

Introduction to the problems surrounding garment textiles

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Garment textiles may contain a number of chemical substances. The dyes, auxiliaries and finishing agents ensure colour fastness during washing, a stable shape or a crease-free garment. Biocides are sometimes used to obtain an anti-microbial effect. If the chemical substances used are not sufficiently bound to the textile, they may be released during wear and – depending on the scale of contact and the harmfulness of the substance – constitute a health risk. For instance allergic reactions may occur.

In the past there have been frequent reports in the media about health hazards linked to garment textiles. Consumer organisations called for the full declaration of all textile finishing agents. Already in 1993 a parliamentary question was submitted on the “Use of harmful substances in textiles” and the Enquête Committee of the 12th German Bundestag “Protection of Humans and the Environment” has addressed this issue.

Within the Federal Institute for Risk Assessment (BfR) a Textiles Working Group looks at the health hazards linked to garment textiles. It was set up in 1992 and advises BfR. The working group consists of scientists, representatives of consumers and industry as well as public agency staff. The task of the Textiles Working Group is to elaborate, from the angle of consumer health protection, statements on the hazard potential of substances used in textile garments. The following introduction to the problems surrounding garment textiles is mainly based on the results of the Textiles Working Group. It gives an overview of their assessments and recommendations.

1 Legal foundations

Under the Textile Labelling Act information need only be provided in the case of garment textiles about textile fibres but not about any auxiliaries used. Garments, including the impregnating agents and other finishing agents used in their production, are consumer articles within the intendment of the Food and Feed Act (LFGB). § 30 of this Act prohibits the manufacture or treatment of consumer products of this kind in such a way that they could harm human health. Compliance with the legal provisions is primarily the responsibility of manufacturers. The federal states, in turn, are responsible for monitoring compliance with the legal provisions. However, as the legislation does not envisage any marketing authorisation or mandatory reporting for these consumer products, the public agencies often do not have comprehensive information on these products.

The Consumer Products Ordinance (BGVO) includes a ban on the use of certain flame-retardants in garment textiles. A second amendment to BGVO on 15 July 1994 banned the use of azo dyes in garments which may form carcinogenic amines. The requirements to be met by dyes have since been laid down throughout Europe as well. According to European Directive 2002/61/EC azo dyes, which can be cleaved into one of the listed carcinogenic amines, may not exceed 30 parts per million (ppm) in products made from leather or textiles which come into direct and prolonged contact with the human skin or mucosa. According to Annex 9 of BGVO textiles whose proper use may involve contact with the skin, which have been given a finish and which contain more than 0.15% free formaldehyde should be labelled as follows, “Contains formaldehyde. It is recommended that this garment be washed before wearing for the first time to improve skin tolerance”. The Prohibited Chemicals Ordinance stipulates that products containing more than 5 mg/kg pentachlorophenol may not be placed on the market.

Hence, in the area of garment textiles there are only detailed statutory regulations for some substances which are deemed to be harmful.

The European Product Safety Directive 2001/95/EC contains general safety requirements to be met by products, including garment textiles. Amongst other things it envisages consideration of foreseeable misuse, labelling and extensive information for consumers as well as the possibility of withdrawal or recall to avoid any product-related hazards. In Germany this Directive has been transposed into national law through the Equipment and Product Safety Act.

2 Textiles Working Group

The concern that garment textiles could lead to health hazards for consumers prompted the setting up of a Textiles Working Group in 1992 within the then Federal Health Office (BGA). This working group continued its activities within the successor institute, the Federal Institute for Consumer Health Protection and Veterinary Medicine (BgVV) and is now attached to BfR. The Working Group consists of textile experts, toxicologists, dermatologists, representatives of consumers and industry and public agency staff. The Working Group pays particular attention to exposure (release of substances, consumer exposure). Given the large number of dyes, auxiliaries and finishing agents for textiles, the following topics were given priority:

- Principles for the toxicological testing of textile dyes and textile auxiliaries for garments
- Exposure assessment
- Allergic reactions
- Mutagenic and carcinogenic substances
- Dye accelerators
- Flame retardants
- Dioxins
- Fluorine surfactants
- Detergent residues and whitening agents
- Anti-bacterial finish
- Functional clothes
- Nano-finish

3 Auxiliaries and finishing agents for garment textiles

The German Catalogue of Textile Auxiliaries 2000 contains 6,972 preparations of auxiliaries and finishing agents for textiles; only some of them are used in textiles [1]. According to information from industry these preparations contain a total of approximately 600 ingredients which can be classified in various categories (Table 1). This list does not yet contain any dyes.

Table 1: Some categories of auxiliaries and finishing agents for garment textiles without reference to dyeing

Name	Chemistry	Comments
Reactant cross-linking agents	N-methylol derivatives (formaldehyde)	Shape stability, "high grade finishing"
Catalysts for above	Dialkylated tin derivatives	
Gripping agents	e.g. polymers	Up to 20% of textile product weight

Flame retardants	e.g. organophosphates	Protective clothing
Anti-microbial agents	Biocides	Footbed, socks (sanitised)
Phagodeterrents	Permethrin	Preservation (transport, storage of uniforms)
Waterproofing agents	Paraffins, fluoropolymers	Water, oil and dirt repellent
Anti-felting finish	Polymers	Wool
Conditioning agents	Oils, greases	Surface enhancement
Lustering finish	Waxes, paraffins	
Coating agents	Polymers	

3.1 Formaldehyde

Amongst the textile auxiliaries, finishing agents to improve crease and shrinking behaviour play an important role (high grade finish to improve shape stability). The applications include fibres on a cellulose basis (cotton and viscose) and their blends with synthetic fibres. Their residues in garment textiles may account for up to 8% of the textile product weight. The main auxiliaries used are synthetic resins (reactant resins containing N-methylol compounds) on a formaldehyde base which may release formaldehyde under certain conditions. In 2004 the International Agency on Research of Cancer (IARC) classified formaldehyde as a human carcinogen. This was prompted by new, very comprehensive studies in workers in the USA in whom there was an increased incidence of tumours in the naso-pharynx after exposure to formaldehyde in respiratory air. For consumers there is no risk of being exposed via respiratory air to problematic formaldehyde concentrations in garment textiles.

However, the substance formaldehyde must be regarded as an important contact allergen. In principle, it cannot be completely ruled out that even very low concentrations of formaldehyde in garment textiles may trigger allergic reactions. It is not possible to state a general threshold value that would be applicable to everyone. In 1989 the Federal Health Office conducted a survey amongst the dermatological departments of German university hospitals in order to ascertain the importance of allergic reactions to formaldehyde in garment textiles. The survey came to the conclusion that allergic reactions to formaldehyde in garment textiles had not been of any relevance in previous years. This situation has remained unchanged up to now. This is also confirmed by the results of a research project conducted by the Information Group of Dermatological Hospitals (IVDK). The conclusion there is that formaldehyde is not an allergen in the private sector and that formaldehyde-containing resins in garment textiles no longer play a role as allergens.

3.2 Glyoxal

As a consequence of the ongoing discussions about formaldehyde, substitute substances were tested in order to develop technological alternatives, in this case synthetic resins based on other aldehydes like glyoxal. Glyoxal-containing reactant type resin is used to give a shrink-free finish to some viscose and cotton fabrics (cotton velvet, viscose velvet) in a manner similar to the above-mentioned formaldehyde-based synthetic resins. However, cross-linking agents on a glyoxal basis are rarely used.

Under the Dangerous Substances Ordinance glyoxal is classified as genotoxic (category 3) and must be labelled Xn (harmful). The same applies to preparations containing 10% or more. The risk phrases prescribed as special warnings are R20 (harmful by inhalation), R36/38 (irritating to eyes and skin), R40 (possible risk of cancer), R43 (may cause sensitisation by skin contact) and R68 (possible risk of irreversible effects). In terms of its chemical structure, reactivity, molecular size and its toxicity, glyoxal is very similar to

formaldehyde. Despite its sensitising potential, there have not been any reports of textile-related allergic reactions to glyoxal in contrast to formaldehyde.

