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European survey on the presence of banned azodyes in textiles

Analysis conducted within the CHEM TEST project
on behalf of DG SANCO

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1. Executive summary

Consumers are increasingly exposed to hundreds of potentially hazardous chemicals in their everyday life. These compounds can come into contact with their bodies through three different pathways: inhalation, ingestion and dermal absorption.

Azodyes are widely used in the dyeing of every type of fibres (natural, artificial and synthetic) and commercially they represent by far the major part of colorants. They can belong to several dye classes such as acid, disperse, direct and reactive dyes.

Directive 2002/61/EC did forbid the use in textile and leather articles of some azodyes which, by reductive cleavage of one or more azo groups, may release one or more carcinogenic aromatic amines which may come into direct and prolonged contact with the human skin or oral cavity. A limit was set for each listed aromatic amine to 30 mg/kg in the finished articles or in the dyed parts thereof.

The scope of this work was threefold: 1) to make a survey on the presence of banned azodyes which can be found in textile products manufactured anywhere in the world and sold on the European market; 2) to evaluate the colour fastness to washing, the fastness to acid and basic perspiration and to acid and basic saliva for textiles which contained some banned azodyes; 3) to evaluate dermal exposure for the analysed samples.

The focus was put on dermal exposure that can result from the direct contact of the skin with textile products. Therefore the sampling was planned with the objective to cover textile clothing in particular.

A total of 116 samples were purchased in 24 out of 27 EU Member States of the European Union. Although it is not compulsory to indicate the origin on labels in Europe, efforts were made to buy samples with labels stating the country of production. Garments were purchased from a variety of sources, including department stores, shops and open air markets, and with various compositions, such as mixtures with cotton, wool, polyester, polyamide and acrylic.

The majority of the samples were textile clothing, whereas 3 % were classified as linen (bedding pillowcases and sofa cushion covers). The target considered was the entire population: clothing samples designed for men, women and children were analysed. Samples were purchased both for babies under the age of two and for children up to the age of 14.

Several types of garments were taken into consideration, such as shirts, T-shirts, underwear, socks, pyjamas, trousers and dresses. Some sweaters, which can be classified either in direct contact with the skin or not depending on the scenarios, were also analysed. In the case of shirts, some samples had an "easy care" label and for the other garments a few had also an "Oeko-Tex" label.

To evaluate the presence of banned azodyes, all the samples were analysed in duplicate with the standard method EN 14362-1 (without previous extraction of dyes from textiles) and 72 samples with high percentage of synthetic fibre were also analysed with the standard method EN 14362-2 (with extraction). Averages and standard deviations were calculated. For comparison purposes, a slightly modified version of method EN 14362-1, which includes a basification step before liquid-liquid extraction in vials instead of using diatomaceous earth columns, was also applied. The comparison showed that usually higher concentrations of aromatic amines were measured using the modified version of the standard method.

Three shirts intended to come into contact with the skin (2.6 % of all analysed samples) exceeded the limit of 30 mg/kg for 4-methoxy-m-phenylendiamine, benzidine and 3,3'- dimethoxybenzidine, established by Directive 2002/61/EC. Ten other samples contained some banned aromatic amines in levels lower than the limit of 30 mg/kg. The positive samples T148, T188 and T292 were two black and one green shirt for men, made either of pure cotton or of binary mixture cotton/polyester. They were bought in a German department store and in shops in Cyprus and Spain respectively. The production country of sample T188 was China. The origin of samples T148 and T292 was not known.

Twelve aromatic amines considered as not carcinogenic were detected in 21 samples. Their concentration was often higher than 30 mg/kg and in certain cases even higher than 100 mg/kg.

In addition, the colour fastness to washing, perspiration and saliva was evaluated for the samples which contained forbidden aromatic amines. Results showed a very high colour fastness in terms of colour degradation, except for some samples including the two positive ones T188 and T292. On the contrary, colour fastness in terms of staining was not high. Staining was generally higher to washing at 60°C than to saliva at 37°C; the lowest staining was obtained to perspiration at 37°C. Staining by washing ranged from 5 to 1/2, while for saliva and perspiration from 5 to 3 and 5 to 3/4 respectively, depending on the adjacent fibres and the analysed specimen.

Essentially no differences were observed among results obtained with acid and basic saliva or with acid and basic perspiration simulants. The three positive samples T148, T188 and T292 were among the worst specimens concerning both colour degradation and staining.

Data on aromatic amines were used to estimate adult and child dermal exposure following the recommendations of the European Chemical Bureau's Technical Guidance Document. From data obtained with the EN-14362-1 standard method and the modified one, the maximum dermal uptakes evaluated in the case of a child were 8.2 and 11.8 mg/kg bw respectively and, in the case of an adult, 3.1 and 4.4 mg/kg bw.

2. Introduction

Directive 2002/61/EC[1], amending for the nineteenth time Council Directive 76/769/EEC[2] relating to restrictions on the marketing and use of certain dangerous substances and preparations, prohibited the use of some azodyes in textile and leather articles which may come into direct and prolonged contact with the human skin or oral cavity, such as:

— clothing, bedding, towels, hairpieces, wigs, hats, nappies and other sanitary items, sleeping bags;

— footwear, gloves, wristwatch straps, handbags, purses/wallets, briefcases, chair covers, purses worn round the neck;

— textile or leather toys and toys which include textile or leather garments;

— yarn and fabrics intended for use by the final consumer.

The azodyes banned by this Directive are those which, by reductive cleavage of one or more azo groups, may release one or more of the aromatic amines listed in the Directive's appendix, in detectable concentrations, i.e. above 30 mg/kg in the finished articles or in the dyed parts thereof, according to the testing methods (EN 14362-1:2003[3] and EN 14362-2:2003[4]). The appendix includes a list of 22 aromatic amines which are classified as carcinogenic except one.

In the frame of its work on human exposure to chemical stressors released from consumer products and the ChemTest project funded by DG Sanco, the Physical and Chemical Exposure Unit (which is part of DG Joint Research Centre's Institute for Health and Consumer Protection) has conducted a European survey on the presence of the banned azodyes in textiles.

Azodyes are compounds containing at least one azo group (-N=N-), they are widely employed and commercially they represent by far the major part of colorants. Depending on the structure, they belong to several dye classes such as for example acid, disperse, direct and reactive dyes. They are used in the dyeing of every type of fibres (natural, artificial and synthetic) depending on the dye class they belong. For example disperse dyes are used with acetate, triacetate and several synthetic fibres, whereas acid dyes are used with wool, silk and polyamide.

Three objectives were pursued during this work: first of all, to verify if textiles on the European market comply with Directive 2002/61/EC; secondly, to evaluate the colour fastness to washing, the fastness to acid and basic perspiration and to acid and basic

saliva for textiles which contained some banned azodyes; thirdly, to evaluate dermal exposure for the same samples.

3. Analytical methods

Two standard methods are available for the determination of 22 aromatic amines (21 of which are carcinogenic), listed in Table 1, derived from the azodyes banned by Directive 2002/61/EC (EN 14362-1 and EN 14362-2). The second method foresees extraction from fibres and the first one not.

Table 1: Aromatic amines derived from the azodyes banned by Directive 2002/61/EC.

		CAS number	Index number	EC number	Substances
A	**1**	92-67-1	612-072-00-6	202-177-1	biphenyl-4-ylamine 4-aminobiphenyl xenylamine
B	**2**	92-87-5	612-042-00-2	202-199-1	benzidine
C	**3**	95-69-2		202-441-6	4-chloro-o-toluidine
D	**4**	91-59-8	612-022-00-3	202-080-4	2-naphtylamine
W	**5**	97-56-3	611-006-00-3	202-591-2	o-aminoazotoluene 4-amino-2',3-dimethylazobenzene 4-o-tolylazo-o-toluidine
X	**6**	99-55-8		202-765-8	5-nitro-o-toluidine
E	**7**	106-47-8	612-137-00-9	203-401-0	4-chloroaniline
F	**8**	615-05-4		210-406-1	4-methoxy-m-phenylenediamine
G	**9**	101-77-9	612-051-00-1	202-974-4	4,4'-methylenediamine 4,4'-diaminodiphenylmethane
H	**10**	91-94-1	612-068-00-4	202-109-0	3,3'-dichlorobenzidine 3,3'-dichlorobiphenyl-4,4'-ylenediamine
I	**11**	119-90-4	612-036-00-X	204-355-4	3,3'-dimethoxybenzidine o-dianisidine
L	**12**	119-93-7	612-041-00-7	204-358-0	3,3'-dimethylbenzidine 4,4'-bi-o-toluidine
M	**13**	838-88-0	612-085-00-7	212-658-8	4,4'-methylenedi-o-toluidine
N	**14**	120-71-8		204-419-1	6-methoxy-m-toluidine p-cresidine
O	**15**	101-14-4	612-078-00-9	202-918-9	4,4'-methylene-bis-(2-chloro-aniline) 2,2'-dichloro-4,4'-methylene-dianiline
P	**16**	101-80-4		202-977-0	4,4'-oxydianiline
Q	**17**	139-65-1		205-370-9	4,4'-thiodianiline
R	**18**	95-53-4	612-091-00-X	202-429-0	o-toluidine 2-aminotoluene
S	**19**	95-80-7	612-099-00-3	202-453-1	4-methyl-m-phenylenediamine
T	**20**	137-17-7		205-282-0	2,4,5-trimethylaniline
U	**21**	90-04-0	612-035-00-4	201-963-1	o-anisidine 2-methoxyaniline
Y	**22**	60-09-3	611-008-00-4	200-453-6	4-aminoazobenzene

The method EN 14362-2 is recommended in the case of synthetic fibre samples. It is based on the extraction of dyes from a weighed amount of sample material (approx. 1.0 g) with an appropriate solvent under reflux. Chlorobenzene, for instance, is recommended in the case of polyester fibres. The sample is not immersed in the extracting solvent, but it is suspended in the headspace of the extractor, so that solvent vapours extract the sample. The extract is concentrated, transferred with methanol, taken up in aqueous citrate-buffer solution and treated in an ultrasonic bath for 30 min at 70 °C in order to disperse dyes. The reductive cleavage of azo groups is

performed in the presence of aqueous sodium dithionite solution at 70 °C for 30 min without ultrasonic action. The solution is then cooled down to room temperature and transferred to t-butyl methyl ether via liquid-liquid extraction using diatomaceous earth columns. The extract is concentrated and the residue taken up to 2 ml in an appropriate solvent, such as methylterbutylether, before GC-MS analysis.

Picture 1: Various steps of method EN 14362: a) extraction; b) concentration.

Picture 2: Various steps of method EN 14362: a) reduction; b) liquid-liquid extraction using diatomaceous earth column.

Picture 3: Various steps of method EN 14362: GC-MS analysis.

The method EN 14362-1 is similar to EN 14362-2, with the exception that azodyes are reduced directly on textile samples without any previous extraction step. This method is used in the case of azodyes which are accessible to reducing agents without extraction, particularly with textiles made of cellulose and protein fibres (e.g. cotton, viscose, wool and silk).

A triple quadrupole from Varian was used for GC-MS analysis (GC model CP 3800, MS model 1200L, auto sampler model CP 8400). The instrument was employed as a single quadrupole in SCAN mode with electron impact ionisation source. The column was a DB-35MS, 60 m long, 0.25 mm internal diameter and 0.25 μm film thickness. The temperature program was the following: 60 °C (2 min) – 10 °C/min – 310 °C (9 min).

