



ETAD recommendations for threshold limits on organic impurities in dyes (rev. 2014)

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Introduction

The question of the presence of impurities in dyes and their potential impact on the environment is a persistent point of discussion. In particular for the main application in textiles, dyes manufacturers are asked to comply with many different standards, any of which typically includes both a specific impurity profile for the dyes and limits for trace impurities in the final textile products that have to be considered in order to provide suitable products for the dyeing process.

Starting from 2013 ETAD has been part of the Technical Advisory Committee of the Zero Discharge of Hazardous Chemicals group (ZDHC)¹, which brings together international brands and retailers seeking to minimize the environmental impact of their products. An important project completed in voluntary collaboration with the ZDHC has been the definition of a Manufacturers Restricted Substance List (MRSL). The scope of the MRSL includes both impurities in the final products **and** in the chemicals used during the textile production. Maximum concentration limits for such impurities are provided and have been agreed upon with chemical suppliers.

As a consequence of the MRSL-related activities, ETAD decided to update its existing recommendations for threshold limits on impurities in dyes. This revised document reflects the results of ETAD's recent collaboration with the ZDHC group.

Origin of impurities

Several sources may contribute to the presence of impurities, e.g.:

- impurities in reactants or raw materials;
- residues of solvents, reactants or reaction by-products;
- particularly in the case of trace metals, use of metal catalysts or corrosion of manufacturing plant equipment.

¹ <http://www.roadmaptozero.com>





General considerations

Dye manufacturers achieve an effective impurity profile by good manufacturing practices such as:

- implementation of a suitable quality management system
- quality specification and control of all chemicals used in the manufacture of colorants
- state-of-the-art manufacturing processes
- proper clarification/purification steps
- automated control of certain process parameters like pH, temperature etc.

Therefore, ETAD is confident that the contamination of dyes with impurities can be kept below the levels recommended in this document without any adverse effect on the coloristic or technical properties of the dye. Additionally, ETAD monitors new eco/toxicological information and issues recommendations, often beyond regulatory requirements, when further action to address impurities is appropriate.

Information needs respecting impurities

Information on impurities in dyes may be required for a variety of reasons, such as:

- compliance with regulatory schemes (e.g., REACH);
- compliance with consent limits for aqueous effluent;
- need to certify that products comply with the requirements of various ecolabelling schemes;
- need to provide information to customers concerning substances of concern in colorants used.

ETAD and ZDHC organic impurity limits

The table on the next page provides ETAD's recommended limits for certain organic impurities that might be present in dye formulations used for consumer goods and the corresponding ZDHC limits². These limits will also achieve at least partial compliance with many other existing textile standards.

ETAD has developed its recommended limits based on its review of available eco/toxicological information, standards established by governments and private organizations, and in certain cases and when feasible, even lower values reflecting the commitment of ETAD members to reducing the impurity profiles of their dye formulations.

ETAD notes that several impurities recently have been singled out for special attention. They are already regulated in some countries and may be relevant for some dyes; in these cases the following table refers to existing official limits.

- Quinoline: Quinoline is an impurity which might be in products due to the use of some dispersing agents. Quinoline has an EU harmonized classification as Carc. 1B, therefore its presence in a quantity >1000 mg/Kg has to be disclosed and will trigger a product classification.

² ZDHC MRS L 2014, published in June 2014





- PCBs: PCBs have been recently identified as relevant impurities for some organic colorants, and the table refers to the current limit for PCBs under US regulation (40 CFR 761.20).
- Dioxins and Furans: Substances, preparations and articles containing dioxins and furans are strictly regulated by the German Chemikalien-Verbotsverordnung. The table refers to the limits in this document.
- Formaldehyde: Formaldehyde limits for textile products already exist in the national legislation of the Netherlands, Norway, Germany, Austria and Finland. The 200 mg/kg limit referenced in the table is a very conservative value derived from these textile products limits.

ETAD plans to update the table as appropriate when new information becomes available or new requirements are enacted.



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Substances/Substance groups	ETAD Limit in mg/kg [ppm]	ZDHC Limit in mg/kg [ppm]	Analytical methods*
PAAs ³ (carcinogenic primary aromatic amines from potential reductive cleavage of dyes)	200	200	Modified DIN EN 14362-1:2012-04
Heavy metals ⁴	ETAD heavy metal limits ⁴ plus 10 for Cr(VI)	ETAD heavy metal limits ⁴ plus 10 for Cr(VI)	AAS
Chlorobenzenes/ Chlorotoluenes ³	200	1,2-dichlorobenzene 1000 Sum of all others 200	GC/MS
Chlorophenols ³	20 (sum of tetra/ pentachlorophenols)	20 (sum of tetra/ pentachlorophenols) 50 (sum of mono-, di-, and tri-)	GC/MS
Organotin compounds ³	5	5 20 for DBT	LRMS
PCBs ³	50	-	HRMS
Short-chained chlorinated paraffins (SCCPs) ³	50	50	GC/MS
AP / APEOs ³	500	500	LC/MS
Dioxins and Furans ³	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-Distillation / Photometry
PAH, polycyclic hydrocarbons ³	20 Benzo[a]pyrene 100 sum	20 Benzo[a]pyrene 200 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

³ See Annex 1 for the detailed list of substances of the class

⁴ See Annex 2 for ETAD metal limits for dyes



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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'-dimethoxybenzidine	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-xylydine	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-Xylydine	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 pentachlorotoluenes



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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
Monooctyltin (MOT)	Multiple
Diocetyl tin (DOT)	Multiple
Tricyclohexyltin (TCyHT)	Multiple
Triocetyl tin (TOT)	Multiple
Tripopyltin (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



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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



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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



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Annex 2

ETAD heavy metal limits for dyes⁵

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
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.

⁵ Background information on the values at www.etad.com

