TECHNICAL REPORT

ISO/TR 16178

Second edition
2012-07-15

Footwear — Critical substances potentially present in footwear and footwear components

Chaussures — Substances critiques potentiellement présentes dans la chaussure et les composants de chaussures

Reference number
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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TR 16178 was prepared by Technical Committee ISO/TC 216, *Footwear*.

ISO/TR 16178 was prepared by the European Committee for Standardization (CEN) Technical Committee CEN/TC 309, *Footwear*, in collaboration with ISO Technical Committee TC 216, *Footwear*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna agreement).

This second edition cancels and replaces the first edition (ISO/TR 16178:2010), which has been technically revised.

Footwear — Critical substances potentially present in footwear and footwear components

1 Scope

This Technical Report establishes a list of critical chemical substances potentially present in footwear and footwear components.

This Technical Report describes the critical chemical substances, their potential risks, the materials in which they can be found and the test method(s) which can be used to quantify them. It does not include requirements; it is the responsibility of the user of this Technical Report to fix his/her level of acceptance, for instance using a defined concentration or detection limit or quantification limit.

NOTE The proposed test methods indicate the state of the art. Some substances do not include a test method, as no test method is available at the time of publication of this Technical Report. If possible, it is intended to include a test method in a revision of this Technical Report.

This Technical Report applies to any kind of footwear and footwear components.

2 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

2.1
allergen
substance that is capable of inducing an allergic reaction

2.2
allergy
immunologically mediated response to certain specific substances

NOTE 1 The specific substances are allergens.

NOTE 2 Type-1 allergy (respiratory allergy) is mediated by IgE antibodies and can cause asthma, rhinitis and urticaria.

NOTE 3 Type-4 allergy (dermal allergy) is mediated by T-cells and can cause dermatitis.

2.3
detection limit
value from which a substance is considered detectable

NOTE This means that the signal associated to the substance is three times bigger than the background noise signal. The limit of detection is determined experimentally by the laboratory for each substance.

2.4
quantification limit
value from which a substance is considered measurable

NOTE It is the value where the uncertainty of measurement is equal to 50 % of the determined value.

2.5
absence of a chemical
state in which a chemical is lacking from a material, where the test method is unable to detect it

NOTE The amount of the chemical is smaller than the detection limit of the test method.

2.6
critical substance
chemical substance that can be found in footwear or footwear components and that can have an effect on the wearer and/or environmental impact due to its chemical reactivity

NOTE 1 The effects caused by critical substances vary. They can be carcinogenic or mutagenic effects, allergy, reaction to toxics, etc.

NOTE 2 Legislations can change; this Technical Report gives the information available at the time of publication. It is the responsibility of the user of this Technical Report to ensure that no changes have occurred.

2.6.1
critical substances category 1
substances with proven dangerous effect on the wearer

NOTE These substances are restricted by regulation at European level.

2.6.2
critical substances category 2
substances with dangerous effect on the wearer

NOTE These substances are restricted by regulation at national level in some countries.

2.6.3
critical substances category 3
substances with environmental impact

NOTE These substances are mentioned in European Ecolabel.

2.6.4
critical substances category 4
substances that are highly suspected to have an effect on the wearer

NOTE Possibly, these substances are not restricted by regulation at the time of publication of this Technical Report.

2.6.5
critical substances category 5
substances that are suspected to have an effect on the wearer

NOTE Possibly, these substances are not restricted by regulation at the time of publication of this Technical Report.

3 Presence of chemicals in footwear materials

A number of chemicals are present in footwear materials. Table 1 gives:

a) materials in which they are supposed to be (for information, see Annex A);

b) the list of the critical chemicals, (for information, see Annex B);

c) test methods which can be used to provoke and quantify them;

d) the potential risk associated with and assessed by the use of the critical substances category scale (see 2.6).

For composite materials, the tests should be conducted on the entire component.

EXAMPLE 1 Coated textile (cotton plus PVC coating): the test on PVC and the test on cellulosic natural fibres should be carried out.

EXAMPLE 2 Mixed textile (PES plus cotton): the test on cellulosic natural textile and the test on PES textile should be carried out.

Table 1 — Critical chemicals potentially present in footwear and footwear components

Substance (see Annex B)		Test method	Leather			Synthetic material									Natural material				Miscellaneous			
			Leather	Coated leather	Leather fibre board	PVC	EVA	Rubber	PU – TPU elasthan	PE- PP	Polyester	Polyamide	Chloride fibre	Polyacrylic	Latex	Cellulosic natural textile	Proteinic natural textile	Wood - cork	Adhesives	Metal hardware	Prints for textile	Cellulosic materials
Acrylonitrile								5						5					5			
AZO - arylamines		ISO 17234-1	1	1	1																	
AZO - arylamines	When 4-aminoazobenzene is suspected	ISO 17234-2	1	1	1																	
AZO - arylamines		EN 14362-1										1	1	1		1	1				1	
AZO - arylamines		EN 14362-2									1										1	
AZO - arylamines	When 4-aminoazobenzene is suspected	EN 14362-3									1	1	1	1		1	1				1	
Cadmium	All plastics (mainly PVC)	EN 1122		1		1	1	1	1	1											1	
Chloroorganic carriers		DIN 54232									3											
Chromium VI		ISO 17075	2	2	2																	
Colophony																			5			
Dimethylformamide (DMF)				4					4													
Dimethylfumarate (DMFU)		ISO/TS 16186	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1			1	1
Disperses dyes and dyestuffs		DIN 54231									2	2	2	2		2	2					
Flame retardant	Only for product claiming FR properties		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1			1	1
Formaldehyde		ISO 17226-1 and ISO 17226-2	2	2	2																	

Table 1 *(continued)*

Substance (see Annex B)		Test method	Leather			Synthetic material									Natural material				Miscellaneous			
			Leather	Coated leather	Leather fibre board	PVC	EVA	Rubber	PU – TPU elasthan	PE- PP	Polyester	Polyamide	Chloride fibre	Polyacrylic	Latex	Cellulosic natural textile	Proteinic natural textile	Wood - cork	Adhesives	Metal hardware	Prints for textile	Cellulosic materials
Formaldehyde		EN 120 EN 717-3																2				2
Formaldehyde		ISO 14184-1									2	2	2	2		2	2					
Heavy metals	Extractible (Sb – As – Pb – Cd – Cr – Co – Cu – Ni – Hg – Zn)	ISO 17072-1	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4		4	4
	Extractible Footwear for children less than 36 months old (Sb – As – Pb – Cd – Cr – Co – Cu – Ni – Hg – Zn – Ba – Se)	ISO 17072-1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2		2	2
	Total content (Sb – As – Pb – Cd – Cr – Co – Cu – Ni – Hg – Zn)	ISO 17072-2	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4		4	4
	Total content (As – Cd – Pb)	EN 14602:2004	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3		3	3
Mercaptobenzothiazole								5														
Extractible latex proteins		EN 455-3													4							
N-ethylphenylamine								5							4							
Nickel	Skin contact	EN 1811 CR 12471 (with or without EN 12472)																		1		
Nitrosamines	Footwear for children less than 36 months old	EN 12868						2														

Table 1 *(continued)*

Substance (see Annex B)		Test method	Leather: Leather	Leather: Coated leather	Leather: Leather fibre board	Synthetic material: PVC	Synthetic material: EVA	Synthetic material: Rubber	Synthetic material: PU – TPU elasthan	Synthetic material: PE- PP	Synthetic material: Polyester	Synthetic material: Polyamide	Synthetic material: Chloride fibre	Synthetic material: Polyacrylic	Natural material: Latex	Natural material: Cellulosic natural textile	Natural material: Proteinic natural textile	Natural material: Wood - cork	Miscellaneous: Adhesives	Miscellaneous: Metal hardware	Miscellaneous: Prints for textile	Miscellaneous: Cellulosic materials
Nitrosamines		EN 12868						3														
OP, NP, OPEO, NPEO Alkylphenols and alkylphenolethoxylates)			4	4	4						3	3	3	3		3	3					
Organotin compounds(TBT, TPT)		ISO/TS 16179	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1
Organotin compounds(MBT, DBT, DOT),		ISO/TS 16179	4	4	4	4	4	4	4	4	3	3	3	3	4	3	3	4	4		4	4
Ortho-phenylphenol		ISO 13365	5	5	5		5				5	5	5	5	5	5	5	5				5
Ozone depleting substances											3	3	3	3		3	3					
PAH – polycyclic aromatic hydrocarbons			4	4	4	4	4	4	4	4												
PCP -TeCP – TriCP - polychlorophenols		ISO 17070	2	2	2																	
PCP -TeCP – TriCP - polychlorophenols		CEN/TR 14823																2				
PCP -TeCP – TriCP - polychlorophenols		XP G 08-015														2	2					
Pesticides			5	5	5											3	3					5
PFOS/PFOA (Perfluorooctane sulfonate/perfluorooctanoic acid)	Only for product claiming FR properties and water resistance	CEN/TS 15968	1	1	1						1	1	1	1		1	1					
pH		ISO 4045	4	4	4																	
pH		ISO 3071									4	4	4	4		4	4					
Phenol			4	4	4			4								4	4		4			4
Phthalates		ISO/TS 16181				3	3	3	3	3												
Phthalates	Footwear for children less than 36 months old	ISO/TS 16181		2		2	2	2	2	2	2	2	2	2		2	2				2	
PCB - Polychlorinated biphenyls			5	5	5						3	3	3	3		3	3					
Polychloroprene or neoprene								5											5			

Table 1 *(continued)*

Substance (see Annex B)	**Test method**	**Leather**			**Synthetic material**									**Natural material**				**Miscellaneous**			
		Leather	Coated leather	Leather fibre board	PVC	EVA	Rubber	PU – TPU elasthan	PE- PP	Polyester	Polyamide	Chloride fibre	Polyacrylic	Latex	Cellulosic natural textile	Proteinic natural textile	Wood - cork	Adhesives	Metal hardware	Prints for textile	Cellulosic materials
PPD Paraphenylene diamine		5	5	5						5	5		5		5	5				5	5
PTBF Paratertiary butyl phenol formaldehyde																		5			
Short-chained chloroparaffins (C_{10}-C_{13})		3	3	3			3			3	3	3	3		3	3					
TCMTB (2-(thiocyanatomethylthio)-1,3-benzothiazole)	ISO 13365	5	5	5																	
Thiuram and thiocarbamate							5														
Vinyl chloride monomer	ISO 6401		4		4																

Annex A
(informative)

Materials used in the footwear industry

A.1 Leather

Leather is a general term for hide or skin, with its original fibrous structure more or less intact, tanned to be rot-proof. The hair or wool can be removed or not. Leather is also made from a hide or skin, which has been split into layers or segmented, either before or after tanning. However, if the tanned hide or skin is disintegrated mechanically and/or chemically into fibrous particles, small pieces or powders and then, with or without the combination of a binding agent, is made into sheets or other forms, such sheets or forms are not leather. If the leather has a surface coating, no matter what is applied, or a glued-on finish, such surface coating layers should not be thicker than 0,15 mm.

