

## JRC SCIENTIFIC AND POLICY REPORTS

# Progress report on the development of standard methods for the characterisation of textile fibres and yarns and for the safety of textile products and toys

P. Piccinini 2013

Report EUR 26466 EN



European Commission

Joint Research Centre

Institute for Health and Consumer Protection

Contact information

Paola Piccinini

Address: Joint Research Centre, Via Enrico Fermi 2749, TP 260, 21027 Ispra (VA), Italy

E-mail: JRC-IHCP-CAT@ec.europa.eu

Tel.: +39 0332 789124 Fax: +39 0332 785707

http://jrc.ec.europa.eu/

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JRC78840

EUR 26466 EN

ISBN 978-92-79-35266-9 (pdf)

ISSN 1831-9424 (online)

doi:10.2788/62275

Luxembourg: Publications Office of the European Union, 2013

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Printed in Luxembourg

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## 1. Executive summary

There is a strong need of standardisation in the field of textile products and toys, in order to allow the enforceability of restrictions established in the EU legislation. The JRC has been actively involved in the progresses made on the development of standard methods for the characterisation of textile fibres and yarns and for the safety of textile products and toy, which are reviewed in this report. A number of standard methods published or under development are entirely or partly based on the JRC work. The JRC contribution ranged from taking part in or organising ring trials, drafting parts of test methods, proposing modifications, giving advice on the basis of its practical experience in chemical analysis of consumer products, drafting questionnaires, statistically evaluating results of collaborative trials and providing test methods that had been developed and validated by the JRC.

The work performed by Working Groups (WGs), of which the JRC is member, is described: CEN/TC 248/WG 26 (on test methods for analysis of EC restricted substances in textiles); CEN/TC 248/WG 30 (on quantitative analysis of fibre mixtures); CEN/TC/52/WG 5 (on chemical properties of toys); and ISO/TC/WG 22 (on composition and chemical testing of textiles). The need for the test methods and their principles are explained, together with their stage in the approval process.

The following standard methods have been published in 2013:

EN ISO 1833-22	Textiles - Quantitative chemical analysis -			
	Part 22: Mixtures of viscose or certain types of cupro or modal or lyocell and flax fibres			
	(method using formic acid and zinc chloride)			
EN ISO 1833-25	Textiles - Quantitative chemical analysis -			
	Part 25: Mixtures of polyester and certain other fibres			
	(method using trichloroacetic acid and chloroform)			
EN ISO 1833-26	Textiles - Quantitative chemical analysis -			
	Part 26: Mixtures of melamine and cotton or aramide fibres			
	(method using hot formic acid)			
EN 71-3	Safety of toys			
	Part 3: Migration of certain elements			
EN 71-12	Safety of toys			
	Part 12: N-nitrosamines and N-nitrosatable substances			

The following standard methods and technical reports are under development or in revision or in publication:

PrEN ISO 16373-1	Textile - Dyestuffs
	Part 1: General principles of testing coloured textiles for dyestuff
PrEN ISO 16373-2	Textile – Dyestuffs
	Part 2: General method for the determination of extractable dyestuffs
	including allergenic and carcinogenic substances
PrEN ISO 16373-3	Textile - Dyestuffs
	Part 3: Method for determination of carcinogenic extractable dyestuffs
	(method using triethylamine/methanol)
PrEN 15777:2009/prA1	Textiles - Test methods for phthalates
Technical report	guidance on health and environmental issues related to the chemical content
	of textile products intended to clothing, interior textiles and upholstery
prEN ISO 18254	Textile – Detection and determination of APEO in textiles by HPLC-MS
WI 00248537	Textile – Determination of metal content
	Part 1: Determination of metals using microw ave digestion
WI 00248536	Textile – Determination of metal content
	Part 2: Determination of metals extracted by acidic artificial perspiration solution
prEN 71-3/pr A1	Safety of toys
	Part 3: Migration of certain elements
WD 18074	Textiles - Identification of some animal fibres by DNA analysis method -
	Cashmere, wool, yak and their blends
ISO/CD 17751-1	Textiles - Quantitative analysis of cashmere, wool, other specialty animal fibers and their blends
	Part 1: Light Microscopy method
ISO/CD 17751-2	Textiles - Quantitative analysis of cashmere, wool, other specialty animal fibers and their blends
	Part 2: Scanning Electron Microscopy method
ISO FDIS 14389	Textiles- Determination of the content of phthalates - tetrahydrofuran
WD 17881-1	Textiles - Determination of certain flame retardants
	Brominated flame retardants
WD 17881-2	Textiles - Determination of certain flame retardants
	Phosphorus flame retardants
WD 17881-3	Textiles - Determination of certain flame retardants
	Short chain paraffin flame retardants
ISO 24362-1	Textiles Methods for determination of certain aromatic amines derived from azo colorants
	Part 1: Detection of the use of certain azo colorants accessible with and without extracting the fibres
ISO 24362-3	Textiles Methods for determination of certain aromatic amines derived from azo colorants
	Part 3: Detection of the use of certain azo colorants, which may release 4-aminoazobenzene

## 2. Introduction

This report summarises the work performed by CEN/TC 248 (textiles and textile products) and ISO/TC 38 (textiles) on the development of standard methods for the characterisation and for the safety of textile products and by CEN/TC 52 (safety of toys) on the development of standard methods for the safety of toys. In particular, the activities of the following Working Groups of CEN/TC 248 were considered: WG 26 (test methods for analysis of EC restricted substances) and WG 30 (quantitative analysis of fibre mixtures). Considering ISO/TC 38, the achievements of Working Group 22 (Composition and chemical testing) were taken into consideration. Finally, for the safety of toys the output of WG 5 (chemical toys) was analysed. The JRC is a member of these WGs and has been actively contributed to their achievements and progresses. For example, the JRC has been taking part in or organising ring trials, drafting parts of test methods, proposing modifications, giving advice on the basis of its practical experience in chemical analysis of consumer products, drafting questionnaires, statistically evaluating results of collaborative trials, providing test methods that had been developed and validated by the JRC in collaboration with the European Network of the National Expert on Textile Labelling (ENNETL).

## 3. Legislative requirements

#### 3.1 Characterisation of textiles

At European level, the proper functioning of the internal market in the textile and clothing sector is assured by the EU regulation 1007/2011 (textile regulation) [1] on textile fibre names and related labelling and marking of the fibre composition of textile products, which sets the rules for the labelling of textile products.

The aim of this regulation is twofold: on the one hand, to avoid hindrances to the proper functioning of the EU internal market; on the other hand, to protect consumer interests by correct information regarding product composition. Validated test methods for the quantification of binary and ternary fibre mixtures are included in the legislation, thus allowing the prevention of frauds and the verification of the accuracy of composition labels by market surveillance authorities in Member States. The regulation repealed and replaced the previous set of Directives (73/44/EEC [2] and 96/73/EC [3] on the analysis of ternary and binary mixtures, respectively, and 2008/121/EC [4] on textile names) and their subsequent amendments. It is applicable in all Member States and it came into force on 8<sup>th</sup> May 2012.

The descriptions of the quantitative test methods that have to be used for compliance purposes are included in Annex VIII of the textile regulation. The possibility to eliminate the test methods from the legislation and to transfer them under the responsibility of standardisation bodies, such as CEN and/or ISO, is under evaluation. In this case, the reference to the standard methods will be added in the regulation.

#### 3.2 <u>Safety of textiles</u>

Another legislation that is relevant to the textile sector is the EC regulation 1907/2006 [5] concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) and, in particular, its Annex XVII on restrictions on the manufacture, placing on the market and use of certain dangerous substances, preparations and articles. Since when Annex XVII of REACH entered into force on 1<sup>st</sup> June 2009, the previous sectorial directives linked to chemicals into textiles were repealed. One of the main scopes of REACH is to ensure a high level of human health and environmental protection from the risks that can be posed by chemicals. The restrictions that are applicable to textile products are reported in Table 1.

**Table 1**: Substances used in textiles restricted by Annex XVII of EC regulation 1907/2006.

Entry	Substance	Acronym	CAS n.	Color Index	Restriction
4	tris (2,3 dibromopropyl) phosphate	TRIS	126-72-7		<ol> <li>They shall not be used in textile articles, such as garments,</li> </ol>
7	tris (aziridinyl)phosphinoxide	TEPA	5455-55-1		undergarments
8	Polybromobiphenyls; Polybrominatedbiphenyls	PBB	59536-65-1		and linen, intended to come into contact with the skin
					Shall not be placed on the market, or used, as substances or in
18	Mercury compounds				mixtures where the substance or mixture is intended for use: (c) in
					the impregnation of heavy-duty industrial textiles and yarn intended
					Dioctyltin (DOT) compound:
	Organostannic compounds				(a) Dioctyltin (DOT) compounds shall not be used after 1 January
20					2012 in the following articles for supply to, or use by, the general
20					public, where the concentration in the article, or part thereof, is
					greater than the equivalent of 0,1 % by weight of tin:
					- textile articles intended to come into contact with the skin,

Substances w hich appear in Part 3 of Annex VI to Regulation (EC) No 1272/2008 classified as carcinogen category 1A or 1B (Table 3.1) or carcinogen category 1 or 2 (Table 3.2) and listed as follows:

