg)	-	-	-	-	ND	ND	-
Cadmium	CPSC-CH-E1002-08 (DL:10mg/Kg)	-	-	-	-	ND	ND	-

Table 2: chemical test results (* for the full list of investigated substances see Table 4)

ND: not detected; **DL:** detection limit; **TEXTILE 1:** 96%cotton 2% polyamide 2% elastane; **TEXTILE 2:** 100% polyester with polyurethane coating; **TEXTILE 3:** 100% polyamide; **LEATHER 1:** lambskin leather; **LEATHER 2:** calf leather.

6. Performance Tests

PERFORMANCE TESTS									
PERFORMED TEST		**TEST METHOD**	**TEXTILE 1**	**TEXTILE 2**	**TEXTILE 3**	**SPLIT-LEATHER application a**	**SPLIT-LEATHER application b**	**LEATHER 1**	**LEATHER 2**
Spray test ISO scale: 1-5	0 washings	UNI EN ISO 4920:2013	ISO 5	ISO 5	ISO 5	ISO 2	ISO 2	ISO 4	-
	After 3 dry washings (30°C)		-	ISO 4	ISO 3	-	-	-	-
	After 3 water washings (40°C; tumbler drying)		-	ISO 4	ISO 2	-	-	-	-
Colour fastness to water spotting		UNI EN ISO 15700:2000	-	-	-	4/5	4/5	4/5	4/5
Soaking-up test (Wicking test)		UNI 11293:2008	Wicking value: 0mm	-	-	Wicking value: 0mm W_a^1: 6,6%	Wicking value: 0mm W_a^1: 11,6%	Wicking value: 42,7mm W_a^1: 101,3%	-
Determination of water resistance of flexible leather (penetrometer)		UNI EN ISO 5403-1:2012	-	-	-	Penetration time: 22mins; W_a^2: 19,2%	Penetration time:56mins; W_a^2: 12,6%	Penetration time: 5mins; W_a^2: 90,6%	-
Water permeability test		UNI EN ISO 20811: 1993	17,1 mbar	-	-	-	-	-	-

Table 3: performance test results

TEXTILE 1: 96%cotton 2% polyamide 2% elastane**; TEXTILE 2:** 100% polyester with polyurethane coating**; TEXTILE 3:** 100% polyamide**;**
application *a:* Ecoperl Active applied in drums; **application *b:*** Ecoperl Active in drums followed by spray application;
LEATHER 1: lambskin leather. Test on grain side; **LEATHER 2:** calf leather. Test on grain side;
W_a^1: percentage of water absorption by capillary action (wicking); **W_a^2**: percentage of water absorption at penetration time.

7. Investigated Substances List

INVESTIGATED SUBSTANCES LIST			
NAME	**CAS**	**NAME**	**CAS**
AZO DYES			
4-Aminobiphenyl	92-67-1	4,4'-Oxydianiline	101-80-4
Benzidine	92-87-5	4,4'- Thiodianiline	139-65-1
4-Chloro-o-toluidine	95-69-2	o-Toluidine	95-53-4
2-Naphthylamine	91-59-8	2,4-Diaminotoluene	95-80-7
2,4-Diaminoanisole	615-05-4	2,4,5- Trimethylaniline	137-17-7
4,4'-Diaminobiphenylmethane	101-77-9	o-Anisidine (2-Methoxyanilin)	90-04-0
3.3'-Dichlorobenzidine	91-94-1	2,4-Xylidine	95-68-1
3,3'-Dimethoxybenzidine	119-90-4	2,6-Xylidine	87-62-7
3,3'-Dimethylbenzidine	119-93-7	o-Aminoazotoluene	97-56-3
3,3'-Dimethyl-4,4'- diaminobiphenylmethane	838-88-0	2-Amino-4-Nitrotoluene	99-55-8
p-Cresidine	120-71-8	p-Chloroaniline	106-47-8
4,4'-Methylene-bis- (2-chloroaniline)	101-14-4	4-Aminoazobenzene	60-09-3
ALKYLPHENOLS (APs), ALKYLPHENOL ETHOXYLATES (APEOs)			
Nonylphenol (NP)	104-40-5; 25154-52-3; Various	Octylphenol (OP)	140-66-9; 27193-28-8; Various
Nonylphenol Ethoxylates[1-18] (NPEO[1-18])	Various	Octylphenol Ethoxylates[1-18]	Various
CHLORINATED PHENOLS			
Pentachlorophenol (PCP) and its salts	87-86-5	2,3,5-Trichlorophenol (TriCP)	933-78-8
2,3,5,6-Tetrachlorophenol (TeCP)	935-95-5	2,3,6-Trichlorophenol (TriCP)	933-75-5
2,3,4,6-Tetrachlorophenol (TeCP)	58-90-2	2,4,5-Trichlorophenol (TriCP)	95-95-4
2,3,4,5-Tetrachlorophenol (TeCP)	4901-51-3	2,4,6-Trichlorophenol (TriCP)	88-06-2
2,3,4-Trichlorophenol (TriCP)	15950-66-0	3,4,5-Trichlorophenol (TriCP)	609-19-8
PFCs (PERFLUORINATED/POLYFLUORINATED COMPOUNDS)			
SEE TABLE 1			

NAME	CAS	NAME	CAS
PHTHALATES			
1,2-Benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich (DIHP)	71888-89-6	1,2-Benzenedicarboxylic acid, dipentylester, branched and linear (DPP)	84777-06-0
Di-n-octylphthalate (DNOP)	117-84-0	Di-nonylphthalate (DNP)	84-76-4
1,2-Benzenedicarboxylic acid, di-C7-11-branched and linear alkyl esters (DHNUP)	68515-42-4	Di-cyclo-hexylphthalate (DCHP)	84-61-7
Di-n-penthylphthalate (DnPP)	131-18-0	Di-iso-decylphthalate (DIDP)	26761-40-0; 68515-49-1
Bis(2-methoxyethyl) phthalate (DMEP)	117-82-8	Di-iso-pentylphthalate (DIPP)	605-50-5
Di-iso-butylphthalate (DIBP)	84-69-5	Di-iso-octylphthalate (DIOP)	27554-26-3
Butylbenzylphthalate (BBP)	85-68-7	Di-n-propylphthalate (DPrP)	131-16-8
Diethylphthalate (DEP)	84-66-2	Di-iso-nonylphthalate (DINP)	288553-12-0; 68515-48-0
Di-(2-ethylhexyl)-phthalate (DEHP)	117-81-7	N-pentyl-iso-pentylphthalate (nPIPP)	776297-69-9
Dimethylphthalate (DMP)	131-11-3	Di-n-hexyl phthalate (DnHP)	84-75-3
Dibutylphthalate(DBP)	84-74-2	Di-hexylphthalate, branched and linear (DHxP)	68515-50-4
HEAVY METALS			
Cr (VI)	18540-29-9	Pb	7439-92-1
Cd	7440-43-9		
OTHERS			
Formaldehyde	50-00-0		

Table 4: investigated substances list according to Valentino's Product RSL