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**Leather — Chemical tests —
Guidelines for testing critical
chemicals in leather**

*Cuir — Essais chimiques — Lignes directrices pour les essais de
produits chimiques critiques sur le cuir*



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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 on 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 the following URL: www.iso.org/iso/foreword.html

This document was prepared by the Chemical Tests Commission of the International Union of Leather Technologists and Chemists Societies (IUC Commission, IULTCS) in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 289, *Leather*, the secretariat of which is held by UNI, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

IULTCS, originally formed in 1897, is a world-wide organization of professional leather societies to further the advancement of leather science and technology. IULTCS has three Commissions, which are responsible for establishing international methods for the sampling and testing of leather. ISO recognizes IULTCS as an international standardizing body for the preparation of test methods for leather.

Introduction

This document was prepared in collaboration by IULTCS and by CEN/TC 289 *Leather* in order to provide an overview of chemical test methods for the leather industry. This can be used by those involved in setting specifications for leather, especially for those parameters relating to restricted chemical substances.

Regulations restrict the use of certain chemicals in consumer products. The leather industry has already taken actions by replacing the restricted substances or assuming the limits imposed by these restrictions. Many brand name manufacturers require certificates of compliance from their suppliers but too often these refer to analytical methods from other industries that are not suitable for use in testing leather.

Through the collaboration of IULTCS and CEN/TC 289, a considerable number of leather specific EN and ISO standard test methods have been developed for the chemical analysis of leather. The International Standards are tested by inter-laboratory studies, have been proven scientifically valid and are subjected to updating processes according to ISO protocols.

Chemical analysis of leather

Leather is a complex substrate to chemically analyse. After tanning, leather typically undergoes wet-processing in aqueous media at low temperatures (<60 °C) and in an acid pH range of 3,5 to 5,5. The characteristic properties of leather are achieved by mostly using a range of anionic retanning agents (natural and/or synthetic), polymers and oils, as well as anionic dyes for achieving the required colour. In analytical procedures, when leather is extracted, some of these substances can be removed and make a complex matrix for the analysis. This should be considered when establishing quantification limits for leather analyses. Too often unrealistic limits established in aqueous solutions, e.g. waste water analysis, are quoted in specifications for leather.

This document gives an overview of those internationally accepted chemical test procedures established specifically for leather.

Leather — Chemical tests — Guidelines for testing critical chemicals in leather

1 Scope

This document gives guidelines to apply the available chemical test methods for leather. This information can be used by those involved in setting specifications for leather, especially for those parameters relating to restricted chemical substances.

Lists of restricted chemicals contain many substances that are not relevant to the leather industry. Those chemical substances that are not mentioned in this document do not need to be determined, thus avoiding unnecessary analytical costs.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 4045, *Leather — Chemical tests — Determination of pH*

ISO 5398-1, *Leather — Chemical determination of chromic oxide content — Part 1: Quantification by titration*

ISO 5398-2, *Leather — Chemical determination of chromic oxide content — Part 2: Quantification by colorimetric determination*

ISO 5398-3, *Leather — Chemical determination of chromic oxide content — Part 3: Quantification by atomic absorption spectrometry*

ISO 5398-4, *Leather — Chemical determination of chromic oxide content — Part 4: Quantification by inductively coupled plasma - optical emission spectrometer (ICP-OES)*

ISO 13365, *Leather — Chemical tests — Determination of the preservative (TCMTB, PCMC, OPP, OIT) content in leather by liquid chromatography*

ISO 17070, *Leather — Chemical tests — Determination of tetrachlorophenol-, trichlorophenol-, dichlorophenol-, monochlorophenol-isomers and pentachlorophenol content*

ISO 17072-1, *Leather — Chemical determination of metal content — Part 1: Extractable metals*

ISO 17072-2, *Leather — Chemical determination of metal content — Part 2: Total metal content*

ISO/17075-1, *Leather — Chemical determination of chromium (VI) content in leather — Part 1: Colorimetric method*

ISO/17075-2, *Leather — Chemical determination of chromium (VI) content in leather — Part 2: Chromatographic method*

ISO 17226-1, *Leather — Chemical determination of formaldehyde content — Part 1: Method using high performance liquid chromatography*

