MANUFACTURING RESTRICTED SUBSTANCES LIST VERSION 1.1





Manufacturing Restricted Substances List Version 1.1 Zero Discharge of Hazardous Chemicals Programme

## 1 Background

In the Zero Discharge of Hazardous Chemicals (ZDHC) Joint Roadmap, Version 2, ZDHC brands committed to define and develop a Manufacturing Restricted Substances List (MRSL) for the apparel and footwear industry. In doing so, brands recognised the value of addressing hazardous substances potentially used and discharged into the environment during manufacturing and related processes deep within our supply chain – not just those substances that could be present in finished products. In June 2014, the ZDHC brands achieved a significant milestone and published the first version of the ZDHC MRSL.

# 2 Purpose

The intent of the ZDHC MRSL is to provide brands and suppliers with a harmonised approach to managing chemicals during the processing of raw materials within the apparel and footwear supply chain. The ZDHC MRSL achieves this by providing a clear list of priority chemicals and specifying the maximum concentration limit of each substance within commercial chemical formulations.

The ZDHC MRSL is divided into sections that focus on a specific raw material. This accounts for the differences between the creation and processing of the material types used within our industry and the need to set applicable limits to reflect the functional use of these chemicals. The MRSL should be communicated to raw material suppliers, including sub-contractors and factories assembling or manufacturing garments and footwear. To support our goal of using MRSL compliant chemical formulations, ZDHC brands also expect that material suppliers and factories will communicate with their chemical suppliers to ensure that listed substances are not present in chemical formulations above established limits.

<u>Note</u>: The ZDHC MRSL does not replace applicable national environmental or workplace safety restrictions. Worker exposure to chemical substances listed in this document, along with other hazardous substances, must not exceed occupational exposure limits. Chemical formulations also must comply with all applicable legal restrictions, including any subsequent restrictions that establish more strict limits. The ZDHC MRSL does not replace legal or brand-specific restrictions on hazardous substances in finished products.

# 3 Definitions

### MRSL

The ZDHC MRSL is a list of chemical substances subject to a usage ban (see Usage Ban, page 2). The MRSL applies to chemicals used in facilities that process materials and trim parts for use in apparel and footwear. Chemicals in the ZDHC MRSL include solvents, cleaners, adhesives, paints, inks, detergents, dyes, colourants, auxiliaries, coatings and finishing agents used during raw material production, wet-processing, maintenance, wastewater treatment, sanitation and pest control. There should be no intentional use of MRSL-listed substances in facilities that process materials used in the production of apparel and footwear. MRSL limits apply to substances in commercially available chemical formulations and not those from earlier stages of chemical synthesis.

<u>Note</u>: Threshold Limit values on restricted substances in chemical formulations are in some cases substantially higher than limits on restricted substances in finished products. This is because restricted substances in finished products are almost always found in smaller concentrations than in the chemical formulations used to produce them. Chemical formulations are highly concentrated before being diluted upon application to textiles and other materials.

### **Chemical Substance**

A chemical substance is a chemical element and its compounds in the natural state or obtained by any manufacturing process (REACH, 2014).<sup>1</sup> A chemical substance is usually identifiable by a single, unique Chemical Abstracts Service (CAS) number or Colour Index (CI) number. The ZDHC MRSL will primarily focus on chemical substances listed by CAS number and CI number, but also will include groups of substances for which listing individual substances is not practical.

### **Commercial Chemical Formulation**

A commercial chemical formulation is usually a proprietary blend of several chemical substances that is available for purchase from chemical suppliers under their own trade name.

#### Usage Ban

A usage ban indicates that the ZDHC MRSL-listed chemical substance or group of substances may not be used to achieve a desired function or effect during production of the raw material or product (that is, no intentional use). This usage ban extends to other uses within a facility like cleaning and maintenance. Due to the existence of manufacturing impurities in chemical formulations, a minor or trace amount of the restricted substance is permitted. Chemical formulations containing restricted substances that exceed limits are not compliant with the ZDHC MRSL.

## **4 MRSL Creation Process**

The ZDHC MRSL includes relevant substances from the original 11 priority chemical groups in the Joint Roadmap<sup>2</sup> along with additional substances discussed with qualified experts from the ZDHC Technical Advisory Committee (TAC) and signatory brands. Several of the listed substances are regulated in finished products and have been successfully restricted by ZDHC brands for years. Though already restricted by ZDHC brands, their inclusion on the list keep it consistent with existing industry standards. Where possible, the content of the ZDHC MRSL was peer-reviewed by independent third-party technical experts and industry associations related to the production of our key raw materials. Collaboration with leading technical experts allows the ZDHC Programme to develop a MRSL that pragmatically represents progress and supports our long-term goal of zero discharge.

### **5 MRSL Instructions**

### **MRSL** Chapters

Chapter 1: MRSL for Textiles and Synthetic Leather Processing

This section applies to chemical formulations and substances used during the creation and wet processing of textile fibres and during the creation and processing of synthetic leather.

• Chapter 2: MRSL for Natural leather Processing

This section applies to chemical formulations and substances used throughout the production of natural leather, from raw-hide to finished leather.

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<sup>&</sup>lt;sup>1</sup> "A chemical element and its compounds in the natural state or obtained by any manufacturing process, including any additive necessary to preserve its stability and any impurity deriving from the process used, but excluding any solvent which may be separated without affecting the stability of the substance or changing its composition." <u>http://www.reachonline.eu/REACH/EN/REACH\_EN/article3.html</u>. Accessed May 8, 2014.

