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## **POSITION PAPER**

# **Aniline - Proposed requirement for Appendix C of the Toy Safety Directive**

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**APRIL 2016**

**Contact Person: Tania Vandenberghe, Senior Programme Manager**  
([tania.vandenberghe@anec.eu](mailto:tania.vandenberghe@anec.eu))

## Summary

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The present paper discusses the need for an aniline limit for toys intended for use by children under 36 months or in other toys intended to be placed in the mouth, taking into account food contact material legislation to be inserted in Appendix C (Article 46 of the Toy Safety Directive).

It reviews existing regulatory and normative provisions including available test methods.

The document provides some evidence on the occurrence of aniline in articles intended for children identified by test magazines and other reports showing that aniline has been found at levels up to 1200 mg/kg in articles for babies (using methods to determine primary aromatic amines after reductive cleavage).

Aniline has been classified as a (suspected) non-threshold carcinogen, i.e. a substance which should not be present in toys.

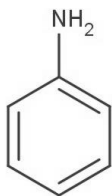
It is recommended to adopt for aniline:

- a limit of 30 mg/kg for toy articles made of textile and leather in line with REACH provisions for carcinogenic primary aromatic amines released from azo colourants including any "free" aniline;
- corresponding test methods given in EN ISO 17234-1 for leather and EN 14362-1 for textiles adapted to detect aniline;
- the application of the provisions included EN 71-7 on finger paints (i.e. 10 mg/kg for the "free" aniline and 30 mg/kg for aniline cleaved from azo dyes) for all liquid toys

It further recommends to consider:

- a broadening of the proposed limit toy articles made of textile and leather to other materials
- to initiate a broader discussion on colourants and related substances in toys

## 1. Aniline basic data



EC / List no.: 200-539-3

CAS no.: 62-53-3



Aniline has the following **harmonised classification and labelling**:

Carc. 2	H351 – Suspected of causing cancer
Muta. 2	H341 – Suspected of causing genetic defects
Acute Tox. 3	H301 – Toxic if swallowed
Acute Tox. 3	H311 – Toxic in contact with skin
Acute Tox. 3	H331 – Toxic if inhaled
STOT RE 1	H372 – Causes damage to organs through prolonged or repeated exposure
Eye Dam. 1	H318 – Causes serious eye damage
Skin Sens. 1	H317 – May cause an allergic skin reaction
Aquatic Acute 1	H400 – Very toxic to aquatic life

## 2. Available comprehensive risk assessment reports

A **European Union Risk Assessment Report** in accordance with Council Regulation (EEC) 793/931 on the evaluation and control of the risks of "existing" substances was published in 2004<sup>1</sup>. Its major conclusion concerning consumers was that "*there is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account*" because of "*concerns for mutagenicity and carcinogenicity as a consequence of exposure arising from use of products containing the substance, as aniline is identified as a non-threshold carcinogen*". Possible releases of aniline from azo colourants by reductive cleavage were not investigated.

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<sup>1</sup> <http://echa.europa.eu/documents/10162/0abd36ad-53de-4b0f-b258-10cf90f90493>

### 3. Aniline limits and test methods relating to toys

#### 3.1. Aniline in REACH Annex XVII

At present aniline included in articles for consumers is not restricted in REACH.

#### 3.2. Aniline limit in the TSD

As a substance classified Carc. 2 and Muta. 2 the aniline limit in (accessible parts of) toys is 1% (= 10.000 mg/kg) based on the generic exclusion of CMR substances and applicable thresholds.

#### 3.2. Aniline limits in standards for toys and related test methods

**EN 71-9:2005+A1:2007 (organic chemical compounds)** contains the following requirement for aniline in Table 2 C – Primary aromatic amines:

Action limit (= 5 mg/kg) when tested in accordance with EN 71-10:2005 and EN 71-11:2005

It applies to a broad range of toys including those intended for children under 3 years of age made of textile and leather where the first action method given in EN 71-10 (colour fastness test) gives a negative result.