A.2 Coated leather

Leather, of which the applied surface coating does not exceed one third of the total thickness of the product, but is in excess of 0,15 mm.

A.3 Leather fibre board

Leather fibre board is the term for materials where tanned hides or skins are disintegrated, mechanically and/or chemically, into fibrous particles, small pieces or powders and then, are made into sheets or other forms, with or without the combination of a binding agent. A minimum amount of 50 % mass fraction of dry leather is necessary to use the term leather fibre board.

A.4 PVC

PVC is a polymer constituted of polymerized vinyl chloride. In footwear material, PVC is used with plasticizer in order to create flexibility. It can also be used as polymeric coating in a coated fabric or patent leather.

A.5 EVA foam

EVA foam is a polymer composed of ethylene vinyl acetate; it can be expanded to foam. It is used as a lightweight midsole in some trainers and as an outsole in some summer sandals where resistance to abrasion is not required.

A.6 Rubber, synthetic rubber and rubber foam

Rubbers are polymers based on either synthetic or natural materials, which are cross-linked to give required physical performance properties and chemical resistance. They are extensively used as outsoles in many styles of footwear (see ISO 1382).

A.7 Thermoplastic polyurethanes

Thermoplastic polyurethanes (TPU) are compounds formed from the condensation of isocyanates and polyols and can be remoulded on the application of heat. They can be moulded in compact or cellular forms.

A.8 Thermoplastic elastomers or thermoplastic rubbers

Thermoplastic elastomers or thermoplastic rubbers (not vulcanized) (TPE or TPR) combine the processability of plastics with the flexibility and durability of rubbers, while more lightweight and formable. These properties provide favourable conditions for the production of thermoplastic materials due to a structure consisting of block copolymers, which combine elastic chain segments with rubbery properties, and very rigid segments (at room temperature). They play the same role as the sulfur bonds formed during vulcanization process, i.e. to prevent the chain displacement against stress. However, due to the absence of a cross-linked structure, cohesion is lost where exceeding the glass transition temperature and the hot material can flow and is suitable for injection moulding. For example:

— Polyethylene (PE) is a thermoplastic polymer consisting of long chains, and produced by combining the ingredient monomer ethylene; it is used in a wide variety of applications, including packaging, textiles, vessels and construction;

— Polypropylene (PP) is a thermoplastic polymer consisting of long chains, and produced by combining the ingredient monomer propylene; it is used in a wide variety of applications, including packaging, textiles (e.g. ropes, thermal underwear and carpets) and construction.

A.9 Latex

Rubber latex is a water-based colloidal solution, which includes spherical rubber particles with a diameter smaller than 1 µm, dispersed in an aqueous continuous phase and relatively stable. Due to its hydrophobic nature, it is non-miscible with water, and the suspension is stabilized because every rubber particle is coated with a layer of natural or synthetic emulsifiers (see ISO 1382).

A.10 Blown material — Foam

Blown material is a synthetic expanded polymer with a closed-cell or open-cell structure, which can be flexible or rigid, and is used for a variety of products.

A.11 Composite materials

Composites, also known as composite materials or reinforced plastics, consist of a polymeric matrix or continuous phase and a discrete phase, made up of one or more loads or reinforcements in the form of mineral and/or synthetic fibres. As a result, a structural material is obtained, whose mechanical properties are, at least, higher than the values obtained from the lineal combination of the individual properties of both constituents. For instance, carbon or glass fibres are commonly used as reinforcing materials.

A.12 Polyurethane

Polyurethane (PU) includes those polymers with urethane groups in the molecular backbone, regardless of the chemical composition of the rest of the chain. Urethane groups (see Figure A.1) are produced through a chemical reaction between a diisocyanate and a polyol. Thus, typical polyurethane may contain, in addition to the urethane linkages, aliphatic and aromatic hydrocarbons, esters, ethers, amides, urea and isocyanates groups. A wide range of properties can be obtained depending on the chemical composition used: thermoplastic, thermoset, rigid or flexible, cellular or compact polyurethanes, etc. Polyurethanes are used as structural materials, coatings, adhesives and sealants.

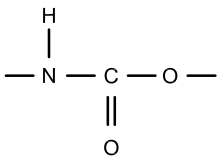

Figure A.1 — Urethane groups

A.13 Textile

The word textile was originally used to describe a woven fabric. The term now applies to fibres, filaments or yarns, which are natural or man-made, and the products obtained from them.

EXAMPLE Threads, cords, ropes, braids, lace, embroidery, nets and fabrics made by weaving, knitting, felting, bonding and tufting are textiles.

A.14 Polyester

Polyester is a polymer with ester bonds in its main string (see Figure A.2). The definition of polyester includes the large family of synthetic polymers, with polycarbonate being the most used and poly(ethylene terephthalate) (PET) the most of all.

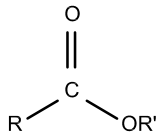

Figure A.2 — Ester bond

A.15 Polyester fibre

Polyester fibre are fibres composed of synthetic linear macromolecules having in the chain at least 85 % (mass fraction) of an ester of a diol and benzene-1,4-dicarboxylic acid (terephthalic acid).

A.16 Polyamides

A synthetic linear polymer in which the linkage of the simple chemical compound or compounds used in its production takes place through the formation of amide groups, for example

$[— R — CO — NH — R — CO — NH —]_n$, or

$[— R_1 — NH — CO — R_2 — CO — NH \ —]_n$,

where R, R_1, and R_2 are generally, but not necessarily, linear divalent hydrocarbon chains $(— CH_2 —)_m$.

Polyamides are distinguished from one another by quoting the number of carbon atoms in the repeating unit or units for polyamides made from two reactants. In the latter case, the number of carbon atoms in the diamine is given first, followed by the number in the dicarboxylic acid, for example

- hexanolactam (E – caprolactam)

[— NH — $(CH_2)_5$ — CO —]$_n$ (Nylon 6)

- 1,6 – diaminohexane + hexanedioic acid (adipic acid)

[— NH — $(CH_2)_6$ — NH — CO — $(CH_2)_4$ — CO —]$_n$ (Nylon 6:6)

- 1,6 – diaminohexane + decanedioic acid

[— NH — $(CH_2)_6$ — NH — CO — $(CH_2)_8$ — CO —]$_n$ (Nylon 6:10)

Polyamide (synthetic fibre) and Nylon[1)] (synthetic fibre) are used to describe fibres composed of synthetic linear macromolecules, having in the chain, recurring amide groups, at least 85 % of which are attached to aliphatic or cyclo-aliphatic groups.

Nylon is a thermoplastic polymer belonging to the polyamide group (PA). It has good tensile properties, high hardness and toughness. Nylon fibres are commonly used by the textile industry in the shape of threads. This material is comprised of long-chain synthetic polyamides containing amide groups (-CONH-), in the core of the polymeric chain. Although there are different varieties of Nylon, the most commonly known are Nylon 6.6 and Nylon 6.

A.17 Chlorofibres

Chlorofibres is a term used to describe fibres composed of synthetic linear macromolecules with more than 50 % (mass fraction) of chloroethene (vinyl chloride) or I,J-dichloroethene (vinylidene chloride) groups in their chains. [More than 65 %, in the case where the rest of the chain is made up of cyanoethene (acrylonitrile) groups, the modacrylic fibres being thus excluded.]

A.18 Polyacrylic

Polyacrylics are a synonym for copolymer fabrics with polyacrylnitrile (PAN) and polymethyl-methacrylates (PMMA). The content of PAN shall be higher than 85 %. Typical materials are Dralon, Orlon or Dolan[2)].

A.19 Natural textile

A.19.1 General

Natural textile describes articles of clothing and textile commodities, which are produced from natural fibres by special criteria. Natural fibres should be untreated or, at least, treated to the least extent possible. The porosity of the fibres should be guaranteed, in any case, and the natural textile articles should be water vapour permeable.

NOTE Natural fibres are fibres made from animals, plants or minerals (cotton, wool, silk, linen, etc.). Fibres of natural origin, which are intended to be spinnable by means of chemical preparation, just like viscose rayon or modal, are not considered natural fibres.

A.19.2 Proteinic textile

Proteinic textile is textile issued from animal fibres.

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1) Nylon is a trademark. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO. Equivalent products may be used if they can be shown to lead to the same results.

2) Dralon, Orlon and Dolan are trademarks. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO. Equivalent products may be used if they can be shown to lead to the same results.

A.19.3 Cellulosic textile

Cellulosic textile is textile issued from vegetable fibres.

A.19.4 Man-made textile fibres

Man-made textile fibres are textiles which are not issued from proteinic or cellulosic fibres.

A.19.5 Mixed textile

Mixed textiles consist of a mix of natural fibres and chemical fibres.

A.20 Print for textile

Textile printing is a process of applying colour to fabric or non-woven textile in definite patterns or designs. In properly printed fabrics, the colour is bonded with the fibre so as to resist washing and friction. Textile printing is related to dyeing but, whereas in dyeing proper the whole fabric is uniformly covered with one colour, in printing, one or more colour(s) are applied to the fabric in certain parts only and in sharply defined patterns.

In printing, wooden blocks, stencils, engraved plates, rollers or silkscreen are used to place colours on fabric. Colourants used in printing contain dyes or pigments.

NOTE Traditional textile printing techniques can be broadly categorized into four styles:

— direct printing, in which colourants containing dyes, thickener and the mordents or substances necessary for fixing the colour on the textile are printed in the desired pattern;

— the printing of a mordent in the desired pattern prior to dyeing cloth; the colours adhere only where the mordent is printed;

— resist dyeing, in which a wax or other substance is printed on to fabric, which is subsequently dyed, leaving uncoloured patterns against a coloured ground;

— discharge printing, in which a bleaching agent is printed into previously dyed fabrics to remove some or the entire colour.