<sup>&</sup>lt;sup>2</sup> These are alkylphenol ethoxylates/alkylphenols (APEOs/APEs), brominated and chlorinated flame retardants, chlorinated solvents, chlorobenzenes, chlorophenols, heavy metals, organotin compounds (e.g., TBT), perfluorinated and polyfluorinated chemicals, (PFCs), phthalates (ortho-phthalates), short-chain chlorinated paraffins (SCCPs) and azo dyes that may release carcinogenic appines as defined in Annex XVII of REACH.

#### **MRSL** Groups

#### • Group A: Raw Material and Finished Product Supplier Guidance

Group A substances are banned from intentional use in facilities that process raw materials and manufacture finished products. Please refer to the AFIRM guidance document for the lowest agreed upon material or finished product limits among AFIRM brands: <u>http://www.afirm-group.com/rsl-guidance/</u>. See brand RSLs for individual requirements.

#### • Group B: Chemical Supplier Formulation Limit

Group B substances are restricted to concentration limits in chemical formulations commercially available from chemical suppliers. These limits ban intentional use while allowing for reasonable expected manufacturing impurities that should be consistently achievable by responsible chemical manufacturers.<sup>3</sup>

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<sup>&</sup>lt;sup>3</sup> Safety Data Sheets (SDS) only list substances present at concentrations of 1000 ppm or greater. Suppliers must communicate with chemical suppliers to ensure MRSL limits are met.

## CHAPTER 1: MRSL for Textiles and Synthetic Leather Processing

CAS No.	Substance	Group A: Raw Material and Finished Product Supplier Guidance	Group B: Chemical Supplier Commercial Formulation Limit	Potential Uses in Apparel and Footwear Textile Processing	General Techniques for Analysing Chemicals
Alkylphenol (AP) and	Alkylphenol Ethoxylates (APEOs): including all i	somers			
104-40-5					
11066-49-2	Nonylphenol (NP), mixed isomers		250 ppm		
25154-52-3			200 ppm		
84852-15-3				APEOs can be used as or found in:	
140-66-9				detergents, scouring agents, spinning	Liquid chromatography- mass spectrometry (LC- MS), gas chromatography- mass spectrometry (GC- MS)
1806-26-4	Octylphenol (OP), mixed isomers		250 ppm	oils, wetting agents, softeners, emulsifier/dispersing agents for dyes	
27193-28-8					
9002-93-1		No intentional use	500 ppm	and prints, impregnating agents, de-	
9036-19-5	Octylphenol ethoxylates (OPEO)			gumming for silk production, dyes and pigment preparations, polyester	
68987-90-6					
9016-45-9				padding and down/feather fillings.	
26027-38-3			500 ppm	padding and down/reather minigs.	
37205-87-1	Nonylphenol ethoxylates (NPEO)				
68412-54-4					
127087-87-0					
Chlorobenzenes and C	Chlorotoluenes				
95-50-1	1,2-dichlorobenzene		1000 ppm	Chlorobenzenes and chlorotoluenes	
Other isomers of mon	Other isomers of mono-, di-, tri-, tetra-, penta- and hexa- chlorobenzene and mono-, di-, tri-, tetra- and penta- chlorotoluene			(chlorinated aromatic hydrocarbons)	
chlorobenzene and me				can be used as carriers in the dyeing	GC-MS
		No intentional use	Sum = 200 ppm	process of polyester or wool/polyester	90-1015
				fibres. They can also be used as solvents.	



CAS No.	Substance	Group A: Raw Material and Finished Product Supplier Guidance	Group B: Chemical Supplier Commercial Formulation Limit	Potential Uses in Apparel and Footwear Textile Processing	General Techniques for Analysing Chemicals
Chlorophenols					
25167-83-3	Tetrachlorophenol (TeCP)		Sum = 20 ppm		
87-86-5	Pentachlorophenol (PCP)				
4901-51-3	2,3,4,5-tetrachlorophenol				
58-90-2	2,3,4,6-tetrachlorophenol				
935-95-5	2,3,5,6-tetrachlorophenol				
95-57-8	2-chlorophenol			Chlorophenols are polychlorinated	
120-83-2	2,4-dichlorophenol			compounds used as preservatives or pesticides. Pentachlorophenol (PCP) and tetrachlorophenol (TeCP) have been used in the past to prevent mould when storing/ transporting, raw hides and leather. They are now regulated and should not be used.	
583-78-8	2,5-dichlorophenol				
87-65-0	2,6-dichlorophenol				GC-MS
95-95-4	2,4,5-trichlorophenol	No intentional use	6		
88-06-2	2,4,6-trichlorophenol		Sum = 50 ppm		EN ISO 17070
591-35-5	3,5-dichlorophenol				
576-24-9	2,3-dichlorophenol				
95-77-2	3,4-dichlorophenol				
108-43-0	3-chlorophenol	-			
106-48-9	4-chlorophenol				
15950-66-0	2,3,4-trichlorophenol				
933-78-8	2,3,5-trichlorophenol				
609-19-8	3,4,5-trichlorophenol	]			