Following reports of the release of, in some cases, considerable amounts of glyoxal from certain garment textiles, the subject was discussed by the Textiles Working Group. According to information from industry, the use of glyoxal-containing cross-linking agents, which had led to the considerable release rates, is no longer considered to be state of art in the Federal Republic of Germany. The release of glyoxal from garment textiles can be assessed by analogy with formaldehyde.

3.3 Flame retardants

In contrast to many other textile auxiliaries and finishing agents, where only small quantities remain on the garment, a flame-retardant coating may account for up to 20% of product weight. In Germany textiles with a flame-retardant finish are used, amongst other things, for protective clothing at workplaces with a particularly high fire hazard. Curtains and upholstered furniture in public areas and car interior furnishings may also be treated with flame-retardants. There are flame-retardant modified polyester fibres which involve practically no exposure of the user to flame retardants. There are also permanent flame retardants made of fibre-active compounds where exposure is assumed to be minor. Some substances involving health risks are also used as semi-permanent flame retardants. Under the Consumer Products Ordinance tri-(t,3-dibromo-propyl)-phosphate (TRIS), tris-(aziridinyl)-phosphine oxide (TEPA) and polybrominated biphenyls (PBB) are banned. Considerable exposure is to be expected when wearing garments with a non-permanent finish. According to the information available to BfR only safe salt products with low skin absorption are used in Germany. They include, for instance, ammonium sulphate, amidosulphonic acid and borax.

In the United Kingdom nightwear and mattresses for children are often given a flame-retardant finish. In scientific publications in the UK there has been some speculation about a possible association between the use of antimony trioxide as a flame retardant in mattresses and sudden infant death syndrome. However, an association of this nature has not been confirmed and is not at all plausible. In the opinion of BfR, however, no flame retardants should be applied to textiles for private use (garments, home fabrics and toys). Or at the very least products of this kind should be labelled accordingly.

The European Standard 71-2 for Textile Toys already includes a test for flammability. The European Committee for Standardisation is also elaborating requirements of this kind for children's nightwear (DIN EN 14878, draft). There are fears that adoption of the standard will lead to an increase in the use of flame retardants in Germany, too.

3.4 Dye accelerators (carriers)

Dye accelerators (carriers) are organic solvents which are used in the dyeing of chemical fibres (polyester, acetate, polyacryl nitrile, polyamide) with disperse dyes as the auxiliaries. They enable the dyes to penetrate the fibres more quickly. Colouring with disperse dyes is of major relevance for the most important chemical fibre for the garment industry in terms of volume, polyester (polyethylene glycol terephthalate). Dyeing is either done with the aid of carriers at 95 °C or under high temperature conditions (HT) at 130 °C. In principle, carriers are not needed for HT dyeing; nevertheless, they are used in small quantities as levelling agents to achieve uniform dyeing. Carriers are also used for dyeing polyester blend fabrics as temperatures have to be limited to 110-115°C because of the wool component.

Depending on the substance and dyeing system, the residual content after dyeing is between 4.9 and 36.5 g/kg fibre. The carrier content may be reduced by various forms of after-treatment but complete elimination is practically impossible. The carrier concentration is less than 0.2% if dyeing has been performed in accordance with state of the art; otherwise levels of up to 2.7% on the textile cannot be ruled out. Amongst the chemicals used as carriers 1,2,4-trichlorobenzene in particular must be rejected. In Germany the view is held that the use of this substance as a carrier no longer corresponds to state of the art. The advisory panel on environmentally relevant substances of the Society of German Chemists (GDCh) already appealed to the textile industry years ago to stop using trichlorobenzenes and received undertakings to that effect. The environmental criteria for awarding the EC eco-label for bed linen and t-shirts specify that halogenated dye accelerators may no longer be used (96/304/EC, Official Journal of the European Communities of 11 May 1996). The quality requirements of various organisations specify that trichlorobenzene should not be detectable either (e.g. Öko-Tex 100, RAL, Tox Proof, Öko-Info DTB). In the opinion of BfR the use of 1,2,4-trichlorobenzene as a carrier for garment textiles is not without health risks and should be banned throughout the EU.