All printing pastes, whether containing colouring matter or not, are known technically as colours and these colours, over colouring matter, contain thickening agents as vehicles in printing. Thickening agents include starch, flour, arabic gum, dextrin or albumen, filler and mordent agent to enable fixing of the colours in textile.

A.21 Wood

Wood is a hard, fibrous, lignified structural tissue produced as secondary xylem in the stems of woody plants, notably trees, but also shrubs. Wood is a heterogeneous, hygroscopic, cellular and anisotropic material. Wood is composed of fibre of cellulose and hemicelluloses, impregnated with lignin.

In the footwear industry, wood can find some application mostly in particular types of shoes, i.e. sandals, where hardness and structural resistance of raw materials are required.

Wood is often preserved by chemical treatments.

A.22 Cork

Cork material is a subset of generic cork tissue, harvested for commercial use primarily from the cork oak tree, *Quercus suber*. Cork's elasticity, light weight combined with is near impermeability makes it a suitable material for many uses.

The cork material is also used in the footwear industry for application where a high structural resistance is not required, typically as an insole material for certain types of shoes.

A.23 Adhesives

An adhesive is a non-metallic substance capable of joining materials by surface bonding (adhesion) and by the bond possessing adequate internal strength (cohesion).

In the footwear industry, many types of adhesives are used in bonding upper and sole as the major joint, but also for the minor joint in footwear.

EN 923 contains a systematic classification of all adhesives, with the corresponding definitions.

The formulation of the adhesives is classified in EN 923. Due to the large number of adhesives used, there are no corresponding typical formulations available for adhesives used for the minor joint in footwear.

A.24 Metallic hardware

Metallic hardware is any material composed entirely of a single metallic element or a combination of metallic elements (alloys). This may be coated to give a desired appearance. This may be achieved by painting, plating or varnishing.

Uses of metallic components include fastenings, ornamental decorations, structural component and assembling.

A.25 Cellulosic material

Cellulosic material is material made from cellulose fibre (for example paper). Where is used as insole material, it contains a binder.

Annex B
(informative)

Critical substances potentially present in footwear and footwear components

B.1 General

This annex describes the critical substances potentially present in footwear and footwear components.

Depending on the tested product and application (see Table 1), different test methods can be used.

B.2 Acrylonitrile

B.2.1 General

Chemical compound with the formula CH_2CHCN.

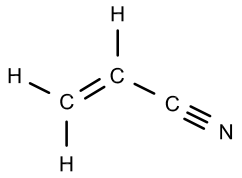


Figure B.1 — Acrylonitrile molecular structure

This pungent-smelling colourless liquid often appears yellow due to impurities. It is an important monomer for the manufacture of useful plastics. In terms of its molecular structure, it consists of a vinyl group linked to a nitrile.

Acrylonitrile is used principally as a monomer in the manufacture of synthetic polymers, especially polyacrylonitrile, which comprises acrylic fibres. Acrylic fibres are, among other uses, precursors for well-known carbon-fibre. It is also a component of synthetic rubber.

Synthetic rubber, essentially based on SBR (styrene-butadiene rubber) and containing acrylonitrile has some properties which are suitable for use as a material for soles, especially for a sole in professional high-resistance footwear.

B.2.2 Potential risks

Acrylonitrile is highly flammable and toxic. It undergoes explosive polymerization. The burning material releases fumes of hydrogen cyanide and oxides of nitrogen. Acrylonitrile is classified as a recognized human carcinogen.

Where polymerized or in composition as synthetic rubber, it is considered inert material and no particular problems rise in using acrylonitrile.

In footwear products, the problems of the use of acrylonitrile are essentially correlated with waste management, in order to avoid uncontrolled burning process, which can release dangerous fumes into the environment.

B.2.3 Test methods

At the time of publication of this Technical Report, there is no standard available for acrylonitrile analysis in footwear and footwear components.

B.3 Aromatic amines

B.3.1 General

Aromatic amines are amines with an aromatic substituent, that is -NH_2, -NH- or nitrogen group(s) attached to an aromatic hydrocarbon, whose structure usually contains one or more benzene rings. Benzidine is an example (see Figure B.2).

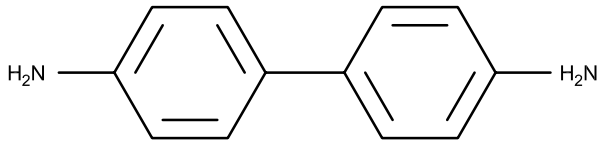


Figure B.2 — Example of aromatic amines molecular structure —Benzidine

Aromatic amines are produced during the degradation of azo-dyes.

The list of the critical amines is given in Table B.1.

Table B.1 — List of critical aromatic amines developed by azo-dyestuffs

Compound	CAS number	Compound	CAS number
4-aminobiphenyl	92-67-1	3,3'-dimethyl-4,4'-diaminodiphenylmethane	838-88-0
Benzidine	92-87-5	*p*-cresidine	120-71-8
4-chloro-*o*-toluidine	95-69-2	4,4'-methylen-bis(2-chloraniline)	101-14-4
2-naphthylamine	91-59-8	4,4'-oxydianiline	101-80-4
o-aminoazotoluene	97-56-3	4,4'-thiodianiline	139-65-1
2-amino-4-nitrotoluene	99-55-8	*o*-toluidine	95-53-4
p-chloroaniline	106-47-8	2,4-toluylendiamine	95-80-7
2,4-diaminoanisole	615-05-4	2,4,5-trimethylaniline	137-17-7
4,4'- diaminodiphenylmethane	101-77-9	2,4-dimethylaniline (=2,4-Xylidine)[a]	95-68-1
3,3'-dichlorobenzidine	91-94-1	2,6-dimethylaniline (=2,6-Xylidine)[a]	87-62-7
3,3'-dimethoxybenzidine	119-90-4	2-methoxyaniline (=*o*-anisidine)	90-04-0
3,3'-dimethylbenzidine	119-93-7	4-aminoazobenzene	60-09-3

[a] This is not requested by the European Directive 2002/95/EC, but may be considered in some other countries.

B.3.2 Potential risks

The aromatic amines given in Table B.1 are known to be carcinogenic (4-aminobiphenyl, benzidine, 4-chlor-*o*-toluidine, 2-naphthylamine) or suspected to be carcinogenic (others). These substances are restricted in many countries.

B.3.3 Test methods

For the purposes of this Technical Report, the content of aromatic amines can be tested with one of the test methods in

— ISO 17234-1,

— ISO 17234-2,

— EN 14362-1,

— EN 14362-2, or

— EN 14362-3.

B.4 Cadmium — Cd

For cadmium (Cd), see B.13.

B.5 Chloroorganic carriers

B.5.1 General

The halogenated carriers, are mainly used in the manufacture of polyester. Table B.2 includes a list of some of these compounds.

Table B.2 — List of chloroorganic carriers

Substance	CAS number	
Dichlorobenzenes	1,2-DICHLOROBENZENE [95-50-1] 1,3-DICHLOROBENZENE [541-73-1]	1,4-DICHLOROBENZENE [106-46-7]
Trichlorobenzenes	1,2,3-TRICHLOROBENZENE [87-61-6] 1,2,4-TRICHLOROBENZENE [120-81-1]	1,3,5-TRICHLOROBENZENE [108-70-3]
Tetrachlorobenzenes	TETRACHLOROBENZENE [634-66-2]	
Pentachlorobenzene	PENTACHLOROBENZENE [608-93-5]	
Hexachlorobenzene	HEXACHLOROBENZENE [118-74-1]	
Chlorotoluene	2-CHLOROTOLUENE [95-49-9] 3-CHLOROTOLUENE [108-41-8]	4-CHLOROTOLUENE [106-43-4]
Dichlorotoluenes	2,3-DICHLOROTOLUENE [32768-54-0] 2,4-DICHLOROTOLUENE [95-73-8] 2,5-DICHLOROTOLUENE [19398-61-9]	2,6-DICHLOROTOLUENE [118-69-4] 3,4 DICHLOROTOLUENE [95-75-0]
Trichlorotoluenes	2,3,6-TRICHLOROTOLUENE [2077-46-5] 2,4,5-TRICHLOROTOLUENE [6639-30-1] alpha, alpha alpha TRICHLOROTOLUENE [98-07-7]	alpha, 2,4 TRICHLOROTOLUENE [94-99-5] alpha, 2,6 TRICHLOROTOLUENE [2014-83-7] alpha, 3,4 TRICHLOROTOLUENE [102-47-6]
Tetrachlorotoluenes	alpha, alpha, 2,6 TETRACHLOROTOLUENE [81-19-6] alpha, alpha, alpha, 2 – TETRACHLOROTOLUENE [2136-89-2]	alpha, 4 – TETRACHLOROTOLUENE [5216-25-1]
Pentachlorotoluene	2,3,4,5,6-PENTACHLOROTOLUENE [877-11-2]	

B.5.2 Potential risks

The substances listed in Table B.2 are toxic and some of them carcinogenic.

B.5.3 Test methods

For the purposes of this Technical Report, the content of chloroorganic carriers can be tested using the test method in DIN 54232.

B.6 Chromium and chromium VI

For chromium and chromium VI, see B.13.

B.7 Colophony

B.7.1 General

Colophony is also called Greek pitch or rosin. The major part of rosin used is obtained as a by-product of the pulp industry and is known as tall oil rosin. These two types of rosin do not have the same composition although

they have major products in common; however, a variation in the amounts of the different compounds is seen. They are often used for the same purposes and, probably, in shoes modified tall oil rosin is found most often .

Both types of rosin consist of 90 % resin acids and 10 % neutral material. In colophony of the gum rosin type, the major resin acid is abietic acid, while dehydroabietic acid dominates in tall oil rosin. 7-Oxo-dehydroabietic acid is a stable oxidation product, which is used as a marker for the presence of other autoxidation products in rosin, e.g. 15-hydroperoxyabietic acid. The latter is identified as the major allergen in colophony. However, this hydroperoxide is not suitable for analysis since it is not stable enough.

Colophony is an ingredient in printing inks, varnishes, adhesives (glues), soap, paper sizing, soda, and, in past times, was an ingredient in sealing wax.

B.7.2 Potential risks

Prolonged exposure to colophony fumes released during soldering can cause occupational asthma in sensitive individuals, therefore, it is considered an allergen.