CAS No.	Substance	Group A: Raw Material and Finished Product Supplier Guidance	Group B: Chemical Supplier Commercial Formulation Limit	Potential Uses in Apparel and Footwear Textile Processing	General Techniques for Analysing Chemicals
Dyes – Azo (Forming	Restricted Amines)				
101-14-4	4,4'-methylene-bis-(2-chloro-aniline)		150 ppm		
101-77-9	4,4'-methylenedianiline		150 ppm		
101-80-4	4,4'-oxydianiline		150 ppm		
106-47-8	4-chloroaniline		150 ppm		
119-90-4	3,3'-dimethoxylbenzidine		150 ppm		
119-93-7	3,3'-dimethylbenzidine		150 ppm		LC, GC
120-71-8	6-methoxy-m-toluidine		150 ppm		
137-17-7	2,4,5-trimethylaniline		150 ppm		
139-65-1	4,4'-thiodianiline		150 ppm	Azo dyes and pigments are colourants that incorporate one or several azo groups (-N=N-) bound with aromatic compounds. Thousands of azo dyes exist, but only those that degrade to form the listed cleavable amines are restricted. Azo dyes that release these amines are regulated and should no longer be used for dyeing of textiles.	
60-09-3	4-aminoazobenzene		150 ppm		
615-05-4	4-methoxy-m-phenylenediamine		150 ppm		
838-88-0	4,4'-methylenedi-o-toluidine		150 ppm		
87-62-7	2,6-xylidine	<ul> <li>No intentional use</li> </ul>	150 ppm		
90-04-0	o-anisidine		150 ppm		
91-59-8	2-naphthylamine		150 ppm		
91-94-1	3,'3-dichlorobenzidine		150 ppm		
92-67-1	4-aminodiphenyl		150 ppm		
92-87-5	Benzidine		150 ppm		
95-53-4	o-toluidine		150 ppm		
95-68-1	2,4-xylidine		150 ppm		
95-69-2	4-chloro-o-toluidine		150 ppm		
95-80-7	4-methyl-m-phenylenediamine		150 ppm		
97-56-3	o-aminoazotoluene		150 ppm		
99-55-8	5-nitro-o-toluidine		150 ppm		
Dyes – Navy Blue Co	lourant				
118685-33-9	Component 1: C39H23ClCrN7O12S·2Na			Navy Blue colourants are regulated and	
Not Allocated	Component 2: C46H30CrN10O20S2·3Na	No intentional use	250 ppm	should no longer be used for dyeing of textiles.	LC



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Dyes – Carcinogenio	c or Equivalent Concern				
1937-37-7	C.I. Direct Black 38		250 ppm		
2602-46-2	C.I. Direct Blue 6	-	250 ppm		
3761-53-3	C.I. Acid Red 26		250 ppm		
569-61-9	C.I. Basic Red 9		250 ppm		
573-58-0	C.I. Direct Red 28		250 ppm		
632-99-5	C.I. Basic Violet 14	-	250 ppm	Most of these substances are regulated	
2475-45-8	C.I. Disperse Blue 1	No intentional use	250 ppm	and should no longer be used for dyeing	LC
2475-46-9	C.I. Disperse Blue 3		250 ppm	of textiles.	
2580-56-5	C.I. Basic Blue 26 (with Michler's Ketone > 0.1%)	-	250 ppm		
569-64-2	C.I. Basic Green 4 (malachite green chloride)		250 ppm		
2437-29-8	C.I. Basic Green 4 (malachite green oxalate)	-	250 ppm		
10309-95-2	C.I. Basic Green 4 (malachite green)		250 ppm		
82-28-0	Disperse Orange 11		250 ppm		
Dyes – Disperse (Se	ensitising)				
119-15-3	Disperse Yellow 1		250 ppm		
12222-97-8	Disperse Blue 102		250 ppm	-	
12223-01-7	Disperse Blue 106		250 ppm		
12236-29-2	Disperse Yellow 39		250 ppm		
13301-61-6	Disperse Orange 37/59/76	-	250 ppm		
23355-64-8	Disperse Brown 1		250 ppm	Disperse dyes are a class of water-	
2581-69-3	Disperse Orange 1		250 ppm	insoluble dyes that penetrate the fibre	
2832-40-8	Disperse Yellow 3		250 ppm	system of synthetic or manufactured	
2872-48-2	Disperse Red 11		250 ppm	fibres and are held in place by physical	
2872-52-8	Disperse Red 1	No intentional use	250 ppm	forces without forming chemical bonds.	LC
3179-89-3	Disperse Red 17		250 ppm	Disperse dyes are used in synthetic fibre (e.g., polyester, acetate, polyamide).	
3179-90-6	Disperse Blue 7		250 ppm	<ul> <li>Restricted disperse dyes are suspected</li> </ul>	
3860-63-7	Disperse Blue 26		250 ppm	of causing allergic reactions and should	
54824-37-2	Disperse Yellow 49		250 ppm	no longer be used for dyeing of textiles.	
12222-75-2	Disperse Blue 35	ľ	250 ppm	- no longer be used for uyeing of textiles.	
61951-51-7	Disperse Blue 124		250 ppm		
6373-73-5	Disperse Yellow 9		250 ppm		
730-40-5	Disperse Orange 3	ľ	250 ppm		
56524-77-7	Disperse Blue 35		250 ppm	7	



