

2014 MANUFACTURING RESTRICTED SUBSTANCES LIST

JOINT ROADMAP DELIVERABLE

Ø ZDHC

ZERO DISCHARGE OF HAZARDOUS CHEMICALS PROGRAMME

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Manufacturing Restricted Substances List

Zero Discharge of Hazardous Chemicals Programme

1 Background

In the Zero Discharge of Hazardous Chemicals (ZDHC) Joint Roadmap, Version 2, ZDHC member brands committed to define and develop a Manufacturing Restricted Substances List (MRSL) for the apparel and footwear industry. The MRSL addresses hazardous substances potentially used and discharged into the environment during manufacturing and related processes, not just those substances that could be present in finished products.

2 Purpose

The ZDHC MRSL will assist brands, their supply chains and the broader industry to adopt a harmonised approach to the control of hazardous substances used to process textile and trim materials in apparel and footwear. Natural leather and metal trim parts are excluded from the scope of this MRSL version.¹ The MRSL should be communicated to raw material suppliers, including wet-processing facilities and sub-contractors and factories assembling or manufacturing garments and footwear. ZDHC brands expect that material suppliers and factories will communicate with their chemical suppliers to ensure that the listed substances are not present in chemical formulations above established limits.

Note: The MRSL does not replace applicable national environmental or workplace safety restrictions. Worker exposure to the listed and other hazardous substances must not exceed occupational exposure limits and chemical formulations must comply with all applicable legal restrictions, including any subsequent restrictions that establish stricter 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, p. 2). The MRSL applies to chemicals used in facilities that process textile materials and trim parts for use in apparel and footwear. The MRSL does not apply to natural leather processing or production of metal trim parts. Chemicals on the MRSL include ingredients potentially used in cleaners, solvents, adhesives, stabilizers, paints, inks, detergents, dyes, pigments, auxiliaries, coatings and finishing agents used for wet-processing, maintenance, waste water treatment, sanitation and pest control. There should be no intentional use of the 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.

Note: 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 substances in finished products are usually found in smaller concentrations than in the chemical formulations used to produce them. Chemical formulations are highly concentrated before dilution upon application to textiles and other materials.

¹ Hazardous substances in metal trim parts are more properly controlled by material or finished product limits. Hazardous substances potentially used during natural leather processing will be addressed in the next version of the MRSL. Special considerations of the chemistry involved made it necessary for the ZDHC Group to separately address leather processing at a later date.

Chemical Substance

A chemical substance is a chemical element and its compounds in the natural state or obtained by any manufacturing process (REACH, 2014).² A chemical substance is usually identifiable by a single, unique Chemical Abstracts Service (CAS) number or Color Index (CI) number. The ZDHC MRSL focuses on chemical substances listed by CAS number and CI number, but it also includes 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 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 MRSL.

4 MRSL Creation Process

The ZDHC MRSL includes relevant substances from the original 11 priority chemical groups in the Joint Roadmap along with additional substances discussed with qualified experts from the ZDHC Technical Advisory Committee (TAC) and member brands. Several of the listed substances are regulated in finished products and have been successfully restricted by brands for years. Their inclusion on the list is consistent with existing industry standards.

5 MRSL Instructions

Group A: Raw Material and Finished Product Supplier Guidance

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

Group B: Chemical Supplier Formulation Limit

- 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.³

² "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."
http://www.reachonline.eu/REACH/EN/REACH_EN/article3.html. Accessed May 8, 2014.

³ Material Safety Data Sheets (MSDS) only list substances present at concentrations of 1000 ppm or greater. Suppliers must communicate with chemical suppliers to ensure MRSL limits are met.