Sampling was performed by cutting five specimens, taken from different areas of each garment with the same colour, into little squares. The pieces were then mixed and part of them was weighted to prepare two replicates of about 1 gram each.

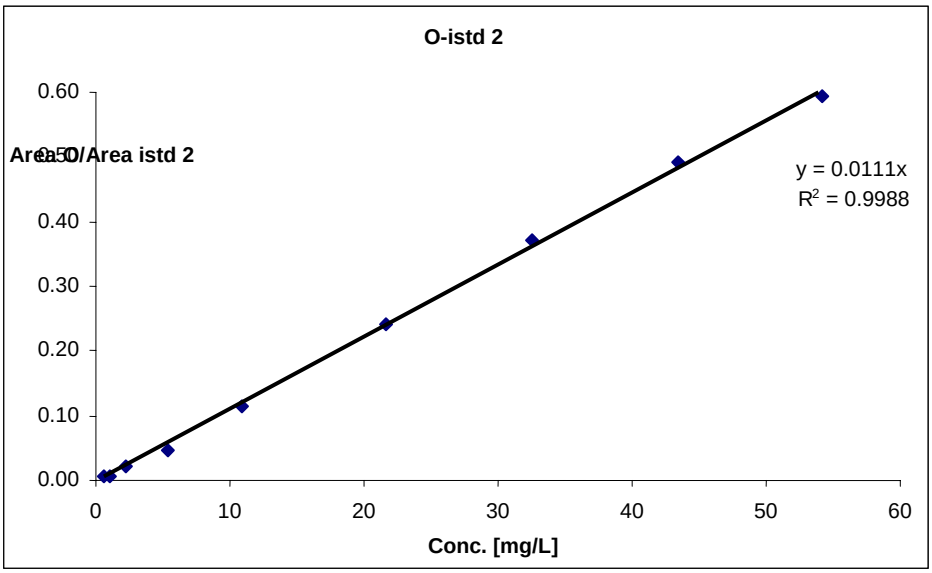


Fig. 1: Calibration curve of 4,4'-methylene-bis(2-chloroaniline) considering 2,3,5-trichloroaniline as internal standard.

A mixture of the following internal standards was added to the solution after the reduction step: naphthalene-d8 (CAS 1146-65-2), 2,4,5-trichloroaniline (CAS 636-30-6), 4-aminoquinaldine (CAS 6628-04-2) and anthracene-d10 (CAS 1719-06-8). The concentration of each internal standard in the solution to be analysed was 20 mg/l. External calibration curves were prepared in the range 0.5 to 50 mg/l, based on

ratios between amine peak areas against internal standard peak areas. As during the procedure loss of 4-aminoquinaldine was experienced, this internal standard was not considered for quantification purposes. Three calibration curves were built for each amine, based on the three remaining internal standards. The final quantitative results were obtained averaging results of two replicates based on the three calibration curves. Calibration curves generally showed a good linearity and correlation coefficients were in the range 0.987 and 0.999 (Fig. 1). Limit of quantification was generally 1 mg/kg, with the exception of few aromatic amines whose quantification limit was 2 mg/kg.

All the samples were analysed in duplicate with method EN 14362-1. The samples containing artificial or synthetic fibres in percentages higher than 20 % were also analysed using method EN 14362-2.

In the case of samples containing one or more listed aromatic amines, experiments were performed in order to evaluate the colour fastness to washing at 60 °C, the fastness to acid and basic perspiration and the fastness to acid and basic saliva.

Picture 4: a) Gyrowash apparatus; b) sample vessel for Gyrowash, grey scale, steel balls and washed specimens.

Colour fastness to washing was measured following the international standard ISO 105-C08[5] and the general principles of testing[6] and assessing change in colour[7] and staining[8]. The aim of this method is to determine the resistance of the colour of textiles to domestic or commercial laundering procedures used for normal household articles using a reference detergent incorporating a low temperature bleach activator. One specimen of about 100 mm x 40 mm is sewed to a piece of multifibre adjacent fabric[9] of equal dimensions and weighed. It is then put in a container of Gyrowash equipment, 25 steel balls are added together with liquor to give a liquor fabric

composite volume of 20:1 (see Picture 4). Test conditions foresee to increase temperature from room temperature up to 60 °C at a speed of 1.5 °C/min. The maximum temperature is then hold for 30 min. Samples are then washed, dried in air and evaluated against grey scale in order to asses the change in colour of the specimen and the staining of the adjacent fabric with reference to the original adjacent fabric. The wash liquor is prepared by dissolving 4 g of the ECE (European Colourfastness Establishment) non-phosphate reference detergent base powder, 0.15 g of tetra-acetylethylenediamine (TAED) (at 100% activity) and 1 g of sodium perborate tetrahydrate per litre of water.

Table 2: Composition of artificial perspiration solutions.

Basic Perspiration Solution	0.5 g/l $C_6H_9O_2N_3$ (L-histidine)*HCl*H_2O 5 g/l NaCl 2.5 g/l Na_2HPO_4*$2H_2O$ pH= 8.0 using a solution of NaOH 0.1 M
Acid Perspiration Solution	0.5 g/l $C_6H_9O_2N_3$ (L-histidine)*HCl*H_2O 5 g/l NaCl 2.2 g/l NaH_2PO_4*$2H_2O$ pH= 5.5 using a solution of NaOH 0.1 M

Picture 5: Perspirometer, multifibre adjacent fabric, grey scale for method EN ISO 105-E04.

Colour fastness to perspiration was measured following the international standard EN ISO 105-E04[10]. The aim of this method is to determine the resistance of the colour of textiles to the action of human sweat. One specimen of about 100 mm x 40 mm is sewed to a piece of multifibre adjacent fabric of equal dimensions and weighed. It is then put in a chrystalliser with liquor to give a liquor fabric composite volume of 50:1 and maintained at room temperature for 30 min, squeezing it from time to time to assure soaking. The composite specimen is then squeezed to eliminate the sweat simulant and put between two pre-heated plastic plates under a pressure of 12.5 kPa.

The equipment is put in oven at 37 ± 2 °C for 4 h. The specimen is then dried in air and evaluated against grey scale in order to asses the change in colour of the specimen and the staining of the adjacent fabric with reference to the original adjacent fabric. The composition of perspiration solutions is reported in Table 2.

A standard method for the determination of colour fastness to saliva is unavailable both at CEN and at ISO level. The method applied to assess colour fastness to saliva is an in-house method similar to the standard for colour fastness to domestic laundering, the only differences being the composition of simulants and the maximum temperature, which in this case is 37 °C. The change in colour and the staining of the adjacent fabric were assessed against grey scale with reference to the original specimen. The composition of acid and basic saliva simulants is reported in Table 3.

Table 3: Composition of artificial saliva solutions.

Acid Saliva Solution	4.5 g/l NaCl 0.3 g/l KCl 0.3 g/l Na_2SO_4 0.4 g/l NH_4Cl 3.0 g/l Lactic Acid 0.2 g/l Urea pH= 2.5 using a solution of NaOH 0.1 M
Basic Saliva Solution	4.2 g/l $NaHCO_3$ 0.5 g/l NaCl 0.2 g/l K_2CO_3 pH= 8.6 using a solution of NaOH 0.1 M

4. Selection of products

One of the purposes of this work was to check if the azodyes banned in textile clothing with Directive 2002/61/EC are still in use or not and if they can be found in textiles bought on the European market.

Directive 2002/61/EC states that the azodyes which, by reductive cleavage of one ore more azo groups, may release one or more of the aromatic amines listed in Table 1, in detectable concentration, i.e. above 30 mg/kg in the finished articles or in the dyed parts thereof, may not be used in textile and leather articles which may come into direct and prolonged contact with the human skin or oral cavity. The testing methods to be used for the analyses are EN 14362-1 and EN 14362-2.

In order to evaluate the current situation in Europe, textile products manufactured anywhere in the world and sold on the European market were taken into consideration. Focus was put on dermal exposure that can result from direct contact of the skin with textile products; therefore, the sampling was planned with the objective to cover as many different categories of textile clothing as possible.

Azodyes are very common dyes; indeed they represent up to 70 % of the global amount of dyes used in textile applications. They can belong to several different dyeing classes, such as for example substantive dyes for cotton, reactive dyes, acid dyes, disperse dyes, etc. For this reason they can be used in the dyeing of a large variety of fibres, both natural and synthetic fibres.

The sampling focused on coloured textile clothing that could contain azodyes for babies, children, women and men.

A total of 116 samples were purchased and analysed. Samples were bought in 24 out of 27 Member States of the European Union, Italy being the most represented for practical reasons.

Although in Europe it is not compulsory to indicate the origin on labels, whenever possible efforts were made to buy samples stating the country of production. About 22 % of samples were produced in Europe, including 4 % in Italy, 17 % in the rest of the world except China, 28 % in China and it was not possible to establish the origin for 33 % of samples.

Table 4: Purchase and production countries of samples.

	Purchase country	Production country
AT	1	
BE	3	
BG	1	
CY	2	
CZ	2	
DE	3	
DK	4	
EE	3	
EL	4	
ES	6	
FI	3	
FR	2	
HU	1	
IE	1	
IT	42	
LT	2	
LV	3	
NL	4	
PL	4	
PT	7	
SE	2	
SI	1	
SK	7	
UK	8	
Europe (except Italy)		21
Italy		5
Outside Europe (except China)		21
China		32
Unknown		37

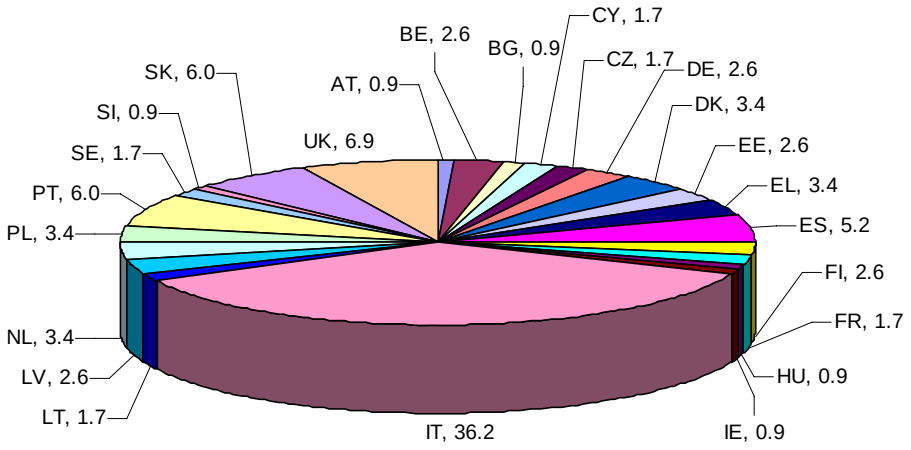


Fig 2: Proportion of samples purchased in European countries.

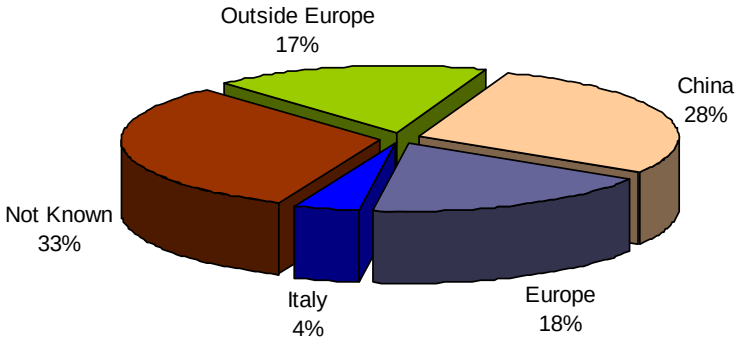


Fig 3: Proportion of samples by manufacturing geographical areas.

