TECHNICAL REPORT

ISO/TR 16178

Third edition 2021-09

Footwear — Critical substances potentially present in footwear and footwear components — Lists of critical chemical substances

Chaussures — Substances critiques potentiellement présentes dans la chaussure et les composants de chaussures — Listes des substances chimiques critiques

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

This third edition cancels and replaces the second edition (ISO/TR 16178:2012), which has been technically revised.

The main changes compared to the previous edition are as follows:

- new <u>Table 1</u> including a new system of grading;
- withdrawn substances:

proteins in latex, substances destroying ozone layer, polychlorobiphenyls, polychloroprene, vinyl chloride;

- added substances:
 - benzene, bisphenol, NMP, DMAC, phenyl mercury, quinoline, VOC;
- biocides are grouped together (CMK, OIT, OPP, TCMTB);
- Annex A is now in ISO 21061^[67]:
- Annex B is now Clause 5:
- bibliography, updated.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Footwear — Critical substances potentially present in footwear and footwear components — Lists of critical chemical substances

1 Scope

This document defines lists of critical chemical substances potentially present in footwear and footwear components.

This document describes the critical chemical substances, their potential risks of nocuousness, in which materials they could be found, and which test method(s) can be used to quantify them.

The test methods listed indicate the state of the art. For some substances, a test method is not available.

This document is applicable to any kind of footwear and footwear components.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

3.1

allergen

substance that is capable of inducing an allergic reaction

3.2

allergy

immunologically mediated response to certain specific substances (allergens)

Note 1 to entry: Type-1 allergy (respiratory allergy) is mediated by IgE antibodies, can cause asthma, rhinitis, urticaria. Type-4 allergy (dermal allergy) is mediated by T-cells, can cause dermatitis.

3.3

limit of detection

value from which a substance is considered as detectable

Note 1 to entry: 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.

3.4

critical substances

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

Note 1 to entry: The effects caused by critical substances vary. It can be carcinogenic or mutagenic effects, allergy, reaction to toxics, etc.

3.4.1

critical substances category 1

substances with proven dangerous effect on the wearer

Note 1 to entry: These substances are widely restricted by national regulation in several countries.

3.4.2

critical substances category 2

substances with dangerous effect on the wearer

Note 1 to entry: These substances are restricted by national regulation in a limited number of countries.

3.4.3

critical substances category 3

substances that are highly suspected to have an effect on the wearer

Note 1 to entry: These substances might not be restricted by regulation at the time of publication but they are frequently requested by the market stakeholders.

3.4.4

critical substances category 4

substances that are suspected to have an effect on the wearer

Note 1 to entry: These substances might not be restricted by regulation. Substances known to have an allergenic effect on the wearer are included in category 4 for reference.

4 Presence of chemicals in footwear materials

A number of chemicals are present in footwear materials. <u>Table 1</u> lists the following:

- a) in which materials they are supposed to be. The possible materials potentially used in the footwear industry are given in ISO 21061:2021^[67], Annex C.
- b) a list of critical chemicals, (see <u>Clause 5</u> for information);
- c) test methods that can be used to quantify them (see Bibliography);
- d) the potential risks associated with their use, assessed by the use of the critical substances' category scale
 - 1) stand for "critical substances category 1";
 - 2) stand for "critical substances category 2";
 - 3) stand for "critical substances category 3";
 - 4) stand for "critical substances category 4".

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

EXAMPLE 1 Coated textile (cotton + PVC coating). Test on PVC and test on cellulosic natural fibres should be done.