ZDHC MRSL					
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 isomers					
104-40-5, 11066-49-2 25154-52-3 84852-15-3	Nonylphenol (NP), mixed isomers	No intentional use	250 ppm	APEOs can be used as or found in: detergents, scouring agents, spinning oils, wetting agents, softeners, emulsifier/dispersing agents for dyes and prints, impregnating agents, de-gumming for silk production, dyes and pigment preparations, polyester padding and down/feather fillings	Liquid chromatography-Mass spectrometry (LC-MS), Gas chromatography-Mass spectrometry (GC-MS)
140-66-9 1806-26-4 27193-28-8	Octylphenol (OP), mixed isomers		250 ppm		
9002-93-1 9036-19-5 68987-90-6	Octylphenol ethoxylates (OPEO)		500 ppm		
9016-45-9 26027-38-3 37205-87-1 68412-54-4 127087-87-0	Nonylphenol ethoxylates (NPEO)		500 ppm		
Chlorobenzenes and Chlorotoluenes					
95-50-1	1,2-dichlorobenzene	No intentional use	1000 ppm	Chlorobenzenes and chlorotoluenes (chlorinated aromatic hydrocarbons) can be used as carriers in the dyeing process of polyester or wool/polyester fibres. They can also be used as solvents.	GC-MS
Other mono-, di-, tri-, and tetra-, hexa-, penta-, chlorobenzenes and mono-, di-, tri-, and tetra-, hexa-, penta-, chlorotoluenes			Sum = 200 ppm		
Chlorophenols					
25167-83-3	Tetrachlorophenol (TeCP)	No intentional use	Sum = 20 ppm	Chlorophenols are polychlorinated compounds used as preservatives or pesticides. Pentachlorophenol (PCP) and tetrachlorophenol (TeCP) are sometimes used to prevent mould and kill insects when growing cotton and when storing/transporting fabrics. PCP/TeCP can also be used as a preservative in print pastes.	GC-MS
87-86-5	Pentachlorophenol (PCP)		Sum = 50 ppm		
Mono-, di-, and tri- chlorophenols					

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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
Dyes – Azo (Forming Restricted Amines)					
101-14-4	4,4'-methylene-bis-(2-chloro-aniline)	No intentional use	200 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 which 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.	LC, GC
101-77-9	4,4'-methylenedianiline		200 ppm		
101-80-4	4,4'-oxydianiline		200 ppm		
106-47-8	4-chloroaniline		200 ppm		
119-90-4	3,3'-dimethoxybenzidine		200 ppm		
119-93-7	3,3'-dimethylbenzidine		200 ppm		
120-71-8	6-methoxy-m-toluidine		200 ppm		
137-17-7	2,4,5-trimethylaniline		200 ppm		
139-65-1	4,4'-thiodianiline		200 ppm		
60-09-3	4-aminoazobenzene		200 ppm		
615-05-4	4-methoxy-m-phenylenediamine		200 ppm		
838-88-0	4,4'-methylenedi-o-toluidine		200 ppm		
87-62-7	2,6-xylydine		200 ppm		
90-04-0	o-anisidine		200 ppm		
91-59-8	2-naphthylamine		200 ppm		
91-94-1	3,3'-dichlorobenzidine		200 ppm		
92-67-1	4-aminodiphenyl		200 ppm		
92-87-5	Benzidine		200 ppm		
95-53-4	o-toluidine		200 ppm		
95-68-1	2,4-Xylydine		200 ppm		
95-69-2	4-chloro-o-toluidine	200 ppm			
95-80-7	4-methyl-m-phenylenediamine	200 ppm			
97-56-3	o-aminoazotoluene	200 ppm			
99-55-8	5-nitro-o-toluidine	200 ppm			
Dyes – Navy Blue Colourant					
118685-33-9	Component 1: C39H23ClCrN7O12S·2Na	No intentional use	250 ppm	Navy Blue colourants are regulated and should no longer be used for dyeing of textiles.	LC
Not Allocated	Component 2: C46H30CrN10O20S2·3Na				

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Dyes – Carcinogenic or Equivalent Concern					
1937-37-7	C.I. Direct Black 38	No intentional use	250 ppm	Most of these substances are regulated and should no longer be used for dyeing of textiles.	LC
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		
2475-46-9	C.I. Disperse Blue 3		250 ppm		
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 (Sensitizing)					
119-15-3	Disperse Yellow 1	No intentional use	250 ppm	Disperse dyes are a class of water-insoluble dyes that penetrate the fibre system of synthetic or manufactured fibres and are held in place by physical forces without forming chemical bonds. Disperse dyes are used in synthetic fibre (e.g., polyester, acetate, polyamide). Restricted disperse dyes are suspected of causing allergic reactions and should no longer be used for dyeing of textiles.	LC
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		
2581-69-3	Disperse Orange 1		250 ppm		
2832-40-8	Disperse Yellow 3		250 ppm		
2872-48-2	Disperse Red 11		250 ppm		
2872-52-8	Disperse Red 1		250 ppm		
3179-89-3	Disperse Red 17		250 ppm		
3179-90-6	Disperse Blue 7		250 ppm		
3860-63-7	Disperse Blue 26		250 ppm		
54824-37-2	Disperse Yellow 49		250 ppm		
12222-75-2	Disperse Blue 35		250 ppm		
61951-51-7	Disperse Blue 124		250 ppm		
6373-73-5	Disperse Yellow 9		250 ppm		
730-40-5	Disperse Orange 3		250 ppm		
56524-77-7	Disperse Blue 35		250 ppm		