Due to the fact that some department stores apply a quality policy that requires producers to guarantee the absence of banned azodyes in textile products and that this could bias the results of the survey, samples were purchased from various sources including not only department stores, but also shops and open air market.

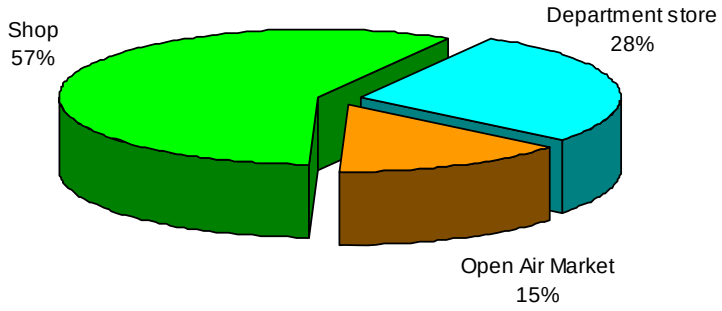


Fig 4: Proportion of samples by sources.

Considering that azodyes can be used in the dyeing of both natural and synthetic fibres, samples were chosen made of cotton, wool, polyester, polyamide, some other fibres such as acrylic, and their mixtures. Based on the composition stated on the label, samples were defined for example “cotton mix”, if cotton was the main component of the mixture.

Samples of different colours were analysed. In order of percentages of analysed samples, the considered colours were black, blue, red, brown, orange, purple, green, pink and grey.

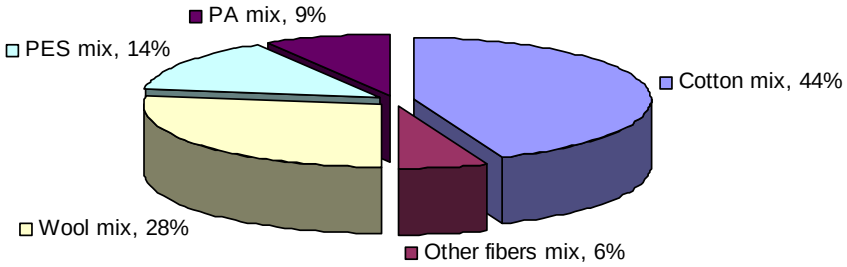


Fig 5: Proportion of samples by composition.

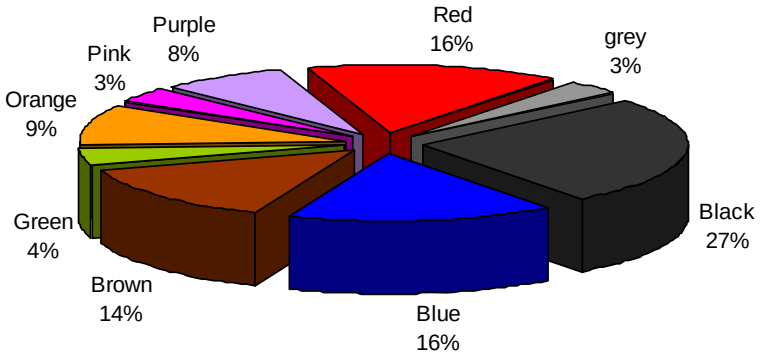


Fig 6: Proportion of samples by colour.

About 97 % of all the samples were textile clothing, while 3 % were classified as linen (bedding pillowcase and sofa cushion covers). The whole population was considered as a target, so clothing samples designed for men, women and children were analysed. With regard to children, samples were purchased both for babies under the age of two and for children up to the age of 14; in particular, 14 out of 22 samples made for children were designed for babies.

Several types of garments were taken into consideration in this study, principally articles in direct contact with the skin (such as shirts, T-shirts, underwear, socks, pyjamas, trousers and dresses) and articles like sweaters which can be either in direct contact with the skin or not, depending on the scenarios. As already mentioned cushions for sofa and bedding pillowcase were considered to represent furnishing textiles which can be in direct contact with the skin. As they were just three specimens they have not been considered in Fig. 10.

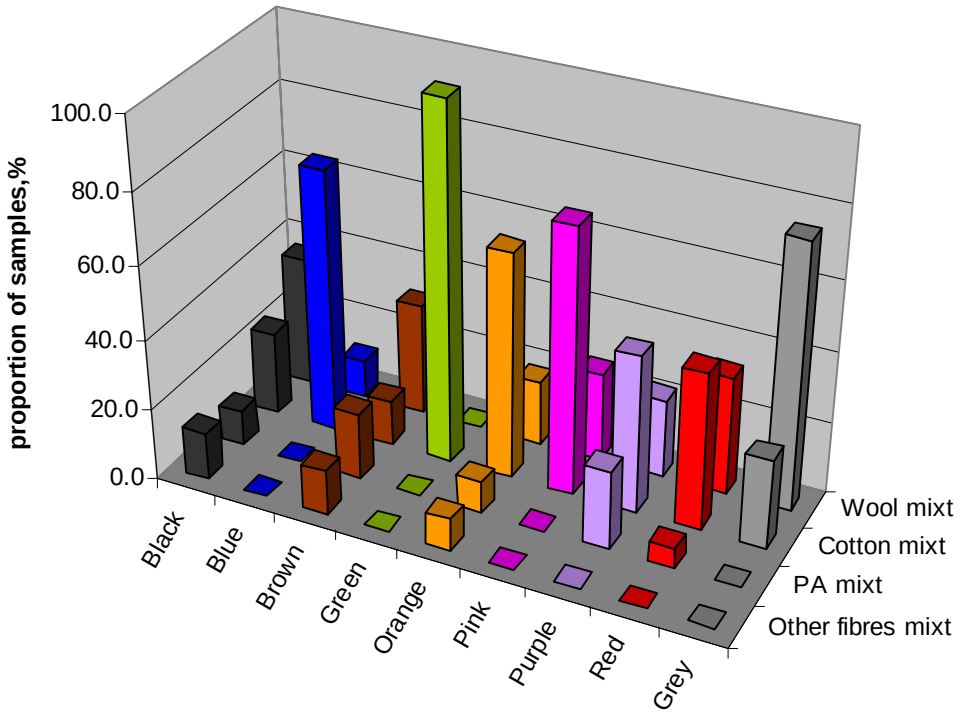


Fig 7: Composition of samples by colour.

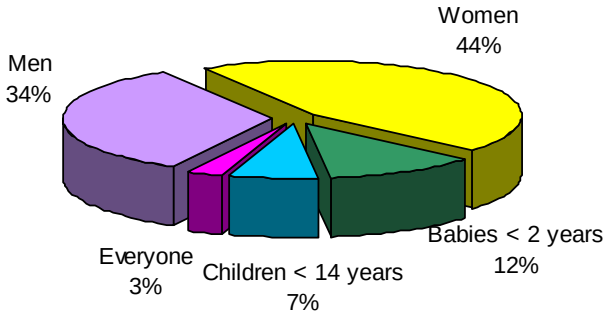


Fig 8: Proportion of samples by target population.

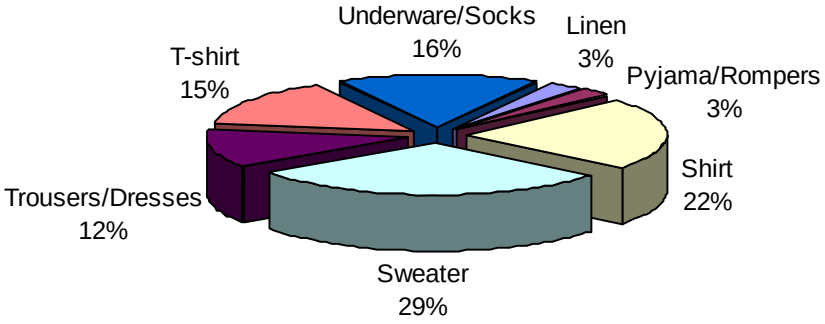


Fig 9: Proportion of samples by textile categories.

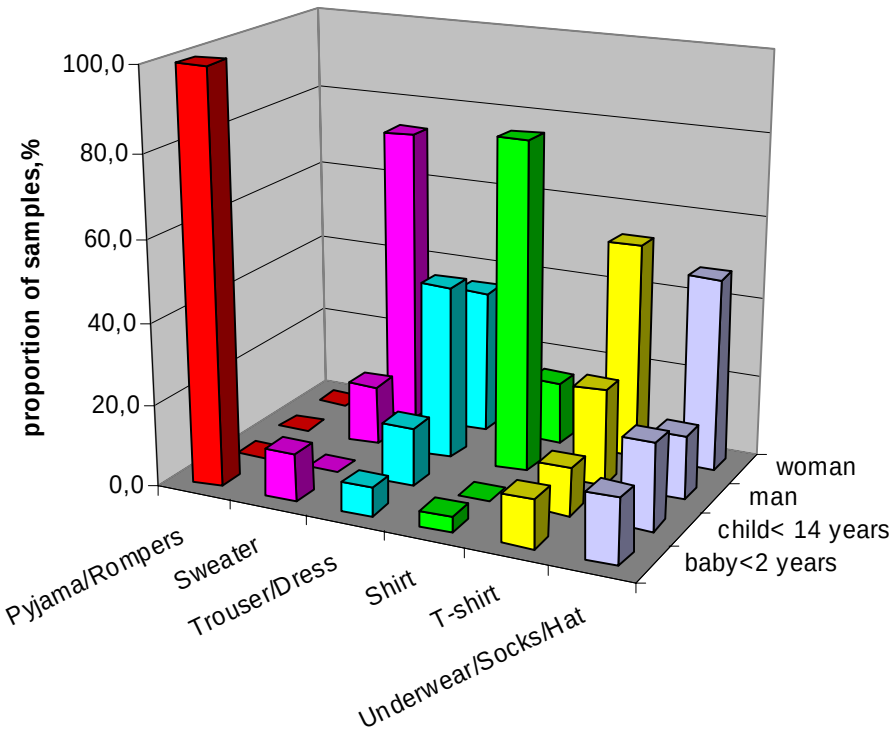


Fig 10: Proportion of samples by target population and textile categories.

5. Results and discussion

Table 1 in Annex I reports the characteristics of all samples including: photo, declared composition, colour, textile category, target population, information about printing, "easy care" or Oeko-Tex, source of purchase, country of purchase and production country. The following abbreviations were used: W (woman), M (man), B 12 m (baby 12 months old), C 3 y (child 3 years old), OAM (open air market), S (shop), DS (department store). The standard abbreviations were used for countries.

All samples (116) were analysed in duplicate with standard method EN 14362-1[3] (without extraction from fibres). Seventy-two samples, see Table 1 in Annex I, were analysed also with standard method EN 14362-2[4] (with extraction from fibres), as they were mixtures containing not only cellulose or protein fibres, such as cotton, viscose, silk and wool, but also synthetic fibres like polyester, acrylic, polyamide, etc. In this case a single measurement was performed.