EXAMPLE 2 Mixed textile (PES + cotton). Test on cellulosic natural textile and test on PES textile should be done

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

		ľ	Leather	nda			Sy	Synthetic material	c mat	erial			-	Natura	Natural material	al	Mi	Miscellaneous	aneo	ns
Substance (see Annex B)	Test method	reather.	Coated leather	Leather board	ЪЛС	EAA		PU – PU – TPU elastane	bE-T pp	Polyester	Polyamide	Chloride fibre	Polyacrylic	Latex Cellulosic natu- ral textile	Proteinic natural	Wood - cork	səvisədbA	Metal hardware	Prints for textile	Cellulose
Acrylonitrile				g/st			4	11					4				4			
Alkylphenols(OP, NP) and Alkylpheno- ISO 18218-1 lethoxylates, (OPEO, NPEO)	ISO 18218-1 ISO 18218-2	33	က	andard		Do	h2.	ng.	:7											
Alkylphenols(OP, NP) and Alkylphenolethoxylates, (OPEO, NPEO)	ISO 18254-1 ISO 21084			s/iso/a	ISO	eun	// 3 L	//c1	Ceh	2	2	2	2	2	2				2	
AZO - arylamines	ISO 17234-1	1	1	la4	/TI	10	a.	91	S											
When 4-aminoa- AZO -arylamines zobenzene is sus- ISO 17234-2 pected	ISO 17234-2	Τ	-	00 <u>32</u> -d8	R 16178	nt l	iua.	nda nda	tan											
AZO - arylamines	ISO 14362-1			3e6	:20	I		ui		1	1	1	1	1	1				Т	
When 4-aminoa-AZO - arylamines zobenzene is suspected	ISO 14362-3			<u>-419f-8</u>	21	'evi		ar Ul Ic it	orda	1	1	Η	1	1	1				1	
Benzene				6d3		W		ما	1	1	1		1	1	1		2			
Biocides (TCMTB, OIT, CMK)	ISO 13365-1 and ISO 13365- 2	4	4	-98401		4		ı.ai		4	4	4	4	4	4	4				4
Biocides (OPP)	ISO 13365-1 and ISO 13365- 2	2	2	4c3048		2				7	2	7	7	2 2	2	2				2
Biocides (triclosan)	EN 17134	2	2	2	2	2	2	2	2	2	2	2	2	2 2	2		2		2	2
Bisphenol		2	2	2																
Cadmium All plastics (mainly PVC)	EN 1122		1	-1617	7	1	1	1	1										1	
Chlorinated paraffin's (Short chained [C10-C13])	ISO 18219-1	2	2	8-201			2			2	2	2	2	2	2				2	
				21																

Table 1 (continued)

				asthar	tps			Cyn	Synthatic material	- tem	riol				atural	Natural material	_	Į.	Miccellanguic	1000	١
Substance (see Annex B)	ance nex B)	Test method	resther	Coated leather	Leather board	ЬΛС	EAA	bΩ − B	TPU elastane	beliacter	Polyester Polyamide	Chloride fibre	Polyacrylic	Latex	Cellulosic naturral tal	roteinic natural textile	Wood - cork	səvisədbA	Metal hardware	erints for textile	esoluliec
Chlorinated paraffin's (Middle chained [C14-C17])		ISO 18219-2	8	3	ai/cata			3			3	3	т С		m	e e			I	- m	
Chlorobenzene and chlorotoluene	hlorotoluene	EN 17137			log	\vdash		M1			2										
Chlorobenzene and chlorotoluene (tetrachorotoluene, trichlorotoluene, αchlorotoluene)	+	EN 17137			standar		Do	IIps	i		2 2	2	2		2	2					
Chromium VI		ISO 17075-1 ISO 17075-2	-	-	ds/iso/a	ISU	cur	://S1	1eh												
Chromium VI W	With ageing	ISO 10195	3	3	3)/T	n	[2]	1												
Colophony					400	'R 1	er.	n	st									4			
Dimethylformamide (DMF)	(DMF)	ISO 16189		2	32	61	lt		2												
Dimethylfumarate (DMFu)	OMFu)	ISO 16186	1		48	75.	1	1	1		1 1	1	1	1	⊣		П			1	\vdash
Disperses dyes and dyestuffs	lyestuffs	ISO 16373-2 ISO 16373-3			e6-419	2021	rev	ds.	lar		2 2	2	2		2	2				2	
Flame retard- ant (Phosphorated ing and brominat- ed)	Only for product claim- ing FR properties ISO 17881-2	ISO 17881-1 ISO 17881-2	1	1	f-86d <u>3</u> -9860	1	iew	iteh.ai	ds T	1	1 1	1	1	1	1	1	1			1	1
Formaldehyde		ISO 17226-1 ISO 17226-2	2	2	1e4c3()													
Formaldehyde		EN 120 EN 717-3)48/isc												2				2
Formaldehyde		ISO 27587			-tr-													3			
Formaldehyde		ISO 14184-1			16						$1 \mid 1$		1		1	1				1	

sdiff **Table 1** (continued)

