TECHNICAL REPORT

ISO/TR 16178

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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

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is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

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

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, in which materials they could be found, and which test method(s) 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 level of acceptance, e.g. using a defined concentration or detection limit or quantification limit, etc.

The proposed test methods indicate the state of the art. Some substances do not include a test method, as no normative test method is available at the moment of the publication of this Technical Report. If possible, it will be included in a further revision of this Technical Report.

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

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 (allergens)

NOTE Type-1 allergy is mediated by IgE antibodies, may cause asthma, rhinitis, urticaria. Type-4 allergy is mediated by T-cells, may cause dermatitis.

2.3
detection limit
value from which a substance is considered as 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 as 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
a chemical is absent from a material, when 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 substances
chemical substance that can be found in footwear or footwear components and can have an effect on the wearer and environmental impact due to its chemical reactivity

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

NOTE 2 Legislations could change; this Technical Report gives the information available at its publication date. It is the responsibility of the user of this Technical Report to ensure that no changes occur.

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 These substances may not be restricted by regulation at the present time.

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

NOTE These substances may not be restricted by regulation at the present time.

3 Presence of chemicals in footwear materials

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

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

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

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

d) the potential risk associated, assessed by the use of the critical substances category scale (see Clause 3.6).

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

Substance (see Annex B)		Test method	leather			Synthetic material									Natural material				Miscellaneous			
			Leather	Coated leather	Leather board	PVC	EVA	Rubber	PU – TPU elasthan	PE-T PP	Polyester	Polyamide	Chloride fibre	Polyacrylic	Latex	Cellulosic natural textile	Proteinic natural textile	Wood - cork	Adhesives	Metal hardware	Prints for textile	Cellulose
Acrylonitrile								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	Special requirement for PVC	EN 1122		1		1	1	1	1	1											1	
Chloroorganic carriers											3											
Chromium VI		ISO 17075	2	2	2																	
Colophony																			5			
Dimethylformamide (DMF)				4					4													
Dimethylfumarate (DMFU)			1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1			1	1
Disperses dyes and dyestuffs		DIN 54231:2005									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																	
Formaldehyde		EN 120																2				2
Formaldehyde		ISO 14184-1									2	2	2	2		2	2					

Table 1 (*continued*)

Substance (see Annex B)		Test method	Leather			Synthetic material									Natural material				Miscellaneous			
			Leather	Coated leather	Leather board	PVC	EVA	Rubber	PU – TPU elasthan	PE-T PP	Polyester	Polyamide	Chloride fibre	Polyacrylic	Latex	Cellulosic natural textile	Proteinic natural textile	Wood - cork	Adhesives	Metal hardware	Prints for textile	Cellulose
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
	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
	Footwear for children less than 36 months (Sb – As – Ba – Cd – Cr – Pb – Hg – Se)	EN 71-3	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2		2	2
Mercapto benzothiazole								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	EN 12868						2														

Table 1 (*continued*)

Substances (see Annex B)		Test method	Leather			Synthetic material									Natural material				Miscellaneous			
			Leather	Coated leather	Leather board	PVC	EVA	Rubber	PU – TPU elasthan	PE-TP	Polyester	Polyamide	Chloride fibre	Polyacrylic	Latex	Cellulosic natural textile	roteinic natural textile	Wood - cork	Adhesives	Metal hardware	Prints for textile	Cellulose
Nitrosamines		EN 12868						3														
Nonylphenol and Alkylphenolethoxylates			4	4	4						3	3	3	3		3	3					
Organic tin (TBT, TPT)		ISO 17353:2004	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1			1	1
Organic tin (MBT, DBT, DOT),		ISO 17353:2004	4	4	4	4	4	4	4	4	3	3	3	3	4	3	3	4			4	4
Ortho-phenylphenol			5	5	5		5				5	5	5	5	5	5	5	5				5
Ozone depleting substances											3	3	3	3		3	3					
PAH						4	4	4	4	4												
PCP -TeCP - TriCP		ISO 17070	2	2	2																	
PCP -TeCP - TriCP		CEN/TR 14823																2				
PCP -TeCP - TriCP		XP G 08-015														2	2					
Pesticides			5	5	5											3	3					5
PFOS/PFOA	Only for product claiming FR properties and water resistance		1	1	1						1	1	1	1		1	1					
pH		ISO 4045	4	4	4																	
pH		ISO 3071									4	4	4	4		4	4					
Phthalates		ISO 18856				1	1	1	1	1												
Phthalates	In textile	EN 15777		1							1	1	1	1		1	1				1	
Phthalates	Footwear for children less than 36 months	EN 71-10 and EN 71-11		1		1	1	1	1	1	1	1	1	1		1	1				1	