Two slight deviations from the procedure described in the standard were introduced in the case of method EN 14362-1. The deviations consisted in: 1) changing the pH of the aqueous solution after the reductive cleavage to 9 by adding sodium hydroxide 0.1 M solution, in order to assure that aromatic amines were in their basic form; 2) performing the liquid-liquid extraction of aromatic amines in t-butyl methyl ether shaking in vials, instead of using the very expensive diatomaceous earth columns.

In case of positive results, samples were reanalysed in duplicate following strictly the procedure of method EN 14362-1. Using method EN 14362-1 azo colorants which were accessible to reducing agent without extraction were detected.

Results obtained with the slightly modified version of the method showed that some samples contained banned azodyes. Out of the 116 tested specimens, 13 (11.2 %) contained one or more carcinogenic aromatic amines and three of them (2.6 %) in concentrations which exceeded the limit of 30 mg/kg (see Table 6 and Fig. 11). Among the specimens which contained the listed aromatic amines, 5 of them were black, 2 were orange, one was pink, one red, one brown, one grey, one green and one blue (specimen colours are represented in Fig. 11). Concerning composition, 2 specimens were made of pure cotton, 9 of binary mixtures (5 polyester/cotton, 1 wool/cotton, 1 wool/polyester, 1 cotton/polyamide and 1 polyamide/elastane) and 2 of ternary mixtures (polyester/acrylic/cotton and polyester/cotton/viscose).

Table 5: Structure of aromatic amines derived from the azodyes banned by Directive 2002/61/EC.

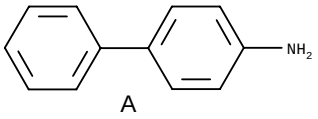
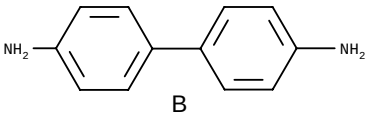
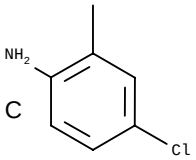
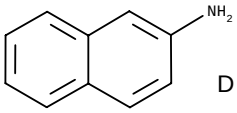
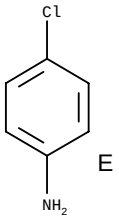
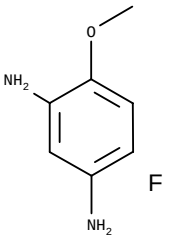
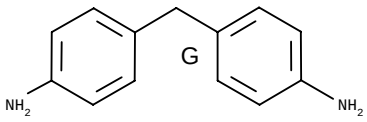
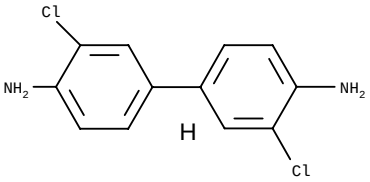
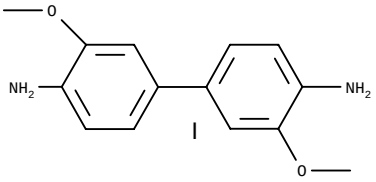
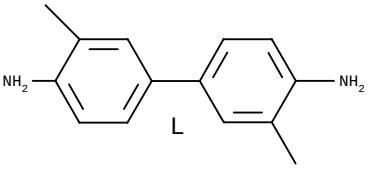
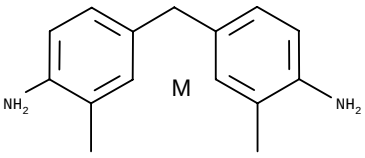
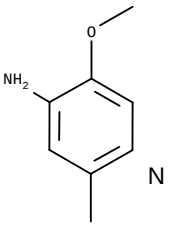
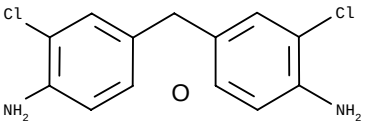
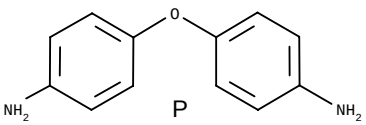
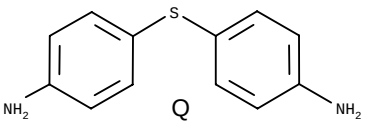
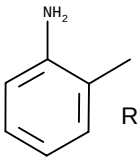
 A	 B
 C	 D
 E	 F
 G	 H
 I	 L
 M	 N
 O	 P
 Q	 R

Table 5: Structure of aromatic amines derived from the azodyes banned by Dir. 2002/61/EC (cont.).

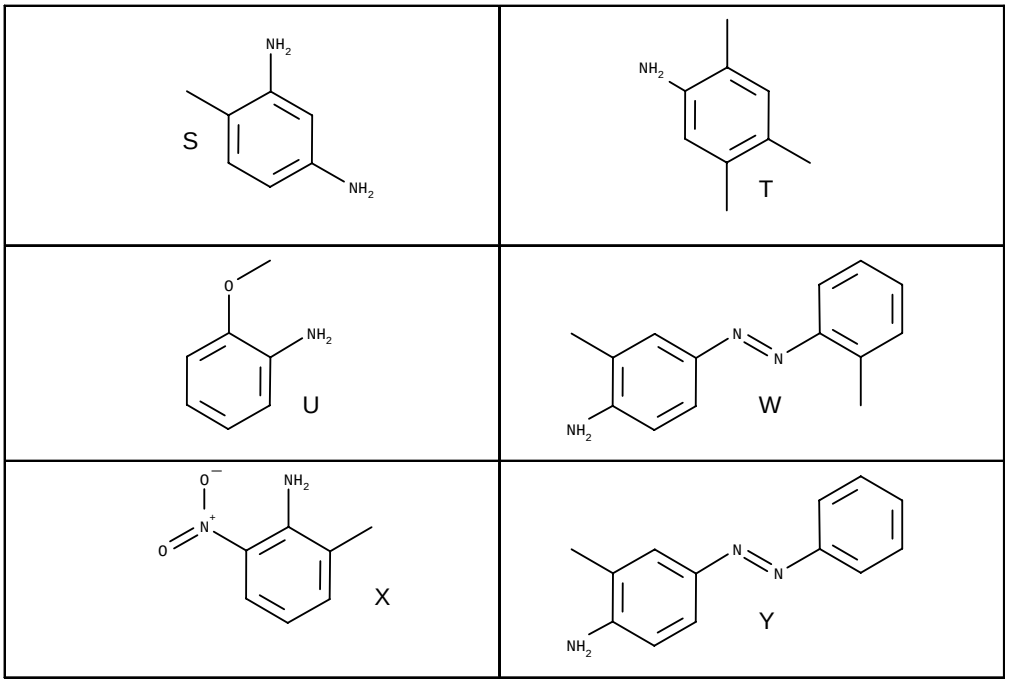


Table 6: Aromatic amines quantified by the modified version of EN 14362-1.

JRC Code	Declared Composition	Textile Category	Target	Analysed Colour	Source	Production Country	Amine	Concentration mg/kg	SD
T005	80% Wool, 20% Cotton	sweater	W	pink	OAM	China	**I**	**2.0**	**1.4**
T064	65% PES, 35% Cotton	shirt	M	red	DS	Bangladesh	**D**	**14.2**	**2.2**
T077	84% Cotton, 16% Polyamide	antislide socks	B 18 m	orange	S	IT	**O**	**4.6**	**1.0**
							Y	**10.5**	**3.0**
							W	**4.4**	**3.5**
T119	42% PES, 31% Acrylic, 27% Cotton	sofa cushion cover	EB	brown	S	UK	**O**	**4.7**	**2.9**
T148	100% Cotton	shirt	M	black	DS	Not Known	**U**	**1.0**	**0.2**
							F	**48.3**	**11.2**
T188	65% PES, 35% Cotton	shirt	M	black	S	China	**B**	**620.7**	**174.7**
							I	**57.2**	**4.5**
							U	**2.1**	**0.3**
T198	100% Cotton	shirt	M	black	S	Morocco	**E**	**2.3**	**0.4**
							F	**10.5**	**2.0**
T232	65% PES, 35% Cotton	shirt	M	black	DS	Not Known	**E**	**2.0**	**0.0**
T239	44% PES, 42% Cotton, 14% Viscose	shirt	W	black	S	PL	**O**	**5.3**	**0.9**
T288	60% Wool, 40% PES	trousers	M	grey	DS	ES	**E**	**6.0**	**0.1**
T292	70% cotton, 30% PES	shirt	M	green	S	Not Known	**I**	**46.3**	**2.9**
							U	**1.7**	**1.1**
T293	70% cotton, 30% PES	shirt	M	blue	S	Not Known	**I**	**6.4**	**3.4**
							D	**4.6**	**0.7**
T401	90% Polyamide, 10% Elastane	t-shirt	W	orange	DS	BG	**E**	**7.1**	**0.6**

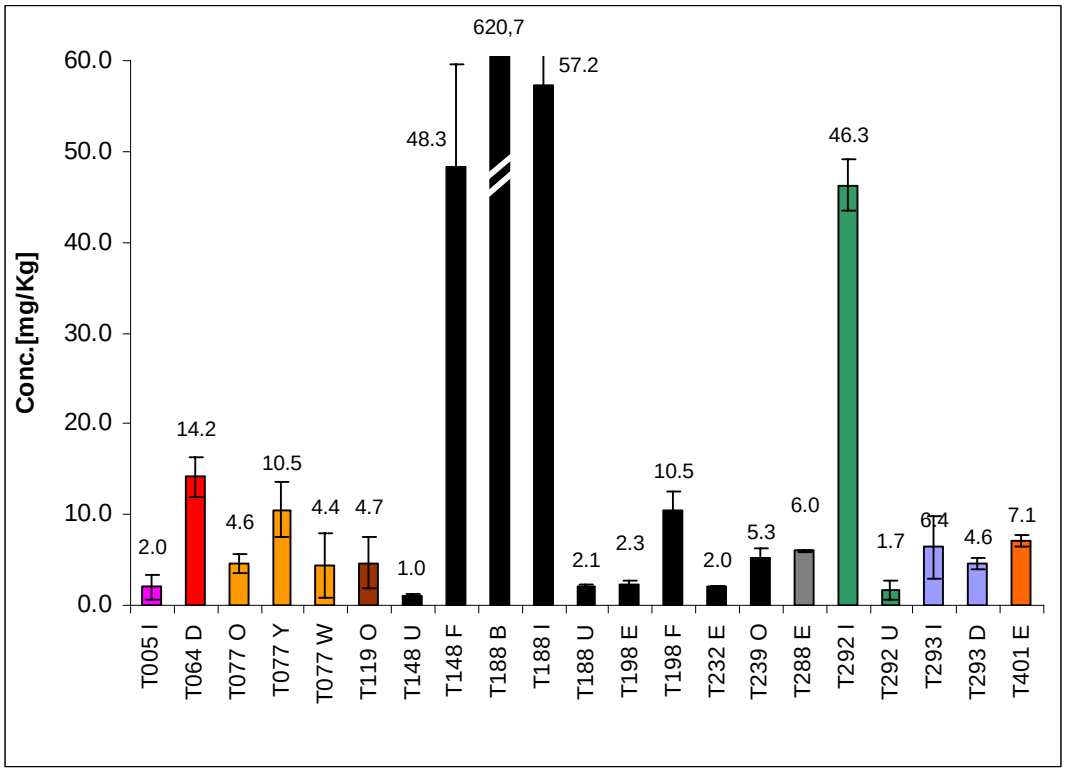


Fig. 11: Aromatic amines quantified by the modified version of EN 14362-1.