3.5 Whitening agents

Whitening agents (optical brighteners, fluorescent brighteners) aim to give the fabric a bright, white appearance through fluorescence. Their effect is based on the absorption of UV rays and their conversion into blue light which is then emitted. The substances used include derivatives of diaminostilbendisulphonic acid (stilbene derivatives), pyrazoline derivatives, coumarin derivatives, benzoxazol derivatives, naphthalimide derivatives, distyrylbiphenyl sulphonate derivatives and pyrene derivatives. Whitening agents are used firstly as textile finishing agents but also on a large scale as ingredients in detergents. Only those compounds which have a high substrate affinity are suitable technically. The group of whitening agents encompasses several hundred substances. Besides distyryl derivatives, the triazinyl flavonates are of economic importance. The former BgVV undertook a health assessment of three economically relevant whitening agents: CI Fluorescent Brightener 220, CI Fluorescent Brightener 260 and distyrylbiphenyl sulphonate [2].

Detergents may contain up to 0.2 % whitening agents, correspondingly finished or washed textiles a maximum 0.5 %. No information is available on the amounts released during wear or absorbed through the skin. However, because of the high molecular weight of the two compounds CI Fluorescent Brightener 220 and CI Fluorescent Brightener 260, there is no significant risk of relevant systemic exposure. For the substance distyrylbiphenyl sulphonate there is a sufficient margin of exposure between the estimated systemic uptake under wear conditions and the biological action concentration identified in animal experiments. 4,4'-diamino-2,2'-stilbene disulphonic acid (DAS) is a by-product of the synthesis of various whitening agents. In its chemical parent structure it has a structural element of the synthetic oestrogen, diethylstilbestrol. In *in vitro* studies this substance did not show any or only a minor hormone impact as oestrogen. In *in vivo* studies, the results of which are of more relevance for risk assessment in humans, have still to be conducted.

3.6 Organotin compounds

In recent years there have been repeated reports of organotin compounds in garment textiles. Organotin compounds, in particular tributyltin (TBT) compounds have an antimicrobial effect. Monotin and dialkylated tin derivatives are used as stabilisers in PVC for coatings, applications and prints on textiles. According to the current German Catalogue of Textile Auxiliaries 2000 three textile auxiliaries are commercially available which contain

organotin compounds. However, they are not used to give a biocide finish to textiles but to provide material protection for heavy textiles like tarpaulins, marquees and tents. According to information from the manufacturers a TBT content of 0.1 % (i.e. 1 g/kg) must be achieved in order to produce an anti-microbial effect. High levels on this scale have not been detected up to now in the measurements of textiles undertaken by various offices. For instance the TBT level in the padding of cycling shorts was 110 mg/kg (equivalent to 0.011 %); in a Dutch study on organotin compounds in textiles a maximum level of 13.2 mg/kg was measured [3].

In studies on the migration of TBT from textiles, 5% TBT could be detected in the eluate of a perspiration test solution. It is, however, likely that the level of release falls with repeated use which means that an average exposure of 1% is plausible [4]. According to estimates of internal consumer exposure whilst wearing textiles of this kind, there is no health hazard. In the context the general reduction in exposure to organotin compounds, they should still not be used in textiles. The use of TBT for the biocidal finishing of garments also goes against manufacturers' recommendations and must, therefore, be interpreted as misuse.

3.7 Sunscreen filter substances

Properties of use like colour fastness or tear resistance of polyurethane and polyester fibres can be impaired through the influence of UV rays via photochemical reactions. UV absorbers which convert UV rays into longer wave rays like light or heat are, therefore, used to protect the fibres and dyes.