				=	an			,	:		[\mid			-	1	=		
			Fe	eather	da			Syn	synthetic material	maı	erial				Natural material	materi	a	MI	Miscellaneous	neor	ıs
ıas)	Substance (see Annex B)	Test method	Leather	Coated leather	Leather board	ЬΛС	ΕΛΨ	Rubber	PU – PT TPU elastane	bE-T pp	Polyester	Polyamide	Chloride fibre	Polyacrylic Latex	Cellulosic natural textile	Proteinic natural textile	Wood - cork	səvisədbA	Metal hardware	Prints for textile	Cellulose
	Extractible (Sb-As-Cd-Cr-Co- Cu-Ni-Hg-Zn)	ISO 17072-1 EN 16711-2	3	33	g/standar	3	3	3	3	8	3	33	т т	3	3	3	3	3		3	33
Heavy metals	E x t r a c t i b l e Footwear for children less than 36 months ISO 17072-1 (Sb - As -Cd - Cr - Co - Cu - Ni - Hg - Zn - Ba - Se)	ISO 17072-1 EN 16711-2	2	2	ds/iso/a_1a40032	ISC ^N TR 161	cument	2//Stand 2		Tob 2540	7	2	5	2 2	7	7	2	2		2	2
	Total content ISO 17072-5 (Sb - As -Cd (leather EN 16711-1 and textile) - Cr - Co - ISO 19050 Cu - Ni - Hg - Zn)	ISO 17072-2 EN 16711-1 ISO 19050	3	8	-d8e6-4191	78:2 % 21	T KeV	ards.	8	3	3	8	8	3	8	33	33	co		8	3
Lead		ISO 17072-2 EN 16711-1	⊣	-	-8643-	-	iew	ten . ¬	18 1471	-	Т-	-		1 1		7	\vdash		-		\vdash
Mercaptobenzothiazole	hiazole				986		r	4													
N-ethylphenyl-amine	mine				501			4	•					4							
N methyl pyrrolidone	idone	ISO 19070			e40	2			2		2	2	2	2	2	2				2	
N,N-dimethylace	N,N-dimethylacetamide (DMAC)				30						2	2	2	2	2	2				2	
Nickel	Skin contact	EN 1811 (with or with- out EN 12472)			48/iso-ti														1		
Nitrosamines	Footwear for children less than 36 ISO 19577 months	ISO 19577			-16178			2													
Nitrosamines		ISO 19577			-20			4													
Organotin comp	Organotin compounds (TBT, TPT)	ISO/TS 16179	1	1	2,1	1	1	1	1	1	1	1	1	$1 \mid 1$	1	1	1	1		7	1

Table 1 (continued)