As confirmation of results, the same 13 samples were reanalysed applying the unmodified EN 14362-1. Comparison among results evidenced that some aromatic amines at low level are detectable with the modified procedure whereas they are not with the unmodified standard method and that the unmodified standard method generally gives lower results, with only few exceptions. The reason is possibly due either to some adsorption phenomena of aromatic amines onto the diatomaceous earth column or to a loss of them because if they are in their acid form they cannot be extracted efficiently from the aqueous solution.

Considering results obtained with the unmodified EN 14362-1, out of the 116 tested specimens, only 7 (6.0 %) contained one or more carcinogenic aromatic amines and three of them (2.6 %) showed concentrations which exceeded the limit of 30 mg/kg (see Table 7 and Fig. 12).

The three positive samples (T148, T188 and T292) were all shirts for man made by pure cotton or mixture cotton/polyester; they were bought in a department store in Germany and shops in Cyprus and Spain respectively. Two shirts were black and one green coloured and the production country was not known for samples T148 and

T292 and China in the case of sample T188. Samples T148 and T188 were "easy care" labelled.

Table 7: Aromatic amines quantified by EN 14362-1.

JRC Code	Declared Composition	Textile Category	Target	Analysed Colour	Source	Production Country	Amine	Concentration mg/kg	SD
T064	65% PES, 35% Cotton	shirt	M	red	DS	Bangladesh	**D**	**3.5**	**0.3**
T148	100% Cotton	shirt	M	black	DS	Not Known	**U**	**0.8**	**0.1**
							F	**25.4**	**5.8**
T188	65% PES, 35% Cotton	shirt	M	black	S	China	**B**	**434.2**	**119.9**
							I	**73.6**	**20.5**
							U	**3.8**	**0.2**
T198	100% Cotton	shirt	M	black	S	Morocco	**E**	**1.5**	**0.1**
T232	65% PES, 35% Cotton	shirt	M	black	DS	Not Known	**E**	**2.4**	**0.1**
T292	70% cotton, 30% PES	shirt	M	green	S	Not Known	**I**	**52.4**	**6.3**
							U	**1.7**	**0.4**
T293	70% cotton, 30% PET	shirt	M	blue	S	Not Known	**D**	**1.8**	**0.3**

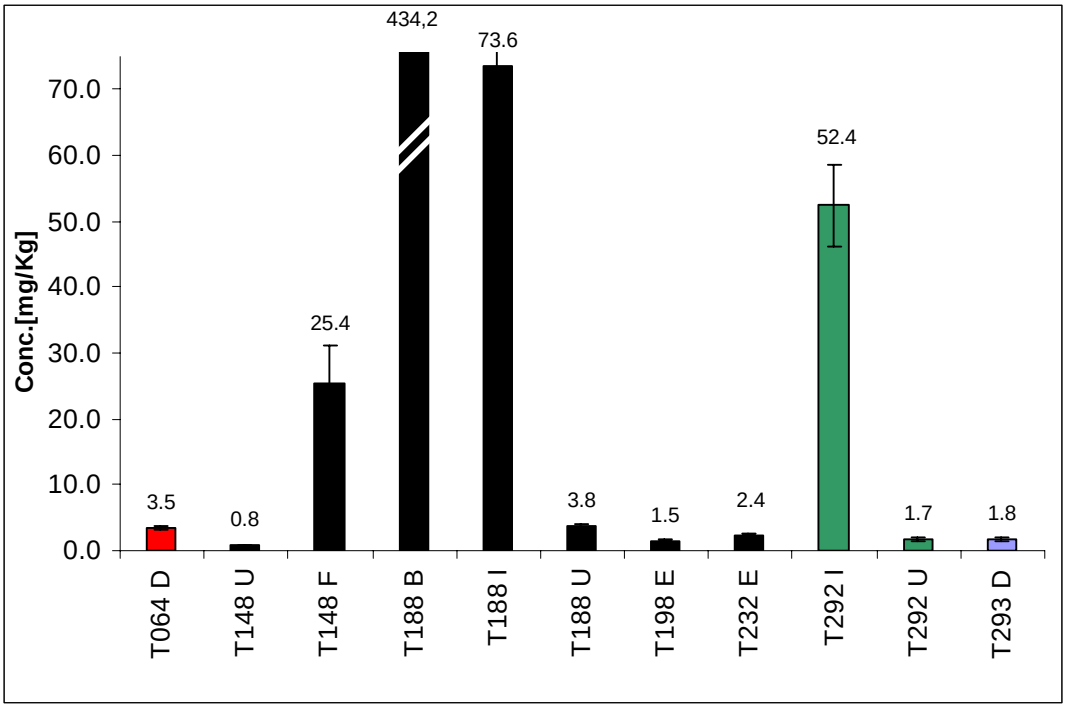


Fig. 12: Aromatic amines quantified by EN 14362-1.

In sample T148, o-anisidine (U) and 4-methoxy-m-phenylendiamine (F) were present at the level of 0.8 and 25.4 mg/kg respectively. However, the analysis conducted with the modified version of the method gave a concentration of 48.3 mg/kg for o-anisidine. Sample T188 contained two aromatic amines, benzidine (B) and 3,3'-dimethoxybenzidine (I), at levels higher than the limit (434.2 and 73.6 mg/kg respectively) and one, o-anisidine (U), at low level. Also sample T292 contained the

aromatic amine 3,3'-dimethoxybenzidine (I) in concentration higher than 30 mg/kg (52.4 mg/kg) and the amine o-anisidine (U) at the level of 1.7 mg/kg.

Seventy-two samples were also analysed with the standard method EN 14362-2 to determine azo colorants accessible by extracting the fibres, as they were mixtures containing not only cellulose or protein fibres. Out of them only sample T188 (0.9 %) contained banned azodyes, as confirmed by the presence of three listed aromatic amines. The three aromatic amines were: 4-aminobiphenyl (A), o-anisidine (U) and benzidine (B). The last one was present in concentration higher than the limit (39.0 mg/kg).

Table 8: Aromatic amines quantified by EN 14362-2.

JRC Code	Declared Composition	Textile Category	Target	Analysed Colour	Source	Production Country	Amine	Concentration mg/Kg
T188	65% PES, 35% Cotton	shirt	M	black	S	China	A	6.0
							B	39.0
							U	24.6

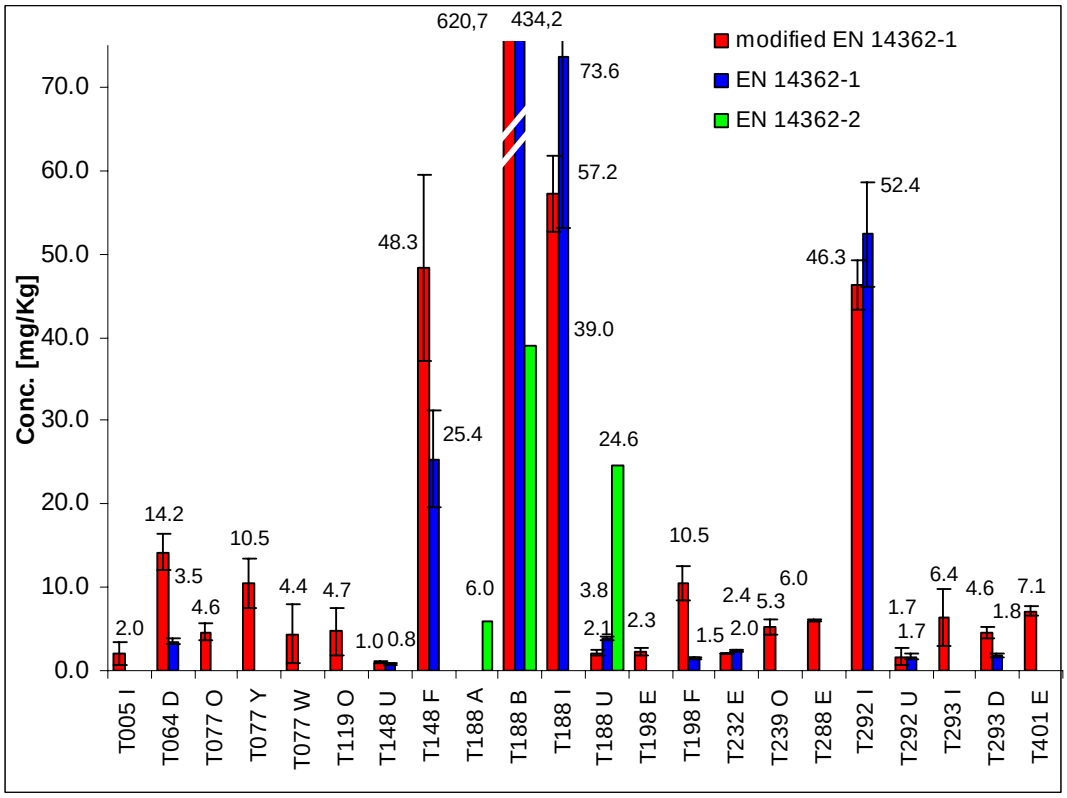


Fig. 13: Aromatic amines quantified by EN 14362 part 1 (modified and not) and 2.

Other aromatic amines, which are not carcinogenic and are not included in the list of Directive 2002/61/EC, were identified during the analysis of several samples on the

base of mass spectrum and the comparison with spectra included in the NIST library. As no external standards were available to compare retention times and the identification of isomers is rarely unequivocal when just based on mass spectra, the isomers reported in Table 9 are to be considered tentative. Semi-quantification was performed based on the calibration curves of aromatic amines of similar structure. The indication of concentration > 100 mg/kg or >> 100 mg/kg was reported in case the amine concentration was moderately of strongly out of the range of the calibration curves (1 – 100 mg/kg).

As shown in Table 9, quite many samples contained aromatic amines, 21 out of 116 which corresponds to 18%. Seven of them also contained some level of banned aromatic amines. It is remarkable that the concentration of these aromatic amines, which are not banned, was higher than 30 mg/kg in 16 cases and in 9 cases even higher 100 mg/kg.

Table 9: Other aromatic amines, tentatively identified by GC-MS and semi-quantified by EN 14362-1.