ISO 17226-3, *Leather — Chemical determination of formaldehyde content — Part 3: Determination of formaldehyde emissions from leather*

ISO 17234-1, *Leather — Chemical tests for the determination of certain azo colorants in dyed leathers — Part 1: Determination of certain aromatic amines derived from azo colorants*

ISO 17234-2, *Leather — Chemical tests for the determination of certain azo colorants in dyed leathers — Part 2: Determination of 4-aminoazobenzene*

ISO 18218-1, *Leather — Determination of ethoxylated alkylphenols — Part 1: Direct method*

ISO 18218-2, *Leather — Determination of ethoxylated alkylphenols — Part 2: Indirect method*

ISO 18219, *Leather — Determination of chlorinated hydrocarbons in leather — Chromatographic method for short-chain chlorinated paraffins (SCCP)*

ISO 19070, *Leather — Chemical determination of N-methyl-2-pyrrolidone (NMP) in leather*

ISO/TS 16179, *Footwear — Critical substances potentially present in footwear and footwear components — Determination of organotin compounds in footwear materials*

ISO/TS 16181, *Footwear — Critical substances potentially present in footwear and footwear components — Determination of phthalates in footwear materials*

ISO/TS 16186, *Footwear — Critical substances potentially present in footwear and footwear components — Test method to quantitatively determine dimethyl fumarate (DMFU) in footwear materials*

ISO/TS 16189, *Footwear — Critical substances potentially present in footwear and footwear components — Test method to quantitatively determine dimethylformamide in footwear materials*

ISO/TS 16190, *Footwear — Critical substances potentially present in footwear and footwear components — Test method to quantitatively determine polycyclic aromatic hydrocarbons (PAH) in footwear materials*

EN 1122, *Plastics — Determination of cadmium - Wet decomposition method*

EN 15987, *Leather — Terminology — Key definitions for the leather trade*

EN 16778, *Protective gloves — The determination of Dimethylformamide in gloves*

CEN/TS 15968, *Determination of extractable perfluorooctanesulphonate (PFOS) in coated and impregnated solid articles, liquids and fire fighting foams - Method for sampling, extraction and analysis by LC-qMS or LC-tandem/MS*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 15987 apply.

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

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

4 Chemical substances potentially found in leather

4.1 Chemical test methods for substances used by the leather industry with no legal restrictions for leather

[Table 1](#) includes those chemical substances conventionally used in the various leather manufacturing processes. While not legally restricted, some of these substances can be restricted in specifications for the final leather article.

4.2 Chemical test methods for substances previously used by the leather industry

[Table 2](#) shows substances that have historically been used in the leather industry, but at the present time are unlikely to be found in leather articles.

4.3 Chemical test methods for substances not used by the leather industry

[Table 3](#) includes those chemical substances that are restricted but not used in the leather industry. The presence of these substances in leather articles is only likely due to external conditions/contamination.

Table 1 — Substances used in the leather industry with no legal restrictions for leather

Substance/material	CAS no.	Suitable method for measurement	Uses
Chromium – total		Total Cr in leather is normally reported as chromic oxide using one of the techniques: ISO 5398-1 ISO 5398-2 ISO 5398-3 ISO 5398-4 Alternatively: ISO 17072-2	Basic chromium (III) sulfate is the most commonly used universal tanning agent for leather. The trivalent Cr(III) form is not hazardous.
Chromium – extractable		ISO 17072-1	Basic chromium (III) sulfate is the most commonly used universal tanning agent for leather. The trivalent Cr(III) form is not hazardous.
Formaldehyde	50-00-0	ISO 17226-1 (formaldehyde in leather – HPLC method) ISO 17226-3 (formaldehyde emission, especially for automotive leathers)	Formaldehyde is used in the manufacture of some leather chemicals, for example, synthetic tanning agents and resins.
Fungicides — 2-(thiocyanomethylthio)-benzothiazole, (TCMTB) — 4-chloro-3-methylphenol, (PCMC) — 2-phenylphenol, (OPP) — 2-octylisothiazol-3(2H)-one, (OIT)	21564-17-0 59-50-7 90-43-7 26530-20-1	ISO 13365	It is necessary to protect the natural product leather in its raw and wet-tanned state from biological damage.
Heavy metals (except Cr) — Cobalt, (Co) — Copper, (Cu)		ISO 17072-1 (extractable metal) ISO 17072-2 (total metal)	A small number of Co and Cu organic metal complex dyes and pigments are used to achieve specific colours.
pH value pH is not a substance but most leather specifications list this chemical parameter		ISO 4045	Typically required to be in the range pH 3,2 to pH 9,5 The pH value indicates the degree of acidity or alkalinity for the chemical reactions during the leather processing. Note: The pH for certain leather articles, e.g. protective products, can be mandatory.