Table 1 (*continued*)

Substances (see Annex B)	Test method	Leather			Synthetic material									Natural material				Miscellaneous			
		Leather	Coated leather	Leather board	PVC	EVA	Rubber	PU – TPU elasthan	PE-TP	Polyester	Polyamide	Chloride fibre	Polyacrylique	Latex	Cellulosic natural textile	Proteinic natural textile	Wood - cork	Adhesives	Metal hardware	Prints for textile	Cellulose
PCB Polychlorinated biphenyls		5	5	5						3	3	3	3		3	3					
Polychloroprene or Neoprene							5											5			
PPD Paraphenylene diamine		5	5	5						5	5		5		5	5				5	5
PTBF Paratertiary butyl phenol formaldehyde																		5			
Short chained Chloroparaffines (C10-C13)		3	3	3			3			3	3	3	3		3	3					
TCMTB		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

A general term for hide or skin with its original fibrous structure more or less intact, tanned to be rotproof. The hair or wool might or might not have been removed. 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, whatever is applied, or a glued on finish, such surface coating layers should not be thicker than 0,15 mm.

A.2 Coated leather

Leather where the surface coating applied to the leather 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

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% in weigh of dry leather is necessary to use the term leather fibre board.

A.4 PVC

Polymer constituted of polymerised 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

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, rubber foam

Rubbers are polymers based on either synthetic or natural materials that are cross-linked to give required physical performance properties and chemical resistance. Extensively used as outersoles in many styles of footwear. (See ISO 1382)

A.7 Thermoplastic polyurethanes (TPU)

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

A.8 Thermoplastic elastomers or thermoplastic rubbers (TPE-TPR)

Thermoplastic elastomers or thermoplastic rubbers (not vulcanized) (TPE or TPR) combine the processability of plastics with the flexibility and durability of rubbers, while more light weight and formable. These properties provide favourable conditions for the production of thermoplastic materials, due to a structure consisting of block copolymers that combine elastic chain segments with rubbery properties, and very rigid segments (at room temperature). They play the same role as the sulphur bonds formed during vulcanisation 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.

A.9 Latex

Rubber latex is a water-based colloidal solution that 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 stabilised due to the fact that every rubber particle is coated with a layer of natural or synthetic emulsifiers (see ISO 1382).

A.10 Blown material, foam

Synthetic expanded polymer with a closed-cell or open-cell structure, which may be flexible or rigid, 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 (PU)

The polyurethane 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 isocyanurates groups. A wide range of properties can be obtained depending on chemical composition used: thermoplastic, thermoset, rigid or flexible, cellular or compact polyurethanes, etc. Polyurethanes are used as structural materials, coatings, adhesives and sealants.

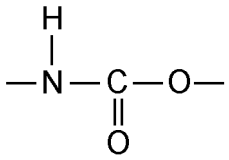

Figure A.1 — Urethane groups

A.13 Textile

Originally used to describe a woven fabric the term now is applied to fibres, filaments, or yarns, natural or man-made, and products obtained from them.

NOTE For example, threads, cords, ropes, braids, lace, embroidery, nets and fabrics made by weavering, knitting, felting, bonding, and tufting are textiles.

A.14 Polyester

Polymer with ester bonds in its main string (See Figure A.2). Today, the definition of polyester includes the big family of synthetic polymer, with the most used polycarbonate and most of all poly(ethylene terephthalate) (PET).

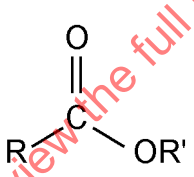

Figure A.2 — Ester bond

A.15 Polyester fibre

Fibres composed of synthetic linear macromolecules having in the chain at least 85 % (by mass) 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, e.g.,

$[— R — CO — NH — R — CO — NH —]_n$, 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, this being followed by the number in the dicarboxylic acid, e.g.,

- 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

Term used to describe fibres composed of synthetic linear macromolecules with more than 50 % (by mass) 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

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

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

A.19.2 Proteinic textile

Textile issue from animal fibres

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

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

A.19.3 Cellulosic textile

Textile issue from vegetal fibres

A.19.4 Manmade textile fibres

Textiles that are not issue 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 are applied to it 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 the fabric. Colorants used in printing contain dyes or pigments.