JRC code	Declared Composition	Textile Category	Target	Analysed Colour	Source	Production Country	Amine	Conc mg/Kg	Quantified on amine
007	70% Wool, 22% PA, 8% Elastane	sweater	W	red	OAM	China	2,4 Dichlorobenzenamine	3.1	C
013	55% Wool, 30% Acrylic, 15% Elastane	sweater	W	orange	OAM	Not Known	2 o-Tolyloxyaniline	71.0	P
064	65% PES, 35% Cotton	shirt	M	red	DS	Bangladesh	2 Chloro 1,4 Benzenediamine	42.1	S
065	65% PES, 35% Cotton	shirt	M	blue	DS	China	2,6 Dichloro 1,4 Benzenediamine	60.0	S
							2 o-Tolyloxyaniline	67.3	P
083	80% Acrylic, 20% PA	socks	W	black	OAM	Not Known	1,4 Naphtalenediamine	>> 100	D
119	42% PES, 31% Acrylic, 27% Cotton	sofa cushion cover	EB	brown	S	UK	2,6 Dichloro 1,4 Benzenediamine	5.3	S
148	100% Cotton	shirt	M	black	DS	Not Known	4 Methoxybenzenamine	13.5	U
							3 Methoxybenzenamine	1.7	U
							5 Amino 2 Methoxyphenol	3.3	U
188	65% PES, 35% Cotton	shirt	M	black	S	China	2 Chloro 1,4 Benzenediamine	12.3	S
							[1,1'Biphenyl]-2-Amine	6.1	A
207	100 % Wool	trousers	W	blue	S	Not Known	2 Aminobenzoic Acid	> 100	R
							5 Chloro 2 Hydroxyanilin	4.8	C
208	80% Wool, 20% PA	sweater	W	black	DS	Italy	2 Aminobenzoic Acid	> 100	R
							5 Chloro 2 Hydroxyaniline	> 100	C
209	95% Cotton, 5% Elastane	T-shirt	W	purple	DS	Turkey	2,5 Dimethoxy 4 Chlorobenzenamine	3.5	C
215	60% Wool, 40% PES	trousers	M	grey	S	HU	2 Aminobenzoic Acid	>> 100	R
230	65% PES, 35% Cotton	shirt	M	brown	S	Not Known	2,6 Dichloro 1,4 Benzenediamine	12.6	S
239	44% PES, 42% Cotton, 14% Viscose	shirt	W	black	S	PL	2 Chloro 1,4 Benzenediamine	8.0	S
281	65% PES, 35% Cotton	shirt	M	black	S	Not Known	2 Chloro 1,4 Benzenediamine	>> 100	S
							2,6 Dichloro 1,4 Benzenediamine	>> 100	S
292	70% cotton, 30% PES	shirt	M	green	S	Not Known	2,6 Dichloro 1,4 Benzenediamine	11.4	S
293	70% cotton, 30% PES	shirt	M	blue	S	Not Known	1,4 Naphtalenediamine	14.6	D
296	50% Wool, 50% Acrylic	sweater	W	blue	S	ES	4 Methoxybenzenamine	35.6	U
							2 o-Tolyloxyaniline	59.0	P
310	60% Wool, 20% Elastane, 20% PES	T-shirt	W	black	S	Not Known	2,6 Dichloro 1,4 Benzenediamine	69.8	S
316	65% PES, 35% Cotton	shirt	M	red	S	SK	4 Methoxybenzenamine	3.1	U
							2 Chloro 1,4 Benzenediamine	> 100	S
376	100% PES	underwear	W	black	S	China	2,6 Dichloro 1,4 Benzenediamine	> 100	S

The samples which contained carcinogenic aromatic amines were analysed to evaluate colour fastness to washing at 60 °C, to acid and basic perspiration at 37 °C

and to acid and basic saliva at 37 °C. Sample T077 was not analysed due to lack of material. International standard methods were used when available. In particular ISO 105-C08[5] was used in the case of colour fastness to domestic laundering and EN ISO 105-E04[10] to determine colour fastness to perspiration. In the absence of a standard method for the evaluation of colour fastness to saliva, an in-house method, described in the analytical methods chapter, was applied.

As reported in Table 10, colour degradation was completely unperceivable in almost all cases. The scale ranges from 1 to 5, 5 meaning no changes in colour. Only in very few cases colour degradation evaluated as 4 resulted from colour fastness to washing (samples T292, T293 and T401) and to saliva (samples T292 and T293). Some samples showed colour degradation of 4/5 to washing (T064) and saliva (T064 and T188). It has to be noted that samples T188 and T292 are positive samples which contained banned azodyes over the limit.

Table 10: Colour fastness to washing, perspiration and saliva (colour degradation).

	FASTNESS				
JRC Code	Basic Saliva 37 °C	Acid Saliva 37 °C	Basic Perspiration 37 °C	Acid Perspiration 37 °C	Washing 60 °C
T005	5	5	5	5	5
T064	4/5	4/5	5	5	4/5
T119	5	5	5	5	5
T148	5	5	5	5	5
T188	4/5	4/5	5	5	5
T198	5	5	5	5	5
T232	5	5	5	5	5
T239	5	5	5	5	5
T288	5	5	5	5	5
T292	4	4	5	5	4
T293	4	4	5	5	4
T401	4/5	4/5	5	5	4

Staining measured via colour fastness to washing, saliva and perspiration was evaluated using a multifibre adjacent fabric (ISO 105-F10)[9] made of wool (W), acrylic (PAN), polyester (PES), polyamide (PA), cotton (C) and acetate (CA).

Staining was measured on every adjacent fibre type. The scale ranges from 1 to 5, 5 meaning no staining on the adjacent fibre. Generally speaking, the worst staining results were obtained by washing at 60 °C and the order of staining was the following: washing > saliva > perspiration (see Tabs 11 and 12). Staining by washing ranged from 5 to 1/2, while for saliva and perspiration it ranged from 5 to 3 and from

5 to 3/4 respectively, depending on the adjacent fibres and the analysed specimen. Almost no differences were observed among results obtained with acid and basic saliva or with acid and basic perspiration simulants. The worst staining results were shown on polyamide and the adjacent fibres were generally stained in the following order: polyamide > acetate ≈ cotton > wool > polyester ≈ acrylic. The two positive samples T188 and T292 were among the worst specimens not only in what concerns colour degradation but also regarding staining, as confirmed for instance by their results on polyamide which were respectively 2 and 2 by washing, 3 and 3 with acid saliva, 3 and 4 with basic saliva, 4 and 4 with acid perspiration and 4/5 and 4 with basic perspiration. Other specimens which did show high stain on polyamide were T064, T148, T293, T288 and T401.

Table 11: Colour fastness to washing and perspiration (staining).

	STAINING																	
	Basic Perspiration 37°C						Acid Perspiration 37°C						Washing 60°C					
JRC Code	W	PAN	PES	PA	C	CA	W	PAN	PES	PA	C	CA	W	PAN	PES	PA	C	CA
T005	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
T064	5	4/5	4/5	4	4	4/5	5	5	5	3/4	4/5	4/5	4	5	4/5	2	4/5	3/4
T119	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4	5	5
T148	5	5	5	4	5	5	5	5	5	5	5	5	5	5	5	2/3	4	4/5
T188	5	5	5	4/5	5	5	5	5	5	4	4/5	5	3/4	5	4	2	2	2/3
T198	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
T232	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	5	5
T239	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	2/3	2/3	4
T288	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	2/3	5	5
T292	5	5	5	4	4/5	4/5	5	5	5	4	4/5	4/5	4/5	5	4/5	2	2/3	4
T293	4/5	5	5	4/5	4/5	4/5	4/5	5	5	4	4/5	4/5	4	5	4	2/3	4	3
T401	5	5	5	5	5	5	5	5	5	4/5	5	5	2	4/5	4	1/2	4	3/4

Table 12: Colour fastness to saliva (staining).

	STAINING											
	Basic Saliva 37°C						Acid Saliva 37°C					
JRC Code	W	PAN	PES	PA	C	CA	W	PAN	PES	PA	C	CA
T005	5	5	5	5	5	5	5	5	5	5	5	5
T064	4/5	4/5	4/5	3	4	3/4	4/5	4/5	4/5	3/4	4	3/4
T119	5	5	5	5	5	5	5	5	5	5	5	5
T148	5	5	5	4	5	4	5	5	5	4	5	4
T188	4/5	5	5	3	5	4	4/5	5	5	3	5	4
T198	5	5	5	5	5	5	5	5	5	5	5	5
T232	5	5	5	5	5	5	5	5	5	4/5	5	5
T239	5	5	5	4/5	5	4/5	5	5	5	4/5	5	4/5
T288	5	5	5	4	5	5	5	5	5	4	5	5
T292	4/5	5	5	4	4/5	4	4/5	5	5	3	4/5	4
T293	4/5	5	5	3	4/5	4	4/5	5	5	3	4/5	4
T401	5	5	4/5	3	4/5	4/5	5	5	5	3/4	5	5

In order to assess human dermal exposure to aromatic amines that can derive from banned azodyes in textiles, the following equation, used in a study made by the Danish Environmental Protection Agency[11] and taken from the European Chemical Bureau's Technical Guidance Document (TGD)[12] after modification to the exposure scenario, was considered:

$$U_{derm} = \frac{Q_{prod} * Fc_{prod} * F_{AREA,derm} * N_{event}}{BW}$$

Where:

U_{derm} is the potential uptake of the compound mg/kg bw/day

Q_{prod} is the amount of textile kg

Fc_{prod} is the fraction of compound in the textile mg/kg

$F_{AREA,derm}$ is the fraction of exposed skin

N_{event} number of exposure events per day

BW bodyweight (bw) kg

The amount of textile in this study was considered as 500 g for an adult. In fact, it has to be noted that for the assessment of dermal exposure, full coverage of the body excepting head, hands and feet is usually used. TGD considers a total body area of 19400 cm^2 for men and 16900 cm^2 for women, the average being 18150 cm^2 with an estimated area including head, neck and feet of 2981 cm^2. Considering an exposed body surface for an adult corresponding to about 85% of the total body area, that is 15000 cm^2, and a textile of 333 g/m^2, the weight of textile that covers the exposed body surface is about 500 g. In the case of a child of about one year old, the total body surface is estimated as 6700 cm^2, the exposed body surface would be about 5700 cm^2 and the weight of textile needed to cover this area is about 190 g.

Body weights of 70 kg and 10 kg for adults and children respectively were considered, as recommended in the TGD.

The potential dermal uptake should be multiplied by the absorption factor (F_{ab}) that takes the dermal absorption into consideration. However, in the absence of

information regarding this parameter, a dermal absorption of 100% was used, as suggested in the TGD.

Data on aromatic amines derived from banned azodyes obtained with the slightly modified EN 14362-1, the standard EN 14362-1 and the standard EN 14362-2 were used to estimate adult and child exposure as reported below.

Calculation example:

Adult dermal exposure: 434.2 (mg/kg) x 0.5 (kg)/ 70 (kg bw) = 4.434 mg/kg bw

Child dermal exposure: 434.2 (mg/kg) x 0.19 (kg)/ 10 (kg bw) = 11.79 mg/kg bw

Table 13: Dermal uptake of aromatic amines (modified EN 14362-1).

JRC Code	Declared Composition	Amine	Concentration mg/kg	Adult mg/kg bw	Child mg/kg bw
T005	80% Wool, 20% Cotton	**I**	2.0	0.014	0.038
T064	65% PES, 35% Cotton	**D**	14.2	0.101	0.270
T077	84% Cotton, 16% Polyamide	**O**	4.6	0.033	0.087
		Y	10.5	0.075	0.200
		W	4.4	0.031	0.084
T119	42% PES, 31% Acrylic, 27% Cotton	**O**	4.7	0.034	0.089
T148	100% Cotton	**U**	1.0	0.007	0.019
		F	48.3	**0.345**	**0.918**
T188	65% PES, 35% Cotton	**B**	620.7	**4.434**	**11.793**
		I	57.2	**0.409**	**1.087**
		U	2.1	0.015	0.040
T198	100% Cotton	**E**	2.3	0.016	0.044
		F	10.5	0.075	0.200
T232	65% PES, 35% Cotton	**E**	2.0	0.014	0.038
T239	44% PES, 42% Cotton, 14% Viscose	**O**	5.3	0.038	0.101
T288	60% Wool, 40% PES	**E**	6.0	0.043	0.114
T292	70% cotton, 30% PES	**I**	46.3	**0.331**	**0.880**
		U	1.7	0.012	0.032
T293	70% cotton, 30% PES	**I**	6.4	0.046	0.122
T401	90% Polyamide, 10% Elastane	**E**	7.1	0.051	0.135

Table 14: Dermal uptake of aromatic amines (EN 14362-1).