28	carcinogen category 1 or 2 (Table 3.2) and listed as follows:			
	— Carcinogen category 1A (Table 3.1)/carcinogen category 1 (Table 3.2)			
	listed in Appendix 1			
	— Carcinogen category 1B (Table 3.1)/carcinogen category 2 (Table 3.2)     listed in Appendix 2			
	C.I. Basic Red 9 4,4'-(4-iminocyclohexa-2,5-dienylidenemethylene) dianiline hydrochloride	548-62-9	42500	
	C.I. Basic Violet 3; 4-[4,4'-bis(dimethylamino) benzhydrylidene] cyclohexa-2,5-dien-1-ylidene]dimethylammonium chloride	548-62-9	42555	Without prejudice to the other parts of this Annex the following shall apply to entries 28 to 30:
	C.I. Direct black 38 disodium 4-amino-3-[[4-1[(2-4-diaminophenyl)]azo][1,1'- biphenyl[-4-yl]azo]-5-hydroxy-6-(phenylazo)naphtalene-2,7- disulphonate	1937-37-7	30235	Shall not be placed on the market, or used,     — as substances,     — as constituents of other substances, or,     — in mixtures,
	C.I. Direct blue 6 tetrasodium 3,3*[[1,1*biphenyl] 4,4*diylbis (azo) bis[5-amino-4-hydroxynaphthalene-	2602-46-2	22610	for supply to the general public when the individual concentration in the substance or mixture is equal to or greater than:  — either the relevant specific concentration limit specified in Part 3 of Annex VI to Regulation (EC) No 1272/2008, or,
	2,7-disulphonate] Cl Direct Brown 95			— the relevant concentration specified in Directive 1999/45/EC where no specific concentration limit is set out in Part 3 of Annex VI to Regulation (EC) No 1272/2008.
	disodium {5-[(4-((2,6-hydroxy-3-((2-hydroxy-5- sulphophenyl)azo)(1,1-bphenyl)-4-y)azo]salicylato(4- ))cuprate(2-) C1. Drect Fed 28	16071-86-6	30145	
	disodium 3,3'-[[1,1'-biphenyl]-4,4'-diylbis (azo)]bis (4-aminonaphthalene-1-sulphonate)	573-58-0	22120	
	C.I. Disperse blue 1 1,4,5,8-tetraaminoanthraquinone C.I. Disperse Yellow 3	2475-45-8	64500	
	N-[4-[(2-hydroxy-5-methylphenyl)azo]phenyl] acetamide	2832-40-8	11855	
	C.I. Pigment Black 25 C.I. Pigment Red 104	68186-89-0 12656-85-8	77332 77605	
	Lead chromate molybdate sulfate red C.I. Rigment Yellow 34	12656-85-8	//605	
	Lead sulfochromate yellow	1344-37-2	77603	
	C.I. Pigment Yellow 157 C.I. Solvent Yellow 14	68610-24-2	77900	
	1-phenylazo-2-naphthol	842-07-9	12055	
	azocolourants and azodyes			
	4-aminobiphenyl or biphenyl-4-ylamine or xenylamine benzidine	92-67-1 92-87-5		<ol> <li>Azodyes w hich, by reductive cleavage of one or more azo groups, may release one or more of the aromatic amines listed in</li> </ol>
	4-chloro-o-toluidine	95-69-2		Appendix 8, in detectable concentrations, i.e. above 30 mg/kg (0,003
	2-naphthylamine	91-59-8		% by w eight) in the articles or in the dyed parts thereof, according to
	o-aminoazotoluene or 4-amino-2',3-dimethylazobenzene or 4-o-tolylazo-	97-56-3		the testing methods listed in Appendix 10, shall not be used, in textile
	otoluidine 5-nitro-o-toluidine	99-55-8		and leather articles which may come into direct and prolonged contact with the human skin or oral cavity, such as:
	5-nitro-o-tolulaine 4-chloroaniline	99-55-8 106-47-8		— clothing, bedding, towels, hairpieces, wigs, hats, nappies and
	4-methoxy-mphenylenediamine	615-05-4		other sanitary items, sleeping bags,
	4,4'-methylenedianiline or 4,4'-diaminodiphenylmethane	101-77-9		<ul> <li>footw ear, gloves, w ristw atch straps, handbags, purses/w allets,</li> </ul>
	3,3'-dichlorobenzidine or 3,3'-dichlorobiphenyl-4,4'-ylenediamine 3,3'-dimethoxybenzidine or o-dianisidine	91-94-1 119-90-4		brief cases, chair covers, purses w orn round the neck, — textile or leather toys and toys w hich include textile or leather
43	3,3'-dimethylbenzidine or 4,4'-bi-o-toluidine	119-90-4		garments,
	4,4'-methylenedi-otoluidine	838-88-0		<ul> <li>yarn and fabrics intended for use by the final consumer.</li> </ul>
	6-methoxy-m-toluidine or p-cresidine	120-71-8		2. Furthermore, the textile and leather articles referred to in
	4,4'-methylene-bis-(2-chloro-aniline) or 2,2'-dichloro-4,4'-methylenedianiline	101-14-4		paragraph 1 shall not be placed on the market unless they conform to
	4,4'-oxydianiline	101-80-4 139-65-1		the requirements set out in that paragraph.
	o-toluidine or 2-aminotoluene	95-53-4		3. Azodyes, which are contained in Appendix 9, 'List of azodyes'
	4-methyl-mphenylenediamine	95-80-7		shall not be placed on the market, or used, as substances, or in
	2,4,5-trimethylaniline o-anisidine or 2-methoxyaniline	137-17-7 90-04-0		mixtures in concentrations greater than 0,1 % by w eight, where the substance or the mixture is intended for colouring textile and leather
	4-amino azobenzene	60-09-3		articles.
	Blu dye (Navy blue) a mixture of component 1 (C39H23ClCn77O12S.2Na) CAS 118685-33-9 and component 2 (C46H30CrN10O20S2.3Na)			
46	(a) Nonylphenol C6H4(OH)C9H19 CAS 25154-52-3			Shall not be placed on the market, or used, as substances or in mixtures in concentrations equal to or greater than 0,1 % by w eight for the following purposes: (3) textiles and leather processing except:
40	(b) Nonylphenol ethoxylates (C2H4O)nC15H24O			<ul> <li>processing with no release into w aste w ater,</li> <li>systems with special treatment w here the process w ater is pretreated to remove the organic fraction completely prior to biological w aste w ater treatment (degreasing of sheepskin);</li> </ul>
61	Dimethylfumarate (DMF)	624-49-7		Shall not be used in articles or any parts thereof in concentrations greater than 0,1 mg/kg. Articles or any parts thereof containing DMF in concentrations greater than 0,1 mg/kg shall not be placed on the

At European level the Commission Decision 2009/567/EC [6] established the ecological criteria for the award of the Community Ecolabel for textile products. This Decision is based on criteria which aim in particular at promoting the reduction of water pollution related to the key processes throughout the textile manufacturing chain, thus promoting the labelling of textile products which have a lower environmental impact. It is a voluntary scheme that established among others textile fibre criteria, as well as processes and chemicals criteria. On this basis, certain chemicals shall not be used and for some others limits were established. The principal chemical restrictions are reported in Table 2.

Table 2: Substances used in textiles restricted by Commission Decision 2009/567/EC (Ecolabel).

Substance	Restriction
Chlorophenols (their salts and esters) PCB organotin compounds	They shall not be used during transportation or storage of products and semi-manufactured products
Heavy metal salts (except of iron) formaldehyde	They shall not be used for stripping or depigmentation
Compounds of cerium	They shall not be used in the weighting of yarn or fabrics
Alkylphenolethoxylates (APEOs) linear alkylbenzene sulfonates (LAS) bis(hydrogenated tallow alkyl) dimethyl ammonium chloride (DTDMAC) distearyl dimethyl ammonium chloride (DSDMAC) di(hardened tallow) dimethyl ammonium chloride (DHTDMAC) ethylene diamine tetra acetate (EDTA) diethylene triamine penta acetate (DTPA)	They shall not be used and shall not be part of any preparations or formulations used
Impurities in dyes	The levels of ionic impurities in the dyes used shall not exceed the follow ing: Ag 100 ppm; As 50 ppm; Ba 100 ppm; Cd 20 ppm; Co 500 ppm; Cr 100 ppm; Cu 250 ppm; Fe 2 500 ppm; Hg 4 ppm; Mn 1 000 ppm; Ni 200 ppm; Pb 100 ppm; Se 20 ppm; Sb 50 ppm; Sn 250 ppm; Zn 1 500 ppm
Impurities in pigments	The levels of ionic impurities for pigments used shall not exceed the follow ing: As 50 ppm; Ba 100 ppm, Cd 50 ppm; Cr 100 ppm; Hg 25 ppm; Pb 100 ppm; Se 100 ppm Sb 250 ppm; Zn 1 000 ppm
Chrome mordant dyeing	It is not allow ed
Azo dyes that may cleave to any one of the following aromatic amines	They shall not be used
4-aminodiphenyl	
Benzidine	
4-chloro-o-toluidine	
2-naphtylamine	
o-amino-azotoluene	
2-amino-4-nitrotoluene	
p-chloroaniline	
2,4-diaminoanisol	
4,4'-diaminodiphenylmethane	
3,3'-dichlorobenzidine	
3,3'-dimethoxybenzidine	
3,3'-dimethylbenzidine	
3,3'-dimethyl-4,4'-diaminodiphenylmethane	
p-cresidine	
4,4'-oxydianiline	
4,4'-thiodianiline	
o-toluidine	
2,4-diaminotoluene	
2,4,5-trimethylaniline	
4-aminoazobenzene	
o-anisidine	
2,4-Xylidine	

