

Annex 2

Summary of studies analysing substances present on finished products

Study 1

Potential impacts of REACH on EU textile supply chains (2005)

Author: Enviro-tex and CAST for DG Enterprise & Industry

Aim: To evaluate the potential impacts of the REACH Regulation on industry

Summary: The study identified six critical functional groups following extensive consultation with industry. The textile industry may be vulnerable to their withdrawal from the market. This is because of their important role as the basis for common chemical formulations and their small production volumes.

Table 2.1 Functional groups identified as being critical by the textile industry

Functional group	Critical substances	Concentration on finished product (% w/w)	Technical notes
Cotton dyestuffs	Reactive dyes	Not identified	Widely applied dyestuff which is of particular importance to cotton.
Dye carriers	benzylbenzoate biphenyl phthalimide chlorobenzene/toluene phenylphenol aromatic hydrocarbons phthalates	Not identified	Required for the low temperature dyeing of synthetic fibres, particularly polyester.

<p>General formulation solvents</p>	<p>ethylene-glycol, diethylene-glycol, triethylene-glycol, propylene-glycol, dipropylene-glycol, tripropylene-glycol <i>and all</i> methyl-, ethyl-, propyl-, butyl-, phenyl-ethers as well as ether-acetates</p>	<p>Not identified</p>	<p>Common to auxiliaries used for pre-treatment, dyeing, printing, top finishing as well as preparations for fibre and yarn processing.</p>
<p>Softeners</p>	<p>Alkanol-amines and Polyamines: - Ethanolamine - Diethanolamine - Triethanolamine - Ethylen-diamine Diethylenetriamine Paraffin substances, Silicone substances Urea</p>	<p>Not identified</p>	<p>Fatty acid condensation products were selected as one example. Precise softening requirements will vary by substrate and the required performance of the finish.</p>
<p>Easy care (cross linkers)</p>	<p>Melamine and DMDHEU resins with different etherification grades and formaldehyde contents</p>	<p>Not identified</p>	<p>These substances lend the final textile an easy care finish as well as being used to improve the performance and permanence of finishing effects such as flame retardancy and water repellency.</p>

Study 2

Chemicals in textiles, report of a Government commission (1997)

Author: Swedish National Chemicals Inspectorate

Aim: To propose measures to reduce risks to human health and the environment caused by chemicals occurring in textiles.

Summary: The extent to which substances remain on the final product depend on their properties and the degree to which they are washed out or evaporated during processing. This means that most detergents, emulsifiers, inorganic salts, acids and bases are likely to be washed out. Substances from dyeing, printing and finishing are the most likely to remain on the fabric. Some substances may remain if washing has not been carried out correctly e.g. poorly fixed dye. The study screened substances into a short list that may be found on the final product, organised by functional groups. The report identifies specific azo dyes that may cleave to form carcinogenic aryl amines.

Table 2.2 Functional groups and their concentration on finished products

Functional group	Critical substances	Concentration on finished product (% w/w)	Technical notes
Dyes	Dyestuff Aryl amines	0.05 – 3.0% >30 ppm	The concentration will depend on the strength and depth of colour. Aryl amines will only be present as degradation products of certain azo dyes.
Carriers		0.1 – 1.0%	
Easy care		0.003 – 0.01%	
Flame retardants		1 – 10%	
Fluorocarbons		0.3 – 8.0%	Provides dirt or water repellency

Biocides	Pentachlorophenol	5 ppm	Can reach 100 ppm
Heavy metals	Mercury	0.01 ppm	
	Copper	1 – 50 ppm	
	Zinc	1 – 50 ppm	

DRAFT

Study 3

Introduction to the problems surrounding garment textiles (2007)

Author: The textile working group of the German Federal Institute for Risk Assessment

Aim: To provide an introduction to consumer health protection issues related to textile products, bringing together the assessments and recommendations of the working group.

