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VALENTINO SPA

**APs/APEOs, PHTHALATES & PFCs CASE
STUDY**

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1. Commitment overview

Following up to its Detox Solution Commitment of February 6th 2013 and in line with the precautionary principle, VALENTINO SPA presents a research on possible sources of contamination in APs/APEOs, Phthalates and PFCs in order to minimize the environmental impacts of manufacturing processes.

2. Introduction

In this paper, we give an example of investigations carried out in order to examine the causes of sources of contaminants found in articles during our screening for hazardous substances.

The focus of this research is on APs/APEOs, Phthalates and PFCs that are substances groups widespread in multiple production processes, formulations as well as in the environment, biota, humans and food items, with the result of residual problems of contaminations in articles.

VALENTINO SPA (VSPA) worked with the supply chain in order to reduce the use of hazardous chemicals in production processes of textiles and apparel and find suitable alternatives.

The complete list of investigated substances is displayed in chapter 5.

3. Substituted substances and their application field

3.1 APs/APEOs

Alkylphenol ethoxylates (APEOs) are surfactants which have an emulsifying and dispersing action, well-known to be suitable for a very large variety of applications (detergents, degreasing agents, softening agents etc...). The most commercially important APEOs, especially for textile and leather industries, are nonylphenol ethoxylates (NPEOs). From the ecotoxicological point of view, APEOs are classified as persistent, bioaccumulative and toxic (PBT) (<https://echa.europa.eu/it/substance-information/-/substanceinfo/100.105.533>). In addition, these compounds exert endocrine disruption effects since they mimic natural hormones by interacting with estrogen receptors.

3.2 PHTHALATES

Phthalates are a group of chemicals used especially as plasticizers or added to plastics to increase their flexibility, transparency, durability and longevity.

Phthalates are used in a large variety of products, such as plastisol prints, paints, high pressure polyester dyeing, cosmetics additives, adhesive tapes, erasers, tubes, lubricants and carpets.

This group of molecules is considered particularly harmful to both human and fauna, due to structural similarities with human and animal cells that foster phthalate absorption; phthalates are also considered allergens and endocrine disruptors.

3.3 PFCs

Poly- and Per- Fluorinated Chemicals (PFCs), are a large group of chemicals that have been used for 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.

4. Case description

This paper presents a research on possible sources of contaminations from APEOs, PHTHALATES and PFCs revealed during our preliminary testing activity and derived from different stages of the production cycle of textiles and leather products. In these researches, we involved the supply chain and we cooperated with suppliers evaluating products SDS, sampling chemicals and their articles, as well as waters in order to fix residual production problems. Tested materials, investigation steps, corrective actions and new implementations are reported in Table 1.

Tested material	Groups of Substances detected	Test Method	Investigation of sources of contaminations steps ¹	Corrective action	Tested material after Corrective Action ¹
Black Calf Leather	APs/APEOs	ISO 18218-1	<ol style="list-style-type: none"> 1. Testing the same calf leather in different colors: only black one showed APs/APEOs; 2. Research of sources of contamination between chemicals employed, especially colorants; (see Table 2) 3. Chemical test on black colorant products found NPEOs in concentrations of 659,6mg/Kg 	Elimination of the contaminated colorants from the production cycle and substitution with a compliant one	No contamination sources of APs/APEOs found. Other parameters compliant
100% cotton jersey fabric treated with a plastisol print	Phthalates	CPSC-CH-C1001-09	<ol style="list-style-type: none"> 1. Print clearly identified as Source of Contamination 2. Phthalate Free alternative identified in <i>Advantage On plastisol ink</i> by Fujifilm 	Elimination of contaminated inks from production cycle and use of the identified alternative	No contamination sources of Phthalates found. Both Chemical and Quality/Performance tests resulted compliant
Calf leather	PFCs	CEN/TS 15968	<ol style="list-style-type: none"> 1. Test of the separate layers of the sample: coated surface and flesh; 2. Higher concentrations of PFCs found in the flesh pointed out that most probably the problem laid in the tanning process; 3. Testing two greasing agents used in tanning process showed no presence of PFCs; 4. A test on the incoming water sampled at the tannery revealed presence of PFCs. 	Installation of a pre-treatment plant in order to prevent the PFCs entering the production cycle.	No contamination sources of PFCs found in products. Other parameters compliant.

Table 1

¹ Test reports, MSDS and other documents are available upon request.