Substance	Restriction
Dyes that are carcinogenic, mutagenic or toxic to reproduction	
C.I. Basic Red 9	
C.I. Disperse Blue 1	
C.I. Acid Red 26	
C.I. Basic Violet 14	
C.I. Disperse Orange 11	They shall not be used
C. I. Direct Black 38	
C. I. Direct Blue 6	
C. I. Direct Red 28	
C. I. Disperse Yellow 3	
Potentially sensitising dyes	
C.I. Disperse Blue 3	
C.I. Disperse Blue 7	
C.I. Disperse Blue 26	
C.I. Disperse Blue 35	
C.I. Disperse Blue 102	
C.I. Disperse Blue 106	
C.I. Disperse Blue 124	
C.I. Disperse Brown 1	
the contract of the contract o	
C.I. Disperse Orange 1	They shall not be used
C.I. Disperse Orange 3	
C.I. Disperse Orange 37	
C.I. Disperse Orange 76	
C.I. Disperse Red 1	
C.I. Disperse Red 11	
C.I. Disperse Red 17	
C.I. Disperse Yellow 1	
C.I. Disperse Yellow 9	
C.I. Disperse Yellow 39	
C.I. Disperse Yellow 49	
Halogenated carriers	They shall not be used
naiogenated carriers	The amount of free and partly hydrolysable formaldehyde
F	the final fabric shall not exceed 20 ppm in products for
Formaldehyde	babies and young children under 3 years old, 30 ppm fo
	products that come into direct contact with the skin, and
	ppm for all other products
flame retardants	Only flame retardants that are chemically bound into the
	polymer fibre or onto the fibre surface (reactive flame
aldrin	
captafol	
ablardana	
chlordane	
DDT	
DDT dieldrin	
DDT dieldrin endrin	
DDT dieldrin endrin heptachlor	
DDT dieldrin endrin heptachlor hexachlorobenzene	
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers)	Cotton and other natural cellulosic seed fibres shall not
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform	
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlorobenzilate	Cotton and other natural cellulosic seed fibres shall not contain more than 0,05 ppm of each of thse substances
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts	
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimef orm chlorobenzilate dinoseb and its salts monocrotophos	
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts	
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimef orm chlorobenzilate dinoseb and its salts monocrotophos	
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol	
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos	
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion	
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion parathion	
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion parathion phosphamidon	
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion parathion phosphamidon y-hexachlorocyclohexane (lindane)	
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimef orm chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion parathion phosphamidon y-hexachlorocyclohexane (lindane) ochexachlorocyclohexane	
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorobenzene (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion parathion phosphamidon γ-hexachlorocyclohexane β-hexachlorocyclohexane	
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion parathion phosphamidon  Y-hexachlorocyclohexane β-hexachlorocyclohexane δ-hexachlorocyclohexane	contain more than 0,05 ppm of each of thse substances
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion parathion phosphamidon  γ-hexachlorocyclohexane β-hexachlorocyclohexane δ-hexachlorocyclohexane aldrin	contain more than 0,05 ppm of each of thse substances  The sum total content of these substances shall not exce
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion parathion phosphamidon y-hexachlorocyclohexane β-hexachlorocyclohexane δ-hexachlorocyclohexane aldrin dieldrin	
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion parathion phosphamidon γ-hexachlorocyclohexane β-hexachlorocyclohexane δ-hexachlorocyclohexane aldrin dieldrin endrin	contain more than 0,05 ppm of each of thse substances  The sum total content of these substances shall not exce
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion parathion phosphamidon y-hexachlorocyclohexane β-hexachlorocyclohexane δ-hexachlorocyclohexane aldrin dieldrin	contain more than 0,05 ppm of each of thse substances  The sum total content of these substances shall not exce
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion parathion phosphamidon γ-hexachlorocyclohexane β-hexachlorocyclohexane δ-hexachlorocyclohexane aldrin dieldrin endrin	contain more than 0,05 ppm of each of thse substances  The sum total content of these substances shall not exce
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion parathion phosphamidon  γ-hexachlorocyclohexane (lindane) α-hexachlorocyclohexane β-hexachlorocyclohexane δ-hexachlorocyclohexane aldrin dieldrin endrin p,p'-DDT p,p'-DDD	contain more than 0,05 ppm of each of thse substances  The sum total content of these substances shall not exce
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DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion parathion phosphamidon  y-hexachlorocyclohexane (lindane) α-hexachlorocyclohexane β-hexachlorocyclohexane δ-hexachlorocyclohexane aldrin dieldrin endrin p,p'-DDT p,p'-DDD diazinon propetamphos chlorfenvinphos dichlofenthion	The sum total content of these substances shall not exce 0,5 ppm in greasy wool and other keratin fibres  The sum total content of the following substances shall results to the following substances
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion parathion phosphamidon γ-hexachlorocyclohexane (lindane) α-hexachlorocyclohexane β-hexachlorocyclohexane δ-hexachlorocyclohexane aldrin dieldrin endrin p,p'-DDT p,p'-DDD diazinon propetamphos chlorfenvinphos dichlofenthion chlorpyriphos	Contain more than 0,05 ppm of each of thse substances  The sum total content of these substances shall not exce 0,5 ppm in greasy w ool and other keratin fibres
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion parathion phosphamidon γ-hexachlorocyclohexane (lindane) α-hexachlorocyclohexane β-hexachlorocyclohexane δ-hexachlorocyclohexane aldrin dieldrin endrin p,p'-DDT p,p'-DDD diazinon propetamphos chlorfenvinphos dichlofenthion chlorpyriphos fenchlorphosq	The sum total content of these substances shall not exce 0,5 ppm in greasy w ool and other keratin fibres
DDT dieldrin endrin heptachlor hexachlorobenzene hexachlorocyclohexane (total isomers) chlordimeform chlorobenzilate dinoseb and its salts monocrotophos pentachlorophenol toxaphene methamidophos methylparathion parathion phosphamidon γ-hexachlorocyclohexane (lindane) α-hexachlorocyclohexane β-hexachlorocyclohexane δ-hexachlorocyclohexane aldrin dieldrin endrin p,p'-DDT p,p'-DDD diazinon propetamphos chlorfenvinphos dichlofenthion chlorpyriphos	The sum total content of these substances shall not exce 0,5 ppm in greasy w ool and other keratin fibres

Substance	Restriction		
cypermethrin			
deltamethrin	The sum total content of the following substances shall not		
fenvalerate	exceed 0.5 ppm in greasy wool and other keratin fibres		
cyhalothrin	exceed 0,5 ppin in greasy wool and other keratiin libres		
flumethrin			
diflubenzuron	The sum total content of the following substances shall not		
triflumuron	exceed 2ppm in greasy wool and other keratin fibres		
dicyclanil	exceed appin in greasy wool and other keratiin hores		
adsorbable organic halogens (AOX)	In man-made cellulose fibres they shall not exceed 250 ppm		
antimony	In polyester fibres it shall not exceed 260 ppm		

It has to be highlighted that no standard methods exist, at CEN or at ISO level, for the determination of the majority of chemicals, which are restricted in textile articles by REACH or Ecolabel.

#### 3.3 Safety of toys

Originally, the safety of toys was assured by Directive 88/378/EEC [7] which harmonised between Member States the safety provisions for these products, thus guaranteeing an equal high level of safety in the whole territory of the European Union.

The new Toy Safety Directive (TSD) 2009/48/EC [8], which substituted the old one, requires that toys sold on the European market fulfill the highest health and safety requirements world-wide, especially those regarding the use of chemical substances. The new Directive introduced new limits for certain substances that may be contained in materials used for toys. For example, substances classified as Carcinogenic, Mutagenic or toxic for Reproduction (CMR) can no longer be used in accessible parts of toys. Limits have been introduced or lowered for certain elements, such as nickel and lead, which may no longer be intentionally used in those parts of toys that are accessible to children. In the case of allergenic fragrances, based on their allergenic potential, they are either completely forbidden or shall be labelled on the toy. The new TSD came into force on 20<sup>th</sup> July 2009, but only on 20<sup>th</sup> July 2013, for the provisions related to chemical content.

The safety criteria which toys must meet are described in the Directive. They cover not only general risks (protection against health hazards or physical injury), but also particular risks (physical and mechanical, flammability, chemical properties, electrical properties, hygiene, radioactivity). In addition, toys must in all cases comply with the relevant Union legislation on chemicals. This include, among others, the EC

regulation 1907/2006 (REACH), so that for example the requirements concerning phthalates, benzene, azo colorants and nickel have to be fulfilled by toys.

In the TSD, the restrictions concerning chemical substances are laid down in Annex II, Part III on chemical properties. Tables 3 and 4 summarise the established restrictions and migration limits.

Table 3: Substances used in toys restricted by Annex II part III of Directive 2009/48/EC.

bstances that are classified as carcinogenic, mutagenic or toxic for reproduction (CMR) of category 1A, 1B or 2 under Regulation (EC) No 1272/2008  nitrosamines  nitrosatable substances		They shall not be used in toys, in components of toys or in micro-structurally distinct parts of toys.  They shall be prohibited for use in toys intended for use by children under 3 months or in other toys intended to be placed in the mouth if the migration of
nitrosamines		They shall be prohibited for use in toys intended for use by children under 3
nitrosatable substances		the substances is equal to or higher than 0,05 mg/kg.
Titi Osatable Substatioes		They shall be prohibited for use in toys intended for use by children under 3 months or in other toys intended to be placed in the mouth if the migration of
		the substances is equal to or higher than 1 mg/kg.
Alanroot oil (Inula helenium)	97676-35-2	
Allylisothiocyanate	57-06-7	
Benzyl cyanide	140-29-4	
4 tert-Butylphenol	98-54-4	
Chenopodium oil	8006-99-3	
Cyclamen alcohol	4756-19-8	
Diethyl maleate	141-05-9	
Dihydrocoumarin	119-84-6 6248-20-0	
2,4-Dihydroxy-3-methylbenzaldehyde 3,7-Dimethyl-2-octen-1-ol (6,7-Dihydrogeraniol)	40607-48-5	
4,6-Dimethyl-8-tert-butylcoumarin	17874-34-9	
Dimethyl citraconate	617-54-9	
7,11-Dimethyl-4.6,10-dodecatrien-3-one	26651-96-7	
6,10-Dimethyl-3.5,9-undecatrien-2-one	141-10-6	
Diphenylamine	122-39-4	
Ethyl acrylate	140-88-5	
Fig leaf, fresh and preparations	68916-52-9	
trans-2-Heptenal	18829-55-5	
trans-2-Hexenal diethyl acetal	67746-30-9	
trans-2-Hexenal dimethyl acetal	18318-83-7	
Hydroabietyl alcohol	13393-93-6	
4-Ethoxy-phenol	622-62-8	
6-Isopropyl-2-decahydronaphthalenol	34131-99-2	
7-Methoxycoumarin	531-59-9	
4-Methoxyphenol	150-76-5 943-88-4	Toys shall not contain the 55 allergenic fragrances listed on the left.
4-(p-Methoxyphenyl)-3-butene-2-one 1-(p-Methoxyphenyl)-1-penten-3-one	104-27-8	How ever, the presence of traces of these fragrances shall be allowed
Methyl trans-2-butenoate	623-43-8	provided that such presence is technically
6-Methylcoumarin	92-48-8	unavoidable under good manufacturing practice and does not exceed 10
7-Methylcoumarin	2445-83-2	mg/kg.
5-Methyl-2,3-hexanedione	13706-86-0	3 3
Costus root oil (Saussurea lappa Clarke)	8023-88-9	
7-Ethoxy-4-methylcoumarin	87-05-8	
Hexahydrocoumarin	700-82-3	
Peru balsam, crude (Exudation of Myroxylon pereirae (Royle) Klotzsch)	8007-00-9	
2-Pentylidene-cyclohexanone	25677-40-1	
3.6,10-Trimethyl-3.5,9-undecatrien-2-one	1117-41-5	
Verbena oil (Lippia citriodora Kunth) Musk ambrette (4-tert-Butyl-3-methoxy-2,6-dinitrotoluene)	12/2/8024 83-66-9	
wusk ambrette (4-tert-butyr-3-metrioxy-2,6-diritirotoluene) 4-Phenyl-3-buten-2-one	122-57-6	
Amyl cinnamal	122-37-0	
Amylcinnamyl alcohol	101-85-9	
Benzyl alcohol	100-51-6	
Benzyl salicylate	118-58-1	
Cinnamyl alcohol	104-54-1	
Cinnamal	104-55-2	
Citral	5392-40-5	
Coumarin	91-64-5	
Eugenol	97-53-0	
Geraniol	106-24-1	
Hydroxy-citronellal	107-75-5	
Hydroxy-methylpentylcyclohexenecarboxaldehyde	31906-04-4	
lsoeugenol Oakmoss extracts	97-54-1 90028-68-5	
Treemoss extracts	90028-67-4	
Anisyl alcohol	105-13-5	
Benzyl benzoate	120-51-4	
Benzyl cinnamate	103-41-3	
Citronellol	106-22-9	The second of the allocation for second listed as the last the first the first terms.
Farnesol	4602-84-0	The names of the allergenic fragrances listed on the left shall be listed on
Hexyl cinnamaldehyde	101-86-0	toy, on an affixed label, on the packaging or in an accompanying leaflet,
	80-54-6	added to a toy, as such, at concentrations exceeding 100 mg/kg in the toy
Lilial		components thereof
Lilial d-Limonene	5989-27-5	
	5989-27-5 78-70-6 111-12-6	

