

2014 MANUFACTURING RESTRICTED SUBSTANCES LIST

JOINT ROADMAP DELIVERABLE

Ø ZDHC

ZERO DISCHARGE OF HAZARDOUS CHEMICALS PROGRAMME



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Manufacturers 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 in the MRSL include solvents, cleaners, adhesives, paints, inks, detergents, dyes, colourants, 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 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.

¹ Hazardous substances in metal trim parts are more properly controlled by material or finished product limits. Hazardous substances potentially used and discharged during leather processing will be addressed separately in the next version of the MRSL, due to the substantially different chemical processes involved.

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 will primarily focus on chemical substances listed by CAS number and CI number, but will also 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 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 Roadmap³ 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 member brands for years. Though already restricted by brand members, their inclusion on the list will keep it 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 guidance document for the lowest 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.⁴

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 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 amines as defined in Annex XVII of REACH.

⁴ 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
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
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.
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.
87-86-5	Pentachlorophenol (PCP)			
Mono-, di-, and tri- chlorophenols			Sum = 50 ppm	
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.
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	

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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
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.
Not Allocated	Component 2: C46H30CrN10O20S2·3Na			
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.
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.
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	

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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
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	
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.
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-aziridinyl)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).
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	

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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).
75-09-2	Methylene chloride		5 ppm	
79-01-6	Trichloroethylene		40 ppm	
127-18-4	Tetrachloroethylene		5 ppm	
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 productions 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.
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).
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			

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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
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 (PFASs) 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).
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 sleeveings • Polymeric coatings
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				
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
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.
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.
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	