Summary: The report has a specific focus on consumer exposure, reviewing the principles for the toxicological testing of the following textile dyes and textile auxiliaries:

- Dye accelerators
- Flame retardants
- Dioxins
- Fluorine surfactants
- Detergent residues and whitening agents
- Anti-bacterial finish
- Functional clothes
- Nano-finish

The evidence brought together suggests that textile chemicals pose a minimal risk to consumer health. However, it does identify specific instances in which a combination of sensitising substances (e.g. disperse dyes), perspiration resistance of <4 and intensive skin contact – particularly in perspiration zones. Damaged skin also poses a risk factor. With regard to dye allergens it concludes that a combination of fibre type, dye (including colour intensity) and test conditions (e.g. pH) are more important than dye fastness as factors influencing migration.

Table 2.3 Functional groups and their concentration on finished products

Functional group	Critical substances	Concentration on finished product (% w/w)	Technical notes
Finishing agents to improve creasing and shrinking behaviour (easy care and shrink-free)	Reactant resins containing N-methylol compounds on a formaldehyde base.	8%	In 2004 the International Agency on Research of Cancer (IARC) classified formaldehyde as a human carcinogen. Formaldehyde is considered a contact allergen. It is not possible to state a general threshold value for exposure that would be applicable to all age groups or skin sensitivities.
	Glyoxal, as an example of a substitute easy care agent	8%	Glyoxal-containing resin is used to give a shrink-free finish to some viscose and cotton fabrics (e.g. cotton velvet, viscose velvet). It is classified as toxic, a skin allergen and possible carcinogen.
Flame retardants		Up to 20%	Exposure is likely to be minimal for modified polyester fibres and fibre-active compounds. Semi-permanent flame retardants can result in considerable levels of exposure. Salt products with low skin absorption are used in Germany e.g. ammonium sulphate, amidosulphonic acid and borax.

Dye carriers	1,2,4-trichlorobenzene	0.2-2.7% depending on dye take-up and finishing stages	<p>In addition to polyester fabrics carriers are also used as levelling agents to achieve uniform dyeing.</p> <p>1,2,4-trichlorobenzene is considered a toxin and is no longer used in Germany.</p> <p>If dyeing using carriers is not carried out in accordance with state of the art, e.g. over dyeing, incorrect dye selection for the substrate or incomplete removal of the carriers, there may be higher consumer exposure. Their small molecular size and high lipophilicity mean that some of them are easily absorbed through the skin.</p>
Whitening agents	<p>derivatives of diaminostilbendisulphonic acid (stilbene derivatives), pyrazoline derivatives, coumarin derivatives, benzoxazol derivatives, naphthalimide derivatives, distyrylbiphenyl</p> <p>sulphonate derivatives and pyrene derivatives.</p>	Up to 0.5%	<p>Only agents which have a high substrate affinity are considered suitable technically. Three whitening agents have been assessed: CI Fluorescent Brightener 220, CI Fluorescent Brightener 260 and distyrylbiphenyl sulphonate. No significant risk of systemic exposure was identified for the former two agents.</p>
Perfluorinated polymers	perfluoro-octane sulphonate (PFOS) and perfluorooctanoic acid (PFOA)	0.04 – 0.25% fluorine	<p>Used for water-repellent and oil-repellent properties. PFOS and PFOA are not the main modern production method. Telomerisation is now more significant. The substances do not occur either as by-products</p>

			<p>or end products in this process.</p> <p>The most frequently used component is tetrafluoroethylene.</p>
Biocide finish	<p>silver ions or nano particles</p> <p>quaternary ammonium salts</p> <p>chitosan compounds</p> <p>isothiazolinones</p> <p>triclosan</p>	<i>Not identified</i>	<p>Relevant to sports and leisure wear, textiles for personal protection, medical products, curtains, carpets and mattresses. Permanent synthetic fibre finishes can be introduced prior to spinning.</p> <p>Anti-microbial finishes should demonstrate skin tolerance, toxicological safety and stability under conditions of use and a clearly proven action. In addition, bacterial skin colonisation should not be negatively impaired.</p> <p>Resistance development is a consideration for textiles with an antibacterial finish. The growing use of biocide substances in the home prompts fears of the selection of resistant germs and multiple antibiotic resistance.</p>

Study 4

Survey of chemical compounds in textile fabrics (2011)

Author: Danish Environmental Protection Agency

Aim: To test selected textile products for selected chemical compounds in order to assess whether the detected amounts of substances are hazardous to health.

