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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 document 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).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at <u>www.iso.org/patents</u>. ISO shall not be held responsible for identifying any or all such patent rights.

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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.

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.

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*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 20137:2017), which has been technically revised.

The main changes are as follows:

- testing standards updated;
- new substances added in <u>Table 1</u> (bisphenols, glutaraldehyde);
- new substance added in <u>Table 3</u> (brominated flame retardants);
- new <u>Tables A.3</u> and <u>A.5</u> added to <u>Annex A</u>.

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 <u>www.iso.org/members.html</u>.

Introduction

1 General

This document is intended to provide an overview of chemical test methods for the leather industry. It 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 action by replacing 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 International and European standard test methods have been developed for the chemical analysis of leather. The International Standards are tested by interlaboratory studies, have been proven scientifically valid and are subjected to updating processes according to ISO protocols.

2 Chemical analysis of leather

Leather is a complex substrate to chemically analyse. After tanning, leather typically undergoes wetprocessing 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, for example waste water analysis, are quoted in specifications for leather.

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

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

1 Scope

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This document provides lists of chemicals that have already been detected in leather and guidelines for applying 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.

Generic lists of restricted chemicals used on the market 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.

NOTE Due to the constantly changing legal requirements and toxicological evaluation of chemical substances, this document cannot address all potentially critical substances.

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 15115, Leather — Vocabulary

EN 15987, Leather — Terminology — Key definitions for the leather trade https://standards.iteh.ai/catalog/standards/sist/983809a8-5fdf-41ad-9746-

Terms and definitions 651e212d3287/iso-fdis

For the purposes of this document, the terms and definitions given in ISO 15115 and EN 15987 apply.

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

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

4 Chemical substances potentially found in leather

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

<u>Table 1</u> includes those chemical substances conventionally used in the various leather manufacturing processes worldwide. While not currently legally restricted (as of May 2023), some of these substances can be restricted in specifications for the final leather article.

Table 1 — Substances used in the leather industry with no current legal restrictions for leather(as of May 2023)

Substance or material	CAS Registry Number ^{® a}	Suitable method for measurement	Uses
Bisphenol S Bisphenol F	80-09-1 620-92-8	ISO 11936	In the leather industry, Bi- sphenol F can be an impurity in synthetic tanning agents. Bisphenol S is a monomer that is used to manufacture synthetic tanning agents, which can lead to residues in the final product.
Chromium – total		Total Cr in leather is normally reported as chromium (III) oxide, using one of the stand- ards: ISO 5398-1 ISO 5398-2	Basic chromium (III) sulfate is the most commonly used universal tanning agent for leather.
		ISO 5398-3	The trivalent Cr form is not
		ISO 5398-4	hazardous.
		Alternatively:	7 7
11eh S	SIANI	ISO 17072-2	VIEW
	(stand	ards.iteh.ai)	Basic chromium (III) sulfate is the most commonly used universal tanning agent for
Chromium – extractable		ISO 17072-1	leather.
	<u>IS</u> itah si/astalas	<u>D/FDIS 20137</u> //standards/sist/082800a8	The trivalent Cr form is not
https://standards.	651e2120	ISO 17226-1	hazardous9746-
		(formaldehyde in leather – HPLC method)	Formaldehyde is used in the
Formaldehyde	50-00-0	ISO 17226-3	manufacture of some leather chemicals, e.g. synthetic tan-
		(formaldehyde emission, especially for automotive leathers)	ning agents and resins.
Biocides			
 — 2-(thiocyanomethylthio)- benzothiazole (TCMTB) 	21564-17-0	ISO 13365-1	I
— 4-chloro-3-methylphenol	59-50-7	(solvent extractable)	It is necessary to protect the natural product leather in
(PCMC)	90-43-7	ISO 13365-2	its raw and wet-tanned state from biological damage.
— 2-phenylphenol (OPP)	26530-20-1	(aqueous extractable)	in oni biological ualliage.
 2-octylisothiazol-3(2H)-one (OIT) 			
^a Chemical Abstracts Service (CAS) R information is given for the convenience product named. Equivalent products may	of users of this d	locument and does not constit	ute an endorsement by ISO of the

^b Cancelled and replaced by ISO 17226-1:2021.