	asolinilaa	<u></u>				~															
Miscellaneous	Cellulose	2	3		4	3					4										_
lane	Prints for textile	2	3	2	4								\vdash	2					1	2	3
scel	Metal hardware																				
Mi	səvisədbA	2	3	1							4		1	2							
=	Wood - cork	2	3															\vdash			
Natural material	Proteinic natural textile	2	3	2	4	3	1			2	4								1	2	3
aturalı	-utan oisolulle Fal textile	2	3	2	4	3	1			2	4								1	2	3
Z	хэтьг	2	3																		
	Polyacrylic	2	3	2	4					2									\vdash		
	Chloride fibre	2	3	2			\vdash			2									П		
_	Polyamide	2	3	2	4					2									1		
teria	Polyester	2	3		4		-			2									\vdash		
c ma	bE-L bb	2	3	\vdash		•	Tol	h	Q.	40	m	7	ords								
Synthetic material	- Uq Sarane - TPU elastane	2	3	1	tr	20	://s	1	o a r		9	1		2 2 1 A							
Sy	Kubber	2	3	7							4		Н	2							
	EAA	2	3	1		0	cu		le	n	l .		CYIC	2							
	bΛC	2	3	\vdash			I	SO	TR	16	17	R-21	021 ₩	2							
ps:	Leather board	2	8	<u>g/</u> s	tan	3	ds/isc	/ <u>a</u> 1	2	003	240	8e	5-419f-86	d3-9860	1,e4	2	8	/iso)-tr	-16	17
eather	Coated leather	2	3	1		3		1	2		4		-	2	1	2	3				
Le	Геатрег	2	3			3			2		4				1	2	3				
	Test method	ISO/TS 16179	ISO/TS 16179	ISO/TS 16190		ISO 22517	CEN/TS 15968	ISO 23702-1	ISO 4045	ISO 3071	ISO 20536		ISO 16181 (all parts) ISO 14389	ISO 16181 (all parts) ISO 14389	ISO 17070	ISO 17070	ISO 17070	CEN/TR 14823	XP G 08-015	XP G 08-015	XP G 08-015
	Substance (see Annex B)	Organotin compounds(DBT, DOT)	Organotin compounds(others)	PAH – polycyclic aromatic hydrocarbons ISO/TS 16190	Paraphenylene diamine	Pesticides	PFCs perfluorinated compounds (PFOS/ PFOA)	PFCs perfluorinated compounds	Hd Hd	l Hd	Phenol	Phenyl mercury	Phthalates Footwear for chil- ISO 16181 (all dren less than parts) 14 years ISO 14389	Phthalates	Polychorophenol (PCP pentachlorophenol) ISO 17070	Polychorophenol TeCP	Polychorophenol TriCP – DiCP	Polychorophenol (PCP pentachlorophenol) CEN/TR 14823	Polychorophenol (PCP pentachlorophenol) XP G 08-015	Polychorophenol TeCP	Polychorophenol TriCP - DiCP - MoCP

(continued)	
https://sqth	1

		Lea	ather	nda			Synthetic materia	tic m	ateri	al			Na	tural n	Natural material	=	Mis	Miscellaneou	neor	S
Substance (see Annex B)	Test method	Leather	Coated leather	Preather board	EΛΨ bΛC	Rubber	- Uq TPU elastane	bE-L bb	Polyester	Polyamide	Chloride fibre	Polyacrylic	Гатех	-uasic natu- Sellulosic natule Tal textile	Proteinic natural slitxet	Моод - согк	səvisədbA	Metal hardware	Prints for textile	Cellulose
PTBF Paratertiary butyl phenol formaldehyde				g/stan		E	ttr										4			
Quinoline				dar		0	2	2	2	2		2	2							
Thiuram and Thiocarbamate				ds/		4	•/	Γ												
Volatile organic compounds			4	<u>18</u> iso	4	4	4	4	4	4	4	4					4			
				000																

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5 Critical substances potentially present in footwear and footwear components

In this document, the chemicals are identified by their CAS Registry Number®¹⁾ (CAS RN®).

5.1 Acrylonitrile

5.1.1 General

Chemical compound with the formula CH₂CHCN.

Figure 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 (CAS RN® 107-13-1) 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 as material for soles, especially for soles in professional high resistance footwear.

5.1.2 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.

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

In footwear products, the presence of acrylonitrile is very rare.

5.1.3 Test methods

No standard is available at the time of publication of this document for acrylonitrile analysis in footwear and footwear components.

5.2 Alkylphenols and Alkylphenol ethoxylates (NP, OP, NPEO, OPEO)

5.2.1 General

Alkylphenols (AP) and alkylphenol ethoxylates (APEO), see <u>Table 2</u>, are used in plastics, as additives, plasticizers and surface-active ingredients in industrial detergents and emulsifiers. Ethoxylated

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