JRC Code	Declared Composition	Amine	Concentration mg/kg	Adult mg/kg bw	Child mg/kg bw
T064	65% PES, 35% Cotton	**D**	3.5	0.025	0.067
T148	100% Cotton	**U**	0.8	0.006	0.015
		F	25.4	0.181	0.483
T188	65% PES, 35% Cotton	**B**	434.2	**3.101**	**8.250**
		I	73.6	**0.526**	**1.398**
		U	3.8	0.027	0.072
T198	100% Cotton	**E**	1.5	0.011	0.029
T232	65% PES, 35% Cotton	**E**	2.4	0.017	0.046
T292	70% cotton, 30% PES	**I**	52.4	**0.374**	**0.996**
		U	1.7	0.012	0.032

Table 15: Dermal uptake of aromatic amines (EN 14362-2).

JRC Code	Declared Composition	Amine	Concentration mg/Kg	Adult mg/kg bw	Child mg/kg bw
T188	65% PES, 35% Cotton	**A**	6.0	0.043	0.114
		B	39.0	**0.279**	**0.741**
		U	24.6	0.176	0.467

The highest estimated dermal uptakes, based on the data obtained with the modified EN 14362-1, were 4.4 and 11.8 mg/kg bw for adult and child respectively, for an "easy care" black shirt made of a mixture polyester/cotton. The same dermal uptakes based on data obtained with the standard method EN 14362-1 were 3.1 and 8.2 mg/kg bw for an adult and a child respectively.

6. Conclusions

A European survey on the presence of banned azodyes in textiles, in particular textile clothing, produced all over the world was performed. The selection of specimens was planned among coloured textile products, in order to cover as many different types of fibres and type of fabrics as possible. Seven categories were considered: 1) trousers and dresses; 2) underwear, socks and hats; 3) sweaters; 4) rompers and pyjamas; 5) shirts; 6) T-shirts; 7) bedding pillowcases and sofa cushion covers. The whole population was considered as target, i.e. men, women, babies under the age of two and children up to 14 years old. Samples were bought in 24 Member States of the European Union, from different sources (shops, department stores and open air market), with different compositions (principally binary mixtures containing cotton ,wool, polyester or polyamide) and various production countries or areas, e.g. Europe, China, rest of the world. Part of them was printed and some were "easy care" or Oeko-Tex labelled.

A total of 116 samples were analysed in duplicate with standard method EN 14362-1 (without extraction from fibres) and 72 with standard method EN 14362-2 (in the case of azo colorants accessible by extracting the fibres). Averages and standard deviations were calculated.

Results obtained with standard method EN 14362-1 were compared with those obtained with a slightly modified version of the same method, which foresaw a basification step after the reductive cleavage and a liquid-liquid extraction of aromatic amines in t-butyl methyl ether, instead of using diatomaceous earth columns. The comparison showed that usually lower concentrations of aromatic amines were determined using the unmodified standard method.

Three samples out of 116 (2.6 %) did not comply with Directive 2002/61/EC, as they did contain some aromatic amines, derived from banned azodyes, in concentration higher than the established limit of 30 mg/kg. The three positive samples T148, T188 and T292 were all shirts for men, two black and one green coloured, made either of pure cotton or of binary mixture cotton/polyester and bought in a German department store and in shops in Cyprus and Spain. Production country was China for sample T188 and not known for the other specimens. In sample T148, analyses made with the modified version of method EN 14362-1 showed the presence of o-anisidine and 4-methoxy-m-phenylendiamine at the level of 1.0 and 48.3 mg/kg respectively.

Sample T188 was marked “easy care” and contained the following aromatic amines determined with EN 14362-1: benzidine (434.2 mg/kg), 3,3’-dimethoxybenzidine (73.6 mg/kg), o-anisidine (3.8 mg/kg). For the same sample, the analysis performed with EN 14362-2 gave the following results: benzidine (39.0 mg/kg), o-anisidine (24.6 mg/kg) and 4-aminobiphenyl (6.0 mg/kg). Sample T292 contained: 3,3’-dimethoxybenzidine (52.4 mg/kg) and o-anisidine (1.7 mg/kg), measured with EN 14362-1. Ten other samples contained some banned aromatic amines in levels lower than the limit of 30 mg/kg. Moreover several not carcinogenic and not banned aromatic amines, different from the ones listed in Directive 2002/61/EC, were detected in 21 samples. They were quantified based on calibration curves of banned aromatic amines of similar structure. Their concentration was often higher than 30 mg/kg and in certain cases even higher than 100 mg/kg.

Colour fastness to washing, perspiration and saliva was evaluated for the samples which contained some forbidden aromatic amines, in order to estimate the tendency of dyes to migrate. Results showed very high colour fastness in terms of colour degradation, except for some samples including two positive ones. Colour fastness in terms of staining was not high, in particular on polyamide. Staining was generally higher to washing at 60°C than to saliva at 37°C, the lowest staining was obtained to perspiration at 37°C. Staining by washing ranged from 5 to 1/2, while for saliva and perspiration it ranged from 5 to 3 and from 5 to 3/4 respectively, depending on the adjacent fibres and the analysed specimen. Almost no differences were observed among results obtained with acid and basic saliva or with acid and basic perspiration simulants. The three positive samples T148, T188 and T292 were among the worst specimens concerning both colour degradation and staining.

Following the recommendations of the European Chemical Bureau’s Technical Guidance Document, data were used to estimate the dermal exposure of an adult and a child. The maximum estimated dermal uptakes were 4.4 and 11.8 mg/kg bw for an adult and a child respectively, with calculation based on data obtained with the modified method EN 14362-1. The maximum estimated dermal uptakes calculated based on data obtained with the unmodified standard method EN 14362-1 were 3.1 and 8.2 mg/kg bw for an adult and a child respectively.

7. References

[1] Directive 2002/61/EC of the European Parliament and of the Council (19 July 2002) amending for the nineteenth time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (azo colourants).

[2] Council Directive 76/769/EEC (27 July 1976), on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations.

[3] EN 14362-1 (2003) Textiles – Methods for the determination of certain aromatic amines derived from azo colorants – Part 1: Detection of the use of certain azo colorants accessible without extraction.

[4] EN 14362-2 (2003) Textiles – Methods for the determination of certain aromatic amines derived from azo colorants – Part 2: Detection of the use of certain azo colorants accessible by extracting the fibres.

[5] ISO 105-C08 (2006) Textiles – Tests for colour fastness – Part C08: Colour fastness to domestic and commercial laundering using a non-phosphate reference detergent incorporating a low temperature bleach activator.

[6] EN ISO 105-A01 (1995) Textiles - Tests for colour fastness – Part A01: General principles of testing.

[7] EN ISO 20105-A02 (1994) Textiles - Tests for colour fastness – Part A02: Grey scale for assessing change in colour.

[8] EN ISO 20105-A03 (1994) Textiles - Tests for colour fastness – Part A03: Grey scale for assessing staining.

[9] ISO 105-F10 (1989) Textiles - Tests for colour fastness – Part F10: Specification for adjacent fabric: Multifibre.

[10] EN ISO 105-E04 (1996) Textiles – Tests for colour fastness – Part E04: Colour fastness to perspiration.

[11] EllebæK Laursen S., Hansen J., Drøjdahl A., Hansen O., Pommer K., Pedersen E., Bernth N., Survey of chemical compounds in textile fabrics, **23**, 2003.

[12] European Chemicals Bureau, Technical Guidance Document on Risk Assessment, 1996.

8. Annex I - Samples

Table 1: Description of samples.

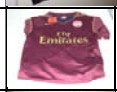
JRC Code	Picture	Declared Composition	Colour	Textile category	Target	Printed Fabric	Source	Purchase Country	Production Country	Easy Care Oeko Tex	EN 14362 Part 2
T001		80% Cotton, 20% Viscose	black	sweater	W		OAM	IT	China		
T002		60% Wool, 35% Acrylic, 5% Elastane	black	sweater	W		OAM	IT	China		Yes
T003		80% Wool, 15% Acrylic, 5% Elastane	red	sweater	W		OAM	IT	China		
T004		80% Wool, 15% Acrylic, 5% Elastane	black	sweater	W		OAM	IT	China		
T005		80% Wool, 20% Cotton	pink	sweater	W		OAM	IT	China		
T006		90% Wool (Merinos), 10% Elastane	black	sweater	W		OAM	IT	China		
T007		55% Wool, 30% Acrylic, 15% Elastane	red	sweater	W		OAM	IT	China		Yes
T011		100% Cotton	blue	sweater	M		OAM	IT	Imported		
T013		70% Wool, 22% Polyamide, 8% Elastane	orange	sweater	W		OAM	IT	Imported		Yes
T014		70% Wool, 22% Polyamide, 8% Elastane	black	sweater	W		OAM	IT	Imported		Yes
T015		70% Wool, 30% Acrylic	brown	sweater	W		S	IT	China		Yes
T016		90% Wool, 10% Elastane	red	sweater	W		S	IT	China		
T017		90% Wool, 10% Elastane	purple	sweater	W		S	IT	China		
T018		90% Wool, 10% Elastane	red	sweater	W		S	IT	China		
T019		100% Cotton	red	sweater	M		DS	IT	Turkey		
T020		100% Cotton	brown	sweater	M		DS	IT	Bangladesh		
T021		100% Cotton	green	trousers	M		DS	IT	Bangladesh		
T023		97% Cotton, 3% Elastane	orange	trousers	W		S	IT	Imported		
T024		80% Wool, 20% Polyamide	orange	sweater	W		DS	IT	China		
T025		60% Wool, 35% Acrylic, 5% Elastane	black	sweater	W		S	IT	Imported		Yes

JRC Code	Picture	Declared Composition	Colour	Textile category	Target	Printed Fabric	Source	Purchase Country	Production Country	Easy Care Oeko Tex	EN 14362 Part 2
T026		80% Wool, 15% Viscose, 5% Elastane	red	sweater	W		S	IT	China		
T027		80% Wool, 20% Viscose	purple	sweater	W		S	IT	Imported		
T028		50% Wool, 30% Angora, 20% Elastane	black	sweater	W		S	IT	China		
T029		70% Wool, 30% Polyamide	red	sweater	W		S	IT	China		Yes
T030		50% Acrylic, 40% Wool, 10% Elastane	orange	sweater	W		S	IT	China		Yes
T036		59% Cotton, 40% Polyester, 1% Elastane	blue	shirt	B 18 m		DS	IT	China		Yes
T040		100% Cotton	red	pyjama	B 12 m		DS	IT	India		
T043		80% Cotton, 15% Polyamide, 5% Elastane	red	socks	C 6-8 y		DS	IT	Syria		Yes
T047		80% Cotton, 15% Polyamide, 5% Elastane	purple	socks	C 6-8 y		DS	IT	Imported		Yes
T051		80% Cotton, 20% Polyester	blue	sweater	B 12 m	Yes	DS	IT	China		Yes
T062		65% Polyester, 35% Cotton	blue	shirt	M	Yes	DS	IT	Imported		Yes
T064		65% Polyester, 35% Cotton	red	shirt	M		DS	IT	Bangladesh		Yes
T065		65% Polyester, 35% Cotton	blue	shirt	M		DS	IT	China		Yes
T067		100% Cotton	orange	T-shirt	M		DS	IT	Bangladesh		
T074		100% Cotton	purple	T-shirt	W		DS	IT	Imported		
T077		84% Cotton, 16% Polyamide	orange	socks	B 24 m	Yes	S	IT	IT		Yes
T078		84% Cotton, 16% Polyamide	blue	socks	C 3 y	Yes	S	IT	IT		Yes
T081		85% Cotton, 15% Polyester	pink	T-shirt	C 10 y	Yes	OAM	IT	China		Yes
T083		80% Acrylic, 20% Polyamide	black	socks	W		OAM	BE	Not Known		Yes
T085		80% Cotton, 20% Polyester	blue	trousers	W		OAM	IT	China		Yes
T093		80% Cotton, 16% Polyamide, 4% Elastane	pink	underwear	C 12-14 y	Yes	OAM	BE	ES		Yes
T096		65% Cotton, 35% Polyester	blue	T-shirt	B 18 m	Yes	S	SK	Not Known		Yes

