Standard methods for determination of restricted substances in textile and leather goods

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Agenda

1. European Union Regulations

2. Dangerous substances restricted in textile and leather goods
   - Azo-dyes
   - Formaldehyde
   - Dimethyle fumarate
   - Heavy metals
European Union Regulations - goals

- Protect humane and environment from dangerous substances
- Harmonisation of regulations in UE ensure effective work of domestic markets
- Improve competitiveness of European Chemical Industry
Regulations apply to various groups of substances in European Union

- Pharmaceuticals
- Drugs
- Cosmetics
- Pesticides
- Fertilisers
- Biocidal Products
- Detergents
- Others chemicals
EU Directives and Regulations

- Directive 67/548/EEC relating to the classification, packaging and labelling of dangerous substances
- Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (substances classified as carcinogenic, mutagenic or toxic to reproduction — c/m/r)
- Directive 98/24/EC - risks related to chemical agents at work
- Council Regulation 793/93 on the evaluation and control of the risks of existing substances
- Regulation 689/2008 concerning the export and import of dangerous chemicals
- EINECS – European Chemical Substances Information System
- ELINCS – European List of Notified Chemical Substances
EU Directives and Regulations

- Regulation 1272/2008 on classification, labeling and packaging of substances and mixtures, amending and repealing
- Directive 87/18/EWG relating to Good Laboratory Practice
- Regulation 684/2004 relating to detergents.
- Regulation 273/2004 on drug precursors
Dangerous substances restricted in textiles and leather goods:

- Pesticides
- Pentachlorophenol
- Formaldehyde
- Monomers
- Heavy metals
- Aromatic amines
- Dimethyl fumarate
AZO Colorants

Azo colorants are the most important class of synthetic dyes representing 60 – 80% of all organic colorants.

Azo colorants may release by reductive cleavage of their azo group(s) one or more of the aromatic amines.

22 aromatic amines are dangerous for humane health (carcinogenic, mutagenic and substances that can harm reproduction).
Table 1. List of forbidden aromatic amines (REACH Regulation)

<table>
<thead>
<tr>
<th>No</th>
<th>Substance</th>
<th>CAS number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-aminodiphenyl</td>
<td>92-67-1</td>
</tr>
<tr>
<td>2</td>
<td>Benzidine</td>
<td>92-87-5</td>
</tr>
<tr>
<td>3</td>
<td>4-chloro-otoluidine</td>
<td>95-69-2</td>
</tr>
<tr>
<td>4</td>
<td>2-naphthylamine</td>
<td>91-59-8</td>
</tr>
<tr>
<td>5</td>
<td>4-amino-2’,3-dimethylazobenzene</td>
<td>97-56-3</td>
</tr>
<tr>
<td>6</td>
<td>2-aminoo-4-nitrotoluene</td>
<td>99-55-8</td>
</tr>
<tr>
<td>7</td>
<td>4-chloroaniline</td>
<td>106-47-8</td>
</tr>
<tr>
<td>8</td>
<td>2,4-diaminoanisole</td>
<td>615-05-4</td>
</tr>
<tr>
<td>9</td>
<td>4,4’-diaminodiphenylomethan</td>
<td>101-77-9</td>
</tr>
<tr>
<td>10</td>
<td>3,3’- dichlorobenzidine</td>
<td>91-94-1</td>
</tr>
<tr>
<td>11</td>
<td>3,3’– dimethoxybenzidine</td>
<td>119-90-4</td>
</tr>
<tr>
<td>12</td>
<td>3,3’– dimethylbenzidine</td>
<td>119-93-7</td>
</tr>
<tr>
<td>13</td>
<td>3,3’; - dimethyl-4,4’-diaminodiphenylomethan</td>
<td>838-88-0</td>
</tr>
<tr>
<td>14</td>
<td>4-cresidine</td>
<td>120-71-8</td>
</tr>
<tr>
<td>15</td>
<td>4,4’-methylene –bis-(2-chloroaniline)</td>
<td>101-14-4</td>
</tr>
<tr>
<td>16</td>
<td>4,4-oxydianiline</td>
<td>101-80-4</td>
</tr>
<tr>
<td>17</td>
<td>4,4-thiodianiline</td>
<td>139-65-1</td>
</tr>
<tr>
<td>18</td>
<td>2-aminotoluene</td>
<td>95-53-4</td>
</tr>
<tr>
<td>19</td>
<td>2,4-diaminotoluene</td>
<td>95-80-7</td>
</tr>
<tr>
<td>20</td>
<td>2,4,5-trimethylaniline</td>
<td>137-17-7</td>
</tr>
<tr>
<td>21</td>
<td>2-methoxyaniline</td>
<td>90-04-0</td>
</tr>
<tr>
<td>22</td>
<td>4-aminoazobenzene</td>
<td>60-09-3</td>
</tr>
</tbody>
</table>
Methods for determination aromatic amines in leather:

- 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 from azo colorants

- EN ISO 17234-1:2010 Leather – Chemical tests for the determination of certain azo colorants in dyed leathers
  Part 1: Determination of 4-aminoazobenzene
Methods for determination aromatic amines in textiles:

- EN 14362-1:2012 Textiles – Methods for determination of certain aromatic amines derived from azo colorant - 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 colorant - Part 1: Detection of the use of certain azo colorants, which may release 4 – aminoazobenzene.
Aromatic amines

Graph 1. Figure of benzidine in leather sample after solvents extraction by HPLC/DAD technique.

Graph 2. Figure of benzidine standard by GC/MS technique.
Formaldehyde

Formaldehyde is an important chemical used widely by industry to manufacture building materials, numerous household products and consumer goods.

Formaldehyde is used to add permanent-press qualities to clothing and draperies, as a component of glues and adhesives, and as a preservative in some paints and coating products.

Formaldehyde is a human carcinogen. It causes cancer of the throat, nose, and blood.
Formaldehyde

<table>
<thead>
<tr>
<th>Product Class</th>
<th>I Baby</th>
<th>II in direct contact with skin</th>
<th>III with no direct contact with skin</th>
<th>IV Decoration material</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH value¹</td>
<td>4.0 - 7.5</td>
<td>4.0 - 7.5</td>
<td>4.0 - 9.0</td>
<td>4.0 - 9.0</td>
</tr>
<tr>
<td>Formaldehyde [mg/kg]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Law 112</td>
<td>n.d.²</td>
<td>75</td>
<td>300</td>
<td>300</td>
</tr>
</tbody>
</table>

Table 2. Limit values according to OEKO – TEX Standard

**Standard method for determination of formaldehyde in textiles:**

- EN ISO 14148 – 1:2011 Textiles – Determination of formaldehyde
  Part 1:Free and hydrolised formaldehyde (water extraction method)
Standard method for determination of formaldehyde in leather:


Formaldehyde

Graph 3. Figure of formaldehyde solution made by spectrophotomic method (UV – VIS)
Dimethyl fumarate (DMFU)

- Dimethyl fumarate is a fungicide.
- Dimethyl fumarate is commonly used as an anti-fungal agent to kill molds that may cause furniture or shoe leather to deteriorate during storage and transportation.
- Sachets containing dimethyl fumarate are placed in orgin inside clothes, shoeboxes from which it spreada and impregnates the consumer product.
Dimethyl fumarate (DMFU)

Exposition to DMFU may causing:

- extreme allergic reaction;
- skin irritation;
- skin redness;
- rash;
- difficulties with breathing;
Dimethyl fumarate (DMFU)

Dimethyl fumarate was banned for use in manufacturing of goods in the EU according to Biocides Directive (98/8/EC).

(substance forbidden in EU science 1998 year)
Dimethyl fumarate (DMFU)

According to EU Regulation 412/2012 the presence of DMFU in products should be determined against the maximum limit of 0,1 (mg/kg) ppm of product.