NOTE Traditional textile printing techniques can be broadly categorised into four styles

- direct printing, in which colorants 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 was printed;
- resist dyeing, in which a wax or other substance is printed onto 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 are known technically as colours and these colours, over colouring matter, contain thickening agents as vehicles in printing as 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 steams of woody plants, notably trees also shrubs. Wood is a heterogeneous, hygroscopic, cellular and anisotropic material. Wood is composed of fibre of cellulose and hemicelluloses impregnated with lignin.

In footwear industry wood can find some application mostly in particular type of shoes, i.e. sandal, where hardness and structural resistance of raw materials is requested.

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 footwear industry for application where a high structural resistance is not required, typically as an insole material for certain type of shoes.

A.23 Adhesives

Non metallic compound that adheres, or bonds, two items together and is able to join these materials with a superficial fixing (adhesion), in such a way that the bond has enough internal resistance (cohesion). In footwear industry many types of adhesives are used in bonding upper and sole as major joint but also for minor joint in footwear.

Adhesives are basically divided into water based and solvent based adhesives, this classification depends on the vehicle in which the bonding resin is dissolved.

Another classification depends on the type of resin adhesives, which is the main adherent agent. More usual classification is from polychloroprenic and polyurethane. More distinction depends on the additive for activation of the cross linking process, in order to obtain a structural resistance able to give adhesion. For activation of adhesives bi-components, cross linking agent based on diisocyanate solved in toluene or ethyl acetate are used.

A.24 Metallic hardware

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, assembling.

A.25 Cellulosic material

Material made from cellulose fibre (for example paper). When 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 Clause 4, Table 1), different test methods can be used.

B.2 Acrylonitrile

B.2.1 General

Chemical compound with the formula CH_2CHCN.

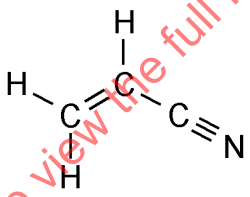

Figure B.1 — Acrylonitrile molecular structure

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 fibers. Acrylic fibers are, among other uses, precursors for well-known carbon-fiber. It is also a component of synthetic rubber.

Synthetic rubber, essentially based on SBR (Styrene-butadiene rubber) and containing acrylonitrile has some properties for which are suitable in using as material for sole, especially for 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.

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

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

B.2.3 Test methods

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

B.3 Aromatic amines

B.3.1 General

Amine 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).

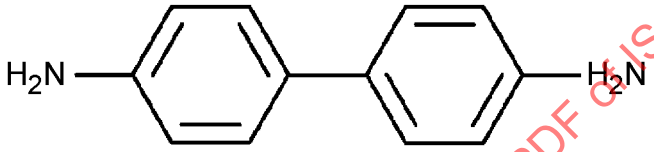

Figure B.2— Example of aromatic amines molecular structure; benzidine

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-chlor-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-chloraniline	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)	95-68-1
3,3'-dichlorbenzidine	91-94-1	2,6-dimethylaniline (=2,6-Xylidine)	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

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 in the world.

B.3.3 Test methods

For the purposes of this document the content of aromatic amines can be tested with one of the following test methods:

— prEN ISO 17234-1;

— prEN ISO 17234-2;

— EN 14362-1;

— EN 14362-2, or;

— prEN 14362-3.

B.4 Cadmium – Cd

See Clause B.13.

B.5 Chloroorganic carriers

B.5.1 General

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

Table B.2 — List of chloroorganic carriers

Substances	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

These products are toxic and some of them carcinogenic.

B.5.3 Test methods

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

B.6 Chromium and Chromium VI

See Clause B.13.

B.7 Colophony

B.7.1 General

Colophony is also called *Greek pitch* or *Rosin*. The major part of rosin used in the world is obtained as by-product from the pulp industry and is known as tall oil rosin. These two types of rosin have not the same composition although the major products are in common, but a variation in the amounts of the different compounds is seen. They are many times used for the same purposes and probably in shoes most often modified tall oil rosin is found.

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 that is used as a marker for the presence of other autoxidation products in rosin, e. g. 15-hydroperoxyabietic acid. The latter has been 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, 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 consider as 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 sensitisation in this aspect.

NOTE Colophony is classified in the EU legislation due to its skin sensitising properties and products containing more than 1 % of colophony should be marked with R 43 (Can cause skin sensitisation). However, in the EU legislation there is no demand for R 42 (lung allergy).

