
**Footwear — Critical substances
potentially present in footwear and
footwear components**

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

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.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.

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

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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	Polycrylic	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																		
When 4-aminoazobenzene is suspected	ISO 17234-2	1	1	1																		
AZO - arylamines	EN 14362-1									1	1	1	1	1	1	1					1	
AZO - arylamines	EN 14362-2									1											1	
When 4-aminoazobenzene is suspected	EN 14362-3									1	1	1	1	1	1	1					1	
All plastics (mainly PVC)	EN 1122									1	1	1	1	1	1	1					1	
Chloroorganic carriers	DIN 54232									3												
Chromium VI	ISO 17075	2	2	2																		
Colophony																					5	
Dimethylformamide (DMF)													4									
Dimethylfumarate (DMFU)	ISO/TS 16186	1	1	1									1	1	1	1	1	1	1	1	1	1
Disperses dyes and dyestuffs	DIN 54231																					
Flame retardant	Only for product claiming FR properties	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							
Heavy metals	Extractible (Sb - As - Pb - Cd - Cr - Co - Cu - Ni - Hg - Zn)	4	4	4	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)	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Heavy metals	Total content (Sb - As - Pb - Cd - Cr - Co - Cu - Ni - Hg - Zn)	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
	Total content (As - Cd - Pb)	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Mercaptobenzothiazole																							
Extractible latex proteins	EN 455-3																						
N-ethylphenylamine																							
Nickel	EN 1811 CR 12471 (with or without EN 12472)																						1
Nitrosamines	EN 12868																						

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	
PTBF Paratertiary butyl phenol formaldehyde																		5					
Short-chained chloroparaffins (C ₁₀ -C ₁₃)		3	3	3					3	3		3		3									
TCMTB (2-(thiocyanatomethylthio)-1,3-benzothiazole)	ISO 13365	5	5	5																			
Thiuram and thiocarbamate																							
Vinyl chloride monomer	ISO 6401		4																				

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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.

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A.3 Leather fibre board (standards.iteh.ai)

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 when 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.

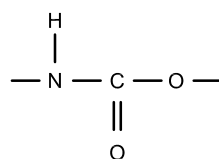


Figure A.1 — Urethane groups

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.

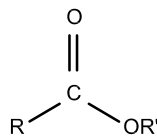


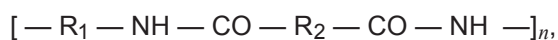
Figure A.2 — Ester bond

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



where R, R₁, and R₂ are generally, but not necessarily, linear divalent hydrocarbon chains (—CH₂—)_m.