Substance or material	CAS Registry Number ^{® a}	Suitable method for measurement	Uses
		In progress	Can be used: — as a tanning agent;
Glutaraldehyde	111-30-8	ISO 17226-1:2018 ^b can be adapted for concentra- tions below 1 000 mg/kg	 as a retanning agent; to give resistance to sweat for certain leather used in military gloves.
Heavy metals (except Cr)		ISO 17072-1	A small number of Co and Cu
— cobalt (Co)		(extractable metal)	organic metal complex dyes and pigments are used to
— copper (Cu)		ISO 17072-2	achieve specific colours. Tita- nium dioxide can be present
— titanium (Ti)		(total metal)	in pigments.
			Typically required to be in the range pH 3,2 to pH 9,5.
pH value pH is an indicator of the leather acidity	NDAF	ISO 4045 REVIE	The pH value indicates the degree of acidity or alkalinity for the chemical reactions during the leather process- ing.
or alkalinity and is a specified pa- rameter	indard	s.iteh.ai)	pH difference figure is impor- tant to evaluate when pH is lower than 4,0.
https://standards.iteh.ai/	<u>ISO/FDIS</u> catalog/standa	20101	The pH for certain leather articles, such as protective products, can be mandatory.
^a Chemical Abstracts Service (CAS) R information is given for the convenience product named. Equivalent products may	of users of this d	ocument and does not constit	ute an endorsement by ISO of the
b Cancelled and replaced by ISO 17226	-1:2021.		

Table 1 (continued)

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

<u>Table 2</u> shows substances that have historically been used in the leather industry worldwide but at the present time are unlikely to be found in leather articles (see <u>Annex A</u>).

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 at the regulated limits

Substance	CAS Registry Number	Suitable method for measurement	Possible uses	Mandatory restriction or legal obligation
Alkylphenols (AP) and alkylphenol ethoxylates (APEO) See <u>Annex A, Table A.1</u>	(see <u>Table A.1</u>)	Https://sta 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, nonyl- phenol (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
Aromaticamines released by the reductive breakdown of azo dyes See <u>Annex A, Table A.2</u>	(see <u>Table A.2</u>)	ISO 17234-1 ISO 17234-2 (for analysis of 4-aminoazobenzene)	Azo colourants 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 Annex XIVSubstance of very high concern Reach (SVHC) candidate substance
Chlorinated paraffins — short-chained chlorinated paraffins, C10 to C13, (SCCP) — middle-chained chlorinated paraffins, C14 to C17, (MCCP)		/standards/sist/ 13287/iso-fdis-2 1-61281 120 18519-5 ISO 18519-5	Chlorinated parafitins were previously used in oil tanning and fat liquor formulations.	Reach EU Regulation No. 1907/2006 Annex XVII – entry 23 Annex XIV Substance of very high concern Reach (SVHC) SCCP is regulated in Persistent Organic Pollutant (POP) EU Regulation No. 2019/1021, Annex 1, Part A
Chlorophenols — pentachlorophenol (PCP) — tetrachlorophenols (TeCP) — trichlorophenols (TCP) — dichlorophenols (DiCP) — monochlorophenols (MCP)		983809a8-5fdf-41 0137 02021 OSI	PCP, TeCP, TCP have been used as biocides. PCP restrictions exist for a considerable time. PCP, TeCP, TCP can sometimes be used as storage vessel preservatives, for example in print paste, and cause trace contamination in leather.	PCP is regulated in Persistent Organic Pollutant (POP) EU Regulation No. 2019/1021, Annex 1, Part A
Dimethylformamide (DMFa)	68-12-2	ISO 16189 (footwear) EN 16778 (protective gloves)	Only for coated leather. Solvent for PU (polyurethane).	Reach EU Regulation No. 1907/2006 Annex XVII – entry 76 Annex XIV Substance of very high concern Reach (SVHC)

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Substance	CAS Registry	Suitable method	Possible uses	Mandatory restriction or legal obligation
			Not used in leather processing.	
Dimethylfumarate (DMFU)	624-49-7	ISO 16186 (footwear)	Problems in recent years have occurred when sa- chets 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
		and	e	Reach EU Regulation No. 1907/2006
N-Methyl-2-pyrrolidone (NMP)	872-50-4	ard 180 19070	Only for coated leather.	Annex XVII – entry 72
, , ,		s.itel	S] (\$	Annex XIV Substance of very high concern Reach (SVHC)
		ISO 16181-1 (with solvent extrac-	ſ⁄	Reach EU Regulation No. 1907/2006
		tion)	Plasticizers or softening agents.	Annex XVII - entry 52 in toys and childcare articles.
Phthalates	(see Table A.3)	ISO 16181-2 (without solvent et extraction)	Denaturation of mineral oils.	Annex XVII – entry 51
See <u>Annex A</u> , <u>Table A.3</u>		(footwear)	Historically, some phthalates have been used in PVC Annex XIV Substance of very high concern Reach and PU finish coat formulations and in fat liquors. (SVHC)	Annex XIV Substance of very high concern Reach (SVHC)
		CPSC-CH-C1001-09.4	A] r(CPSC regulation (USA)
Polyaromatic hydrocarbons (PAH)	(1) A Alder (1)	arc (reantpol (180	DAH can ha found in carbon black nimment	Reach EU Regulation No. 1907/2006
See <u>Annex A</u> , <u>Table A.4</u>				Annex XVII – entry 50