Colophony is one of the most common causes of skin (contact) allergy, which is caused by contact with colophony on the skin. It is on the ten top list of all skin allergens tested worldwide. Colophony in shoes is considered to be a dominating cause of sensitization in this aspect.

NOTE Colophony is classified in the EU legislation due to its skin sensitizing properties and products containing more than 1 % of colophony are marked with R 43 (i.e. can cause skin sensitization). However, in the EU legislation, there is no demand for R 42 (lung allergy).

B.7.3 Test methods

At the time of publication of this Technical Report, there is no standard available for colophony analysis in footwear and footwear components.

B.8 Dimethylformamide

B.8.1 General

Dimethylformamide (DMF) is the organic compound with the formula $(CH_3)_2NC(O)H$. Commonly abbreviated as DMF, this colourless liquid is miscible with water and the majority of organic liquids. DMF is a common solvent for chemical reactions. Pure dimethylformamide is odourless, whereas technical grade or degraded dimethylformamide often has a fishy smell due to impurity of dimethylamine (CAS number is [68-12-2]).

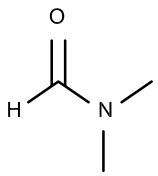


Figure B.3 — Dimethylformamide molecular structure

Its name is derived from the fact that it is a derivative of formamide, the amide of formic acid. The primary use of dimethylformamide is as a solvent with low evaporation rate. Dimethylformamide is used in the production of acrylic fibres and plastics. It is also used in the manufacture of adhesives, synthetic leathers, fibres, films, and surface coatings.

B.8.2 Potential risks

Dimethylformamide is harmful by inhalation, ingestion or skin contact and can act as a carcinogen. Ingestion or absorption through skin can be fatal. Exposure can result in foetal death. Long-term exposure can result in kidney or liver damage. It is also an irritant.

B.8.3 Test methods

At the time of publication of this Technical Report, there is no standard available for DMF analysis in footwear and footwear components.

B.9 Dimethylfumarate

B.9.1 General

Dimethylfumarate (DMFU) (CAS number [624-49-7]) is used to treat psoriasis. It is a lipophilic, highly mobile molecule in human tissue. However, as an α,β-unsaturated ester, dimethylfumarate reacts rapidly with the detoxifying agent glutathione by Michael addition.

Another use for dimethylfumarate is mould inhibition. Dimethylfumarate is used also as a biocide.

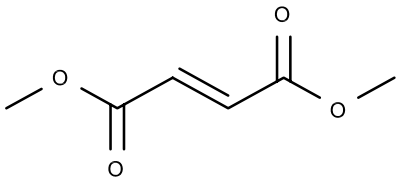


Figure B.4 — Dimethylfumarate molecular structure

B.9.2 Potential risks

Dimethylfumarate has been found to be a sensitizer at very low concentrations, producing extensive, pronounced eczema, which is difficult to treat. Low concentrations of about 1 ppm (0,998 859 mg/L) can produce allergic reactions.

NOTE The extreme sensitizing risk was brought to public attention by the “poison chair” incident, where a Chinese manufacturer produced two-seater sofas, which contained DMFU sachets in the interior in order to inhibit mould while they were in storage or transport. The cause was identified as dimethylfumarate-induced allergic reaction.

B.9.3 Test methods

For the purposes of this Technical Report, the content of DMFU can be tested using the test method in ISO/TS 16186.

B.10 Disperses dyes

B.10.1 General

A dye can generally be described as a coloured substance, which has an affinity for the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and can require a mordant to improve the fastness of the dye on the fibre. Both dyes and pigments appear to be coloured because they preferentially absorb some wavelengths of light. In contrast with a dye, a pigment generally is insoluble and has no affinity for the substrate. Some dyes can be precipitated with an inert salt to produce a lake pigment.

A list of allergenic dyes and of carcinogenic dyes is included in Table B.3 and Table B.4, respectively.

Table B.3 — List of allergenic disperse dyes

Name of dye	Abbreviated term	CAS number	Colour index (CI)
Disperse blue 3	DB 3	2475-46-9	61505
Disperse blue 7	DB 7	3179-90-6	62500
Disperse blue 26	DB 26	3860-63-7	63305
Disperse blue 102	DB 102	69766-79-6	—
Disperse brown 1	—	23355-64-8	—
Disperse yellow 1	DG 1	119-15-3	10345
Disperse yellow 9	DG 9	6373-73-5	10375
Disperse yellow 39	DG 39	12236-29-2	—
Disperse yellow 49	DG 49	54824.37-2	—
Disperse orange 1	DO1	2581-69-3	11080
Disperse red 11	DR 11	2872-48-2	62015
Disperse red 17	DR 17	3179-89-3	11210
Disperse yellow 7	DG 7	6300-37-4	—
Disperse yellow 56	DG 56	54077-16-6	—
Disperse red 151	—	—	—
Solvent red 23	—	—	—

Disperse dyes (see Table B.3 and B.4) were originally developed for the dyeing of cellulose acetate and are not substantially water soluble. The dyes are finely ground in the presence of a dispersing agent and then sold as a paste or spray-dried and sold as a powder.

They can also be used to dye nylon, cellulose triacetate, polyester and acrylic fibres. In some cases, a dyeing temperature of 130 °C is required, and a pressurized dyebath is used. The very fine particle size gives a large surface area that aids dissolution to allow uptake by the fibre. The dyeing rate can be significantly influenced by the choice of dispersing agent used during the grinding.

Table B.4 — List of carcinogenic dyes

Name of dye	Abbreviated term	CAS number	Colour index (CI)
Navy blue	Navy blue	118685-33-9	611-070-00-2
Disperse blue 1	DB1	2475-45-8	64500
Disperse blue 35	DB 35	12222-75-2	—
Disperse blue 106	DB 106	12223-01-7	—
Disperse blue 124	DB 124	61951-51-7	—
Disperse yellow 3	DG 3	2832-40-8	11855
Disperse orange 3	DO3	730-40-5	11005
Disperse orange 37/59/76[a]	DO 37	12223-33-5	—
Disperse red 1	DR1	2872-52-8	11110
Basic red 9	—	569-61-9	—
Violet 3	—	—	—
Disperse yellow 23	DY 23	6250-22-3	—

[a] Disperse orange 59 and disperse orange 76 are synonymic names for disperse orange 37.

B.10.2 Potential risks

A certain number of these dyes are carcinogenic or allergenic.

B.10.3 Test methods

For the purposes of this Technical Report, the content of disperse dyes can be tested using the test method in DIN 54231.

B.11 Flame retardants

B.11.1 General

Flame retardants (see Table B.5) are materials which inhibit or resist the spread of fire. They can be naturally occurring substances, such as asbestos as well as synthetic materials, usually halocarbons, such as polybrominated diphenyl ether (PBDEs) and polychlorinated biphenyls (PCBs).

Flame retardants are added to polymers used in a wide range of materials, such as electric and electronic equipment, paint and textiles. Polybrominated diphenyl ethers (PBDE) are so-called additive flame retardants. PBDEs are used as commercial mixtures, with different degrees of bromination. Typically, PBDEs can comprise up to 5 % to 20 % of the total mass of the product to which they are added. Since these chemicals are not chemically bound they can “leak” from the polymer product, thus entering the environment.

B.11.2 Potential risks

PBDEs can be accumulated in human body and have harmful effects on human health and the environment. There is growing evidence that indicates these chemicals can cause liver toxicity, thyroid toxicity and neurodevelopmental toxicity.

A list of critical flame retardants is included in Table B.5.

Table B.5 — List of critical flame retardants

Substance		CAS number
OBDE	2,2’,3,3’,4,4’,5,6 octabrominated diphenyl ether 196	446255-38-3
	2,2’,3,3’,4,4’,6,6’ octabrominated diphenyl ether 197	446255-39-6
	2,2’,3,4,4’,5,5’,6 octabrominated diphenyl ether 203	337513-72-1
	2,3,3’,4,4’,5,5’,6 octabrominated diphenyl ether 205	446225-56-7
	Technical mixture of the 4 substances	32536-52-0
PBDE	2,2’,4,4’,5 pentabrominated diphenyl ether - 99	60348-60-9
	2,2’,4,4’,6 pentabrominated diphenyl ether 100	189084-64-8
TEPA	Tris-(azirinidyl)-phosphinoxid	5455-55-1
TRIS	Tris(2,3-dibromopropyl) phosphate	126-72-7
PBB	Polybrominated biphenyls	
TCEP	Tris(2-chloroethyl) phosphate	115-96-8
NOTE These substances can be used in children’s slippers to meet flammability requirements.		

B.11.3 Test methods

At the time of publication of this Technical Report, there is no standard available for flame retardant analysis in footwear and footwear components.

B.12 Formaldehyde

B.12.1 General

Formaldehyde (methanal) is the chemical compound with the formula H_2CO. Formaldehyde exists in several forms aside from H_2CO: the cyclic trimer trioxane and the polymer paraformaldehyde. Its CAS number is [50-00-0].

Formaldehyde is an intermediate in the oxidation (or combustion) of methane as well as other carbon compounds. It can be found in the smoke from forest fires, in automobile exhaust, and in tobacco smoke. In the atmosphere, formaldehyde is produced by the action of sunlight and oxygen on atmospheric methane and other hydrocarbons. It thus becomes part of smog pollution.

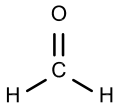


Figure B.5 — Formaldehyde molecular structure

B.12.2 Potential risks

Formaldehyde can be toxic, allergenic and carcinogenic. Because formaldehyde resins are used in many construction materials, formaldehyde is one of the more common indoor air pollutants. At concentrations above 0,1 ppm (0,998 859 mg/L) in air, formaldehyde can irritate the eyes and mucous membranes, resulting in watery eyes. If inhaled, formaldehyde at this concentration can cause headaches and a burning sensation in the throat, and difficulty breathing, as well as triggering or aggravating asthma symptoms. Formaldehyde is classified as a probable human carcinogen. Sufficient evidence exists that formaldehyde can cause nasopharyngeal cancer in humans by the International Agency for Research on Cancer. Formaldehyde can cause allergies and is part of the standard patch test series.

B.12.3 Test methods

For the purposes of this Technical Report, the content of formaldehyde can be tested with one of the test methods in

— EN 120,

— EN 717-3,

— ISO 17226-1,

— ISO 17226-2, or

— ISO 14184-1.