Table 2 — Substances that have historically been used in the leather industry, but at the present time are unlikely to be found in leather articles

Substance	CAS no.	Suitable method for measurement	Possible uses	Mandatory restriction or legal obligation
Alkylphenols (AP) and alkylphenol ethoxylates (APEO)	(see Table A.1)	ISO 18218-1 (NPEO, OPEO) ISO 18218-2 (NP, OP)	Soaking, degreasing, finishing. In the leather industry the nonylphenol ethoxylate (NPEO) and octylphenol ethoxylate (OPEO) surfactants have been used, but are now mostly replaced with alternative surfactants. However, the water insoluble substances, nonylphenol (NP) and octylphenol (OP), were not used by the leather industry.	Reach EU Regulation No. 1907/2006 Annex XVII – entry 46, in treatment of leather
Aromatic amines released by the reductive breakdown of azo dyes	(see Table A.2)	ISO 17234-1 ISO 17234-2 (for analysis of 4-aminoazobenzene)	Azo colorants releasing these forbidden amines are not manufactured today.	Reach EU Regulation No. 1907/2006 Annex XVII – entry 43 GB 20400-2006, Chinese Standard
Cadmium	87-86-5	ISO 17072-2 EN 1122 (for PVC)	Only for coated leather. [cadmium is a polymer stabilization agent for polyvinyl chloride (PVC)]	Reach EU Regulation No. 1907/2006 Annex XVII – entry 23 Substance of Very High Concern (SVHC) Candidate substance
Chlorinated paraffins — Short chained chlorinated paraffins, C10 to C13, (SCCP)		ISO 18219	SCCP were previously used in oil tanning and fatliquor formulations. The use of SCCP is legally restricted in the EU.	Reach EU Regulation No. 1907/2006 SVHC Candidate substance Persistent Organic Pollutant (POP) EU Regulation No. 850/2004, Annex 1, Part B
Chlorophenols — Pentachlorophenol, (PCP) — Tetrachlorophenols, (TeCP) — Trichlorophenols, (TCP)	87-86-5	ISO 17070	Biocides. Restrictions exist for a considerable time, these substances are no longer used.	Reach EU Regulation No. 1907/2006 Annex XVII – entry 22 Biocide EU Regulation No. 528/2012
Dimethylformamide, (DMFa)	68-12-2	ISO/TS 16189 (footwear) EN 16778 (protective gloves)	Only for coated leather. Solvent for PU (polyurethane).	Reach EU Regulation No. 1907/2006 SVHC Candidate substance

Table 2 (continued)

Substance	CAS no.	Suitable method for measurement	Possible uses	Mandatory restriction or legal obligation
Dimethylfumarate, (DMFU)	624-49-7	ISO/TS 16186 (footwear)	Not used in leather processing. Problems in recent years have occurred when sachets of DMFU have been added into the packaging of upholstery and shoes to protect them from mould during shipping.	Reach EU Regulation No. 1907/2006 Annex XVII – entry 61
N-methyl pyrrolidone (NMP)	872-50-4	ISO 19070	Only for coated leather.	Reach EU Regulation No. 1907/2006 SVHC Candidate substance
Phthalates	(see Table A.3)	ISO/TS 16181 (footwear)	Only for coated leather. Plasticizers/softening agents. Historically some phthalates have been used in PVC and PU finish coat formulations and in fatliquors.	Reach EU Regulation No. 1907/2006 Annex XIV and Annex XVII – entry 51-52 in toys and childcare articles. SVHC Candidate substance
Polyaromatic hydrocarbons, (PAH)	(see Table A.4)	ISO/TS 16190 (footwear)	Only for coated leather.	Reach EU Regulation No. 1907/2006 Annex XVII – entry 50