B.7.3 Test methods

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

B.8 Dimethylformamide (DMF)

B.8.1 General

Dimethylformamide is the organic compound with the formula $(CH_3)_2NC(O)H$. Commonly abbreviated 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]).

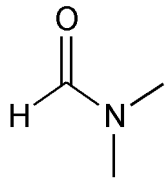

Figure B.3 — Dimethylformamide molecular structure

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

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

B.8.3 Test methods

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

B.9 Dimethylfumarate (DMFU)

B.9.1 General

Dimethylfumarate (CAS N° [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.

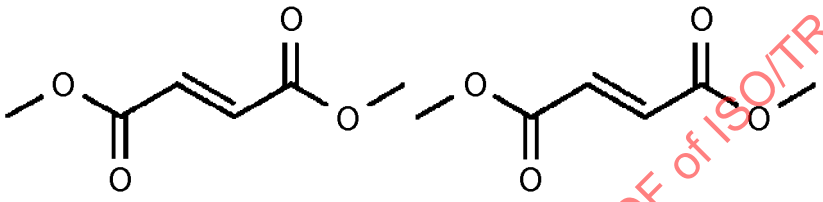

Figure B.4 — Dimethylfumarate molecular structure

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 (about 1 ppm) might produce allergic reactions.

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

B.9.3 Test methods

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

B.10 Disperses dyes

B.10.1 General

A **dye** can generally be described as a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and might require a mordant to improve the fastness of the dye on the fiber. Both dyes and pigments appear to be colored 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 dyes

Name of dye	Abbreviation	CAS number	C.I. (colour index)
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			

Table B.4 — List of carcinogenic disperse dyes

Name of dye	Abbreviation	CAS number	C.I. (colour index)
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			

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 fibers. 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 fiber. The dyeing rate can be significantly influenced by the choice of dispersing agent used during the grinding.

B.10.2 Potential risks

Certain of these dyes are carcinogenic or allergenic.

B.10.3 Test methods

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

B.11 Flame retardants

B.11.1 General

Flame retardants (see Table B.5) are materials that inhibit or resist the spread of fire. Naturally occurring substances such as asbestos as well as synthetic materials, usually halocarbons such as polybrominated diphenyl ether (PBDEs), 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 weight of a product to which they are added. Since these chemicals are not chemically bound they might "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 might 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

Substances		N° CAS
OBDE	2,2',3,3',4,4',5,6 octabrominated diphenyl ether 196 2,2',3,3',4,4',6,6' octabrominated diphenyl ether 197 2,2',3,4,4',5,5',6 octabrominated diphenyl ether 203 2,3,3',4,4',5,5',6 octabrominated diphenyl ether 205	32536-52-0
PBDE	2,2',4,4',5 pentabrominated diphenyl ether - 99 2,2',4,4',6 pentabrominated diphenyl ether 100	60348-60-9 189084-64-8
TEPA	(Tris-(azirinidyl)-phosphinoxid)	5455-55-1
TRIS	(Tri-o-cresyl phosphate, tris(2,3-dibromopropyl) phosphate)	126-72-7
PBB	(Polybrominated biphenyls)	
TCEP	(Tris(2-chloroethyl) phosphate)	
Note: These substances can be used in children slippers to meet with flammability requirements		

B.11.3 Test methods

No standard is available at the time of publication of this document, 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 H2CO. Formaldehyde exists in several forms aside from H2CO: 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.

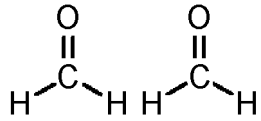

Figure B.5 — Formaldehyde molecular structure

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 in air, formaldehyde can irritate the eyes and mucous membranes, resulting in watery eyes. If inhaled, formaldehyde at this concentration may cause headaches, 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 might 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 document the content of formaldehyde can be tested with one of the following test methods:

— EN 120;

— EN ISO 17226-1;

— EN ISO 17226-2, or;

— EN ISO 14184-1.

B.13 Heavy metals

B.13.1 General

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

In this document, 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 as 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) is the amount of metal that can be extracted from a material or a product using an extraction solution. The choices of the solution depend of the test goal. For example:

— water is used for waste leaching;

— hyfrochloric acid solution to simulate ingestion;

— artificial perspiration to simulate the wear.