In the table of Annex XVII to Regulation (EC) No 1907/2006, the following entry 61 is added:

<table>
<thead>
<tr>
<th>61. Dimethylfumarate (DMF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS No 524-49-7</td>
</tr>
<tr>
<td>EC 210-849-0</td>
</tr>
<tr>
<td>Shall not be used in articles or any parts thereof in concentrations greater than 0,1 mg/kg</td>
</tr>
<tr>
<td>Articles or any parts thereof containing DMF in concentrations greater than 0,1 mg/kg shall not be placed on the market</td>
</tr>
</tbody>
</table>

Table 3. Forbidden dimethyl fumarate according to Annex XVII to REACH
Graph 4. Figure of dimethyl fumarate in leather sample after solvents extraction by GC/MS technique

Graph 5. Figure of dimethyl fumarate by GC/MS technique
Heavy metals

Heavy metals are used in producing textiles, leather goods, jewellery, furniture, cosmetics, household products……

The determination of heavy metals in consumer products is crucial for the safety appraisal and sources classification of human and environmental exposures.
## Heavy metals

<table>
<thead>
<tr>
<th>Product Class</th>
<th>I Baby</th>
<th>II in direct contact with skin</th>
<th>III with no direct contact with skin</th>
<th>IV Decoration material</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>pH value</strong></td>
<td>4.0 - 7.5</td>
<td>4.0 - 7.5</td>
<td>4.0 - 9.0</td>
<td>4.0 - 9.0</td>
</tr>
<tr>
<td><strong>Formaldehyde [mg/kg]</strong></td>
<td>Law 112</td>
<td>n.s.</td>
<td>75</td>
<td>300</td>
</tr>
<tr>
<td><strong>Extractable heavy-metals [mg/kg]</strong></td>
<td>Sb (Antimony)</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
</tr>
<tr>
<td></td>
<td>As (Arsenic)</td>
<td>0.2</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Pb (Lead)</td>
<td>0.2</td>
<td>1.0&lt;sup&gt;3&lt;/sup&gt;</td>
<td>1.0&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Cd (Cadmium)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Cr (Chromium)</td>
<td>1.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>Cr(VI)</td>
<td>under detection limit&lt;sup&gt;5&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co (Cobalt)</td>
<td>1.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>Cu (Copper)</td>
<td>25.0&lt;sup&gt;6&lt;/sup&gt;</td>
<td>50.0&lt;sup&gt;6&lt;/sup&gt;</td>
<td>50.0&lt;sup&gt;6&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Ni (Nickel)&lt;sup&gt;7&lt;/sup&gt;</td>
<td>1.0&lt;sup&gt;8&lt;/sup&gt;</td>
<td>4.0&lt;sup&gt;9&lt;/sup&gt;</td>
<td>4.0&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Hg (Mercury)</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 4. Limit values according to OEKO – TEX Standard
Heavy metals

Standard method for determination of heavy metals in leather:

- ISO 17072-1:2011 Leather - Chemical determination of metal content
  Part 1: Extractable metals

- ISO 17072-1:2011 Leather - Chemical determination of metal content
  Part 1: Extractable metals, footwear for children less than 36 months old

- ISO 17072-2:2011 Leather - Chemical determination of metal content
  Part 2: Total metal content

- EN 14602:2004 Footwear. Test methods for the assessment of ecological criteria
Dangerous example - Cadmium

- Cadmium is found in soil and ocean water, and up to 10% of the cadmium ingested from dietary sources, such as food and water, is absorbed by the body.

- It is readily absorbed (40-60%) through the inhalation of cigarette smoke and can be absorbed through the skin.

- Cadmium binds to red blood cells and is transported throughout the body where it concentrates in the liver and kidneys, significant amounts are also found in the pancreas, and spleen.
Thank you for your attention

Contact details

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