**Table 4:** Elements used in toys restricted by Annex II part III of Directive 2009/48/EC.

	mg/kg	mg/kg	mg/kg
⊟ement	in dry, brittles, powder-like	in liquid or sticky	in scraped-off
	or pliable toy material	toy material	toy material
Aluminium	5625	1406	70000
Antimony	45	11.3	560
Arsenic	3.8	0.9	47
Barium	4500	1125	56000
Boron	1200	300	15000
Cadmium	1.9	0.5	23
Chromium (III)	37.5	9.4	460
Chromium (VI)	0.02	0.005	0.2
Cobalt	10.5	2.6	130
Copper	622.5	156	7700
Lead	13.5	3.4	160
Manganese	1200	300	15000
Mercury	7.5	1.9	94
Nickel	75	18.8	930
Selenium	37.5	9.4	460
Strontium	4500	1125	56000
Tin	15000	3750	180000
Organic tin	0.9	0.2	12
Zinc	3750	938	46000

#### 4. CEN activities

The members of CEN (European Committee for Standardization) are the National Standards Bodies (NSBs) of the 28 European Union countries, the former Yugoslav Republic of Macedonia, and Turkey plus three countries of the European Free Trade Association, EFTA (Iceland, Norway and Switzerland). There is only one member per country. The members of CEN work to develop voluntary European Standards (ENs). These standards are also national standards in each of its 33 member countries. In addition, after the adoption of a new European Standard, every conflicting national standard should be immediately withdrawn.

The development of an EN follows several steps:

- 1. proposal of a New Work Item Proposal (NWIP);
- 2. acceptance of the proposal, done by the relevant CEN Technical Committee (TC), at this point the member countries shall put all national activity within the scope of the project on hold;
- 3. drafting done by experts of the designed Working Group (WG);
- 4. CEN enquiry during which public comments at national level are collected;
- adoption in which the final version of the standard, prepared on the basis of the comments resulting from the CEN enquiry, is submitted to the CEN national members for a weighted formal vote;
- 6. publication, after which a European Standard must be given the status of national standard in all CEN member countries, which also have the obligation to withdraw any national standards that would conflict with it.

In 1991, CEN and ISO (International Organization for Standardization) signed the Vienna Agreement. This contract ensures technical cooperation, mutual representation and coordination, together with the adoption of the same text, as both an ISO Standard and a European Standard, on the issues developed under the umbrella of this agreement.

#### 4.1 CEN/TC 248 on textiles and textile products

# 4.1.1 <u>CEN/TC 248/WG 26 on test methods for analysis of EC restricted</u> substances

WG 26 takes care of the development of test methods for the analysis of substances that can be found in textile products and that are either restricted at EU level by law or limited by voluntary schemes such as for example the European Ecolabel and the world widespread Oeko-Tex Standard 100. This last document is a private voluntary scheme, which consider ecological and consumer protection criteria, and that is published by the International Association for Research and Testing in the field of Textile Ecology (Oeko-Tex) that presently include 68 members. It specifies the conditions to be fulfilled to obtain the authorisation to mark textile products with the Oeko-Tex Standard 100 mark. It is applicable to textile and leather products and articles, including accessories.

#### PrEN ISO 16373 Textile – Dyestuffs

The new standard for the analysis of dyestuffs (16373) was planned in three parts: Part 1 on general principles of testing coloured textiles for dyestuff; Part 2 on general method for the determination of extractable dyestuffs including allergenic and carcinogenic substances; Part 3 on method for determination of carcinogenic extractable dyestuffs (method using triethylamine/methanol). The standard is under development, under Vienna agreement, by both CEN and ISO, in particular Parts 1 and 2 are under the responsibility of CEN, whereas Part 3 is under ISO lead. The standard is important as many countries worldwide have introduced regulations regarding carcinogenic dyestuffs in textile articles.

Part 1 was approved as Preliminary Work Item (PWI). A draft text was prepared, that includes the definition of the dyestuff classes and the description of some procedures to identify qualitatively the dyestuff class used in textile material. The classes of dyes taken into consideration are acid, azoic, basic (also called cationic), chrome, direct, disperse, metal-complex, reactive, sulphur, VAT and azo dyes. The test methods proposed for the identification of the dyestuff class are for example based on their solubility, oxidation, dyeing and bleeding properties. Annex A of the draft standard reports the use of dyestuffs in various textile materials.

Table 5: List of carcinogenic dyes quantifiable with prEN ISO 16373-2.

Carcinogenic dyestuff	Color Index	CAS	REACH	Ecolabel	OekoTex 100
Disperse Blue 1	64500	2475-45-8	Х	Х	Х
Solvent Yellow 1	11000	60-09-4			
Solvent Yellow 2	11020	60-11-7			
Solvent Yellow 3	11160	97-56-3			
Basic Red 9	42500	548-62-9	Х	Х	X
Basic Violet 14	42500	632.99.5		Х	X
Disperse Yellow 3	11855	2832-40-8	Х	Х	X
Acid Red 26	16150	3761-53-3		Х	X
Direct Black 38	30235	1937-37-7	Х	Х	X
Direct Blue 6	22610	2602-46-2	Х	Х	X
Direct Red 28	22120	573-58-0	Х	Х	X
Disperse Orange 11	60700	82-28-0		Х	X
Acid Red 114	23635	6459-9-5			

**Table 6**: List of allergenic dyes quantifiable with prEN ISO 16373-2.

Allergenic dyestuff	Color Index	CAS	REACH	Ecolabel	OekoTex 100
Disperse Blue 1	64500	2475-45-8		Х	Х
Disperse Blue 3	61505	2475-46-9		Х	X
Disperse Blue 7	62500	3179-90-6		Х	X
Disperse Blue 26	63305	3860-63-7		Х	X
Disperse Blue 35		56524-77-7		Х	X
Disperse Blue 35		56524-76-6		Х	X
Disperse Blue 102	11945	12222-97-8		Х	X
Disperse Blue 106	111935	12223-01-7		Х	X
Disperse Blue 124	111938	61951-51-7		Х	X
Disperse Brow n 1	11152	23355-64-8		Х	X
Disperse Orange 1	11080	2581-69-3		Х	X
Disperse Orange 3	11005	730-40-5		Х	X
Disperse Orange 37/76/59	11132	13301-61-6		Х	X
Disperse Red 1	11110	2872-52-8		Х	X
Disperse Red 11	62015	2872-48-2		Х	X
Disperse Red 17	11210	3179-89-3		Х	X
Disperse Yellow 1	10345	119-15-3		Х	Х
Disperse Yellow 3	11855	2832-40-8			Х
Disperse Yellow 9	10375	6373-73-5		Х	X
Disperse Yellow 39	480095	12236-29-2		Х	X
Disperse Yellow 49		54824-37-2		Х	X

Table 7: List of other dyes quantifiable with prEN ISO 16373-2.

	Other dyestuff	Color Index	CAS	REACH	Ecolabel	OekoTex 100
Ī	Disperse Yellow 23	26070	6250-22-3			Х
	Disperse Orange 149		85136-74-9			X
	Navy Blue 018112		118685-33-9			
	Disperse Orange 61	111355	55281-26-0			

Part 2 undergone a parallel enquiry at CEN and ISO level and the WG subsequently addressed all the comments received. If members accept the revised version proposed by the WG, the formal vote on the draft standard will be launched soon. The draft standard describes how to detect extractable dyestuffs in textile products. The JRC experience on the analysis of allergenic dyes in textile products provided a valuable

contribution. Literature experimental results proved that a solution pyridine-water (1:1) is the most efficient in the extraction of a large variety of dyes, including allergenic and carcinogenic ones. For this reason, the principle of the test method is based on the extraction of dyes using this solution at 100 °C followed by an analysis made by liquid chromatography/diode array detection (LC/DAD) and/or by liquid chromatography/mass spectrometry (LC/MS). The lists of carcinogenic, allergenic and other dyestuffs that can be quantified using this method are reported in Tables 5, 6, and 7, respectively.

The method is applicable to quantify all the dyes restricted by Ecolabel and OekoTex 100, some dyes restricted by Annex XVII of REACH plus some others.

Part 3 is described later on in the section linked to ISO activities.

#### PrEN 15777:2009/prA1 Textiles - Test methods for phthalates

The objective of the revision of EN 15777:2009 (textiles - test methods for phthalates) is the inclusion of diisobutyl phthalate (DiBP), CAS 84-69-5. DiBP is listed in REACH regulation in Appendix 6, which includes substances which are classified as toxic to reproduction either category 1B or category 2 (entry 30 of Annex XVII). Diisobutyl phthalate is also mentioned in Annex XIV of the same regulation as a substance subject to authorisation. As from 21<sup>st</sup> August 2014, in the absence of an authorisation the use and placing on the market of DiBP will be forbidden.

The draft should be submitted by the end of 2013, so that the public enquiry can be launched by February 2014.

