ETAD

Implementation of Chapter 4 of the Code of Ethics

Pursuant to Chapter 4 of the Code of Ethics, ETAD members may not manufacture or sell dyes referred to in Annexes A and B.

Annex A

Dyes or preparations of dyes used in textile and leather articles, which may come into direct and prolonged contact with the human skin or oral cavity.

These dyes:
- contain, or release by reductive cleavage of azo bonds to any of the specified amines;
- contain any of the specified organic impurities;
- contain any of the specified trace metals.

Details on the different groups of impurities, corresponding detection limits and additional information are contained in the following pages.

Annex B
Individual Dyestuffs

CAS-No.	C.I. No.	C.I. Name	EU	IARC
569-61-9	42500	Basic Red 9	Cat. 1B[a]	Group 2b
3761-53-3	16150	Acid Red 26	Cat. 2[b]	Group 2b
60-11-7	11020	Solvent Yellow 2	Cat. 2[c]	Group 2b
6358-53-8	12156	Solvent Red 80	Cat. 2[b]	Group 2b

[a] Annex VI CLP

[b] C&L inventory, same classification for all notifications

[c] C&L inventory, classification for most notifications

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ETAD' impurity limits for the dyes described in Annex A of the Code of Ethics

Substances/Substance groups	ETAD Limit in mg/kg [ppm]	Analytical methods*
PAAs[1] (carcinogenic primary aromatic amines from potential reductive cleavage of dyes)	150	Modified DIN EN 14362-1:2012-04 (see next page for important false positive information)
Heavy metals[2]	ETAD heavy metal limits[2] plus 10 for Cr(VI)	AAS
Chlorobenzenes/ Chlorotoluenes	200	GC/MS
Chlorophenols[1]	20 (sum of tetra/ pentachlorophenols)	GC/MS
Organotin compounds[1]	5	LRMS
PCBs[1]	50	HRMS
Short-chained chlorinated paraffins (SCCPs)[1]	50	GC/MS
APs[1]	250	LC/MS
APEOs[1]	500	LC/MS
Dioxins and Furans[1]	sum of substances in group I: 0.001 sum of substances in group I and II: 0.005 sum of substances in group I, II and III: 0.1	HRMS
Formaldehyde (CAS 50-00-0)	200	Derivation + GC/MS or Steam-Destillation / Photometry
PAH, polycyclic hydrocarbons[1]	20 Benzo[α]pyrene 100 sum	GC/MS
Quinoline (CAS 91-22-5)	1000	

* The detailed analytical method depends on the laboratory, since no dyes-specific standard methods are available for these impurities

[1] See Annex 1 for the detailed list of substances of the class
[2] See Annex 2 for ETAD metal limits for dyes

False positives in the determination of PAAs through reductive cleavage

Cases of false positives under the conditions of the analytical test for the detection of PAAs in textiles are well known. Since modified tests used on the dyes also use reductive cleavage of the azo-bond, even when testing dyes it is necessary to know which specific false positives may occur.

Most common cases when the amine is an artifact of the test procedure are the following:

1. **Detection of 4-aminobiphenyl from dyes containing an aniline moiety, e.g. C.I. Acid Red 1, C.I. Solvent Yellow 7**. The detection of 4-aminobiphenyl should always be treated with suspicion as no known azo dyes or pigments would form this amine by cleavage of one or more azo bonds. However it is known that, in cases where the reductive cleavage of the azo bond would produce an aniline moiety, 4-aminobiphenyl can be formed as a byproduct. This byproduct will then show as impurity.

2. **Detection of 2-naphthylamine from dyes based on Tobias acid.** Although the cited method yields smaller amounts of 2-naphthylamine than detected under more aggressive test conditions, the results are false positive as the responsible dyes do not fall within the scope of the limits.

Testing facility should always take into account the possibility of such false positive whenever dyes (and textiles) are checked for PAAs under reductive cleavage conditions.

Annex 1

Specific substances included in the chemical classes

Primary (carcinogenic) aromatic amines from potential reductive cleavage of dyes (PAAs)

Name	CAS Nr.
4,4'-methylene-bis-(2-chloro-aniline)	101-14-4
4,4'-methylenedianiline	101-77-9
4,4'-oxydianiline	101-80-4
4-chloroaniline	106-47-8
3,3'-dimethoxylbenzidine	119-90-4
3,3'-dimethylbenzidine	119-93-7
6-methoxy-m-toluidine	120-71-8
2,4,5-trimethylaniline	137-17-7
4,4'-thiodianiline	139-65-1
4-aminoazobenzene	60-09-3
4-methoxy-m-phenylenediamine	615-05-4
4,4'-methylenedi-o-toluidine	838-88-0
2,6-xylidine	87-62-7
o-anisidine	90-04-0
2-naphthylamine	91-59-8
3,'3-dichlorobenzidine	91-94-1
4-aminodiphenyl	92-67-1
Benzidine	92-87-5
o-toluidine	95-53-4
2,4-Xylidine	95-68-1
4-chloro-o-toluidine	95-69-2
4-methyl-m-phenylenediamine	95-80-7
o-aminoazotoluene	97-56-3
5-nitro-o-toluidine	99-55-8