**EN 71-7:2014 (finger paints)** contains the following requirement for aniline in 4.5.1.2:

10 mg/kg when tested in accordance with Annex D

In addition, 4.2.2 disallows azo colourants that by cleavage of one or more azo groups can produce the primary aromatic amines listed in Tables 1 and 2 (including aniline) when tested in accordance with the test method specified in Annex D. This Annex provides that "*A prohibited azo colourant is deemed to be present in the finger paint if, on reductive cleavage, one or more of the amines listed in Tables 1 and 2 is present in a concentration exceeding 30 mg/kg*".

### 4. Other aniline limits and related test methods

#### 4.1. Cosmetics Regulation

The Cosmetics Regulation (Regulation (EC) No 1223/2009) disallows the use of aniline, its salts and its halogenated and sulphonated derivatives (Annex II, Reference number 22).

#### 4.2. Food contact materials

The Commission Regulation "on plastic materials and articles intended to come into contact with food" (No 10/2011) includes a provision for PAAs covering also aniline:

"Plastic materials and articles shall not release primary aromatic amines, excluding those appearing in Table 1 of Annex I, in a detectable quantity into food or food simulant. The detection limit is 0,01 mg of substance per kg of food or food simulant. The detection limit applies to the sum of primary aromatic amines released".

#### 4.3. Child use and care articles

CEN/TR 13387-2 "Child use and care articles - General safety guidelines - Part 2: Chemical hazards" recommends to use the aniline provisions included in EN 71-9 for standards addressing child use and care articles.

#### 4.4. EU ecolabel criteria and test methods

The EU Ecolabel criteria generally do not allow the use of CMRs of all categories unless a derogation is granted subject to conditions.

### 5. Aniline found in articles for children

The German test magazine ÖKO-TEST found aniline frequently in products for children as shown in the list below:

- **Toys** ("Kinderspielzeug") - 9/2009 - found in 3 hand puppets
- **Children's pyjamas** ("Kinderschlafanzüge") - 11/2011 - found in 2 pyjamas
- **Baby shoes** ("Krabbelschuhe") - 10/2013 - found in 4 shoes
- **Plastic and textile picture books** ("Plastik- und Stoffbilderbücher") - 2/2014 - found in 1 picture book
- **Finger paints** ("Fingermalfarben") - 2/2015 - found in 1 finger paint
- **Children's low shoe** ("Kinderhalbschuhe") - 4/2015 - found in 9 shoes
- **Children's carpets** ("Kinderteppiche") - 9/2015 - found in 2 carpets
- **Baby shoes** ("Krabbelschuhe") - 11/2015 - found in 1 shoe
- **Sleeping aids** ("Einschlafhilfen") - 1/2016 - found in 1 sleeping aid
- **Children's backpacks** ("Kinderrucksäcke") - 3/2016 - found in 1 backpack
- **Street painting crayons** ("Straßenmalkreide") - 4/2016 - found in 2 products

The concentrations were in the range 5 - 350 mg/kg according to ÖKO-TEST (answer to our enquiry). The highest concentration was found in one hand puppet.

The tests were performed in accordance with EN 14362-1 "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". The test was modified to detect aniline.

A survey published by the Danish EPA in 2008 entitled "Survey and health assessment of chemical substances in hobby products for children" (Survey of Chemical

Substances in Consumer Products 93)<sup>2</sup> identified aniline in 2 marker pens in concentrations up to 0.22 mg/kg.

Another survey published by the Danish EPA in 2015 was entitled "CMR Substances in Toys – Market Surveillance and Risk Assessment" (Survey of Chemical Substances in Consumer Products 141)<sup>3</sup> identified aniline in a green paint on the handle of a skipping rope (650 mg aniline/kg). No migration of aniline to artificial saliva or artificial sweat under static conditions was demonstrated.