Furthermore, garment textiles are explicitly finished with UV-absorbing substances in order to reduce consumer exposure to UV rays. The UV permeability of textiles depends on fibre material, porosity, thickness of the textile surface, the dye used and colour intensity. Generally speaking, synthetic fibres like polyester absorb more UV radiation than natural fibres like cotton. The main area of use of a finishing treatment with UV-absorbing substances is, therefore, cotton textiles. The active substance is bound covalently to the fibres similar to the reactive dyes; the levels are between 0.2 and 0.8 %. In the case of viscose UV absorption can be achieved through pigmentation with titanium dioxide; UV absorbers have been developed for polyester which – similar to the disperse dyes – are applied to the tissue. At the present time special detergents are being developed to apply these active substances to garments.

In accordance with the EN 13758-1 Standard on the permeability of UV radiation, the protective properties against ultra-violet solar radiation are determined between 290 and 400 nm and are given as an ultraviolet protection factor UPF.

3.8 Perfluorinated polymers

Perfluorinated polymers (fluoropolymers) are known for their water-repellent and oil-repellent properties and are, therefore, used to finish textiles, particularly for waterproof clothing. Because of the possible residual content of perfluoro-octane sulphonate (PFOS) and perfluorooctanoic acid (PFOA) in fluoropolymers, the persistence and ubiquitous occurrence of PFOS and PFOA, this category of compounds has moved centre stage of public interest.

According to information from trade associations neither PFOS nor PFOA is used in the main production method today, telomerisation. The substances do not occur either as by-products or end products in this process. Generally speaking, no fluorinated monomer substances are used in textile enhancement but polymers with a molecular weight (MW) > 20,000 Dalton, so-called fluoropolymers or fluorocarbon resins.

In the case of telomerisation perfluorinated C2 parent structures (tetrafluoroethylene) are converted to perfluoroalkyl iodides, the chain is lengthened through the addition of other tetrafluoroethylene units (telomerised) and finally converted with ethylene to perfluoroalkyl alcohols, so-called telomer alcohols (FTOH). This leads to the formation of linear chains whose length is determined by the number of parent substances added and always has an even number of C-atoms. Normally between three and six parent substances are added which means that the number of fluorinated C-atoms is as a rule between six and twelve. The terminal, fluorine-free ethyl group is then derivatised into various reactive intermediate products, e.g. into acrylates, methacrylates or polyurethanes.

A second method is electrofluorination. In this process organic parent substances are dissolved in hydrofluoric acid (HA) and the H-atoms in the substance are exchanged for fluorine by applying an electric current. The starting substances are C4 parent substances which are converted to perfluorobutanoic sulphonic acid and then used to produce other fluorine surfactants. No details are known about the method. A method involving C8 parent substances leading to the formation of PFOS and PFOA was withdrawn by the market leader on his own initiative in 2000. The fluorocarbon resins on the basis of RTOH used in the textile industry consist of a reactive parent structure with perfluoroalkyl monomers and alkyl monomers as the side chains. As a rule the polymer contains 20-50 weight % fluorine and is commercially available as an aqueous dispersion with a polymer content of 20-100 g/L. Dispersion, the last step in the finishing process, is mainly applied using a foulard to the textile. Fixing is done by means of a covalent bond (cross-linking) to the fibres in a tenter at 120-180 °C. The typical amounts of polymer applied to the fibres are 0.2 - 0.5 weight % which means that the fabric then contains 0.04 – 0.25 weight % fluorine.

Toxicological data indicate that the polymer is of little dermatological relevance firstly because of the rigid binding to the fibres and secondly because of the high molecular weight. In the case of oral intake there is no metabolism. Toxicological data and exposure calculations are available for PFOA in the literature which were undertaken on the basis of the maximum extractable content of the substance from treated textiles (various extraction agents) and a skin penetration rate for perfluorooctanoic acid [5]. Based on these data the annual uptake from garment textiles, calculated for various groups in the population, is far lower than the values which are assumed as the threshold values for toxicological effects. The margin of exposure (MOE) is 10^6 - 10^8 .