B.13.1.1.2 Total heavy metals

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

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

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

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

B.13.2 Potential risks

Table B.6 include a list of list of heavy metals and theirs 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 fibers.	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 will lead 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 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. Current research has found that cadmium toxicity might 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 certain hazardous substances in electric or electronic products
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.

Table B.6 — List of heavy metals and associated risks *(Continued)*

Metals	General	Potential risks
Chromium – Cr	In the footwear sector, there are three oxidation states, stable in nature, 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.
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 that 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 PbO2) 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 and 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; 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 is believed to be carcinogenic, and various other nickel compounds might 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 might cause lung oedema. Inhalation of fume might cause symptoms of asphyxiation, chills and fever and bronchitis. The effects might be delayed. Repeated or prolonged contact with skin might cause dermatitis. The substance might have effects on the respiratory tract, gastrointestinal tract and skin. Resulting in nausea, vomiting, cough, 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 document the content of heavy metals can be tested with one of the following test methods:

— EN 71-3;

— EN 14602;

— prEN ISO 17072-1, or;

— prEN ISO 17072-2.

B.13.4 Special cases

B.13.4.1 Cadmium

Cadmium is used largely in plastic products, especially PVC and the use of Cd in PVC is covered by a European Union's Directive

Cadmium could 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 amount of parameters (washing of leather, storage conditions, tanning agents, etc.).

In the past, Chromium VI was used for mordant dying 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 EN ISO 17075

B.13.4.3 Nickel

Nickel coating are often used for the finishing of the metallic pieces. Metallic fastening or ornamental pieces could be used in manufacturing shoes. These components are made with 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 reached with different process as burnishing, sandblasting, nickel-plating, etc.

Only the metallic pieces in prolonged contact with the skin (eyelet, buckle, slide fastener, etc.) are concerned by this technical report.

Sensitized individuals might show an allergy to nickel affecting their skin.

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

B.14 Mercaptobenzothiazole

B.14.1 General

Mercaptobenzothiazole is a substance used in the manufacturing of rubbers (natural or synthetic). It is added to latex or synthetic to improve the vulcanisation and to decrease the speed of ageing (ant oxidising agent). Its CAS number is [149-30-4].

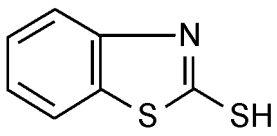

Figure B.6 — Mercaptobenzothiazole molecular structure

B.14.2 Potential risks

Mercaptobenzothiazole is an allergen.

B.14.3 Test methods

No standard is available at the time of publication of this document, 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 when vulcanised. When 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 might be capable of inducing anaphylactic shock in sensitised individuals. This is referred to as a "type 1 rubber allergy".

B.15.3 Test methods

For the purposes of this document 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].

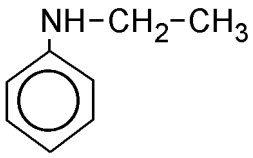

Figure B.7 — N-ethylphenylamine molecular structure

B.16.2 Potential risks

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

B.16.3 Test methods

No standard is available at the time of publication of this document, for N-ethylphenylamine analysis in footwear and footwear components.

B.17 Nickel – Ni

See Clause 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 might be carcinogenic.

Nitrosamines can be use in rubber products, pesticides, certain cosmetics

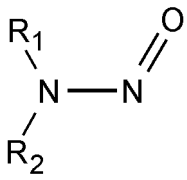

Figure B.8 — Nitrosamines molecular structure

B.18.2 Potential risks

Nitrosamines can cause cancers in a wide variety of animal species, a feature which suggests that they might also be carcinogenic in humans. Epidemiological data suggests that nitrosamines in preserved food 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 document the content of nitrosamines can be determined by EN 12868.

B.19 Nonylphenol and alkylphenolethoxylates (NP, NPEO, APEO)

B.19.1 General

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

AP commonly used are nonylphenol (NP) and, to a lesser extent, octylphenol (OP), in both cases predominantly 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 used than octylphenol ethoxylate (OPEO). AP are moderately soluble in water while the APIEO 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 on the final products).

B.19.3 Test methods

No standard is available at the time of publication of this document, for nonylphenol 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) has been extensively used as a wood preservative. Tributyltin compounds are used as marine anti-biofouling agents.