Colorant	Method	Detection Limits	NPs (mg/kg)	OPs (mg/kg)	NPEOs (mg/kg)	OPEOs (mg/kg)
Black colorant 1	Ref. to ISO 18218-1	1 mg/kg	N.D.	N.D.	27,1	N.D.
Black colorant 2			N.D.	N.D.	N.D.	N.D.
Black colorant 3			N.D.	N.D.	N.D.	N.D.
Black colorant 4			N.D.	N.D.	N.D.	N.D.
Black colorant 5			N.D.	N.D.	659,6	N.D.

Table 2

5. Investigated Substances List

ALKYLPHENOLS (APs), ALKYLPHENOL ETHOXYLATES (APEOs)			
NAME	CAS	NAME	CAS
Nonilphenol (NP)	104-40-5; 25154-52-3; Various	Nonilphenol Ethoxylates _[1-18] (NPEO _[1-18])	9016-45-9; Various
Octylphenol (OP)	140-66-9; 27193-28-8; Various	Octylphenol Ethoxylates _[1-18] (OPEO _[1-18])	9002-93-1; Various

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

PFCs (PERFLUORINATED/POLYFLUORINATED COMPOUNDS)			
NAME	CAS	NAME	CAS
Perfluorooctane sulfonate (PFOS) and related substances	Various	Perfluorohexanesulfonate Na-salt (PFHxS-Na)	82382-12-15
Perfluorooctanesulfonamide (PFOSA)	754-91-6	Perfluoroheptanesulfonate Na-salt (PFHpS-Na)	68555-66-8
N-Methyl-Perfluorooctanesulfonamide (N-Me-FOSA)	31506-32-8	Perfluorodecanesulfonate Na-salt (PFDS-Na)	2806-15-7
N-Ethyl-Perfluorooctanesulfonamide (N-Et-FOSA)	4151-50-2	Perfluorodecanesulfonate K-salt (PFDS-K)	2806-16-8
N-Methyl-Perfluorooctanesulfonamidoethanol (N-Me-FOSE)	24448-09-7	Perfluorodecanesulfonate NH ₄ -salt (PFDS-NH ₄)	67906-42-7
N-Ethyl-Perfluorooctanesulfonamidoethanol (N-Et-FOSE)	1691-99-2	Perfluorobutane sulfonic acid (PFBS)	375-73-5; 59933-66-3; 749861-23-2
7H-Dodecafluoroheptanoic acid (HPFHpA)	1546-95-8	Perfluorohexane sulfonic acid (PFHxS)	355-46-4
2H,2H-Perfluorodecanoic acid (H ₂ PFDA)	27854-31-5	Perfluoroheptane sulfonic acid (PFHpS)	375-92-8
Perfluorooctanoic acid (PFOA)	335-67-1	Perfluorodecane sulfonic acid (PFDS)	335-77-3
Perfluorobutanoic acid (PFBA)	375-22-4	Perfluoro-3,7-dimethyloctanoic acid (PF-3,7-DMOA)	172155-07-6
Perfluoropentanoic acid (PFPeA)	2706-90-3	1H,1H,2H,2H-Perfluorooctane sulfonic acid (1H,1H,2H,2H-PFOS)	27619-97-2
Perfluorohexanoic acid (PFHxA)	307-24-4	2H,2H,3H,3H-Perfluoroundecanoic acid (H ₄ PFUnA)	34598-33-9
Perfluoroheptanoic acid (PFHpA)	375-85-9	1H,1H,2H,2H-Perfluorohexane-1-ol (4:2 FTOH)	2043-47-2
Perfluorononanoic acid (PFNA)	375-95-1	1H,1H,2H,2H-Perfluoro-1-octanol (6:2 FTOH)	647-42-7
Perfluorodecanoic acid (PFDA)	335-76-2	1H,1H,2H,2H-Perfluoro-1-decanol (8:2 FTOH)	678-39-7
Perfluoroundecanoic acid (PFUnA)	2058-94-8	1H,1H,2H,2H-Perfluorododecane-1-ol (10:2 FTOH)	865-86-1
Perfluorododecanoic acid (PFDoA)	307-55-1	1H,1H,2H,2H-Perfluorooctylacrylate (6:2-FTA)	17527-29-6
Perfluorotridecanoic acid (PFTrA)	72629-94-8	1H,1H,2H,2H-Perfluorodecylacrylate (8:2-FTA)	27905-45-9
Perfluorotetradecanoic acid (PFTeA)	376-06-7	1H,1H,2H,2H-Perfluorododecylacrylate (10:2-FTA)	17741-60-5
Perfluorobutanesulfonate K-salt (PFBS-K)	29420-49-3	Perfluoro-1-octanesulfonyl fluoride (POSF)	307-35-7