Chlorobenzenes and chlorotoluenes

- All mono-, di-, tri-, and tetra-, hexa- chlorobenzenes and pentachlorobenzene
- All mono-, di-, tri-, and tetra-, hexa-, penta- chlorotoluenes and pentachlorotoluene

Chlorophenols

- All mono-, di-, and tri- chlorophenols, plus

Name	CAS No.
Tetrachlorophenol (TeCP)	25167-83-3
Pentachlorophenol (PCP)	87-86-5

Organotin compounds

Name	CAS No.
Dibutyltin (DBT)	Multiple
Dimethyltin (DMT)	Multiple
Monobutyltin (MBT)	Multiple
Monoctyltin (MOT)	Multiple
Dioctyltin (DOT)	Multiple
Tricyclohexyltin (TCyHT)	Multiple
Trioctyltin (TOT)	Multiple
Tripropyltin (TPT)	Multiple
Tributyltin (TBT)	Multiple
Trimethyltin (TMT)	Multiple
Triphenyltin (TPhT)	Multiple
Tetrabutyltin (TebT)	Multiple

Polychlorinated biphenyls (PCBs)

Name	CAS No.
209 individual congeners with 1 to 10 chlorine atoms attached to biphenyl, with general formula $C_{12}H_{10-x}Cl_x$	1336-36-3

Short-chain chlorinated paraffins (SCCP)

Name	CAS No.
C_{10}-C_{13} molecules with general formula $C_xH_{(2x-y+2)}Cl_y$ where x = 10-13; y = 3-12	85535-84-8

Alkylphenol (AP) and alkylphenol ethoxylates (APEOs)

Name	CAS No.
Nonylphenol (NP), mixed isomers	104-40-5 11066-49-2 25154-52-3 84852-15-3
Octylphenol (OP), mixed isomers	140-66-9 1806-26-4 27193-28-8
Octylphenol ethoxylates (OPEO)	9002-93-1 9036-19-5 68987-90-6
Nonylphenol ethoxylates (NPEO)	9016-45-9 26027-38-3 37205-87-1 68412-54-4 127087-87-0

Dioxins and furans

Group	Name	CAS No.
Group I	2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746-01-6
	1,2,3,7,8-Pentachlorodibenzo-p-dioxin	40321-76-4
	2,3,7,8-Tetrachlorodibenzofuran	51207-31-9
	2,3,4,7,8-Pentachlorodibenzofuran	57117-31-4
Group II	1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	39227-28-6
	1,2,3,7,8,9- Hexachlorodibenzo-p-dioxin	19408-74-3
	1,2,3,6,7,8- Hexachlorodibenzo-p-dioxin	57653-85-7
	1,2,3,7,8-Pentachlorodibenzofuran	57117-41-6
	1,2,3,4,7,8-Hexachlorodibenzofuran	70648-26-9
	1,2,3,7,8,9-Hexachlorodibenzofuran	72918-21-9
	1,2,3,6,7,8-Hexachlorodibenzofuran	57117-44-9
	2,3,4,6,7,8-Hexachlorodibenzofuran	60851-34-5
Group III	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	35822-46-9
	1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	3268-87-9
	1,2,3,4,6,7,8-Heptachlorodibenzofuran	67562-39-4
	1,2,3,4,7,8,9-Heptachlorodibenzofuran	55673-89-7

Polycyclic aromatic hydrocarbons (PAHs)

Name	CAS No.
Benzo[a]pyrene (BaP)	50-32-8
Anthracene	120-12-7
Pyrene	129-00-0
Benzo[ghi]perylene	191-24-2
Benzo[e]pyrene	192-97-2
Indeno[1,2,3-cd]pyrene	193-39-5
Benzo[j]fluoranthene	205-82-3
Benzo[b]fluoranthene	205-99-2
Fluoranthene	206-44-0
Benzo[k]fluoranthene	207-08-9
Acenaphthylene	208-96-8
Chrysene	218-01-9
Dibenz[a,h]anthracene	53-70-3
Benzo[a]anthracene	56-55-3
Acenaphthene	83-32-9

Phenanthrene	85-01-8
Fluorene	86-73-7
Naphthalene	91-20-3

Annex 2

ETAD heavy metal limits for dyes[3]

Antimony	50
Arsenic	50
Cadmium	20
Chromium	100
Lead	100
Mercury	4
Zinc	1500
Copper	250
Nickel	200
Tin	250
Barium	100
Cobalt	500
Iron	2500
Manganese	1000
Selenium	20
Silver	100

Notes

1. All values are in mg/kg (ppm).
2. These limits do not apply to products containing a listed metal as an inherent part of the molecular structure, e.g. metal-complex dyes or the double salts of certain cationic dyes.

[3] Background information on the values at www.etad.com