B.13 Heavy metals

B.13.1 General

Heavy metals or metallic elements can be determined for different purposes.

In this Technical Report, antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se) and zinc (Zn) are considered heavy metals.

B.13.1.1 List of heavy metals

B.13.1.1.1 Extractible heavy metals

Extractible heavy metals (Sb, As, Ba, Pb, Cd, Cr, Co, Cu, Ni, Hg, Se and Zn) are the amount of metal which can be extracted from a material or a product using an extraction solution. The choices of the solution depend on the test goal. For example:

— water is used for waste leaching;

— hydrochloric acid solution to simulate ingestion (never used for footwear);

— artificial perspiration to simulate the wear.

NOTE Barium is not a heavy metal and Selenium is a non-metal. However, they are generally included in the list of heavy metals .

B.13.1.1.2 Total heavy metals

Total heavy metals (Sb, As, Ba, Pb, Cd, Cr, Co, Cu, Ni, Hg, Se and Zn) are the total amount of metal contained in a material or a product. The test method includes firstly a total digestion of the sample and, afterwards, a metal quantification.

The heavy metal content is used most of the time to determine whether a waste can be landfilled or not.

B.13.1.1.3 Heavy metal in footwear for children less than 36 months old

Extractible heavy metals (Sb, As, Ba, Cd, Cr, Pb, Hg and Se) are the amount of metals which can be extracted from a material or a product by an acid solution. This test should be carried out only in the cases where ingestion is possible.

B.13.2 Potential risks

Table B.6 includes a list of list of heavy metals and their associated potential risks.

Table B.6 — List of heavy metals and associated risks

Metals	General	Potential risks
Antimony Sb	Antimony is used in flame-proofing, paints, ceramics, enamels, a wide variety of alloys, electronics, and rubber. Antimony has been used in the production of polyester textile fibres.	Antimony and many of its compounds are toxic. Clinically, antimony poisoning is very similar to arsenic poisoning. In small doses, antimony causes headache, dizziness, and depression. Larger doses cause violent and frequent vomiting, and leads to death in a few days.
Arsenic As	Arsenic and its compounds are used as pesticides, herbicides, insecticides and various alloys.	Arsenic and many of its compounds are especially potent poisons. Arsenic disrupts ATP (adenosine triphosphate) production through several mechanisms.
Barium Ba	—	All water- or acid-soluble barium compounds are extremely poisonous. At low doses, barium acts as a muscle stimulant, while higher doses affect the nervous system, causing cardiac irregularities, tremors, weakness, anxiety, dyspnea and paralysis.
Cadmium Cd	Cadmium is used largely in batteries and pigments, for example in plastic products, especially PVC.	Cadmium and several cadmium-containing compounds are known carcinogens and can induce many types of cancer. Research has found that cadmium toxicity can be carried into the body by zinc-binding proteins. Cadmium is also a potential environmental hazard. Cadmium is one of six substances banned by the European Union's Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment.

Table B.6 *(continued)*

Metals	General	Potential risks
Cobalt Co	Cobalt and his compounds are used in the production of inks, paints, and varnishes.	Cobalt compounds should be handled with care due to cobalt's slight toxicity. Cobalt is known as an allergen can cause dermatitis (contact allergy).
Copper Cu	—	All copper compounds, unless otherwise known, should be treated as if they were toxic. Symptoms of copper poisoning are very similar to those produced by arsenic. Fatal cases are generally terminated by convulsions, palsy, and insensibility.
Chromium Cr	In the footwear sector, there are three oxidation states, which are stable in nature, i.e. metallic Cr, Cr(III) and Cr(VI), and one substance can convert to another. Chromium compounds are used in dyes and paints, plating of metallic components and the tanning of leather.	Chromium metal and trivalent chromium [Cr(III)] compounds are not usually considered health hazards; chromium is an essential trace mineral. However, hexavalent chromium [Cr(VI)] compounds can be toxic if orally ingested or inhaled (see B.13.4.2).
Lead Pb	Lead is used in building construction, lead-acid batteries, bullets and shot, weights for model railroad cars, and is part of solder, pewter and fusible alloys. Lead is also often used as a pigment in paint.	Lead is a potent neurotoxin, which accumulates in soft tissues and bone over time. Lead is a poisonous metal, which can damage nervous connections (especially in young children) and cause blood and brain disorders. Long-term exposure to lead or its salts (especially soluble salts or the strong oxidant PbO_2) can cause nephropathy. The concern about lead's role in cognitive deficits in children has brought about widespread reduction in its use (lead exposure has been linked to schizophrenia).
Mercury Hg	Mercury occurs in deposits throughout the world. It is harmless in an insoluble form, such as mercuric sulfide, but it is poisonous in soluble forms such as mercuric chloride or methylmercury.	Metallic mercury can be biologically transformed into the organic methylmercury, which means that all release of the metal is potentially dangerous. Mercury and most of its compounds are extremely toxic and are generally handled with care; for CAS numbers of spills involving mercury (such as from certain thermometers or fluorescent light bulbs), specific cleaning instructions should be used to avoid toxic exposure.
Nickel Ni	—	Exposure to nickel metal and soluble compounds is strictly controlled. Nickel sulfide fume and dust are believed to be carcinogenic; various other nickel compounds can be as well.
Selenium Se	The greatest use of selenium compounds is in electronic and photocopier components, but they are also widely used in glass, pigments, rubber, metal alloys, textiles, petroleum, medical therapeutic agents and photographic emulsions.	The substance is irritating to the eyes and the respiratory tract; inhalation of dust can cause lung oedema. Inhalation of fume can cause symptoms of asphyxiation, chills and fever and bronchitis. The effects can be delayed. Repeated or prolonged contact with skin can cause dermatitis. The substance can have effects on the respiratory tract, gastrointestinal tract and skin, resulting in nausea, vomiting, coughing, yellowish skin discolouration, loss of nails, garlic breath and bad teeth.
Zinc Zn	Zinc is currently used in plating of metallic components.	Even though zinc is an essential requirement for a healthy body, too much zinc can be harmful. Excessive absorption of zinc can also suppress copper and iron absorption. The free zinc ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish.

B.13.3 Test methods

For the purposes of this Technical Report, the content of heavy metals can be tested using one of the test methods in

— EN 14602,

— ISO 17072-1, or

— ISO 17072-2.

B.13.4 Special cases

B.13.4.1 Cadmium

Cadmium is used largely in plastic products, especially PVC.

Cadmium can be tested according to the method described in EN 1122.

B.13.4.2 Chromium VI

Chromium VI can appear in chrome tanned leather due to undesirable chemical reaction, depending on a large number of parameters (washing of leather, storage conditions, tanning agents, etc.).

In the past, chromium VI was used for mordant dyeing process of textile.

Cr(VI) compounds are irritating to eyes, skin and mucous membranes. Chronic exposure to Cr(VI) compounds can cause permanent eye injury, unless properly treated. Cr(VI) is an established human carcinogen and allergen.

Chromium VI can be determined directly from leather or after an ageing of leather using a specific test method, i.e. ISO 17075.

B.13.4.3 Nickel

Nickel coating is often used for the finishing of the metallic pieces. Metallic fastening or ornamental pieces can be used in the manufacture of shoes. These components are made from different types of metal or specific alloys. The external finishing for these elements is important in order to give the final desired aspect as brilliant, stained, old style, etc.

This external finishing is achieved with different processes, such as burnishing, sandblasting and nickel-plating.

This Technical Report applies only to the metallic pieces in prolonged contact with the skin (eyelet, buckle, slide fastener, etc.).

Sensitized individuals can show a skin allergy to nickel.

Nickel can be tested according to the method described in EN 1811, EN 12472 and CEN CR 12471.

B.14 Mercaptobenzothiazole

B.14.1 General

Mercaptobenzothiazole is a substance used in the manufacture of rubbers (natural or synthetic). It is added to latex or synthetics to improve the vulcanization and decrease the speed of ageing (anti-oxidizing agent). Its CAS number is [149-30-4].

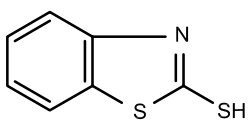


Figure B.6 — Mercaptobenzothiazole molecular structure

B.14.2 Potential risks

Mercaptobenzothiazole is an allergen.

B.14.3 Test methods

At the time of publication of this Technical Report, there is no standard available for mercaptobenzothiazole analysis in footwear and footwear components.

B.15 Extractible latex proteins

B.15.1 General

Natural rubber latex (*cis*-1,4-polyisoprene) is used in a wide variety of products, if vulcanized. Where latex is used as a concentrate to produce dipped products such as medical examination gloves, contraceptives, elastic threads and adhesives, it can contain residual proteins.

B.15.2 Potential risks

These substances are allergens, which can be capable of inducing anaphylactic shock in sensitized individuals. This is referred to as a “type 1 rubber allergy”.

B.15.3 Test methods

For the purposes of this Technical Report, the content of extractible latex proteins can be tested with one of the methods described in EN 455-3 (for biological evaluation).

B.16 N-ethylphenylamine

B.16.1 General

N-ethylphenylamine (N-ethylaminobenzene) is a secondary amine used as an intermediate for dyestuffs. Its CAS number is [103-69-5].

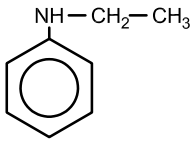


Figure B.7 — N-ethylphenylamine molecular structure

B.16.2 Potential risks

It is toxic by inhalation, through contact with the skin and if swallowed.

B.16.3 Test methods

At the time of publication of this Technical Report, there is no standard available for N-ethylphenylamine analysis in footwear and footwear components.

B.17 Nickel – Ni

For nickel, see B.13.

B.18 Nitrosamines

B.18.1 General

Nitrosamines are chemical compounds of the chemical structure $R_1N(-R_2)-N=O$, some of which can be carcinogenic.

Nitrosamines can be used in rubber products, pesticides and certain cosmetics.

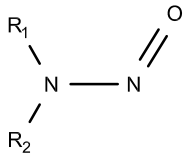


Figure B.8 — Nitrosamines molecular structure

B.18.2 Potential risks

Nitrosamines can cause cancers in a wide variety of animal species, a feature which suggests that they can also be carcinogenic in humans. Epidemiological data suggests that nitrosamines in preserved food can cause stomach cancer.

These substances should be determined in footwear for children less than 36 months old.

B.18.3 Test methods

For the purposes of this Technical Report, the content of nitrosamines may be determined by EN 12868.