Table 3 — Substances not used in the leather industry, presence in leather articles is only likely due to external conditions/contamination

Substance	CAS no.	Suitable method for measurement	Possible uses	Mandatory restriction or legal obligation
Bisphenol-A	80-08-7		Used in synthetic materials, it is not used in leather.	
Chromium (VI), Hexavalent chromium, (Cr VI)		ISO 17075-1 ISO 17075-2	Not used for leather tanning. Traces of Cr (VI) oxidation state can develop if oxidative conditions are allowed to occur. Experience has shown that the use of reductive processes can hinder the formation of these trace levels.	Reach EU Regulation No. 1907/2006 Annex XVII – entry 47 SVHC Candidate substance
Flame retardants - Polybrominated diphenyl ether			Organic polybromo complexes are restricted. Used in synthetic materials, not used in leather.	Reach EU Regulation No. 1907/2006 Annex XVII – entry 45 POP EU Regulation No. 850/2004
Heavy metals — Arsenic (As) — Barium (Ba) — Mercury (Hg)		ISO 17072-1 (extractable metal) ISO 17072-2 (total metal)		EU Directive 2009/48/EC on toy safety
Heavy metals — Lead (Pb)		ISO 17072-1 (extractable metal) ISO 17072-2 (total metal)		Reach EU Regulation No. 1907/2006 SVHC Candidate substance California Proposition 65 List Consumer Product Safety Improvement Act (CPSIA, USA)
Organotin (Sn) compounds	(see Table A.5)	ISO/TS 16179 (footwear)	Fungicides in certain organic chemical auxiliaries. Catalysts for polyurethane manufacture and stabilizers for PVC.	Reach EU Regulation No. 1907/2006 Annex XVII – entry 20 EU Directive 2009/48/EC on toy safety
Perfluoro octyl sulfonic acid, (PFOS)	3825-26-1	CEN/TS 15968	Soil, oil and water resistant products based on octyl (C8) type fluorocarbons. The C8-type have been replaced with shorter chain fluorocarbons.	POP EU Regulation No. 850/2004

Annex A (informative)

Substances lists

Tables A.1 to A.5 report the specific chemical substances listed with a general name in Tables 2 and Table 3.

Table A.1 — Alkylphenols and alkylphenol ethoxylates

Chemical name	Abbreviation	CAS number
4-tert-octylphenol	OP	140-66-9
octylphenol ethoxylate (from OP2EO → OP16EO)	OPEO	9002-93-1
4-nonylphenol (mix of isomers)	NP	84852-15-3
4-nonylphenol ethoxylate (from NP2EO → NP16EO)	NPEO	68412-54-4

Table A.2 — Aromatic amines^a

Restricted aromatic amines (24)	CAS number
4-aminobiphenyl	92-67-1
Benzidine	92-87-5
4-chloro-o-toluidine	95-69-2
2-naphtylamine	91-59-8
o-aminoazotoluene	97-56-3
5-nitro-o-toluidine	99-55-8
4-chloroaniline	106-47-8
4-methoxy-m-phenylenediamine	615-05-4
4,4'-diaminobiphenylmethane	101-77-9
3,3'-dichlorobenzidine	91-94-1
o-dianisidine	119-90-4
3,3'-dimethylbenzidine	119-93-7
4,4'-dimethylenedi-o-toluidine	838-88-0
p-cresidine	120-71-8
4,4'-methylene-bis-(2-chloro-aniline)	101-14-4
4,4'-oxydianiline	101-80-4
4,4'-thiodianiline	139-65-1
o-toluidine	95-53-4
4-methyl-m-phenylenediamine	95-80-7
2,4,5-trimethylaniline	137-17-7
o-anisidine	90-04-0
4-aminoazobenzene	60-09-3
2,4-xylidine	95-68-1
2,6-xylidine	87-62-7

^a Amines according to EU Regulation 1907/2006, Annex XVII and Chinese Standard GB 20400-2006