JRC Code	Picture	Declared Composition	Colour	Textile category	Target	Printed Fabric	Source	Purchase Country	Production Country	Easy Care Oeko Tex	EN 14362 Part 2
T112		100% Cotton	blue	shirt	M		S	FR	Not Known	EC	
T115		100% Cotton	gray	shirt	M		DS	FR	Turkey		
T119		42% Polyester, 31% Acrylic, 27% Cotton	brown	sofa cushion cover	EB		S	UK	UK		Yes
T128		100% Cotton	pink	shirt	M		S	BE	SK	OT / EC	
T133		100% Cotton	blue	bedding pillowcase	EB		S	EE	India	OT	
T135		100% Cotton	blue	sofa cushion cover	EB		S	PT	India		
T140		100% Cotton	orange	T-shirt	M	Yes	DS	CZ	Not Known		
T144		100% Cotton	green	shirt	M		DS	DE	Germany		
T146		100% Cotton	blue	shirt	M		DS	DE	SK	OT	
T148		100% Cotton	black	shirt	M		DS	DE	Not Known	EC	
T182		80% Polyamide, 20% Elastane	black	trousers	M		DS	IT	RO		Yes
T186		100% Cupro	black	shirt	M		S	CY	Not Known		
T188		65% Polyester, 35% Cotton	black	shirt	M		S	CY	China	EC	Yes
T191		80% Cotton, 20% Polyester	red	sweater	B 3 m		S	CZ	Not known		Yes
T198		100% Cotton	black	shirt	M	Yes	S	UK	Morocco		
T201		53% Polyester, 45% Wool, 2% Elastane	brown	trousers	W		DS	UK	China		Yes
T202		77% Cotton, 23% Polyester	red	T-shirt	B 9-12 m		S	UK	China		Yes
T206		100% Cotton	black	shirt	M		DS	DK	Turkey		
T207		100% Wool	blue	trousers	W		S	DK	Not Known		
T208		80% Wool, 20% Polyamide	black	sweater	W		DS	DK	Italy		
T209		95% Cotton, 5% Elastane	purple/white	T-shirt	W	Yes	DS	DK	Turkey		Yes
T215		60% Wool, 40% Polyester	grey	trousers	M		S	HU	HU		Yes

JRC Code	Picture	Declared Composition	Colour	Textile category	Target	Printed Fabric	Source	Purchase Country	Production Country	Easy Care Oeko Tex	EN 14362 Part 2
T220		55% Silk, 45% Cashmere	black	sweater	W		DS	PT	China		
T224		80% Cotton, 20% Polyamide	blue	rompers	B 3 m		OAM	NL	Not Known		Yes
T226		100% Cotton	red	underwear	M	Yes	OAM	NL	Not Known		
T228		100% Cotton	black	underwear	M	Yes	OAM	NL	Not Known		
T230		65% Polyester, 35% Cotton	brown	shirt	M		S	NL	Not Known		Yes
T232		65% Polyester, 35% Cotton	black	shirt	M		DS	IE	Not Known		Yes
T239		44% Polyester, 42% Cotton, 14% Viscose	black	shirt	W		S	PL	PL		Yes
T243		Wool-Polyester	black/white	trousers	W		S	PL	PL		Yes
T244		80% Acrylic, 20% Wool	brown	sweater	W		S	PL	PL		Yes
T249		80% Wool, 20% Polyamide	brown	sweater	M		S	LT	Not Known		
T250		55% Cotton, 45% Polyester	blue	shirt	M		S	LT	Not Known		Yes
T255		100% Cotton	blue	shirt	M		S	LV	DE	EC	
T256		80% Wool, 20% Acrylic	brown	sweater	M		S	LV	Oman		
T261		100% Cotton	black	underwear	B 18 m	Yes	S	LV	Turkey		
T265		100% Cotton	purple	skirt	C 4-6 y		S	EE	Not known		
T267		50% Cotton, 50% Viscose	black	T-shirt	W	Yes	S	EE	Turkey		
T274		80% Cotton, 20% Polyester	orange	sweater	B 3 m		S	EL	Not known		Yes
T276		95% Polyamide, 5% Elastane	black	underwear	W		S	EL	Not known		Yes
T277		90% Viscose, 10% Elastane	brown	T-shirt	C 10 y	Yes	S	EL	Not known		
T279		95% Cotton, 5% Elastane	orange	underwear	C 6-8 y	Yes	S	EL	China		Yes
T281		65% Polyester, 35% Cotton	black	shirt	M		S	FI	Not known	EC	Yes
T284		80% Cotton, 20% Polyester	brown	sweater	B 6 m		S	FI	China		Yes

JRC Code	Picture	Declared Composition	Colour	Textile category	Target	Printed Fabric	Source	Purchase Country	Production Country	Easy Care Oeko Tex	EN 14362 Part 2
T285		60% Wool, 38% Polyester, 2% Elastane	brown	trousers	M		S	FI	Not known		Yes
T288		60% Wool, 40% Polyester	grey	trousers	M		DS	ES	ES		Yes
T292		70% Cotton, 30% Polyester	green	shirt	M		S	ES	Not known		Yes
T293		70% Cotton, 30% Polyester	blue	shirt	M		S	ES	Not known		Yes
T294		50% Wool, 50% Acrylic	black	T-shirt	W		S	ES	ES		Yes
T296		50% Wool, 50% Acrylic	blue	sweater	W		S	ES	ES		Yes
T300		80% Cotton, 20% Polyester	blue	pyjama/rompers	B 18 m	Yes	DS	ES	China		Yes
T306		65% Cotton, 35% Polyester	red	T-shirt	W		S	SK	China		Yes
T310		60% Wool, 20% Elastane, 20% Polyester	black	T-shirt	W		S	SK	Not known		Yes
T311		75% Wool, 23% Polyamide, 2% Elastane	black	T-shirt	W		S	Sk	IT		Yes
T314		65% Cotton, 35% Polyester	orange	T-shirt	M	Yes	S	SK	Vietnam		Yes
T316		65% Polyester, 35% Cotton	red	shirt	M		S	SK	Not known	EC	Yes
T318		70% Wool, 30% Polyester	brown	trousers	M		S	SK	SK		Yes
T327		50% Wool, 50% Acrylic	black	sweater	M		S	SI	SI		Yes
T330		59% Viscose, 36% Polyester, 5% Elastane	black	underwear	M	Yes	S	AT	DE		Yes
T338		60% Cotton, 40% Polyester	green	skirt	B 12 m	Yes	S	BG	Thailand		Yes
T362		82% Polyamide, 18% Elastane	black	underwear	W		S	IT	Not known		Yes
T365		85% Cotton, 15% Polyester	red	baby gym pants	C 8 y	Yes	S	IT	China		Yes
T369		90% Polyamide, 10% Elastane	brown	shirt	W		DS	PT	BG		Yes
T372		80% Polyamide, 20% Elastane	brown	underwear	W		S	PL	Not known		Yes
T375		100% Polyester	purple	underwear	W		S	UK	China		Yes
T376		100% Polyester	black	underwear	W		S	UK	China		Yes

JRC Code	Picture	Declared Composition	Colour	Textile category	Target	Printed Fabric	Source	Purchase Country	Production Country	Easy Care Oeko Tex	EN 14362 Part 2
T379		95% Polyamide, 5% Elastane	purple	tights	W		S	UK	IT		Yes
T382		100% Polyester	red	T-shirt	M		S	UK	Thailand		Yes
T387		100% Polyester	brown	shirt	W		S	SE	Not known		Yes
T389		90% Polyamide, 10% Elastane	purple	underwear	W		S	SE	China		Yes
T395		90% Polyamide, 10% Elastane	brown	underwear	W		S	PT	Not known		Yes
T401		90% Polyamide, 10% Elastane	orange	T-shirt	W		DS	PT	BG		Yes
T402		97% Polyester, 3% Elastane	blue	shirt	W		DS	PT	Marocco		Yes
T404		90% Polyamide, 10% Elastane	red	T-shirt	W		DS	PT	BG		Yes

List of abbreviations

W	woman
M	man
B	baby
C	children
EB	everybody
S	shop
DS	department store
OAM	open air market
EC	easy care
OT	Oeko-Tex

The standard abbreviations were used for European countries.

European Commission

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Abstract
A European survey on the presence of banned azodyes in textiles, in particular textile clothing, produced all over the world was performed. The selection of fabrics was planned among coloured textile products, in order to cover as many different types of fibres and type of garments as possible. The whole population was considered as target. Samples were bought in 24 Member States of the European Union, from different sources, with different compositions and various production countries or areas. Part of them was printed and some were “easy care” or Oeko-Tex labelled. A total of 116 samples were analysed with standard method EN 14362-1 (without extraction) and 72 also with standard method EN 14362-2 (with extraction). Measurements were performed in duplicate and standard deviations were calculated.
In the case of the method without extraction, 2.6 % of samples (3 out of 116) intended to be in direct contact with skin contained over 30 mg/kg of some banned aromatic amines, which is the limit established by Directive 2002/61/EC. The highest concentration (434.2 mg/kg) was measured for benzidine. Other ten samples (8.6 %) contained some prohibited aromatic amines in levels lower than the limit. Comparison between method EN 14362-1 and a slightly modified version of it showed that generally the standard method gave lower results than the ones obtained with the modified one.
Considering the method with extraction from fibres, only one sample T188 contained some banned aromatic amines, one of which, benzidine, in concentration of 39.0 mg/kg.
Several not carcinogenic aromatic amines, different from the ones listed in Directive 2002/61/EC, were detected in 21 samples. They were quantified based on calibration curves of some banned aromatic amines of similar structure. Their concentration was often higher than 30 mg/kg and in certain cases even higher than 100 mg/kg.
Colour fastness to washing, perspiration and saliva was evaluated for the samples which contained some forbidden aromatic amines, in order to estimate the tendency of dyes to migrate. Results showed a very high colour fastness in terms of colour degradation, except for some samples including the two positive ones T188 and T292. On the contrary, colour fastness in terms of staining was not high, in particular on polyamide. Staining was generally higher to washing at 60°C than to saliva at 37°C; the lowest staining was obtained to perspiration at 37°C. Almost no differences were observed among results obtained with acid and basic saliva or with acid and basic perspiration simulants. The three positive samples T148, T188 and T292 were among the worst specimens concerning both colour degradation and staining.
Following the recommendations of the European Chemical Bureau’s Technical Guidance Document, data were used to estimate adult and child dermal exposure to carcinogenic aromatic amines. From data obtained with the EN-14362-1 standard method and the modified one, the maximum dermal uptakes evaluated in the case of a child were 8.2 and 11.8 mg/kg bw and, in the case of an adult, 3.1 and 4.4 mg/kg bw respectively.

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