## Technical report on guidance on health and environmental issues related to the chemical content of textile products intended to clothing, interior textiles and upholstery

WG 26 prepared a comprehensive draft document on the general requirements for textile products with direct skin contact and that can be close to the human body, such as interior textiles and upholstery. The JRC contributed drafting some chapters of the document. Member of CEN will decide by the end of January 2014 if they agree on the activation of a Preliminary Work Item (PWI) to produce a technical report on this topic.

The document includes environmental and health recommendations for textile products (including accessories) with direct skin contact and in the surroundings of the human body. The document was planned to help stakeholders to comply with the European chemical regulations and recommendations in force in the EU. The report addresses the properties of both the intended used chemicals and the unintended released substances. For each substance the document explains the use, the reason why it is considered critical to the environment or to human health, if national or European legislations are in place and the standardised test methods if existing. The list of chemicals considered in the report includes: carcinogenic, mutagenic or reprotoxic chemicals (CMR), persistent, bio accumulating and toxic substances (PBT) and very persistent and very bio accumulating substances (vPvB), formaldehyde, chlorophenols (pentachlorophenol, isomers of tetrachlorophenol), orthophenylphenol (OPP), heavy metals, flame retardants, carcinogenic dyes, suspected dyes and derived substances, irritating and sensitizing colorants, irritating and sensitizing substances (others than colorants), pesticides, herbicides and antifungi, chloroorganics including carriers (chlorinated benzenes, chlorinated toluenes and chlorinated naphtalenes), phthalates, organotins, perfluorooctanesulfonates (PFOS) and perfluorooctanoic acid (PFOA), dimethylfumarate (DMFu), alkyl phenol ethoxylate (APEO) and residual solvents.

#### prEN ISO 18254 Detection and determination of APEO in textiles by HPLC-MS

APEO is an acronym that stands for alkylphenol ethoxylates. APEO are products commonly used in industrial and consumer detergents and cleaners, some plastics and many industrial applications. In the textile industry, they are used in detergents and as scouring, coating or waterproofing agents, in printing pastes and adhesives, and in dyeing. The most important APEOs for the textile industry are NPEO (nonylphenol ethoxylates) and OPEO (octylphenol ethoxylates), due to their detergent properties. Their use may result in their presence in wastewater streams, rivers and lakes. Nonylphenol ethoxylate is a non-ionic surfactant. When biodegraded it releases branched nonylphenols which are difficult to biodegrade. Even though APEOs are not classified as carcinogenic, teratogenic or mutagenic, their degradation byproducts show toxicity, estrogenic activity, persistence and tendence to bioaccumulate higher than APEOs themselves. Nonylphenol and nonylphenol ethoxylates are restricted by Annex XVII of REACH (entry 46). They shall not be placed on the market, or used,

as substances or in mixtures in concentrations equal to or greater than 0,1 % by weight for several purposes, among which textiles and leather processing with the exception of processing with no release into waste water, or systems with special treatment where the process water is pre-treated to remove the organic fraction completely prior to biological waste water treatment (degreasing of sheepskin). The restrictions for nonylphenol and nonylphenol ethoxylate were originally put in place by the EU Directive 2003/53/EC [9], which was then included in REACH. The use of alkylphenol ethoxylates is also forbidden by Ecolabel. In addition, OekoTex 100 established limits for the sum of octylphenol and nonylphenols and the sum of octylphenol, nonylphenols, octylphenol ethoxylate (n = 1-2) and nonylphenol ethoxylate (n = 1-9).

The development of a new EN ISO standard method, under the responsibility of CEN, for the detection of extractable alkylphenolethoxylates (nonylphenolethoxylates and octylphenolethoxylates) in textile products was approved. The degree of ethoxylation of the substances covered by the method can be anything higher than 1. A preliminary draft was prepared by WG 26 and it is expected to be circulated for public enquiry by February 2014. The test method is based on the ultrasonic extraction of the textile sample in methanol followed by liquid chromatography/mass spectrometry (LC/MS) analysis using gradient elution, Electro Spray Ionisation (ESI) and a single quadrupole. Experimental results proved that better extraction performances can be obtained using 70 instead of 40 °C as extraction temperature. Critical points of the test methods are the purity of reference standards and the quantification. In fact, nowadays it is not possible to obtain individual standards for quantifying accurately each congener, as APEO are available only as technical mixtures. APEOs are commonly identified by their average number of ethoxy moieties. Various standards with different numbers of ethoxy moieties (normally from 1 to 20) in various ratios can be found on the market. The consequence is that test results are hugely dependent on the technical mixture used for the calibration curve. It seems that the better the match between the APEOs ratio in the samples and in the standards the better the quantitative results are. The proposed quantification is based on the calculation of weight fraction (R) of each congener APEO, which is equal to the ratio between the area response in each isomer by LC/MS (Liquid Chromatography)/Mass Spectrometry) and the total sum of APEOs area response. The drawback of this

approach, however, is that it could provide an overestimation of low m/z fraction and an underestimation of high m/z fraction because mole fractions are calculated from MS counts. Normally in MS higher counts are obtained for low ethoxylates and lower counts for high ethoxylates as the molar responses are not constant with ethoxylate numbers with this technique.

The draft should be submitted by the end of 2013 so that the public enquiry can be launched by February 2014.

#### **Determination of metal content**

Part 1: Determination of metals using microwave digestion (WI 00248537)

# Part 2: Determination of metals extracted by acidic artificial perspiration solution (WI 00248536)

On the one hand, the level of ionic impurities that can be found in dyes and pigments used in textile products are restricted by Ecolabel, in which limits for several elements were established (e.g Ag, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sb, Sn, Zn). On the other hand, OekoTex 100 established limits for extractable heavy metals on the final textile products and for heavy metals on digested textile samples. As no standard methods are available to perform such kind of analyses, WG 26 started working on the development of these test methods.

Part 1 of the standard describes a procedure for determination of the total content after microwave digestion of the following metals, antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), mercury (Hg) and nickel (Ni), both in natural and in man-made textiles and in garment components, such as for example buttons and zips. Different test specimen sampling and digestion procedures are foreseen for natural and man-made textiles, garment components with painted and other similar surface coatings, metallic products, non-metal products, ceramics, glass and crystal and other siliceous materials, plastics, polymers and other non-siliceous materials. Digestion solutions include mixtures of nitric acid and hydrogen peroxide, or nitric and hydrochloric acids, or concentrated nitric and hydrofluoric acids, or concentrated nitric acid. The analysis of the metals is then performed with appropriate analytical techniques of Atomic Absorption, Inductively Coupled Plasma and Mass Spectrometry (e.g. ICP-MS, ICP-OES (Optical Emission Spectrometry), AAS (Atomic Absorption Spectroscopy), CVAAS (Cold Vapor Atomic Absorption

Spectrometry), etc.). Calibration is performed either with calibration solutions in the appropriate matrix or via standard addition.

Part 2 specifies a procedure for the determination of Sb, As, Cd, Cr, Co, Cu, Pb, Hg and Ni in natural and man-made textile fibres after extraction with acidic artificial perspiration solution. This method provides the quantification of the chemical release of metals mimicking the real condition of use of textile products (extraction carried out in acidic conditions for 1 hour at 37 °C). In fact, for the determination of soluble metals the textile specimen is cut into small pieces and is extracted with acidic artificial perspiration solution. After filtration, the analysis is performed with appropriate analytical techniques of atomic absorption and mass spectrometry (e.g. ICP-MS, ICP-OES, AAS, CVAAS, etc.). The perspiration solution to be used is the same described in EN ISO 105-E04 [10]. It has a pH of 5.5 and includes L-histidine-monohydrochloride-1-hydrate, sodium chloride and sodium dihydrogenphosphate-2-hydrate.

Both parts were originally based on DIN standard methods, in particular DIN 54233-1 and -3. The drafts of both parts should be submitted by the end of 2013, so that the public enquiry can be launched by February 2014.

#### 4.1.2 CEN/TC 248/WG 30 on quantitative analysis of fibre mixtures

The WG was established at the moment when the European Commission decided to prepare a textile regulation to replace the European Directives related to textile names, labelling and composition. This was created in consideration of the possibility of transferring the quantification methods for textiles, described in the legislation, to the standardisation field. The new EU textile Regulation 1007/2011 was published in October 2011, it is applicable since 8<sup>th</sup> May 2012. According to Article 19 of the Regulation, market surveillance checks to determine the conformity of fibre composition of textile products have to be carried out in accordance with the methods set out in Annex VIII or with the harmonised standards to be introduced in that annex.

As until 2009 no standard methods were available at CEN level for the quantification of textiles, WG 30 decided to adopt the ISO standards of the series 1833 on the quantitative chemical analysis of textiles. The decision was taken to use the quickest procedure existing at CEN level, which is the Unique Acceptance Procedure (UAP).

This procedure foresees a formal vote during which CEN members cannot propose technical modifications to the text of the standard, but can only approve, disapprove or abstain.

The WG did not meet in 2013 and the last meeting was held in Helsinki on 13<sup>th</sup> September 2010.

Following the UAP procedure, the Parts 1-21 of EN ISO 1833 [11-31] on quantitative chemical analysis of textiles were published in 2010, Part 24 in 2011 [32] and Parts 22, 25 and 26 [33-35] in 2013. These test methods are exactly the same published by ISO and the JRC contribution to them is described later on in section 5.1.1. Even though some ISO standards are similar to the test methods in Annex VIII of the regulation 1007/2011, some differences exist both in terms of experimental conditions and coefficients to be used in the calculation of composition. In addition, the ISO standards are more numerous than the test methods in the textile regulation. An important difference among the EN ISO standards and the test methods described in the textile regulation is the fact that the first were not validated, whereas the second were all fully validated.

Table 8: Correlation table for test methods in Annex VIII of EU Reg. 1007/2011 and EN ISO 1833.