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Flame Retardants					
115-96-8	Tris(2-chloroethyl)phosphate (TCEP)		250 ppm		
1163-19-5	Decabromodiphenyl ether (DecaBDE)		250 ppm		
126-72-7	Tris(2,3,-dibromopropyl)-phosphate (TRIS)		250 ppm		
32534-81-9	Pentabromodiphenyl ether (PentaBDE)		250 ppm		
32536-52-0	Octabromodiphenyl ether (OctaBDE)		250 ppm	- Flame retardant chemicals are recelu	
5412-25-9	Bis(2,3-dibromopropyl)phosphate (BIS)		250 ppm	Flame retardant chemicals are rarely used to meet flammability	
545-55-1	Tris(1-aziridinyl)phosphine oxide) (TEPA)	No intentional use	250 ppm	requirements in children's clothing and	GC-MS
59536-65-1	Polybromobiphenyls (PBB)	NO IIIteritional use	250 ppm	- adult products. They should no longer	96-1013
79-94-7	Tetrabromobisphenol A (TBBPA)		250 ppm	be used in apparel and footwear.	
3194-55-6	Hexabromocyclodecane (HBCDD)		250 ppm		
3296-90-0	2,2-bis(bromomethyl)-1,3-propanediol (BBMP)		250 ppm		
13674-87-8	Tris(1,3-dichloro-isopropyl) phosphate (TDCP)		250 ppm		
85535-84-8	Short-chain chlorinated Paraffins (SCCP) (C10-C13)		50 ppm		
Glycols	· · · · · · · · · · · · · · · · · · ·			·	•
111-96-6	Bis(2-methoxyethyl)-ether		50 ppm		
110-80-5	2-ethoxyethanol		50 ppm	In apparel and footwear, glycols have a	
111-15-9	2-ethoxyethyl acetate		50 ppm	wide range of uses including as solvents	
110-71-4	Ethylene glycol dimethyl ether		50 ppm	for finishing/cleaning, printing agents,	High-performance liquid
109-86-4	2-methoxyethanol	No intentional use	50 ppm	and dissolving and diluting fats, oils and	chromatography (HPLC), LC- MS
110-49-6	2-methoxyethylacetate		50 ppm	adhesives (e.g., in degreasing or	IVIS
70657-70-4	2-methoxypropylacetate		50 ppm	cleaning operations).	
112-49-2	Triethylene glycol dimethyl ether		50 ppm		
Halogenated Solven					
107-06-2	1,2-dichloroethane		5 ppm	In apparel and footwear, solvents are	
75-09-2	Methylene chloride		5 ppm	used as finishing/cleaning and printing	
79-01-6	Trichloroethylene	No intentional use	40 ppm	agents, for dissolving and diluting fats,	GC-MS
127-18-4	Tetrachloroethylene		5 ppm	oils and adhesives (e.g., in degreasing or cleaning operations).	



CAS No.	Substance	Group A: Raw Material and Finished Product Supplier Guidance	Group B: Chemical Supplier Commercial Formulation Limit	Potential Uses in Apparel and Footwear Textile Processing	General Techniques for Analysing Chemicals
rganotin Compound	S				•
Multiple	Dibutyltin (DBT)		20 ppm	Organotins are a class of chemicals	
Multiple	Mono-, di- and tri-methyltin derivatives		5 ppm	combining tin and organics such as butyl	
Multiple	Mono-, di- and tri-butyltin derivatives	]	5 ppm	and phenyl groups. Organotins are	
Multiple	Mono-, di- and tri-phenyltin derivatives		5 ppm	predominantly found in the environment	
Multiple	Mono-, di- and tri-octyltin derivatives	No intentional use	5 ppm	as antifoulants in marine paints, but they can also be used as biocides (e.g., antibacterials), catalysts in plastic and glue production and heat stabilisers in plastics/rubber. In textiles and apparel, organotins are associated with plastics/rubber, inks, paints, metallic glitter, polyurethane products and heat transfer material.	GC-MS, low resolution mass spectrometry (LRMS)
olycyclic Aromatic Hy	ydrocarbons (PAHs)				
50-32-8	Benzo[a]pyrene (BaP)		20 ppm	Polycyclic aromatic hydrocarbons (PAHs)	
120-12-7	Anthracene			are natural components of crude oil and	
129-00-0	Pyrene			are a common residue from oil refining.	
191-24-2	Benzo[ghi]perylene			PAHs have a characteristic smell similar	
192-97-2	Benzo[e]pyrene			to the smell of car tires or asphalt. Oil	
193-39-5	Indeno[1,2,3-cd]pyrene			residues containing PAHs are added to	
205-82-3	Benzo[j]fluoranthene			rubber and plastics as a softener or	
205-99-2	Benzo[b]fluoranthene			extender and may be found in rubber,	
206-44-0	Fluoranthene			plastics, lacquers and coatings. PAHs are	
207-08-9	Benzo[k]fluoranthene			often found in the outsoles of footwear	
208-96-8	Acenaphthylene	No intentional con-		and in printing pastes of screen prints.	CC 145
218-01-9	Chrysene	No intentional use	Sum = 200 ppm	PAHs can be present as impurities in	GC-MS
53-70-3	Dibenz[a,h]anthracene			Carbon Black. They also may be formed from thermal decomposition of recycled	
56-55-3	Benzo[a]anthracene			materials during reprocessing.	
83-32-9	Acenaphthene				
85-01-8	Phenanthrene			Naphthalene: Dispersing agents for	
86-73-7	Fluorene			textile dyes may contain high residual	
91-20-3	Naphthalene			naphthalene concentrations due to the use of low quality naphthalene derivatives (e.g., poor quality naphthalene sulphonate formaldehyde condensation products).	x estima 123
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CAS No.	Substance	Group A: Raw Material and Finished Product Supplier Guidance	Group B: Chemical Supplier Commercial Formulation Limit	Potential Uses in Apparel and Footwear Textile Processing	General Techniques for Analysing Chemicals
Perfluorinated and	Polyfluorinated Chemicals (PFCs)				
	nd stain repellent finishes and soil release finishes (f				
	ng to the Organisation for Economic Co-operation a acids (C8 and higher) and on long-chain perfluoroall			<u>/pfc/)</u> are based on long-chain	
Perfluoroalkyl sulfor	ants of this technology include: nates (PFSAs) with carbon chain lengths C6 and high				
Perfluorocarboxylic	acids with carbon chain lengths C8 and higher (e.g.,	PFOA, perfluorooctano	ic acid)		
Multiple	Perfluorooctane sulfonate (PFOS) and related substances		Sum = 2 ppm	PFOA and PFOS may be present as unintended by-products in long-chain	
Multiple	Perfluorooctanoic acid (PFOA) and related substances	No intentional use	2 ppm	commercial water, oil and stain repellent agents. PFOA also may be in use for polymers like polytetrafluoroethylene (PTFE).	LC-MS
Phthalates – includi	ing all other esters of ortho-phthalic acid				
117-81-7	Di(ethylhexyl) phthalate (DEHP)				
117-82-8	Bis(2-methoxyethyl) phthalate (DMEP)			Esters of ortho-phthalic acid (phthalates) are a class of organic	
117-84-0	Di-n-octyl phthalate (DNOP)				
26761-40-0	Di-iso-decyl phthalate (DIDP)				
28553-12-0	Di-isononyl phthalate (DINP)			compounds commonly added to plastics	
84-75-3	Di-n-hexyl phthalate (DnHP)			to increase flexibility. They sometimes	
84-74-2	Dibutyl phthalate (DBP)			are used to facilitate moulding of plastic by decreasing its melting temperature.	
85-68-7	Butyl benzyl phthalate (BBP)			by accreasing its menting temperature.	
84-76-4	Dinonyl phthalate (DNP)	No intentional use	Sum of all phthalates	Phthalates can be found in:	GC-MS
84-66-2	Diethyl phthalate (DEP)	No intentional d3e	= 250 ppm	Flexible plastic components	
131-16-8	Di-n-propyl phthalate (DPRP)			(e.g., PVC)	
84-69-5	Di-isobutyl phthalate (DIBP)			<ul> <li>Print pastes</li> </ul>	
84-61-7	Di-cyclohexyl phthalate (DCHP)			Adhesives	
27554-26-3	Di-iso-octyl phthalate (DIOP)			Plastic buttons	
68515-42-4	1,2-benzenedicarboxylic acid, di-C7-11-branched and linearalkyl esters (DHNUP)			<ul> <li>Plastic sleevings</li> <li>Polymeric coatings</li> </ul>	
71888-89-6	1,2-benzenedicarboxylic acid,di-C6-8-branched alkyl esters,C7-rich (DIHP)			Polymeric coatings	