The German UBA published a report in 2011 entitled "Karzinogene, mutagene, reproduktionstoxische (CMR) und andere problematische Stoffe in Produkten" ("Substances classified as carcinogenic, mutagenic and toxic for reproduction (CMR) and other substances of concern in consumer products")<sup>4</sup>. It identified aniline in 2 toy samples (no details given). Aniline was included in the "master list", i.e. *"a list of those substances and groups of substances that are considered to be "of concern" in this research project. The list provides a guide as to which substances or groups of substances should not be present in mixtures and articles, if possible, from the point of view of the German Environmental Agency"*.

One RAPEX notification could be identified which was related to aniline in baby textiles. Finland notified<sup>5</sup> a "dark red baby's body made of cotton" (1100 mg/kg) and a "dark red baby's overall made of cotton" (1200 mg/kg) in 2010.

## 6. Test methods used for the determination of aniline in toys

It is important to note that the requirement in **EN 71-9** concerning aniline relates to the "free" amine (as for all other listed primary aromatic amines). The final action method for primary aromatic amines (PAAs) in accordance with EN 71-10 is based on an extraction of the sample reduced to small pieces not exceeding 3 mm with water ("agitate on a Vortex® mixer for 30 s") at room temperature followed by centrifugation (15 min) and extraction of the supernatant fluid with tert-butyl methyl ether (MTBE) using a kieselguhr column. The extract is analysed in accordance with EN 71-11 (GC-MS).

By contrast, the requirement in **EN 71-7** covers the "free" aniline as well as the aniline (and other listed PAAs) released from azo dyes by reductive cleavage. The method described in Annex D relies on mixing the sample with buffer (pH 6, 70°), keeping the contents for 30 min, adding sodium dithionite solution (for reductive cleavage) and - after thoroughly shaking - keeping the content for another 30 min.

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<sup>2</sup> <http://mst.dk/service/publikationer/publikationsarkiv/2008/apr/survey-and-health-assessment-of-chemical-substances-in-hobby-products-for-children/>

<sup>3</sup> <http://www2.mst.dk/Udgiv/publications/2015/10/978-87-93352-79-7.pdf>

<sup>4</sup> <https://www.umweltbundesamt.de/publikationen/karzinogene-mutagene-reproduktionstoxische-cmr>

<sup>5</sup>

[http://ec.europa.eu/consumers/consumers\\_safety/safety\\_products/rapex/alerts/main/?event=main.notification&search\\_term=0432/10&exclude\\_search\\_term=0&search\\_year=2010](http://ec.europa.eu/consumers/consumers_safety/safety_products/rapex/alerts/main/?event=main.notification&search_term=0432/10&exclude_search_term=0&search_year=2010)

For the determination of "free" amines the addition of dithionite solution is replaced by addition of buffer (the temperature in this case is only 37°). The liquid is extracted with tert-butyl methyl ether (MTBE) following its transfer on a kieselguhr column. The analysis of the amines is done using HPLC/DAD or GC-MS.

**EN 14362-1** is used to verify the absence of PAAs cleaved from azo dyes according to the REACH restriction (see below) in textiles. It addresses azo colorants accessible with and without extracting the fibres. Azo colorants accessible to reducing agent without extraction are those used to dye:

- cellulosic fibres (e.g. cotton, viscose);
- protein fibres (e.g. wool, silk);
- synthetic fibres (e.g. polyamide, acrylic).

However, in some cases extraction is also needed: for cellulose and/or protein fibres blended with man-made fibres. Azo colorants which need extraction are those used to dye man-made fibres with disperse dyes (for polyester, polyamide, acetate, triacetate, acrylic and chlorofibre). In some cases, a combined procedure is used.

Where necessary, extraction is done using boiling chlorobenzene (30 min). Reductive cleavage with sodium dithionite in a citrate buffered aqueous solution similar to EN 71-7. A variety of different chromatographic techniques can be used for analytical determination of the PAAs. The method was used by Öko-Test to determine among other PAAs aniline.