ZDHC MRSL					
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Flame Retardants					
115-96-8	Tris(2-chloroethyl)phosphate (TCEP)	No intentional use	250 ppm	Flame retardant chemicals are rarely used to meet flammability requirements in children's clothing and adult products. They should no longer be used in apparel and footwear.	GC-MS
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		
5412-25-9	Bis(2,3-dibromopropyl)phosphate (BIS)		250 ppm		
545-55-1	Tris(1-aziridiny)phosphine oxide (TEPA)		250 ppm		
59536-65-1	Polybromobiphenyls (PBB)		250 ppm		
79-94-7	Tetrabromobisphenol A (TBBPA)		250 ppm		
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	No intentional use	50 ppm	In apparel and footwear, glycols have a 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).	High-performance liquid chromatography (HPLC), LC-MS
110-80-5	2-ethoxyethanol		50 ppm		
111-15-9	2-ethoxyethyl acetate		50 ppm		
110-71-4	Ethylene glycol dimethyl ether		50 ppm		
109-86-4	2-methoxyethanol		50 ppm		
110-49-6	2-methoxyethylacetate		50 ppm		
70657-70-4	2-methoxypropylacetate		50 ppm		
112-49-2	Triethylene glycol dimethyl ether		50 ppm		
Halogenated Solvents					
107-06-2	1,2-dichloroethane	No intentional use	5 ppm	In apparel and footwear, solvents are used as finishing/cleaning and printing agents, for dissolving and diluting fats, oils and adhesives (e.g., in degreasing or cleaning operations).	GC-MS
75-09-2	Methylene chloride		5 ppm		
79-01-6	Trichloroethylene		40 ppm		
127-18-4	Tetrachloroethylene		5 ppm		

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Organotin Compounds					
Multiple	Dibutyltin (DBT)	No intentional use	20 ppm	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 production and heat stabilizers 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)
Multiple	Dimethyltin (DMT)		5 ppm		
Multiple	Monobutyltin (MBT)		5 ppm		
Multiple	Monooctyltin (MOT)		5 ppm		
Multiple	Diocetyl tin (DOT)		5 ppm		
Multiple	Tricyclohexyltin (TCyHT)		5 ppm		
Multiple	Triocetyl tin (TOT)		5 ppm		
Multiple	Tripropyltin (TPT)		5 ppm		
Multiple	Tributyltin (TBT)		5 ppm		
Multiple	Trimethyltin (TMT)		5 ppm		
Multiple	Triphenyltin (TPHT)		5 ppm		
Multiple	Tetrabutyltin (TebT)		5 ppm		
Polycyclic Aromatic Hydrocarbons (PAHs)					
50-32-8	Benzo[a]pyrene (BaP)	No intentional use	20 ppm	Polycyclic aromatic hydrocarbons (PAHs) are natural components of crude oil and are a common residue from oil refining. PAHs have a characteristic smell similar to the smell of car tires or asphalt. Oil residues containing PAHs are added to rubber and plastics as a softener or extender and may be found in rubber, plastics, lacquers and coatings. PAHs are often found in the outsoles of footwear and in printing pastes of screen prints. PAHs can be present as impurities in Carbon Black. They also may be formed from thermal decomposition of recycled materials during reprocessing. <u>Naphthalene</u> : Dispersing agents for textile dyes may contain high residual naphthalene concentrations due to the use of low quality naphthalene derivatives (e.g., poor quality naphthalene sulphonate formaldehyde condensation products).	GC-MS
120-12-7	Anthracene		Sum = 200 ppm		
129-00-0	Pyrene				
191-24-2	Benzo[ghi]perylene				
192-97-2	Benzo[e]pyrene				
193-39-5	Indeno[1,2,3-cd]pyrene				
205-82-3	Benzo[j]fluoranthene				
205-99-2	Benzo[b]fluoranthene				
206-44-0	Fluoranthene				
207-08-9	Benzo[k]fluoranthene				
208-96-8	Acenaphthylene				
218-01-9	Chrysene				
53-70-3	Dibenz[a,h]anthracene				
56-55-3	Benzo[a]anthracene				
83-32-9	Acenaphthene				
85-01-8	Phenanthrene				
86-73-7	Fluorene				
91-20-3	Naphthalene				