CAS No.	Substance	Group A: Raw Material and Finished Product Supplier Guidance	Group B: Chemical Supplier Commercial Formulation Limit	Potential Uses in Apparel and Footwear Textile Processing	General Techniques for Analysing Chemicals
otal Heavy Metals					
isted metals are banned fr				eer, nickel, tin, barium, cobalt, iron, Organic Pigments Manufacturers (ETAD)	
7440-38-2	Arsenic (As)		50 ppm	Arsenic and its compounds can be used in some preservatives, pesticides and defoliants for cotton. It is also associated with synthetic fibres, paints, inks, trims and plastics.	
7440-43-9	Cadmium (Cd)		20 ppm (50 ppm for pigments)	Cadmium compounds are found in or used as: pigments (particularly red, orange, yellow and green), a stabiliser for PVC plastic and in fertilisers, biocides and paints (e.g., surface paints on zippers and buttons).	Inductively coupled plasma- optical emission
7439-97-6	Mercury (Hg)	No intentional use	4 ppm (25 ppm for pigments)	Mercury compounds can be present in pesticides and can be found as contamination in caustic soda (NaOH). Mercury compounds may be used in paints (e.g., surface paints on zippers and buttons).	spectrometry (ICP-OES), atomic absorption spectroscopy (AAS)
7439-92-1	Lead (Pb)		100 ppm	In apparel and footwear, lead may be associated with plastics, paints, inks, pigments and surface coatings.	
18540-29-9	Chromium (VI)		10 ppm	Although typically associated with leather tanning, chromium VI also may be used in the dyeing of wool (after the chroming process).	
olatile Organic Compound	ds (VOC)	· · ·			
71-43-2	Benzene		50 ppm	These volatile organic compounds	
1330-20-7	Xylene		500 ppm	should not be used in textile auxiliary	
95-48-7	o-cresol		500 ppm	chemical preparations. They are	
106-44-5	p-cresol	No intentional use	500 ppm	associated with solvent-based processes	GC-MS
108-39-4	m-cresol		500 ppm	like solvent- based polyurethane coatings and glues/adhesives. They should not be used for any kind of facility cleaning or spot cleaning.	
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# Chapter 2: MRSL for Leather Processing

CAS No.	Substance	Group A: Raw Material and Finished Product Supplier Guidance	Group B: Chemical Supplier Commercial Formulation Limit	Potential Uses in Leather Processing for Apparel and Footwear	General Techniques for Analysing Chemicals within commercial formulations
Alkylphenol (AP) and	Alkylphenol Ethoxylates (APEOs): including a	all isomers			
104-40-5 11066-49-2 25154-52-3 84852-15-3	Nonylphenol (NP), mixed isomers		250 ppm	APEOs can be used in leather processing or found in a variety of formulations such as	Liquid chromatography-mass spectrometry (LC-MS), gas chromatography-mass spectrometry (GC-MS) EN ISO 18219 -1 EN ISO 18219 - 2
140-66-9 1806-26-4 27193-28-8	Octylphenol (OP), mixed isomers		250 ppm	detergents, wetting agents, emulsifier/ dispersing agents/dedusting agents for dyes and prints, dyes and pigment preparations, degreasing and fur scouring agents, fat liquors and greases, water borne dispersions and emulsions used in the beamhouse and finishing	
9002-93-1 9036-19-5 68987-90-6	Octylphenol ethoxylates (OPEO)	No intentional use	500 ppm		
9016-45-9 26027-38-3 37205-87-1 68412-54-4 127087-87-0	Nonylphenol ethoxylates (NPEO)		500 ppm	agents. NP and OP are not used by the leather industry, but could be present as contaminants.	LIN 130 18219 - 2
Chlorobenzenes and	Chlorotoluenes				
95-50-1	1,2-dichlorobenzene		1000 ppm	Chlorobenzenes and chlorotoluenes can be	
	no-, di-, tri-, tetra-, penta- and hexa- nono-, di-, tri-, tetra- and penta-	No intentional use	Sum = 200 ppm	used for degreasing sheep and pig skins. They can also be used as solvents (e.g., in chemical synthesis).	GC-MS