Reg. 1007/2011	EN ISO 1833	Reagent/type of method	
Method	Part		
1	3	acetone	
2	4	sodium hypochlorite	
3	6	formic acid/zinc chloride	
4	7	80 % m/m formic acid	
5	9	benzyl alcohol	
6	10	dichloromethane	
7	11	75 % m/m sulphuric acid	
8	12	dimethylformamide	
9	13	55.5 /44.5 v/v CS2 and acetone	
10	14	glacial acetic acid	
11	18	75 % m/m sulphuric acid	
12	15	by determing nitrogen content	
13	16	xylene	
14	17	concentrated sulphuric acid	
15	21	cyclohexanone	
16	26	hot formic acid	
-	1	general principles	
	2	ternary fibre mixtures	
	5	sodium zincate (stock solution)	
	8	acetone 70% v/v	
	19	method by heating	
	20	dimethylacetamide	
	22	formic acid and zinc chloride	
	24	phenol and tetrachloroethane	
	25	trichloroacetic acid and chloroform	

On 21<sup>st</sup> June 2013, at the meeting of the Commission Expert Group on Textile Names and Labelling in Brussels, the Commission services proposed to give a mandate to CEN to bring the two systems close to each other. The purpose would be to examine the differences and, where appropriate, plan standardisation work including the validation of the methods other than those included in Annex VIII.

#### 4.2 CEN/TC 52 on safety of toys

#### 4.2.1 <u>CEN/TC 52/WG 5 on chemical properties</u>

The work of WG 5 and its Task Groups (TG) was carried out under the umbrella of the standardisation mandate n. 445, signed in 2009, within the framework of Directive 2009/48/EC revising Directive 88/378/EEC concerning the safety of toys. The objective of the mandate was to revise existing European standards or draw up new European standards in order that they could meet the essential requirements of Directive 2009/48/EC, the so-called new Toy Safety Directive (TSD). The TSD established that toys shall not endanger the safety or health of users or third parties when they are used as intended or in a foreseeable way, bearing in mind the behaviour of children (art. 10). In particular, they have to comply with the essential safety requirements set out in Annex II of the Directive, which is divided in six parts: physical and mechanical properties, flammability, chemical properties, electrical properties, hygiene and radioactivity, respectively. As foreseen in article 13, when toys are in conformity with harmonised standards, the references of which have been published in the Official Journal of the European Union, they shall be presumed to be in conformity with the requirements covered by those standards, set out in Article 10 and in Annex II.

This document focusses on the work carried out by WG 5/TG 2 (migration of certain elements) and WG 5/TG 3 (N-Nitrosamines and N-nitrosatable substances) to which the JRC has contributed.

#### EN 71-3:2013 Safety of toys - Part 3: Migration of certain elements

The development of the test method to quantify the migration of certain elements from toys was carried out by WG 5/TG 2. The elements restricted and the limits applicable to the three categories of toy materials: 1) dry, brittles, powder-like or

pliable; 2) liquid or sticky; 3) scraped-off, are reported in Table 4. The standard method was published in 2013.

The principle of the method is based on the extraction of the soluble elements in conditions that simulate the permanence of the material in contact with gastric juices for a period of time after swallowing. Three different quantification methods are described: one for organotin compounds, one for the speciation of chromium (III) and (VI) and one for all the other elements. Sample preparation varies depending on the category and type of toy materials. The extraction is carried out in hydrochloric aqueous solution of pH between 1.0 and 1.5 for one hour at 37 °C under constant shaking conditions and for another hour at the same temperature without shaking. The solution is then filtrated to remove solid material. The final extract is analysed by ICP-MS, ICP-OES, CVAAS, GC-MS (Gas Chromatography) or other suitable techniques.

In the case of the analysis of chromium, to prevent interconversion of chromium (III) and (VI), the migration solution is neutralised immediately after the migration step up to pH 7.1. A mobile phase containing EDTA (potassium ethylenediamine tetraacetic acid) is added, so that EDTA reacts to form a complex with chromium (III) and the solution is kept at 50 °C for one hour. LC-ICP-MS technique is then used to separate and quantify chromium (III) and (VI). It has to be noted that the method is able to determine compliance with the migration limit for category III toy materials (scraped-off), but not for categories I (dry, brittles, powder-like or pliable) and II (liquid or sticky) toy materials. In fact, for those two categories the limit of quantification of the method is higher than the migration limits.

The method for organotin compounds foresees a derivatisation step which transforms the non per-alkylated organotin compounds in per-alkylated organotin substances that can be analysed via GC-MS. The derivation agent used is tetraethylborate in order to produce ethyl organic tin derivatives. The migration of organic tin shall be calculated by adding the migration values for all the single organic tin compounds that have been detected. The migration of organic tin is expressed as tributyltin.

A validation study, organised according to ISO 5725-2 [36], was carried out for this standard method. The JRC has been involved particularly in the planning of the

collaborative trial and in the critical evaluation of its results. Twentysix samples (reference materials) were sent to the participants which were 12, 19 and 24 for chromium (III) and (VI), organic tin compounds and the standard elements, respectively. Despite the fact that several test batches had been produced by the lead laboratory trying to obtain reference materials with migration values near the limit ones, in many cases this was not achieved. Among the 48 combinations element/toy category studied in the round robin test, the JRC considered relevant only 27 of them, because the migration of the elements in these combinations was in the range 0.1 to 10 times the migration limit specified in the toy safety directive. In fact, the objective of the validation was to evaluate the precision of the test method close to the migration limits set by the TSD. The 27 combinations element/toy category considered adequate were Al, Sb, As, B, Co, Cu, Sr in category I toy material, Al, Sb, As, Ba, B, Co, Cu, Mn, Ni, Se, Sr in category II toy material and As, B, Cd, Cr (III), Co, Cu, Pb, Sr and organotin compounds in category II toy material.

The Horrat parameter was used as acceptance criterion. The Horwitz ratio, called HORRAT parameter, is a normalised performance parameter that indicates the acceptability of a method of analysis with regards to the reproducibility, which is the among-laboratory precision [37]. The HORRAT value is equal to the ratio of the observed coefficient of variation among laboratories, calculated from the data of the collaborative trial, to the corresponding predicted coefficient of variation calculated with the Horwitz equation. The empirical interpretation of the HORRAT parameter considers that the precision of a method, in terms of reproducibility, is acceptable if this parameter is in the range 0.5 - 2. Results showed that the method was satisfactory in the case of Co, Cu and Sr in category II. Ten results were judged questionable: 3 for category I (As, Co, Sr); 3 for category II (B, Mn, Se) and 4 for category III (B, Cr(III), Sr, organotin compounds). The remaining fourteen results were evaluated unsatisfactory: 4 for dry, brittle, powder like or pliable materials (Al, Sb, B, Cu); 5 for liquid or sticky materials (Al, Sb, As, Ba, Ni); 5 for scraped-off materials (As, Cd, Co, Cu, Pb). Applying an acceptance criterion less severe than the Horwitz one, which considers acceptable test results showing a relative standard deviation of the reproducibility lower than 30 %, the results obtained in the quantification of B and Sr in all the three categories, Pb in category II and Cu in categories I and II can be accepted as satisfying.

In order to understand the reason of the unsatisfactory results, the lead laboratory in collaboration with the JRC drafted a questionnaire. The analysis of the results of the validation study, of the questionnaire filled-in by participants and of further experimentation indicated that a large variation among test results obtained in different laboratories was most probably due to a too big range of pH (1.0-1.5) accepted in the standard method for the extraction solution. For this reason an amendment of the standard method is under development now. The range of pH would be restricted to 1.1-1.3 and a UAP procedure will be launched as soon as possible to adopt the amendment.

At the same time, a novel standard method able to quantify Cr (III) and Cr (VI) in categories I and II needs to be prepared to allow the enforceability of the restrictions established in the TSD.

# EN 71-12:2013 Safety of toys - Part 12: N-nitrosamines and N-nitrosatable substances

The development of the test method to quantify the migration of N-nitrosamines and N-nitrosatable substances from toys was carried out by WG 5/TG 3. The standard method was published in 2013. The JRC has been involved particularly in the planning of the collaborative trial and in the critical evaluation of its results.

The test method can quantify N-nitrosamines and N-nitrosatable substances in toys made from elastomers and intended for use by children under 36 months; toys made from elastomers and intended to be placed in the mouth; and finger paints for children under 36 months. Teethers and ballons can be analysed using this standard methods. The limits of the TSD are reported in Table 3. In the case of finger paints at least Nnitrosodiethanolamine should be quantified. In the case of elastomers at least the following thirteen N-nistrosamines should be analysed: N-nitrosodiethanolamine, N-N-nitrosodiethylamine, nitrosodimethylamine, N-nitrosodipropylamine, N-N-nitrosodibutylamine, nitrosodiisopropylamine, N-nitrosodiisobutylamine, Nnitrosodiisononylamine, N-nitrosomorpholine, N-nitrosopiperidine, Nnitrosodibenzylamine, N-nitroso-N-methyl-N-phenylamine, N-nitroso-N-ethyl-Nphenylamine.

The principle of the method is based on the migration of N-nitrosamines and N-nitrosatable substances into a test solution at 37 °C. The test solution is water, in the case of N-nitrosamines in finger paints, and saliva simulant solution, in the case of N-nitrosatable substances in finger paints and N-nitrosamines and N-nitrosatable substances in elastomers. After migration, N-nitrosatable substances are converted to N-nitrosamines by acidification before quantification. The quantification can be carried out with LC-MS/MS. The saliva solution is an aqueous solution at pH 9.0 containing sodium hydrogen carbonate, sodium chloride, potassium carbonate, sodium nitrite.

Round robin tests for the determination of N-nitrosamines and N-nitrosatable substances in elastomeric toys and for the determination of N-nitrosamines in finger paints were conducted according to the principles of ISO 5725-2.

In the case of elastomeric toys, two balloons and one rubber sheet were tested by 14 laboratories. The statistical evaluation was performed following the rules laid down in ISO 5725-2 and the Horrat parameter was used as acceptance criterion. Results showed that the method is satisfactory for the determination of N-nitrosamines and N-nitrosodimethylamine from elastomeric toys, whereas it is either questionable of unsatisfactory for the determination of N-nitrosatable substances.

In the case of finger paint, one sample was measured by 11 laboratories and the method was considered satisfactory on the basis of the results of the quantification of N-nitrosodiethanolamine (NDELA).

## 5. ISO activities

ISO is the International Organization for Standardization. It is a network of national standards bodies where there is only one member per country. There are three member categories: full members (P-members) that can participate and vote in ISO technical and policy meetings; observer members (O-members) that can attend ISO technical and policy meetings as observers; and subscriber members that can be kept up to date on ISO's work but cannot participate in it.