**EN ISO 17234-1** uses a similar approach for leather products (see below). There is an additional degreasing step using n-hexane in an ultrasonic bath at 40°C prior to the reductive cleavage. No extraction of colourants is foreseen.

## 7. Excursus: REACH restriction concerning azocolourants and azodyes

The REACH restriction concerning azocolourants and azodyes in a broad range of textile and leather articles including toys which may come into direct and prolonged contact with the human skin or oral cavity (entry 43) also relies on the concept of reductive cleavage of azo dyes. It disallows azo dyes which, by reductive cleavage of one or more azo groups, may release one or more of the aromatic amines listed in Appendix 8, in detectable concentrations, i.e. above 30 mg/kg (0,003 % by weight). Appendix 8 includes currently 22 substances but does not list aniline.

This restriction was introduced in European law with Directive 2002/61/EC "amending for the nineteenth time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (azocolourants)". It was based on provisions originally introduced in the German Consumer Goods Ordinance (Bedarfsgegenständeverordnung) in 1994. In contrast to the REACH restriction the latter was not limited to textile and leather materials.

The provisions are based on the finding that azo dyes can be metabolically cleaved by bacteria on the skin and in the human digestive tract or by enzymatic reduction in some organs (e.g. in the liver). For example, it could be demonstrated that about

10% of the lipophilic azo dye "Disperse Orange 3" released from a textile into a saliva solution was cleaved by the skin bacterium *Staphylococcus epidermidis* in just 4 hours (T. Platzek and Chr. Lang, Freisetzung aromatischer Amine aus Azofarbstoffen in Textilien durch Hautbakterien)<sup>6</sup>.

The applied test methods are intended to simulate these biological degradation mechanisms.

Appendix 10 to Annex XVII of REACH specifies a "List of testing methods":

- EN ISO 17234-1:2010 Leather — Chemical tests for the determination of certain azo colorants in dyed leathers — Part 1: Determination of certain aromatic amines derived from azo colorants
- EN ISO 17234-2:2011 Leather — Chemical tests for the determination of certain azo colorants in dyed leathers — Part 2: Determination of 4-aminoazobenzene
- EN 14362-1:2012 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
- EN 14362-3:2012 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

A separate method is needed for the determination of 4-aminoazobenzene (4-AAB, no 22 in REACH Appendix 8 PAA list). This PAA is itself an azo compound which is cleaved under the conditions of the test method to aniline and *p*-phenylenediamine (PPD). However, the detection of aniline is no evidence for the presence of 4-AAB as it may be released from many other azo colourants which are not restricted in REACH. These include<sup>7</sup>:

- C.I. Disperse Orange 13 (6253-10-7),
- C.I. Solvent Orange 1 (2051-85-6),
- C.I. Solvent Yellow 56 (2481-94-9),
- C.I. Solvent Black 3 (4197-25-5),
- C.I. Solvent Yellow 16 (4314-14-1),
- C.I. Solvent Yellow 2 (60-11-7),
- C.I. Disperse Yellow 4 (6407-80-3),
- C.I. Solvent Yellow 14 (842-07-9),
- C.I. Acid Black 1 (1064-48-8),
- C.I. Acid Black 234 (157577-99-6),
- C.I. Reactive Red 2 (17804-49-8),
- C.I. Acid Orange 10 (1936-15-8),
- C.I. Direct Red 23 (25188-34-5),

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<sup>6</sup> [www.bfr.bund.de/cm/343/forschung\\_azo.pdf](http://www.bfr.bund.de/cm/343/forschung_azo.pdf)

<sup>7</sup> Brüsweiler et al., Identification of non-regulated aromatic amines of toxicological concern which can be cleaved from azo dyes used in clothing textiles, *Regulatory Toxicology and Pharmacology* 69 (2014) 263–272



- C.I. Direct Red 23 (3441-14-3),
- C.I. Basic Orange 1 (4438-16-8),
- C.I. Acid Brown 289 (52587-68-5),
- C.I. Basic Orange 2 (532-82-1),
- C.I. Acid Yellow 11 (6359-82-6),
- C.I. Direct Orange 102 (6598-63-6),
- C.I. Acid Red 106 (6844-74-2),
- C.I. Acid Brown 298 (70236-62-3),
- C.I. Direct Black 168 (85631-88-5)

These colourants are, therefore, possible sources of the presence of aniline in articles made of textile, leather and possibly other materials.