B.19 Alkylphenols and alkylphenolethoxylates (NP, OP, NPEO, OPEO)

B.19.1 General

Alkylphenols (AP) and alkylphenolethoxylates (APEO) are used in plastics, as additives, plasticizers and surface-active ingredients in industrial detergents and emulsifiers. Ethoxylated alkylphenols and alkylphenolethoxylates (APEO) are used as industrial surfactants in the manufacture of wool and metal, as emulsifiers for emulsion polymerization, in laboratory detergents, and pesticides.

Commonly used AP are nonylphenol (NP) and, to a lesser extent, octylphenol (OP), in both cases pre-dominantly the para-substituted isomers (> 90 %). APEO are produced by a condensation reaction of AP with ethylene oxide. While the lower condensates (number of ethoxylate units about 4) are used as emulsifiers, the higher ethoxylates are used in textile and carpet cleaning and as emulsifiers in solvents and agricultural pesticides. As with the AP, nonylphenol ethoxylate (NPEO) is more widely used than octylphenol ethoxylate (OPEO). AP are moderately soluble in water while the APEO are generally more water soluble than the parent AP themselves.

NOTE APEs are a component of some household detergents outside of Europe; within Europe, due to environmental concerns, they are replaced by more expensive, but safer alcohol ethoxylates.

B.19.2 Potential risks

Nonylphenol and nonyphenol ethoxylates (NPEO) are a hazard to human and environmental safety in the chemical preparation (not in the final products).

B.19.3 Test methods

At the time of publication of this Technical Report, there is no standard available for alkylphenol and alkylphenolethoxylates analysis in footwear and footwear components.

B.20 Organotins

B.20.1 General

Organotins compounds or stannanes are chemical compounds based on tin. Tributyltin oxide (or tributyltin for short) is extensively used as a wood preservative. Tributyltin compounds are used as marine anti-biofouling agents.

There are three major applications for organotin compounds. Firstly, the use of tributyltin (TBT) in anti-fouling paints for ships, secondly, the use of triphenyltin (TPhT) as a pesticide, and third, the use of butyl- and octyltin compounds as stabilizers in polymers. Therefore, many textile products containing polymer parts, such as T-shirts with prints, sanitary bandages, plasters and diapers can contain organotin compounds. In some cases, organotin compounds are used as fungicides on textiles that are exposed to extreme weather conditions such as canvas.

B.20.2 Potential risks

Triorganotins are very toxic. Tri-n-alkyltins are phytotoxic and therefore cannot be used in agriculture. Depending on the organic groups, they can be powerful bactericides and fungicides. Tributyltins are used as industrial biocides, e.g. as antifungal agents in textiles and paper, wood pulp and paper mill systems, breweries, and industrial cooling systems. Tributyltins are also used in marine anti-fouling paint. Triphenyltins are used as active components of antifungal paints and agricultural fungicides. Other Triorganotins are used as miticides and acaricides.

Diorganotins have no antifungal activity, low toxicity, and low antibacterial activity, except for diphenyltins. They are used in polymer manufacturing, as PVC heat stabilizers, and as catalysts in the manufacture of polyurethane and silicone curing.

Monoorganotins have no biocidal activity and their toxicity to mammals is very low. Methyltin, butyltin, octyltin and monoestertins are used as PVC heat stabilizers.

B.20.3 Test methods

For the purposes of this Technical Report, the content of organotins can be tested using the test method in ISO/TS 16179.

B.21 Orthophenylphenol

B.21.1 General

2-Phenylphenol, or *o*-phenylphenol, is an organic compound, which consists of two linked benzene rings and a phenolic hydroxyl group. It is a biocide used as a preservative.

The primary use of 2-phenylphenol is as an agricultural fungicide. It is also used for disinfection on fibres and other materials. It is used to sterilize hospital and veterinary equipment. Other uses are in the rubber industry and as a laboratory reagent. It is also used in the manufacture of other fungicides, dye stuffs, resins and rubber chemicals. Its CAS number is [90-43-7].

The sodium salt of orthophenylphenol, sodium orthophenylphenol, is used as a preservative.

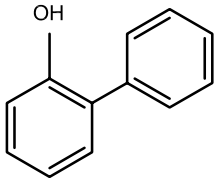


Figure B.9 — Orthophenylphenol molecular structure

B.21.2 Potential risks

Eye contact can cause severe irritation and burns with possible eye damage. For some individuals, 2-phenylphenol can also irritate the skin. It is linked with hyperactivity in children.

B.21.3 Test methods

For the purposes of this Technical Report, the content of orthophenylphenol can be tested using the test method in ISO 13365.

B.22 Ozone-depleting substances

B.22.1 General

Chlorofluorocarbons (CFCs) (see Table B.7) were used in air conditioning/cooling units, as aerosol spray propellants prior to the 1980s, and in the cleaning processes of delicate electronic equipment. They also occur as by-products of some chemical processes. No significant natural sources have ever been identified for these compounds. Their presence in the atmosphere is due almost entirely to human manufacture.

Two classes of substance can be defined:

a) class I substance: one of several groups of chemicals with an ozone-depletion potential of 0,2 or higher;

b) class II substance: one of several groups of chemicals with an ozone-depletion potential of less than 0,2.

A list of class I ozone-depleting substances is included in Table B.7.

B.22.2 Potential risks

Whenever ozone-depleting chemicals reach the stratosphere, they are dissociated by ultraviolet light to release chlorine atoms. The chlorine atoms act as a catalyst and each can break down tens of thousands of ozone molecules before being removed from the stratosphere. Given the longevity of CFC molecules, recovery times are measured in decades. It is calculated that a CFC molecule takes an average of 15 years to go from the ground level up to the upper atmosphere, and it can stay there for about a century, destroying up to one hundred thousand ozone molecules during that time.

B.22.3 Test methods

At the time of publication of this Technical Report, there is no standard available for ozone-depletion substance analysis in footwear and footwear components.

Table B.7 — List of ozone-depleting substances of class I

Name of compound		Formula	CAS number
Trichlorofluoromethane	CFC-11	$CFCl_3$	75-69-4
Dichlorodifluoromethane	CFC-12	CF_2Cl_2	75-71-8
1,1,1-trichlorotrifluoroethane	CFC-113	$C_2F_3Cl_3$	354-58-5
1,1,2-trichlorotrifluoroethane	CFC-113	$C_2F_4Cl_2$	76-13-1
Dichlorotetrafluoroethane	CFC-114	$C_2F_4Cl_2$	76-14-2
Monochloropentafluoroethane	CFC-115	C_2F_5Cl	76-15-3
Bromochlorodifluoromethane	Halon-1211	CF_2ClBr	353-59-3
Bromotrifluomethane	Halon-1301	CF_3Br	75-63-8
Dibromotetrafluoroethane	Halon-2402	$C_2f_4Br_2$	124-73-2
Chlorotrifluomethane	CFC-13	CF_3Cl	75-72-9
Pentachlorofluoroethane	CFC-111	C_2FCl_5	354-56-3
Tetrachlorodifluoroethane	CFC-112	$C_2F_2Cl_4$	76-12-0
Heptachlorofluoropropane	CFC-211	C_3FCl_7	422-78-6
Hexachlorodifluoropropane	CFC-212	$C_3F_2Cl_6$	3182-26-1
Pentachlorotrifluoropropane	CFC-213	$C_3F_3Cl_5$	2354-06-5
Tetrachlorotetrafluoropropane	CFC-214	$C_3F_4Cl_4$	29255-31-0
Trichloropentafluoropropane	CFC-215	$C_3F_5Cl_3$	1599-41-3
Dichlorohexafluoropropane	CFC-216	$C_3F_6Cl_2$	661-97-2
Monochloroheptafluoropropane	CFC-217	C_3F_7Cl	422-86-6
Carbon tetrachloride	CC14	CCl_4	56-23-5
1,1,1-trichloroethane	Methyl chloroform	$C_2H_3Cl_3$	71-55-6
Methyl bromide		CH_3Br	74-83-9
Monochlorodifluoromethane	HCFC-22	CHF_2Cl	75-45-6
2,2-dichloro-1,1,1-trifluoroethane	HCFC-123	$C_2HF_3Cl_2$	306-83-2
2-chloro-1,1,1,2-tetrafluorethane	HCFC-124	C_2HF_4Cl	2837-89-0
1,1-dichloro-1-fluoroethane	HCFC-141B	$C_2H_3FCl_2$	1717-00-6
1-chloro-1,1-difluoroethane	HCFC-142B	$C_2H_3F_2Cl_1$	75-68-3

B.23 Pesticides

B.23.1 General

A pesticide (see Tables B.8 and B.9) is a substance or mixture of substances intended for preventing, destroying, repelling, or lessening the damage of any pest. A pesticide can be a chemical substance, biological agent (such as a virus or bacteria), an antimicrobial or a disinfectant.

B.23.2 Potential risks

Many pesticides can be poisonous to humans.

Table B.8 — Pesticides for textiles

Substance	CAS number	Substance	CAS number
DDT op’	789-02-6	Aldrin	309-00-2
DDT pp’	50-29-3	Dieldrin	60-57-1
DDD op’	72-54-8	Endrin	72-20-3
DDD pp’	72-55-9	Endosulfan	
DDE		Mirex	2385-85-5
HCHs without Lindane		Toxaphene	8001-35-2
Lindane	58-89-9	Heptachlor	76-44-8
Hexachlorobenzene	118-74-1	Heptachloroepoxide	93-76-5
Carbaryl	63-25-2	2,4-D	94-75-7
Trifluralin	1582-09-8	2,4,5-T	93-76-5
Methoxychlor	72-43-5		

Table B.9 — Pesticides for leather

Substance	CAS number	Substance	CAS number
DDT op’	789-02-6	Dieldrin	60-57-1
DDT pp’	50-29-3	Ethylparathion	56-38-2
DDD op’	72-54-8	Endosulfan	
DDD pp’	72-55-9	Mirex	2385-85-5
DDE		Dichlofluanide	1085-98-9
HCHs without Lindane		Heptachloroepoxide	93-76-5
Lindane	58-89-9	Pentachloroanisole	1825-21-4
Malathion	121-75-5	Permethrin	52645-53-1
Methoxychlor	72-43-5	Tolyfluanide	731-27-1
Aldrin	309-00-2	Chlorthalonil	1897-45-6

B.23.3 Test methods

At the time of publication of this Technical Report, there is no standard available for pesticide analysis in footwear and footwear components

B.24 Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA)

B.24.1 General

Perfluorooctanoic acid (PFOA), also known as C8, is an artificial acid that has many industrial uses. PFOA can designate the acid itself or its principal salts (e.g. ammonium perfluorooctanoate).