ISO only develops standards for which there is a clear market requirement. International Standards are the result of the agreement between the member bodies of ISO. An ISO International Standard represents a global consensus on the state of the art in the subject of that standard. They are developed by ISO technical committees (TC) and subcommittees (SC) in a six-step process:

- 1. proposal stage during which a new work item proposal (NWIP, NP) is submitted for vote by the members of the relevant TC or SC to determine the inclusion of the work item in the programme of work;
- 2. preparatory stage in which a Working Group (WG) of experts prepares a working draft;
- 3. committee stage during which the Committee Draft (CD) is distributed for comment and voting by the P-members of the TC/SC;
- enquiry stage in which the Draft International Standard (DIS) is circulated to all ISO member bodies for voting and comment within a period of five months;
- 5. approval stage during which the Final Draft International Standard (FDIS) is circulated to all ISO member bodies for a final yes/no vote within a period of two months;
- 6. publication stage in which only minor editorial changes, if and where necessary, are introduced into the final text and the final text is then published.

#### 5.1 ISO/TC 38 on textiles

Currently, the ISO technical committee 38 on textiles include 30 P-members (Australia, Austria Belgium, Botswana, Brazil, Czech Republic, China, Egypt, Finland, France, Germany, India, Islamic Republic of Iran, Italy, Japan, Kenya,

Republic of Korea, Netherlands, Norway, Pakistan, Poland, Portugal, South Africa, Spain, Sri Lanka, Sweden, Switzerland, Turkey, USA, United Kingdom) and 44 Omembers (Argentina, Bangladesh, Bosnia and Herzegovina, Bulgaria, Cameroon, Colombia, Croatia, Cuba, Cyprus, Côte-d'Ivoire, Denmark, Ecuador, Ethiopia, Greece, Hong Kong, Hungary, Iceland, Indonesia, Iraq, Jamaica, Dem. P. Rep. of Korea, Libya, Lithuania, Malaysia, Mali, Mauritius, Mexico, Rep. of Moldova, Mongolia, Morocco, New Zealand, Philippines, Romania, Russian Federation, Saudi Arabia, Serbia, Slovakia, Slovenia, Syrian Arab Republic, United Rep. of Tanzania, Thailand, Tunisia, Ukraine, Vietnam).

Seven organisations have the status of A-liaisons to TC 38, among which the JRC (BISF: Bureau International pour la Standardisation des Fibres Artificielles, EDANA: European Disposables and Nonwovens Association, EURATEX: European Apparel and Textile Organisation, IWTO: International Wool Textile Organisation, JRC: Joint Research Centre of the European Commission, TWC: The Woolmark Company, CINET: International Committee of Textile Care).

#### 5.1.1 ISO/TC 38/WG 22 on composition and chemical testing

#### ISO 1833 Textiles - Quantitative chemical analysis

In 2013, under the responsibility of WG 22, the following three standard methods related to the quantification of binary fibre mixtures were published:

- ISO 1833-22:2013 Textiles Quantitative chemical analysis Part 22: Mixtures of viscose or certain types of cupro or modal or lyocell and flax fibres (method using formic acid and zinc chloride)
- ISO 1833-25:2013 Textiles Quantitative chemical analysis Part 25: Mixtures of polyester and certain other fibres (method using trichloroacetic acid and chloroform)
- ISO 1833-26:2013 Textiles Quantitative chemical analysis Part 26: Mixtures of melamine and cotton or aramide fibres (method using hot formic acid)

ISO 1833-26 is a standard method entirely based on the method that the JRC had fully validated in the frame of the work done on the novel fibre melamine and that had already been published as method 16 in the EU Regulation 1007/2011 and in the EUR

report 23482 EN [38]. In addition, the JRC took part in the restricted collaborative trials that were organised on Parts 22 and 25 to check their applicability and to determine some correction factors d (mass loss of the insoluble component due to the application of the method).

#### ISO 2076:2013 Textiles - Man-made fibres - Generic names

In 2013, also ISO 2076:2013 (Textiles - Man-made fibres - Generic names) was published.

All the novel fibres that had been evaluated by the JRC and included in the EU Regulation 1007/2011 (polylactide [39], elastomultiester [40], elastolefin [41], melamine and polypropylene/polyamide bicomponent [42]) were added in the revised standard. However, the definition of polylactide in ISO 2076:2013 is different from the definition which is accepted in Europe.

In the EU, polylactide was established on the basis of a petition presented by Cargill Dow, which is a joint venture of Cargill and Dow Chemical. The polylactide which was accepted in Europe is a synthetic fibre, but it is derived from natural renewable resources (agricultural crops such as corn, sugar beet etc.). To make sure that polylacide is produced from natural renewable resources and not from oil, the definition in EU Regulation 1007/2011, which was developed by the JRC, includes a reference to the melting point of the fibre: "fibre formed of linear macromolecules having in the chain at least 85 % (by mass) of lactic acid ester units derived from naturally occurring sugars, and which has a melting temperature of at least 135 °C". Due to strong pressures of some WG members and despite very long discussions, the definition that was selected for the ISO standard does not contain neither the reference to the natural renewable resources (present in the EU and US definitions) nor to the fibre melting point (present in the EU definition). This means that fibres made by a polylactide polymer entirely derived from oil can be named polylactide in ISO documents and test method, according to ISO rules. Even though the legally binding definitions of fibres are published by the Federal Trade Commission (FTC) in the US and in the Textile Regulation in EU, this could finally result in some confusion at customs and maybe in the presence on the EU and on the US market of products that are not allowed by our respective legislation.

# WD 18074 Textiles - Identification of some animal fibres by DNA analysis method - Cashmere, wool, yak and their blends

Analysis of composition for textile products is very important, as several legislations in the world require composition labelling of textiles. In particular, the correct labelling of cashmere is of high relevance due to its high price and to the need of avoid frauds on the market. Cashmere shows physical and chemical properties very similar to the ones observed in other animal wool fibres, such as sheep's wool, yak, camel etc., this makes difficult to achieve their identification based on both mechanical and chemical methods. Currently, there is only one method to determine the animal fibre composition, which is ISO 17751:2007 (Textiles - Quantitative analysis of animal fibres by microscopy - Cashmere, wool, speciality fibres and their blends). The method is based on microscopy and it needs very experienced technician to be applied successfully. Difficulties have been experienced with this method in the identification of fibres, mainly due to the fact that textile products have broad varieties of colours and finishings, and include many blends in animal fibres. The new draft standard tries to overcome these difficulties using DNA (deoxyribonucleic acid) analysis.

The method is qualitative and its scope is the identification of cashmere, wool, yak and their blends using extraction, amplification by polymerase chain reaction (PCR) method and detection process of DNA. The DNA is specific for each animal and the mitochondrial one is used for this analysis. The method has been proved to work well when the textile products to be analysed were processed with low dye concentration levels or dyed in light colours. On the contrary, in case textiles were processed in severe conditions or high temperature, the identification may be difficult due to possible damages occurred to the mitochondrial DNA and the consequent failure of DNA amplification.

A chemical and enzyme reaction is used to extract mitochondrial DNA from animal fibre samples. The extracted DNA is then purified with a precipitation method and amplified with PCR method. In the PCR method, primers for cashmere, yak and wool have to be tested in parallel. If the sample is cashmere, only cashmere primer can amplify the constant length of DNA fragments. Then, the constant length of DNA fragments is detected by the electrophoretic migration method. The sample fibres are

identified by knowing whether the amplification was observed or not for the tests using all primers. The limit o detection has been established as 0.5 % m/m.

The project has reached the stage of the DIS vote.

## ISO/CD 17751 Textiles - Quantitative analysis of cashmere, wool, other specialty animal fibers and their blends

#### Part 1: Light Microscopy method

#### Part 2: Scanning Electron Microscopy method

The revision of the current standard ISO 17751:2007 (Textiles - Quantitative analysis of animal fibres by microscopy - Cashmere, wool, speciality fibres and their blends) was agreed to improve several part of the standard. In particular, the following items needed to be either increased or added: the amount of cashmere micrographs showing appearances and characteristics of cashmere types produced in main cashmere producing countries around the world; descriptions to micrographs, such as cashmere diameter, scale frequency, scale height, scale appearance etc.; information about those fibers which are frequently and easy to be blended into cashmere for adulteration, such as native Chinese sheep wool, decolored yak etc. In addition, the sampling and fiber diameter measurement methods needed to be modified and the precision of Light Microscope method needed to be added.

As this standard is widely applied in the world, its improvement will be beneficial to both textile testing laboratories, woolgrowers, cashmere traders, cashmere manufacturers, dealers and cashmere products consumers all across the world.

It was decided to split the standard method in two parts, the first one dealing with Light Microscope method and the second one with Scanning Electron Microscopy (SEM) method. The two parts were approved for registration as DIS as no comments were obtained in the CD vote.

# ISO FDIS 14389: Textiles- Determination of the content of phthalates - tetrahydrofuran

WG 22 worked on the development of a test method for the quantification of a number of phthalates in textile articles, in collaboration with CEN/TC 248/WG 26. ISO has the responsibility of this standard. Phthalates are commonly used as

plasticizers in polymers and in the field of textile products that can be found within motifs, coated fabrics, plastisol prints, buttons, etc.

In support of ISO/TC 38/WG 22 and CEN/TC 248/WG 26, the JRC organised a collaborative trial for method validation, with the aim of evaluating the precision (repeatability and reproducibility) of four methods, which were used in various countries to determine phthalates in textiles, in order to compare them and select the best one for standardisation purposes [43]. Thirteen laboratories, 8 European and 5 from outside EU, took part in the exercise. The JRC carried out the homogeneity study of the 6 samples that were used in the validation; all of them were proved to be sufficiently homogeneous. The following phthalates were tested: bis (2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), di-n-octyl phthalate (DNOP) and diisobutyl phthalate (DIBP). Three levels of phthalates were tested (200, 1000 and 5000 mg/kg of PVC), which were in the range of the current limits applicable to toys and childcare articles. On the basis of statistical evaluation of results, done by the JRC and reported in Annex D of the standard, the method based on tetrahydrofuran extraction was selected for the standard method as it showed the best performance in terms of recovery of phthalates.

In addition, the JRC in-house developed a method for the quantification of the mass percentage of PVC in coated textiles, which was successfully validated and it was included in Annex C of the standard. The method would be used in case of textile products coated with PVC layer to evaluate the corrected mass of the specimen (corresponding to the PVC coated part of the sample) against which results have to be calculated.