There are three major applications for organotin compounds. First, the use of tributyltin (TBT) in anti-fouling paints for ships, secondly, the use of triphenyltin (TPT) as a pesticide and third, the use of butyl- and octyltin compounds as stabilizers in polymers. Therefore, many textile products containing polymer parts, like T-shirts with prints, sanitary bandages, plasters and diapers can contain organotin compounds. In some occasions 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, catalysts, in the manufacturing 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

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

B.21 Orthophenylphenol

B.21.1 General

2-Phenylphenol, or *o*-phenylphenol, is an organic compound that 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 fibers and other materials. It is used to sterilize hospital and veterinary equipment. Other uses are in 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

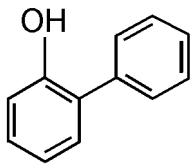

Figure B.9 — Orthophenylphenol molecular structure

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

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

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: a chemical with an ozone-depletion potential of less than 0,2.

A list of ozone depleting substances, Class 1, in included in Table B.7

Table B.7 — List of ozone depleting substances class 1

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
Monochlorofiluoromethane	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.22.2 Potential risks

When 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

No standard is available at the time of publication of this document, for ozone-depletion substances analysis in footwear and footwear components.

B.23 Pesticides

B.23.1 General

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

B.23.2 Potential risks

Many pesticides might be poisonous to humans.

B.23.3 Test methods

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

Table B.8 — Pesticides for textiles

Substances	CAS N°	Substances	CAS N°
DDT op'	789-02-6	Aldrine	309-00-2
DDT pp'	50-29-3	Dieldrine	60-57-1
DDD op'	72-54-8	Endrine	72-20-3
DDD pp'	72-55-9	Endosulfanes	
DDE		Mirex	2385-85-5
HCH's without Lindane		Toxaphene	8001-35-2
Lindane	58-89-9	Heptachlor	76-44-8
Hexachlorobenzene	118-74-1	Heptachloroepoxide	93-76-5
Carbaryle	63-25-2	2,4-D	94-75-7
Trifluraline	1582-09-8	2,4,5-T	93-76-5
Methoxychlor	72-43-5		

Table B.9 — Pesticides for leather

Substances	CAS N°	Substances	CAS N°
DDT op'	789-02-6	Dieldrine	60-57-1
DDT pp'	50-29-3	Ethylparathione	56-38-2
DDD op'	72-54-8	Endosulfanes	
DDD pp'	72-55-9	Mirex	2385-85-5
DDE		Dichlofluanide	1085-98-9
HCH's without Lindane		Heptachloroepoxide	93-76-5
Lindane	58-89-9	Pentachloroanisole	1825-21-4
Malathione	121-75-5	Permethrine	52645-53-1
Methoxychlor	72-43-5	Tolyfluanide	731-27-1
Aldrine	309-00-2	Chlorthalonil	1897-45-6

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 (like ammonium perfluorooctanoate).

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

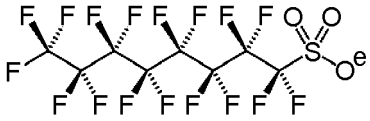

Figure B.10 — PFOS molecular structure

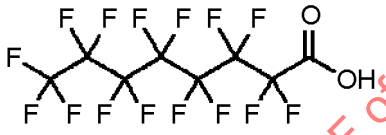

Figure B.11 — PFOA molecular structure

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 only used in certain parts, or in the coating of, certain products, such as textiles, and only the use of specific octanesulphonates 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 to 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 perfluorooctanesulphonate (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 chemically firmly bonded to the substrate (e.g. to the fibers 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 might 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.

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

B.24.2 Potential risks

PFOS are categorised as possibly carcinogenic to humans. The toxicity of PFOS is not clear, more research is necessary.

B.24.3 Test methods

No standard is available at the time of publication of this document, for PFOS-PFOA analysis in footwear and footwear components.

B.25 pH

B.25.1 General

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

B.25.2 Potential risks

Strong acidic (pH less than 3,2) or strong alkaline pH (higher than 9,5) material can irritate the skin.

B.25.3 Test methods

For the purposes of this document the content of pH can be tested with one of the following test methods:

— EN ISO 4045, or;

— EN 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. When 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.

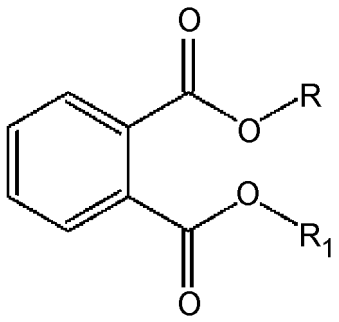

Figure B.12 — Phthalates molecular structure