Summary: The study consisted of a testing survey of a sample of clothing, curtains, table clothes, upholstery, napkins and bed linen from shops in Copenhagen. The worst case was tested i.e. assuming that that consumer does not wash the item before using it.

A screening was also carried out for additional organic compounds, the results of which are presented in table 2.5. The budget for analysis was not sufficient to test for all compounds in all fabrics. The following organic compounds from the main test list were detected in the textile samples:

- DEHP
- 4-Chloroaniline
- Formaldehyde
- Napthalene
- Nicotine
- Nonylphenol, nonylphenol mono- and diethoxylate
- o-Toluidine

A health assessment was carried out for each of these compounds based on the latest toxicological knowledge about each substance and the level of contact, oral and inhalation exposure routes.

Table 2.4 Functional groups and their concentration on finished products

Functional group	Critical substances	Concentration on finished product	Technical notes
Selected organic compounds	Nicotine, naphthalene, o-chlorophenol, C3-C4-alkylbenzenes, tetrachloroethylene, nitrobenzene and DEHP	DEHP 1.0 - 8.6 mg/kg Naphthalene 0.04 – 3.8 mg/kg Nicotine 0.02 - 0.25 mg/kg	<ul style="list-style-type: none"> - DEHP (bis(2-ethylhexyl)phthalate) was detected in all 10 tested samples. - Nicotine was detected in 9 out of 10 tested samples, - Naphthalene was detected in 5 out of 10 tested samples. - The other organic compounds were below limit of detection
Dyes	26 known aromatic amine compounds	o-Toluidine: 0.82 ± 3.4 % 4-Chloroaniline: 1.22 ± 3.4 %	<ul style="list-style-type: none"> - Only 2 out of 10 samples contained levels above the limit of detection
Surfactants	nonyl phenol ethoxylates	5.5 – 26.4 mg/kg	<ul style="list-style-type: none"> - In 3 out of 4 tested samples nonyl phenol ethoxylates were found in levels above the limit of detection.

Metals	Arsenic (As), barium (Ba), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), antimony (Sb) and tin (Sn).	<p>Where samples were positive the concentrations were:</p> <p>Barium 0.44 – 9.7 mg/kg</p> <p>Chromium 0.20 – 64 mg/kg</p> <p>Copper 1.1 – 680 mg/kg</p> <p>Cobalt 0.45 – 48 mg/kg</p> <p>Antimony 0.63 – 215 mg/kg</p> <p>Lead 0.51 – 1.6 mg/kg</p>	<ul style="list-style-type: none"> - Cadmium and mercury were not found in any of the 15 samples above the limit of detection. - Barium was detected in 14/15 samples. - Chromium was detected in 12/15 samples, - Copper was detected in 10/15 samples, - Cobalt was detected in 5/15 samples - Antimony and lead was detected in 4/15 samples. - Arsenic, nickel and tin were only detected in 1/15 sample. <p>Testing of six samples was also carried out for extractable antimony. Only one sample produced extractable (10% of the total antimony in the sample).</p>
Easy care	Formaldehyde	35 – 82 mg/kg	Only 3 out of 10 samples contained formaldehyde above limit of detection (20 mg/kg)