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Chlorophenols					
25167-83-3	Tetrachlorophenol (TeCP)		Sum - 20 nnm		
87-86-5	Pentachlorophenol (PCP)		Sum = 20 ppm		
4901-51-3	2,3,4,5-tetrachlorophenol				
58-90-2	2,3,4,6-tetrachlorophenol				
935-95-5	2,3,5,6-tetrachlorophenol				
95-57-8	2-chlorophenol		used as preservatives or pesticides. Pentachlorophenol (PCP) and tetrachlorophenol		
120-83-2	2,4-dichlorophenol			Pentachlorophenol (PCP) and tetrachlorophenol	
583-78-8	2,5-dichlorophenol				
87-65-0	2,6-dichlorophenol				GC-MS
95-95-4	2,4,5-trichlorophenol	No intentional use			EN ISO 17070
88-06-2	2,4,6-trichlorophenol		Sum = 50 ppm	(TeCP) have been used in the past to prevent mould when storing/transporting, raw hides	EN 130 17070
591-35-5	3,5-dichlorophenol			and leather. They are now regulated and should	
576-24-9	2,3-Dichlorophenol			not be used.	
95-77-2	3,4-Dichlorophenol				
108-43-0	3-Chlorophenol				
106-48-9	4-Chlorophenol	]			
15950-66-0	2,3,4-Trichlorophenol				
933-78-8	2,3,5-Trichlorophenol	7			
609-19-8	3,4,5-Trichlorophenol	]			



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Dyes – Azo (Forming	g Restricted Amines)			·	
101-14-4	4,4'-methylene-bis-(2-chloro-aniline)		150 ppm		
101-77-9	4,4'-methylenedianiline		150 ppm		
101-80-4	4,4'-oxydianiline		150 ppm		
106-47-8	4-chloroaniline		150 ppm		
119-90-4	3,3'-dimethoxylbenzidine		150 ppm		
119-93-7	3,3'-dimethylbenzidine		150 ppm		
120-71-8	6-methoxy-m-toluidine		150 ppm	Azo dyes and pigments are colourants that	
137-17-7	2,4,5-trimethylaniline		150 ppm	incorporate one or several azo groups	
139-65-1	4,4'-thiodianiline	]	150 ppm	(-N=N-) bound with aromatic compounds. Thousands of azo dyes exist, but only those which degrade to form the listed cleavable amines are restricted. Azo dyes that release these amines are regulated and should no	
60-09-3	4-aminoazobenzene		150 ppm		
615-05-4	4-methoxy-m-phenylenediamine	]	150 ppm		LC, GC-MS
838-88-0	4,4'-methylenedi-o-toluidine		150 ppm		EN ISO 17234 – 1 EN ISO 17234 – 2
87-62-7	2,6-xylidine	No intentional use	150 ppm		
90-04-0	o-anisidine		150 ppm	longer be used for dyeing of leather.	
91-59-8	2-naphthylamine		150 ppm	Restricted amines also may be present or formed during cleavage of unintended	
91-94-1	3,'3-dichlorobenzidine	]	150 ppm		
92-67-1	4-aminodiphenyl	]	150 ppm	impurities in raw materials used for dyestuff	
92-87-5	Benzidine	1	150 ppm	production.	
95-53-4	o-toluidine	1	150 ppm		
95-68-1	2,4-xylidine		150 ppm		
95-69-2	4-chloro-o-toluidine		150 ppm		
95-80-7	4-methyl-m-phenylenediamine		150 ppm	7	
97-56-3	o-aminoazotoluene		150 ppm	7	
99-55-8	5-nitro-o-toluidine		150 ppm	7	
Dyes – Navy Blue Co	blourant				
118685-33-9	Component 1: C39H23ClCrN7O12S·2Na			Navy Blue colourants are regulated, were not	LC
Not Allocated	Component 2: C46H30CrN10O20S2-3Na	No intentional use	250 ppm	sold commercially, and should not have been used for dyeing of leather	(No test reference available)