Table A.3 — Phthalates

Substance	Abbreviation	CAS number	Phthalates in the SVHC Candidate list	Phthalates in Annex XIV	Phthalates in Annex XVII
Diisobutyl phthalate	DiBP	84-69-5	X	X	—
Dibutyl phthalate	DBP	84-74-2	X	X	X, entry 51-b
Bis(2-methoxyethyl) phthalate	DMEP	117-82-8	X	—	—
BenzylButyl phthalate	BBP	85-68-7	X	X	X, entry 51-c
Di(ethylhexyl) phthalate	DEHP	117-81-7	X	X	X, entry 51-a
Di(n-octyl) phthalate	DnOP	117-84-0	—	—	X, entry 52-c
Diisononyl phthalate	DiNP	28553-12-0 68515-48-0	—	—	X, entry 52-a
Diisodecyl phthalate	DiDP	26761-40-0 68515-49-1	—	—	X, entry 52-b
1,2-benzenedicarboxylic acid, di C6-8 branched alkylesters C7 rich, Di-isoheptylphthalate	DiHP	71888-89-6	X	—	—
1,2-benzenedicarboxylic acid, di C7-11 branched and linear alkylesters	DHNUP	68515-42-4	X	—	—
Di-n-hexylphthalate	DnHP	84-75-3	X	—	—
Di-n-pentyl phthalate	DnPP	131-18-0	X	—	—
Diisopentyl phthalate	DiPP	605-50-5	X	—	—
N-pentyl-isopentylphthalate	nPiPP	776297-69-9	X	—	—
1,2-Benzenedicarboxylic acid, dipentylester, branched and linear (including DnPP dipentylester)	(DnPP+DiPP +nPiPP)	84777-06-0	X (sum)	—	—

Table A.4 — Polyaromatic hydrocarbons (PAH)

PAH substances (8)	CAS number
Benzo(a)anthracene, BaA	56-55-3
Benzo(a)pyrene, BaP	50-32-8
Benzo(b)fluoranthene, BbFA + Benzo(j)fluoranthene, BjFA	205-99-2 205-82-3
Benzo(e)pyrene, BeP	192-97-2
Benzo(k)fluoranthene, BkFA	207-08-9
Chrysene, Chr	218-01-9
Dibenzo(a,h)anthracene, DBahA	53-70-3

Table A.5 — Organotin (Sn) compounds

Organotin compounds
Dibutyltin (DBT)
Monobutyltin (MBT)
Monooctyltin (MOT)
Dioctyltin (DOT)
Tricyclohexyltin (TCyHT)
Trioctyltin (TOT)
Tributyltin (TBT)
Triphenyltin (TPhT)
Tetrabutyltin (TebT)

Bibliography

- [1] ISO/TR 16178, *Footwear — Critical substances potentially present in footwear and footwear components*
- [2] CEN/TR 16417, *Footwear. Footwear industry guideline for substances of very high concern (Annex XIV of REACH)*
- [3] REGULATION E.U. 1907/2006 (Original work published 1907) Registration, Evaluation, Authorisation and Restriction of Chemicals. REACH, 2006. <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2007:136:0003:0280:en:PDF>
- [4] GB 20400-2006, Leather and fur – Limit of harmful matter. <http://www.chinesestandard.net/PDF-Excerpt/ShowPDFexcerpt.aspx?ExcerptID=GB%2020400-2006>
- [5] REGULATION EU 850/2004, Persistent organic pollutants (POP). <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2004:158:0007:0049:EN:PDF>
- [6] REGULATION EU 528/2012, Use of biocidal products. <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2012:167:FULL:EN:PDF>
- [7] Candidate List of substances of very high concern for Authorisation, SVHC Candidate and Annex XIV substances. <http://echa.europa.eu/web/guest/candidate-list-table>
- [8] State of California, Safe Drinking Water and Toxic Enforcement Act of 1986, Proposition 65 List. <http://oehha.ca.gov/proposition-65/proposition-65-list>
- [9] The Consumer Product Safety Improvement Act (CPSIA), USA. <http://www.cpsc.gov/en/Regulations-Laws-Standards/Statutes/The-Consumer-Product-Safety-Improvement-Act/>
- [10] EU Directive 2009/48/EC on the safety of toys. <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32009L0048&from=en>