## 8. Discussion of limits

Aniline is suspected to be a non-threshold carcinogen. In its opinion concerning the "Risk from organic CMR substances in toys" (May 2010) SCHER stated:

*"In accordance with previous opinions by CSTEE, CMR categories 1 and 2 (now categories 1A, 1B according to the CLP regulation) non-thresholded carcinogens should not be present in toys as intentionally added components. Indeed, the acceptance for those chemicals of a non-threshold mechanism makes the definition of a safe level virtually impossible".*

Apparently SCHER associated non-threshold CMR substances with categories 1A and 1B (CLP). However, the example aniline shows that a category 2 CMR substance may be also a non-threshold substance. It is also not understandable why such substances should be excluded only if they are "intentionally added components". The more so as SCHER itself reiterated in this document recommendations included in an earlier opinion on "CEN's response in the opinion of the CSTE on the assessment of CEN report on the risk assessment of organic chemicals in toys" (2007) where it stated:

*"Action limits for CMR and very toxic compounds are not acceptable as these compounds should not be present in toys. Thus, they should be determined directly in the toy using appropriate extraction procedures and sensitive chemical-analytical procedures".*

This statement was neither restricted to intentionally added substances nor to any particular CMR category. From this follows that aniline should not be present in toys (irrespective of the fact that SCHER seems to misinterpret the meaning of the term "action limit" as a migration limit).

In view of the frequently observed occurrence of aniline in articles for children a restriction in Appendix C of the TSD seems warranted. The restriction should cover the aniline released from azo dyes by reductive cleavage including any "free" aniline which may be present. A limit of 30 mg/kg for articles made of textile and leather in line with REACH provisions for PAAs released from azo colourants seems adequate. The test methods referred to in Appendix 10 to Annex XVII could be used, i.e. EN ISO

17234-1 for leather and EN 14362-1 for textiles. These methods are likely to include also any "free" aniline. It should be discussed whether the restriction should be broadened to toy articles made of other materials.

The provisions for aniline in finger paints included in the standard EN 71-7 are already addressing aniline released from azo dyes by reductive cleavage and any "free" aniline. They could be simply taken over for all toys in liquid form.

## **9. Final remark**

Aniline is just one of the substances of concern associated with colourants. It seems useful to cover the issue of colourants in toys in a more comprehensive manner with a particular view to identifying colourants with CMR or sensitising properties.

## **Acknowledgements**

*Special thanks go to Dr. Franz Fiala, ANEC expert on chemicals in toys, main author of this paper.*

## About ANEC

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ANEC is the European consumer voice in standardisation, defending consumer interests in the processes of technical standardisation and conformity assessment, as well as related legislation and public policies.

ANEC was established in 1995 as an international non-profit association under Belgian law and is open to the representation of national consumer organisations in 33 countries.

ANEC is funded by the European Union and EFTA, with national consumer organisations contributing in kind. Its Secretariat is based in Brussels.



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**European association for the coordination  
of consumer representation in standardisation aisbl**

Avenue de Tervuren 32, box 27, B-1040 Brussels, Belgium  
Tel.: +32 2 743 24 70 / Fax: +32 2 706 54 30  
E-mail: [anec@anec.eu](mailto:anec@anec.eu)

EC Register of Interest Representatives:  
Identification number 507800799-30

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ANEC is supported financially by the European Union & EFTA

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