Perfluorooctane sulfonate is a related compound, used as a surfactant.

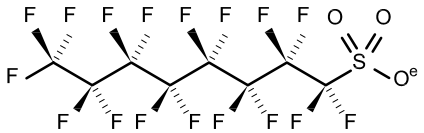


Figure B.10 — PFOS molecular structure

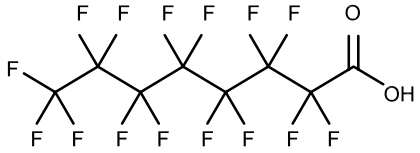


Figure B.11 — PFOA molecular structure

Perfluorooctane sulfonate (PFOS, or perfluorooctanyl sulfonate) is the anion with the formula $C_8F_{17}SO_3^-$. It is the conjugate base of perfluorooctane sulfonic acid. Salts of this anion are used as surfactants.

PFOS are possibly used only in certain parts, or in the coating of, certain products, such as textiles, and only the use of specific octanesulfonates is forbidden.

PFOS are substances which can be degraded only with difficulty in the environment, are accumulative, and are toxic to mammals according to an Organization for Economic Cooperation and Development (OECD) study dating from 2002. Risk assessment has established the necessity of reducing the risk to human health and danger to the environment posed by PFOS.

PFOS belongs to the perfluorinated surfactants. Perfluorinated surfactants are very stable towards chemicals and heat and also towards light (UV radiation). They have excellent dirt, oil and water repelling properties. Compound derived from perfluorooctanesulfonate (PFOS), therefore, have numerous applications in the surface finishing of packaging materials, carpets, textiles, leather and furniture. Polymeric compounds are often used for such applications. They are firmly bonded chemically to the substrate (e.g. to the fibres of a carpet) to prevent washing out. Perfluorinated surfactants are also found in cosmetics, paints, plant protection agents and fire extinguishers.

PFOS are organic surfactants in which all the hydrogen atoms attached to the carbon skeleton have been replaced by fluorine atoms. This leads to highly stable molecules which can be strongly bio accumulative and toxic. The chemical bond between fluorine and carbon number is one of the most stable bonds known. Certain polyfluorinated compounds, such as PFOS, are practically indestructible.

PFOS do not occur naturally. Owing to their special properties they are produced industrially and used in a wide range of products.

There is a general ban against the use of substances containing the PFOS sub-component $C_8F_{17}SO_2X$, where X represents all kinds of derivative, including polymers. There are discussions about similar regulations for PFOA and substances degrading to PFOA, but so far restrictions in force apply only for some countries such as Canada.

NOTE Since 2002, German chemical companies have ceased to produce PFOS anywhere in the world.

B.24.2 Potential risks

PFOS are categorized as possibly carcinogenic to humans. The toxicity of PFOS has been demonstrated; this substance is considered very persistent and very bioaccumulative (vPvB).

B.24.3 Test methods

For the purposes of this Technical Report, the content of PFOS can be tested using the test method in CEN/TS 15968.

B.25 pH

B.25.1 General

Potential of hydrogen (pH) is a measure of the acidity or alkalinity of a solution. Aqueous solutions at 25 °C with a pH of less than seven are considered acidic, while those with a pH of greater than seven are considered basic (alkaline).

B.25.2 Potential risks

Material of strong acidic (pH < 3,2) or strong alkaline (pH > 9,5) can irritate the skin.

B.25.3 Test methods

For the purposes of this Technical Report, the content of pH can be tested with the test methods in

— ISO 4045, or

— ISO 3071.

B.26 Phthalates

B.26.1 General

Phthalates, or phthalate esters, are a group of chemical compounds that are mainly used as plasticizers (substances added to plastics to increase their flexibility). They are chiefly used to turn polyvinyl chloride from a hard plastic into a flexible plastic.

Phthalate esters are the dialkyl or alkyl aryl esters of 1,2-benzenedicarboxylic acid; the name phthalate derives from phthalic acid. Where added to plastics, phthalates allow the long polyvinyl molecules to slide against one another. The phthalates show low water solubility, high oil solubility and low volatility.

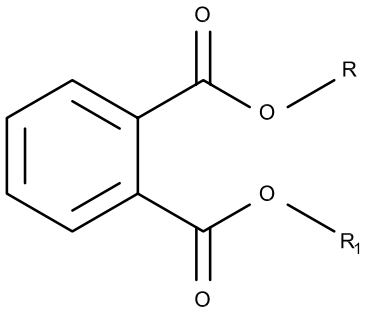


Figure B.12 — Phthalates molecular structure

The most widely used phthalates are di-2-ethylhexyl phthalate (DEHP), diisodecyl phthalate (DIDP) and diisononyl phthalate (DINP). DEHP is the dominant plasticizer used in PVC, due to its low cost.

Phthalates (see Table B.10) are also frequently used in nail polish, fishing lures, adhesives, caulk and paint pigments. Phthalates are controversial because high doses of many phthalates have shown hormonal activity in rodent studies.

Table B.10 — List of phthalates

Name of phthalate	Abbreviated term	CAS number	Regulation 1907/2006/CE REACH Annex 14
Di-*iso*-nonylphthalate	DINP	28553-12-0	no
Di-*n*-octylphthalate	DNOP	117-84-0	no
Di-(2-ethylhexyl)-phthalate	DEHP	117-81-7	yes
Di-*iso*-decylphthalate	DIDP	26761-40-0	no
Butylbenzylphthalate	BBP	85-68-7	yes
Dibutylphthalate	DBP	84-74-2	yes
Di-isobutylphthlate	DIBP	84-69-5	yes

B.26.2 Potential risks

Phthalates, which are suspect as human cancer-causing agents, can damage the liver and kidneys, and the development of reproductive organs. They can also interfere with development by acting as a mimic of the sex hormone oestrogens and act as anti-androgens. Research has found a strong link between allergies in children and the phthalates DEHP and BBP; a study reported that phthalates can mimic the female hormone oestrogen.

B.26.3 Test methods

For the purposes of this Technical Report, the content of phthalates can be tested using the test methods in ISO/TS 16181.

B.27 Polychlorinated biphenyls

B.27.1 General

Polychlorinated biphenyls (PCBs) are a class of organic compounds with 1 to 10 chlorine atoms attached to biphenyl and a general chemical formula of $C_{12}H_{10-x}Cl_x$. Most PCBs were manufactured as cooling and insulating fluids for industrial transformers and capacitors, and also as stabilizing additives in flexible PVC coatings of electrical wiring and electronic components, pesticide extenders, cutting oils, flame retardants, hydraulic fluids, sealants (used in caulking, etc.), adhesives, wood floor finishes, paints, de-dusting agents, and in carbonless copy paper. PCBs have already been detected in the products used for the surface treatment of textiles.

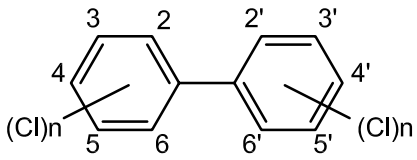


Figure B.13 — Polychlorinated biphenyls molecular structure

B.27.2 Potential risks

The toxicity of PCBs varies considerably among congeners. The coplanar PCBs, known as non-ortho PCBs, because they are not substituted at the ring positions ortho to (next to) the other ring (i.e. PCBs 77, 126, 169, etc.), tend to have dioxin-like properties, and generally are among the most toxic congeners.

NOTE PCB production was stopped in the 1970s due to the high toxicity of most PCB congeners and mixtures. PCBs are classified as persistent organic pollutants.

PCBs have been found to have effects on the brain and nervous system, endocrine system, cancer, reproduction and fertility, birth or developmental effects, persistent and bio accumulative, immune system (including sensitization and allergies).

B.27.3 Test methods

At time of publication of this Technical Report, there is no standard available for PCB analysis in footwear and footwear components.

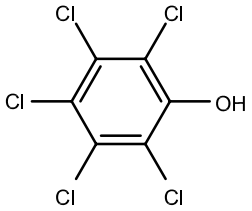
B.28 Polychlorophenols

B.28.1 General

Pentachlorophenol (PCP) is a synthetic substance which was first produced in the 1930s. It can be found in two forms: PCP itself or as the sodium salt of PCP, which dissolves easily in water. In the past, it has been used as an herbicide, insecticide, fungicide, algaecide, disinfectant and as an ingredient in antifouling paint. Some applications were in agricultural seeds (for non-food uses), leather, masonry, wood, cooling tower water, rope and paper mill system.

Tetrachlorophenol (TeCP) is an insecticide and a bactericide and is used as a preservative for latex, wood, and leather.

Trichlorophenol (TriCP) is any organochloride of phenol which contains three covalently bonded chlorine atoms. Trichlorophenols are produced by electrophilic halogenations of phenol with chlorine. Different isomers of trichlorophenol exist according to which ring positions on the phenol contain chlorine atoms. 2,4,6-Trichlorophenol, for example, has two chlorine atoms in the *ortho* positions and one chlorine atom in the *para* position.



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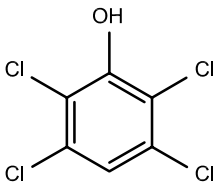

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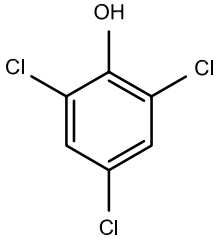

c)

Figure B.14 — Molecular structure and CAS number for polychlorophenols

Table B.11 — List of chlorophenols

Substance	Name	Abbreviated name	CAS number
Trichlorophenols	2,4,5-Trichlorophenol	245-TriCP	95-95-4
	2,4,6-Trichlorophenol	246-TriCP	88-06-2
	2,3,5-Tichlorophenol	235-TriCP	933-78-8
	3,4,5-Trichlorophenol	345-TriCP	609-19-8
	2,3,6-Trichlorophenol	236-TriCP	933-75-5
	2,3,4-Trichlorophenol	234-TriCP	15950-66-0
Tetrachlorophenols	2,3,4,6-Tetrachlorophenol	2346-TeCP	58-90-2
	2,3,5,6-Tetrachlorophenol	2356-TeCP	935-95-5
	2,3,4,5-Tetrachlorophenol	2345-TeCP	4901-51-3
Pentachlorophenol		PCP	87-86-5

B.28.2 Potential risks

Short-term exposure to large amounts of polychlorophenols can cause harmful effects on the liver, kidneys, blood, lungs, nervous system, immune system and gastrointestinal tract.