Table 2.5 Additional compounds detected following product screening

Sample	Detected compounds
B) 100% cotton, yellow (children)	Phthalate, fatty acids, C _x H _y (C ₈₋₂₀), C _x H _y (C ₂₀₋₄₀), 2-2'-oxybis ethanol, squalene, aliphatic alcohols, aliphatic amide
E) Cotton/PET brown	fatty acids, aliphatic amide
G) 100% (animal motive)	fatty acids, 2-2'-oxybis ethanol
I) 100% cotton (flowers)	fatty acids, C _x H _y (C ₈₋₂₀), C _x H _y (C ₂₀₋₄₀), 2-2'-oxybis ethanol, propylene glycol, aliphatic amide
J) 100% flax	bis(2-ethylhexyl)maleate, 2-2'-oxybis ethanol, squalene
L) 100% viscose	Phthalate, 5-hydroxy-methyl-furfural
M) 100% wool	fatty acids, C _x H _y (C ₂₀₋₄₀), 2-2'-oxybis ethanol, 2-(2-butoxy-ethoxy)ethanol
O) 100% cotton (bear)	fatty acids, C _x H _y (C ₂₀₋₄₀)
Q) 100% cotton (oilcloth)	C _x H _y (C ₂₀₋₄₀), bis(2-ethylhexyl)maleate, benzylbenzoate, 2-2'-oxybis ethanol
T) 100% PET (cushion)	fatty acids, C _x H _y (C ₂₀₋₄₀)

Study 5

Chemical requirements for consumer products (2010)

Author: Consumer Council at the Austrian Standards Institute

Aim: To review European legislation relating to chemicals in consumer products and the regulatory framework to protect consumers

Summary: The report contains a compilation of the findings from a range of studies that have tested textile products on the market. The studies cited were:

- Nanosilver treatments, National Nanotechnology Centre of Thailand (2010)
- Jackets and mittens, Norwegian Climate and Pollution Agency (2010) and Danish EPA (2009)
- Womens bras, Øko-test (2009)
- Children's bed linen and t-shirts, Øko-test (2009)
- T-shirts, Swedish Society for Nature Conservation (2009)
- Bed linen, Øko-test (2008)
- Bath towels, Swedish Society for Nature Conservation (2007)
- Waterproof jackets. Friends of the Earth Norway (2006)

The findings of the studies cited by the report are compiled in table 2.6. The findings are presented only as an indication of the results of the literature review in the report. A more detailed review of each study would be required to normalize the data and reporting methods.

Table 2.6 Functional groups and substances found to be present on finished products

Functional group	Critical substances	Concentration on finished product	Technical notes
Biocides	Dibutyltin	> 250 micro g/kg	Testing of womens bras. 18/20 showed trace amounts and 2/20 elevated levels (see concentration levels).
	Tributyltin	>2,500 micro g/kg	
	Triclosan	<i>Not specified</i>	Testing of childrens bed linen and t-shirts.
	Nanosilver	36 – 425 mg/kg ¹	Laboratory testing of 6 commercial fabrics. Artificial perspiration releases of 0 – 322 mg/kg were measured.
Plastics	DEHP and DBP	Up to 22%	Migration of phthalates from rubber zippers of jackets and gloves.
Dyes	Aromatic amines: p-aminoazobenzol, aniline, benzidine, and disperse orange 37/76	<i>Not specified</i>	Testing of womens bras (6/25 samples).
Carriers	Halogenated hydrocarbons	<i>Not specified</i>	Present in bras and bed linen samples tested.
Optical brighteners		<i>Not specified</i>	Present in bra, bed linen and t shirt samples tested.
Surfactants	Nonylphenoethoxylate	1%	Testing of Bath towels. All samples contained measurable concentrations.
Softeners	DEHP	<i>Not specified</i>	Testing of womens bras (1/25 samples).

Printing	Plastisol coatings containing phthalates (DEHP, DBP, BBP, DINP, DIDP, DOP)	By weight of print: DEHP 22% BBP 7.3% DINP 7.9% DIDP 2.6%	Testing of samples of 20 different t-shirts.
Easy care	Formaldehyde	10/25 samples >20 ppm 1/20 samples 120 ppm	Testing of bed linen. Testing of nightwear.
Water repellents	perfluorooctanyl sulfonate (PFOS), fluorotelomer alcohols (FTOH), perfluorocarboxylic acids (PFCA).	FTOH 139-5215 ng/g PFCA (including PFOA) 14.5 - 1406 ng/g PFOS 0.3 – 66.2 ng/g	Testing of jackets with branded waterproof membranes or treatments.

Notes

1. In the referenced study some nanosilver samples were below limit of detection.