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Dyes – Carcinogeni	c or Equivalent Concern			·	
1937-37-7	C.I. Direct Black 38		250 ppm		
2602-46-2	C.I. Direct Blue 6		250 ppm		
3761-53-3	C.I. Acid Red 26		250 ppm		
569-61-9	C.I. Basic Red 9		250 ppm		
573-58-0	C.I. Direct Red 28		250 ppm		
632-99-5	C.I. Basic Violet 14		250 ppm		
2475-45-8	C.I. Disperse Blue 1		250 ppm	Most of these substances are regulated in many countries. All should no longer be used for dyeing of leather.	
2475-46-9	C.I. Disperse Blue 3	No intentional use	250 ppm		LC
2580-56-5	C.I. Basic Blue 26 (with Michler's Ketone > 0.1%)		250 ppm		
569-64-2	C.I. Basic Green 4 (malachite green chloride)		250 ppm		
2437-29-8	C.I. Basic Green 4 (malachite green oxalate)		250 ppm		
10309-95-2	C.I. Basic Green 4 (malachite green)		250 ppm		
82-28-0	Disperse Orange 11		250 ppm		
Dyes – Disperse (Se	nsitizing)	•			
		Disperse dyes have r	no applicability to leather pr	ocessing.	
Fat liquoring agent	5				
85535-84-8	Short-chain chlorinated paraffin ( $C_{10} - C_{13}$ )	No intentional use	250 ppm	Short-chain chlorinated paraffins can be found as contaminants within long-chain chlorinated paraffins and sulfo-chlorinated paraffin's, used as fat liquoring agents.	Gas chromatography/ electron capture negative ion-mass spectrometry (GC/ECNI-MS) EN ISO 18219



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Flame Retardants	·	•			•
115-96-8	Tris(2-chloroethyl)phosphate (TCEP)		250 ppm		
1163-19-5	Decabromodiphenyl ether (DecaBDE)		250 ppm	Flame retardant chemicals are rarely used to meet flammability requirements in children's clothing and adult products, but they could be used in processing leather for technical/	GC-MS
126-72-7	Tris(2,3,-dibromopropyl)-phosphate (TRIS)		250 ppm		
32534-81-9	Pentabromodiphenyl ether (PentaBDE)		250 ppm		
32536-52-0	Octabromodiphenyl ether (OctaBDE)		250 ppm		
5412-25-9	Bis(2,3-dibromopropyl)phosphate (BIS)		250 ppm		
545-55-1	Tris(1-aziridinyl)phosphine oxide) (TEPA)		250 ppm		
59536-65-1	Polybromobiphenyls (PBB)	No intentional use	250 ppm	industrial purposes (e.g., drive belts) and	
79-94-7	Tetrabromobisphenol A (TBBPA)		250 ppm	upholstery leather for trains and planes. The mentioned substances should no longer be used in apparel and footwear.	
3194-55-6	Hexabromocyclodecane (HBCDD)		250 ppm		
3296-90-0	2,2-bis(bromomethyl)-1,3-propanediol (BBMP)		250 ppm		
13674-87-8	Tris(1,3-dichloro-isopropyl) phosphate (TDCP)		250 ppm		
Glycol Ethers	·				
111-96-6	Bis(2-methoxyethyl)-ether		50 ppm	In apparel and footwear, glycol ethers have a	
110-80-5	2-ethoxyethanol		50 ppm	wide range of uses including as solvents for finishing/cleaning, printing agents and dissolving and diluting fats, oils and adhesives (e.g., in degreasing or cleaning operations). Some polar solvents (glycol ethers) are necessary for the use of water-based leather finishing systems.	High-performance liquid chromatography (HPLC), LC- MS
111-15-9	2-ethoxyethyl acetate		50 ppm		
110-71-4	Ethylene glycol dimethyl ether		50 ppm		
109-86-4	2-methoxyethanol	No intentional use	50 ppm		
110-49-6	2-methoxyethylacetate		50 ppm		
112-49-2	Triethylene glycol dimethyl ether		50 ppm		
70657-70-4	2-methoxypropylacetate		1000 ppm	The mentioned glycol ethers are classified as carcinogenic, mutagenic or reprotoxic substances and should not be used in processing leather.	
Halogenated Solver	nts				
107-06-2	1,2-dichloroethane		5 ppm	In apparel and footwear, solvents are used as	
75-09-2	Methylene chloride		5 ppm	finishing/cleaning and printing agents, for	CC MS
79-01-6	Trichloroethylene	No intentional use	40 ppm	dissolving and diluting fats, oils and adhesives	GC-MS
127-18-4	Tetrachloroethylene	] [	5 ppm	(e.g., in degreasing or cleaning operations).	



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Organotin Compound	ds	L	1			
Multiple	Dibutyltin (DBT)	No intentional use	20 ppm (*EXCEPTION* 100 ppm for polyurethane based thickeners used at <20% loading)	Organotins are a class of chemicals combining tin and organics such as butyl and phenyl groups. Organotins are predominantly found in the environment as antifoulants in marine paints, but they can also be used as biocides (e.g., antibacterials), catalysts in plastic and glue	GC-MS, low resolution mass	
Multiple	Mono-, di- and tri-methyltin derivatives		5 ppin	productions and heat stabilizers in	spectrometry (LRMS)	
Multiple	Mono-, di- and tri-butyltin derivatives		5 ppm	plastics/rubber.		
Multiple	Mono-, di- and tri-phenyltin derivatives		5 ppm	Polyurethane thickeners, which could contain traces of DBT, are commonly used for viscosity adjustments of leather chemicals formulations.		
Multiple	Mono-, di- and tri-octyltin derivatives		5 ppm			
olycyclic Aromatic I	Hydrocarbons (PAHs)					
50-32-8	Benzo[a]pyrene (BaP)		20 ppm	_		
120-12-7	Anthracene					
129-00-0	Pyrene					
191-24-2	Benzo[ghi]perylene	4				
192-97-2	Benzo[e]pyrene	4				
193-39-5	Indeno[1,2,3-cd]pyrene	4		Polycyclic aromatic hydrocarbons (PAHs) are		
205-82-3	Benzo[j]fluoranthene	4		natural components of crude oil and are a		
205-99-2	Benzo[b]fluoranthene			common residue from oil refining. PAHs are		
206-44-0	Fluoranthene			Sum = 200 ppm	typically found as contaminants within leather	GC-MS
207-08-9	Benzo[k]fluoranthene		2000 200 ppm	formulations.		
208-96-8	Acenaphthylene	No intentional use				
218-01-9	Chrysene	4				
53-70-3	Dibenz[a,h]anthracene	_				
56-55-3	Benzo[a]anthracene					
83-32-9	Acenaphthene	4				
85-01-8	Phenanthrene	-				
86-73-7 91-20-3	Fluorene Naphthalene		300 ppm	In the leather chemical industry, naphthalene is used as a raw material for manufacture of synthetic tanning agents (syntans) and for manufacture of active substances in dispersing agents used during leather processing.	GC-MS, LC	