Contact with polychlorophenols (particularly in the form of vapour) can irritate the skin, eyes and mouth. Long-term exposure to low levels, such as those which occur in the workplace, can cause damage to the liver, kidneys, blood and nervous system. Finally, exposure to polychlorophenols are also associated with carcinogenic, renal and neurological effects. Polychlorophenols CP are classified in the group of probable human carcinogen.

B.28.3 Test methods

For the purposes of this Technical Report, the content of polychlorophenols can be tested with the test methods in

— CEN/TR 14823, or

— ISO 17070, or

— XPG 08-015.

B.29 Polychloroprene

B.29.1 General

Polychloroprene is an elastomer with special properties, which is produced from the polymerization of chloroprene. It is produced both in the form of homopolymer and copolymer.

B.29.2 Potential risks

This substance can be an allergen.

B.29.3 Test methods

At time of publication of this Technical Report, there is no standard available for polychloroprene analysis in footwear and footwear components.

B.30 Paraphenylene diamine

B.30.1 General

Para-ethylene-diamine or *p*-phenylenediamine (PPD) is an aromatic amine compound, with formula $C_6H_8N_2$ or $C_6H_4(NH_2)_2$ and with CAS number [106-50-3].

Para-ethylene-diamine is used with dyes in leather and textile industries.

B.30.2 Potential risks

The substance can be irritating to the eyes. Inhalation of dust can cause asthmatic reactions. Swelling of mouth and throat can be observed following ingestion. The substance can cause effects on the blood, resulting in the formation of met haemoglobin. Exposure can result in death.

Repeated or prolonged contact can cause skin sensitization. Repeated or prolonged inhalation exposure can cause asthma. The substance can have effects on the kidneys, resulting in kidney impairment.

B.30.3 Test methods

At the time of publication of this Technical Report, there is no standard available for paraphenylenediamine analysis in footwear and footwear components.

NOTE Paraphenylenediamine can be detected in leather and textile with the test method used for aromatic amines (see B.3).

B.31 Paratertiary butyl phenol formaldehyde

B.31.1 General

Paratertiary butyl phenol formaldehyde (PTBF) is a tackifying resin for adhesives, with CAS number [25085-50-1].

B.31.2 Potential risks

The substance can be an allergen.

B.31.3 Test methods

At the time of publication of this Technical Report, there is no standard available for paratertiary butyl phenol formaldehyde analysis in footwear and footwear components.

B.32 Short-chain chlorinated paraffins (C10-C13)

B.32.1 General

Chlorinated paraffins (CPs) are a complex mixture of polychlorinated n-alkanes and were introduced in the 1930s. The chlorination degree of CPs can vary between 30 % and 70 %. CPs are subdivided according to their carbon chain length into short-chain chlorinated paraffins (SCCPs, $C_{10\text{-}13}$), medium-chain CPs (MCCPs, $C_{14\text{-}17}$) and long-chain CPs (LCCPs, $C_{>17}$). Over 200 CP formulations are in use for a wide range of industrial applications, such as flame retardants and plasticisers, and as additives in metal-working fluids, sealants, paints and coatings.

B.32.2 Potential risks

Short-chain chlorinated paraffins ($C_{10\text{-}13}$) are classified as persistent and their physical properties imply a high potential for bioaccumulation. Furthermore, CPs are classified as toxic to aquatic organisms, and carcinogenic to rats and mice. SCCPs was categorized in group 2B as possibly carcinogenic to humans.

B.32.3 Test methods

At the time of publication of this Technical Report, there is no standard available for short-chain chlorinated paraffins (C_{10-13}) analysis in footwear and footwear components.

B.33 2-(thiocyanatomethylthio)-1,3-benzothiazole (TCMTB)

B.33.1 General

TCMTB [2-(thiocyanatomethylthio)-1,3-benzothiazole] is a biocide used as a fungicide. Its CAS number is [21564-17-0].

NOTE The other name for TCMTB is (2-benzothiazolylthio)methyl thiocyanate.

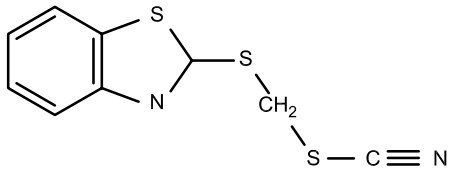

Figure B.15 — TCMTB molecular structure

B.33.2 Potential risks

TCMTB is able to produce allergenic reactions. Furthermore, TCMTB can be irritating to eyes, respiratory system and skin; it can be harmful if swallowed.

B.33.3 Test methods

For the purposes of this Technical Report, the content of TCMTB can be tested using the test method in ISO 13365.

B.34 Thiuram and thiocarbamate

B.34.1 General

Thiuram and thiocarbamate are secondary accelerators used in the manufacture of vulcanized rubber.

B.34.2 Potential risks

Thiuram and thiocarbamate can be contact allergens and can irritate the skin.

B.34.3 Test methods

At the time of publication of this Technical Report, there is no standard available for thiuram and thiocarbamate analysis in footwear and footwear components.

B.35 Vinyl chloride monomer

B.35.1 General

Vinyl chloride monomer is an important industrial chemical chiefly used to produce its polymer, polyvinyl chloride (PVC). Its CAS number is [75-01-4].

NOTE The other name for vinyl chloride monomer is chloroethene.

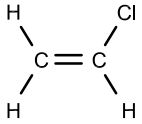

Figure B.16 — Vinyl chloride monomer molecular structure

B.35.2 Potential risks

At room temperature, vinyl chloride is a toxic, colourless gas with a sickly sweet odour. Vinyl chloride monomer is classified in the group of carcinogenic substances for humans.

Due to the hazardous nature of vinyl chloride to human health, there are no end products that use vinyl chloride in its monomer form. Once vinyl chloride has been polymerized, it is very stable and non-hazardous and can be used for a great number of end products.

B.35.3 Test methods

For the purposes of this Technical Report, the content of vinyl chloride monomer may be determined according to ISO 6401.

B.36 Polycyclic aromatic hydrocarbons

B.36.1 General

The polycyclic aromatic hydrocarbons (PAH) include some 100 different substances. They share a similar molecular structure, as they are all compounds with at least two condensed aromatic hydrocarbon rings. However, interest is focussed mainly on polyaromatic compounds in which four to seven rings are fused together, such as naphthalene, anthracene, chrysene or benzo(a)pyrene (see Table B.12).

Anthracene is an example (see Figure B.17).

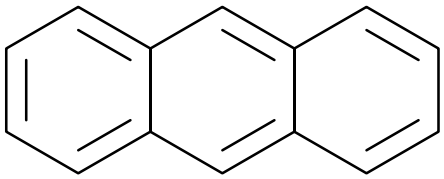

Figure B.17 — Anthracene structure

Table B.12 — List of Polycyclic aromatic hydrocarbons

Substance	CAS number	EINECS
BENZO[*A*]PYRENE	50-32-8	No: 200-028-5
BENZO[*E*]PYRENE	192-97-2	205-892-7
BENZO[*A*]ANTHRACENE	56-55-3	200-280-6
DIBENZO[*A,H*]ANTHRACENE	53-70-3	200-181-8
BENZO[*B*]FLUORANTHENE	205-99-2	205-911-9
BENZO[*J*]FLUORANTHENE	205-82-3	205-910-3
BENZO[K]FLUORANTHENE	207-08-9	205-916-6
CHRYSENE	218-01-9	205-923-4

NOTE 1 The US Environmental Protection Agency (EPA) classifies 16 PAH as primary pollutants: naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*a*)pyrene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, dibenzo(*a*,*h*)anthracene and indeno[1,2,3-*cd*]perylene.

NOTE 2 In order to avoid hazards to health, German consumer products have to meet legal requirements according to Section 30 of the German Food and Animal Feed Code, Section 3 of ProdSG, or the Chemicals Prohibition Ordinance. For this reason, the German committee for technical work equipment and consumer products decided in November 2007 to include PAH testing in the conditions for awarding the GS mark introduced as long ago as 1977. The reason for this additional testing lies in the possibility of PAH contamination by plasticiser oils in rubber and flexible plastics, by lampblack as pigment in rubber and plastics, in paints, and by naphthalene used for preserving products during transport or storage.

B.36.2 Potential risks

These PAH, and above all benzo[a]pyrene, are banned because of their various hormonal, mutagenic, carcinogenic and fertility-impairing actions. Upon entering the body, they accumulate in adipose tissue, and can even enter through the lungs if they are attached to soot particles. Moreover, not only can PAH be hazardous to health, but they can also be extremely long-lived and ubiquitous. PAH are natural constituents of coal and petroleum, hence also occur in products made from these raw materials, such as tar, bitumen or asphalt. They are also admixed with plastics as additives in order to improve their properties. And they arise on combustion of organic materials such as wood or tobacco. Use of combustion residues as low-cost colourants inevitably introduces PAH into the corresponding products.

B.36.3 Test methods

At the time of publication of this Technical Report, there is no standard available for PAH analysis in footwear and footwear components.

B.37 Phenol

B.37.1 General

The major uses of phenol involve its conversion to plastics or related materials. For example, condensation with formaldehyde gives phenolic resins. Non-ionic detergents are produced by alkylation of phenol to give alkylphenols.

Phenol is also a versatile precursor to a large collection of drugs and many pesticides.

Phenol (see Figure B.18) was used in the past as a biocide.

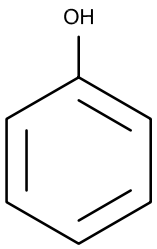

Figure B.18 — Phenol structure

B.37.2 Potential risks

Phenol and its vapours are corrosive to the eyes, the skin and the respiratory tract. Repeated or prolonged contact with the skin can cause dermatitis, or even second and third-degree burns due to phenol's caustic and degreasing properties. Inhalation of phenol vapour can cause lung oedema. Long-term or repeated exposure of the substance can have harmful effects on the liver and kidneys. There is no evidence that phenol causes cancer in humans.

B.37.3 Test methods

At the time of publication of this Technical Report, there is no standard available for phenol analysis in footwear and footwear components.

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