ZDHC MRSL					
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Perfluorinated and Polyfluorinated Chemicals (PFCs)					
<p>Beginning January 1, 2015: Durable water, oil and stain repellent finishes and soil release finishes (fluorinated polymers) based on long-chain technology are banned from intentional use by ZDHC signatory brands. Long-chain compounds according to the OECD definition (http://www.oecd.org/ehs/pfc/) are based on long-chain perfluorocarboxylic acids (C8 and higher) and on long-chain perfluoroalkyl sulfonates (C6 and higher).</p> <p>The main contaminants of this technology include:</p> <ul style="list-style-type: none"> Perfluoroalkyl sulfonates (PFSAs) with carbon chain lengths C6 and higher (e.g., PFOS, perfluorooctane sulfonate) Perfluorocarboxylic acids with carbon chain lengths C8 and higher (e.g., PFOA, perfluorooctanoic acid) 					
Multiple	Perfluorooctane sulfonate (PFOS) and related substances	No intentional use	2 ppm (sum)	PFOA and PFOS may be present as unintended by-products in long-chain commercial water, oil and stain repellent agents. PFOA also may be in use for polymers like polytetrafluoroethylene (PTFE).	LC-MS
335-67-1	Perfluorooctanoic acid (PFOA)		2 ppm		
Phthalates – including all other esters of ortho-phthalic acid					
117-81-7	Di(ethylhexyl) phthalate (DEHP)	No intentional use	Sum of all phthalates = 250 ppm	<p>Esters of ortho-phthalic acid (phthalates) are a class of organic compounds commonly added to plastics to increase flexibility. They are sometimes used to facilitate moulding of plastic by decreasing its melting temperature.</p> <p>Phthalates can be found in:</p> <ul style="list-style-type: none"> Flexible plastic components (e.g., PVC) Print pastes Adhesives Plastic buttons Plastic sleeves Polymeric coatings 	GC-MS
117-82-8	Bis(2-methoxyethyl) phthalate (DMEP)				
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)				
85-68-7	Butyl benzyl phthalate (BBP)				
84-76-4	Dinonyl phthalate (DNP)				
84-66-2	Diethyl phthalate (DEP)				
131-16-8	Di-n-propyl phthalate (DPRP)				
84-69-5	Di-isobutyl phthalate (DIBP)				
84-61-7	Di-cyclohexyl phthalate (DCHP)				
27554-26-3	Di-iso-octyl phthalate (DIOP)				
68515-42-4	1,2-benzenedicarboxylic acid, di-C7-11-branched and linearalkyl esters (DHNUP)				
71888-89-6	1,2-benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich (DIHP)				

ZDHC MRSL					
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Total Heavy Metals					
Listed metals are banned from intentional use in textile manufacturing/finishing. Additionally, residual traces of antimony, zinc, copper, nickel, tin, barium, cobalt, iron, manganese, selenium and silver in colourants are expected to comply with the Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD) concentration limits (http://www.etad.com/).					
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.	Inductively coupled plasma-optical emission spectrometry (ICP-OES), atomic absorption spectroscopy (AAS)
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 stabilizer for PVC plastic, and in fertilizers, biocides and paints (e.g., surface paints on zippers and buttons).	
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).	
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).	
Volatile Organic Compounds (VOC)					
71-43-2	Benzene	No intentional use	50 ppm	These volatile organic compounds should not be used in textile auxiliary chemical preparations. They are associated with solvent-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
1330-20-7	Xylene		500 ppm		
95-48-7	o-cresol		500 ppm		
106-44-5	p-cresol		500 ppm		
108-39-4	m-cresol		500 ppm		