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	Polyfluorinated Chemicals (PFCs)				
				gy are banned from intentional use. Long-chain	
	ng to the Organisation for Economic Co-operatic acids (C8 and higher) and on long-chain perfluor			<pre>cd.org/ehs/pfc/</pre> ) are based on long-chain	
	nts of this technology include:				
•	ates (PFSAs) with carbon chain lengths C6 and I		-		
Perfluorocarboxylic	acids with carbon chain lengths C8 and higher (e	e.g., PFOA, perfluorooctano	ic acid)		
Multiple	Perfluorooctane sulfonate (PFOS) and related substances	No intentional use	Sum = 2 ppm	PFOA and PFOS may be present as unintended by-products in long-chain commercial water, oil	
Multiple	Perfluorooctanoic acid (PFOA) and related substances		2 ppm	and stain repellent agents. PFOA also may be in use for polymers like polytetrafluoroethylene (PTFE).	LC-MS
Phthalates – includi	ng all other esters of ortho-phthalic acid				
117-81-7	Di(ethylhexyl) phthalate (DEHP)				
117-82-8	Bis(2-methoxyethyl) phthalate (DMEP)		class of organic compounds common	Esters of ortho-phthalic acid (phthalates) are a class of organic compounds commonly added to	
117-84-0	Di-n-octyl phthalate (DNOP)				
26761-40-0	Di-iso-decyl phthalate (DIDP)				
28553-12-0	Di-isononyl phthalate (DINP)				
84-75-3	Di-n-hexyl phthalate (DnHP)				
84-74-2	Dibutyl phthalate (DBP)			plastics to increase flexibility. They are	
85-68-7	Butyl benzyl phthalate (BBP)	1		sometimes used to facilitate moulding of plastic	
84-76-4	Dinonyl phthalate (DNP)	No intentional use	Sum of all phthalates = 250 ppm	GC-MS	
84-66-2	Diethyl phthalate (DEP)				Ge Wis
131-16-8	Di-n-propyl phthalate (DPRP)			Polymeric coatings for leather finishing,	
84-69-5	Di-isobutyl phthalate (DIBP)			dedusting agents in colourants, fat liquors and	
84-61-7	Di-cyclohexyl phthalate (DCHP)			greases could be a source for phthalates in	
27554-26-3	Di-iso-octyl phthalate (DIOP)			formulations for leather processing.	
	1,2-benzenedicarboxylic acid, di-C7-11-				
68515-42-4	branched and linearalkyl esters (DHNUP)				
71888-89-6	1,2-benzenedicarboxylic acid,di-C6-8- branched alkyl esters,C7-rich (DIHP)				



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Total Heavy Metals		•			
manganese, seleniun	ned from intentional use in textile manufactur n and silver in colourants are expected to comp ( <u>http://www.etad.com/</u> ).		•	zinc, copper, nickel, tin, barium, cobalt, iron, Dyes and Organic Pigments Manufacturers (ETAD)	
7440-38-2	Arsenic (As)	No intentional use	50 ppm	Arsenic and its compounds can be used in some preservatives, pesticides and defoliants for cotton. It is also associated with synthetic fibres, paints, inks, trims and plastics. Arsenic is not a typical residue in leather chemicals.	
7440-43-9	Cadmium (Cd)		20 ppm (50 ppm for pigments)	Cadmium compounds are found in or used as: pigments (particularly red, orange, yellow and green), a stabiliser for PVC plastic and in fertilisers, biocides and paints (e.g., surface paints on zippers and buttons).	Inductively coupled plasma- optical emission spectrometry (ICP-OES), atomic absorption
7439-97-6	Mercury (Hg)		4 ppm (25 ppm for pigments)	Mercury compounds can be present in pesticides and can be found as contamination in caustic soda (NaOH). Mercury compounds may be used in paints (e.g., surface paints on zippers and buttons). Mercury is not a typical residue in leather	spectroscopy (AAS)
				chemicals.	Cr (III) Tanning agents can be monitored for Cr(VI)
7439-92-1	Lead (Pb)		100 ppm	In apparel and footwear, lead may be associated with plastics, paints, inks, pigments and surface coatings.	EN ISO 17075 (Current Use) ISO/DIS 19071 (Draft)
18540-29-9	Chromium (VI)		10 ppm	The two-bath process for tanning using potassium dichromate (VI) is no longer used by the leather industry. Potassium dichromate (VI) and other chromium (VI) compounds are banned and chromium (VI) residues in chromium (III) tanning agents are restricted.	



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Volatile Organic Compounds (VOC)							
71-43-2	Benzene	No intentional use	50 ppm	These volatile organic compounds should not			
95-48-7	o-cresol		500 ppm	be used in textile and leather auxiliary chemical			
106-44-5	p-cresol		500 ppm	preparations. They are associated with solvent-			
108-39-4	m-cresol		500 ppm	based processes like solvent-based polyurethane coatings and glues/adhesives. They should not be used for any kind of facility cleaning or spot cleaning.	GC-MS		