The phthalates are extracted from textile specimen with tetrahydrofuran by ultrasonic generator. The plastic polymer is either partially or completed dissolved, depending on its nature, and it is then re-precipitated by mean of an appropriate solvent (e.g. acetonitrile, n-hexane, etc.). The solution is then centrifuged to get rid of the solid and the liquid analysed by Gas Chromatography-Mass Spectrometry (GC-MS). Dicyclohexyl phthalate (DCHP) is used as internal standard.

The standard is ready for the Final Draft International Standard (FDIS) vote, after which it will be published.

# ISO DIS 16373-3 Textiles- Dyestuffs- Part 3: Method for determination of carcinogenic extractable dyestuffs (method using triethylamine/methanol)

As already mentioned, the new standard for the analysis of dyestuffs (16373) was planned in three parts. Part 3 is under the responsibility of ISO/TC 38/WG 22. In 2013, the standard went through the Draft International Standard (DIS) vote which was positive. The comments received will be dealt in the next meeting of WG 22 in February 2014, after which the draft standard can be sent to the final FDIS vote.

The scope of the test method covers the quantification of carcinogenic dyestuffs, reported in Tables 1-2, in dyed, printed or coated textile products. The coloured textile samples are extracted by means of 0.25 % (v/v) tri-ethylamine methanol solution in an ultrasonic bath at 50 °C for 3 h. The extract is then evaporated, the residue dissolved in methanol, which is filtered before the HPLC analysis. Either photodiode array detector (DAD) or a mass spectrometer (MS) can be used as detector.

The JRC took part in the round robin test that was organised on 4 textile samples each one containing either Acid red 114 or Acid red 26 at two different levels. In total 10 laboratories did participate in the exercise and the results of the JRC were in line with the global average calculated.

**Table 9**: List of carcinogenic dyestuffs covered by draft ISO 16373-3.

C.I. generic name	CAS	C.I. constitution number
C.I. Basic Red 9	569-61-9	42500
C.I. Disperse Orange 11	82-28-0	60700
C.I. Disperse Yellow 3	2832-40-8	11855
C.I. Acid Red 114	6459-94-5	23635
C.I. Acid Red 26	3761-53-3	16150
C.I. Direct Black 38	1937-37-7	30235
C.I. Direct Red 28	573-58-0	22120
C.I. Disperse Blue 1	2475-45-8	64500
C.I. Basic Violet 14	632-99-5	42510
C.I. Direct Blue 6	2602-46-2	22610
C.I. Direct Brown 95	16071-86-6	30145

#### WD 17881: Textiles - Determination of certain flame retardants

The standard under development for the quantification of certain flame retardants is structured in three parts. Part 1 deals with brominated flame retardants, part 2 with phosphorus flame retardants and part 3 with short chain paraffin flame retardants. The

three parts went through the Committee Draft (CD) ballot. The first two parts received just few minor comments and after the required corrections they will proceed to DIS stage immediately. Major comments were received on part 3, which will need to be discussed in WG22 meeting before DIS registration.

Part 1 is based on the extraction of flame retardants from textile samples by ultrasonic generator with toluene, followed by a GC-MS analysis using internal standard method. Two subsequent extractions are performed at room temperature for 30 and 15 min. The solution is filtered, concentrated near the dry by rotary evaporator. The internal standard is added before the analysis. The list of brominated flame retardants that can be analysed with this method is reported in Table 10.

Part 2 covers the determination of some phosphorous flame retardants, reported in Table 11, in all kinds of textile products. The principle of the method is based on an extraction in acetone carried out by ultrasonic generator. Two subsequent extractions are performed at 40 ° C for 40 and 20 min. The solution is filtered, concentrated near the dry by rotary evaporator and then the residue is dissolved in acetonitrile. The extracted compounds are determined by Liquid Chromatography Tandem Mass Spectrometry (HPLC-MS/MS) after filtration and quantified by using external standard method.

**Table 10**: List of brominated flame retardants covered by draft ISO 17881-1.

Brominated flame retardant	Acronym	CAS
Monobromobiphenyl	MonoBB	2052-07-5
Dibromobiphenyl	DiBB	57422-77-2
Tribromobiphenyl	TriBB	59080-34-1
Tetrabromobiphenyl	TetraBB	60044-24-8
Pentabromo-1,1'-biphenyl	PentaBB	59080-39-6
Hexabromobiphenyl	HexaBB	60044-26-0
Heptabromo-1,1'-biphenyl	HeptaBB	88700-06-5
Octabromobiphenyl	OctaBB	67889-00-3
Nonabromobiphenyl	NonaBB	69278-62-2
Decabromobiphenyl	DecaBB	13654-09-6
Tetrabromodiphenylether	TetraBDE	5436-43-1
Pentabromodiphenylether	PentaBDE	32534-81-9
Hexabromodiphenylether	HexaBDE	207122-15-4
Heptabromodiphenylether	HeptaBDE	207122-16-5
Octabromodiphenylether	OctaBDE	337513-72-1
Decabromophenylether	DecaBDE	1163-19-5
Hexabromocyclododecane	HBCDD	25637-99-4

Table 11: List of brominated flame retardants covered by draft ISO 17881-2.

Phosphorous flame retardant	Acronym	CAS
Tris (2,3-dibromopropyl) phosphate	TRIS	126-72-7
Tris (1-aziridinyl) phosphate	TEPA	545-55-1
Tris (2-chloroethyl) phosphate	TCEP	115-96-8

Part 3 deals with the analysis of short chain chlorinated paraffins (C10-C13) (SCCPs) in textiles. These compounds are extracted by ultrasonic generator with n-hexane/acetone (1:1) from textile samples. Again two subsequent extractions are carried out at room temperature for 30 and 15 min. The solution is filtered, concentrated near to dryness by rotary evaporator and then the residue is dissolved in n-hexane. The extract is purified by use of SPE column, eluted with n-hexane/diethyl ether 90/10 v/v, concentrated again near to dryness by rotary evaporator and finally the residue is dissolved in n-hexane and analysed. For the time being the draft standard foresees a pre-test done via GC-ECD, followed in case of presence of SCCPs by a quantification performed by GC-FID using external standard method. Before the quantification, a dechlorination step, based on reaction with hydrogen, is foreseen to generate straight-chain alkane (C10-C13) in the presence of PdCl2 as catalyst. However, further discussions are needed as several comments were received concerning the method of analysis. The detection limit of GC-ECD or GC-FID method is 20 mg/kg.

# ISO 24362 Textiles -- Methods for determination of certain aromatic amines derived from azo colorants

Part 1: Detection of the use of certain azo colorants accessible with and without extracting the fibres

Part 3: Detection of the use of certain azo colorants, which may release 4-aminoazobenzene.

WG 22 proposed to adopt at ISO level the European standards EN 14362, parts 1 and 3 for determination of certain aromatic amines derived from azo colorants by reductive cleavage. The aromatic amines that are covered by the scope of the methods are those restricted in Annex XVII of REACH (entry 43) reported in Table 1. The European test methods were essentially agreed upon with only minor changes and the FDIS vote was positive. The standard methods are now in publication.

The European standards EN 14362, parts 1 and 3, were partly based on the experimental work performed by the JRC on aromatic amines derived from azo colorants by reductive cleavage, published as EUR report [44].

#### 6. Conclusions

Standard methods are essential to guaranty the enforceability of EU legislation that established in the field of textile products and toys requirements, both in terms of labelling and chemical content. However, many standard methods are still lacking. The development of such methods is carried out both at CEN and ISO level, due to the global market that characterises our society.

In 2013, standards on quantitative chemical analysis of textiles, generic names of man-made fibres and safety of toys (migration of certain elements, N-nitrosamines and N-nitrosatable substances) were published. At the same time, standards on the detection of allergenic and carcinogenic dyestuffs, phthalates, alkylphenol ethoxylates, metals, carcinogenic aromatic amines derived from azo colorants, flame retardants in textiles are under development, as well as test methods for the identification and quantitative analysis of cashmere in blends with wool, yak, etc.

The JRC has actively participated in the standardisation process and a number of standard methods published or under development are entirely or partly based on the JRC work, such as for example PrEN ISO 16373, the technical report on guidance on health and environmental issues related to the chemical content of textile products intended to clothing, interior textiles and upholstery, EN 71-3:2013, EN 71-12:2013, ISO 1833-22:2013, ISO 1833-25:2013, ISO 1833-26:2013, ISO 2076:2013, ISO FDIS 14389 and ISO 24362.

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European Commission

EUR 26466 - Joint Research Centre - Institute for Health and Consumer Protection

Title: Progress report on the development of standard methods for the characterisation of textile fibres and yarns and for the safety of textile products and toys

Author: P. Piccinini

Luxembourg: Publications Office of the European Union

2013 – 42 pp. – 21.0 x 29.7 cm

EUR - Scientific and Technical Research series - ISSN 1831-9424 (online)

ISBN 978-92-79-35266-9 (pdf)

doi: 10.2788/62275

#### Abstract

There is a strong need of standardisation in the field of textile products and toys, in order to allow the enforceability of restrictions established in the EU legislation. The JRC has been actively involved in the progresses made on the development of standard methods for the characterisation of textile fibres and yarns and for the safety of textile products and toy, which are reviewed in this report. A number of standard methods published or under development are entirely or partly based on the JRC work. The JRC contribution ranged from taking part in or organising ring trials, drafting parts of test methods, proposing modifications, giving advice on the basis of its practical experience in chemical analysis of consumer products, drafting questionnaires, statistically evaluating results of collaborative trials and providing test methods that had been developed and validated by the JRC.

The work performed by Working Groups (WGs), of which the JRC is member, is described: CEN/TC 248/WG 26 (on test methods for analysis of EC restricted substances in textiles); CEN/TC 248/WG 30 (on quantitative analysis of fibre mixtures); CEN/TC/52/WG 5 (on chemical properties of toys); and ISO/TC/WG 22 (on composition and chemical testing of textiles). The need for the test methods and their principles are explained, together with their stage in the approval process.

As the Commission's in-house science service, the Joint Research Centre's mission is to provide EU policies with independent, evidence-based scientific and technical support throughout the whole policy cycle. Working in close cooperation with policy Directorates-General, the JRC addresses key societal challenges while stimulating innovation through developing new methods, tools and standards, and sharing its know-how with the Member States, the scientific community and international partners.