During telomerisation a mixture is formed of fluorotelomer alcohols of varying chain lengths. The most frequently found component consists of four tetrafluoroethylene units. In line with the number of fluorinated and non-fluorinated C-atoms it is called 8:2 FTOH. Toxicological data and information from impregnated textiles on extracted volumes (extraction agent: water or ethylacetate) are available in the literature both for the mixtures and for the individual component 8:2 FTOH. These data are the basis for an exposure and risk assessment which has been published [5]. The calculation model is based on brand new textiles in which the mean contents extractable with ethylacetate are 27 ng/cm² for total FTOH and 22 ng/cm² for 8:2 FTOH; approximately 10 % can reach the skin. The assumed penetration rate is 0.14 % per hour (h). With an exposure of 12 h/day and a wear frequency of 365 days a year, this leads – calculated for the entire skin surface (child, adolescent, adult) - to intakes of 8:2 FTOH of 9×10^{-6} up to 10^{-5} mg/kg and day and to intakes of total FTOH of around 10^{-5} mg/kg and day. This results in values for the margin of exposure of around 10^5 . Based on the calculation of aqueous extraction values, the absorbed amounts are far lower and the MOE is approximately 10^7 . The model is based on conservative assumptions.

The model calculation was also used to estimate possible exposure to PFOA. Here a conversion rate of 1 % was used to convert FTOH to PFOA. Both were carcinogenic and for non-carcinogenic effects this led to values for the MOE of at least 4×10^7 in conjunction with extraction with ethylacetate and 9×10^8 using water as the extraction agent. This leads to a good correlation in terms of scale of the model calculation presented with exposure from other published data. When impregnation is carried out properly there does not seem to be any hazard for consumers because of the low migration rates. However, difficulties are encountered when it comes to converting general exposure to serum values. Furthermore, there is a need for more elucidation about the relatively high PFOA values in serum in humans described in the literature. A possible disproportionate accumulation, particularly at low concentrations, was discussed in the literature. In the meantime the EU has adopted Directive 2006/122/EC which has introduced extensive constraints for the placing on the market and use of PFOS.

3.9 Biocide finish

For a long time the finishing of technical textiles and material protection were to the fore in conjunction with biocidal finishing. Because of increased awareness about hygiene, however, textiles worn next to the skin are also increasingly being given this finish. The application areas for textiles with an anti-microbial finish are sports and leisure wear for outdoors but also textiles for personal protection, medical products like bandages, technical textiles, curtains, carpets and mattresses.

In textiles the main action is to prevent the decomposition of perspiration by bacteria and to counteract odour development. The requirements to be met by an anti-microbial finish are skin tolerance, toxicological safety and stability under conditions of use as well as a clearly proven effect in the final product. In addition, bacterial skin colonisation may not be negatively impaired by wearing garments of this kind. Active anti-microbial substances normally have a non-specific effect: for instance they impair cell wall structures, inhibit enzymes or denature proteins.

The most commonly used substances are metal ions, in particular silver ions, quaternary ammonium salts, chitosan compounds, isothiazolinones and, above all, triclosan. The anti-microbial effect of these substances can be impaired by processing methods and interaction with other textile auxiliaries and dyes. An anti-microbial finish is frequently achieved by post-processing of the textiles in an application bath. In the case of synthetic fibres it is also possible to integrate the active substances prior to spinning. More recent methods are based on the permanent fixing of supramolecules (e.g. cyclodextrins) on the textile surface which in turn can bind and incorporate active substances. This technique opens up diverse opportunities for textile finishing.

Active anti-microbial substances are subject to statutory regulation. In Europe the Biocides Directive has been transposed into national law, too. According to this Biocides Act, biocides products must go through an authorisation procedure. This authorisation procedure will impact on new future biocide products. In the case of biocide products, which were placed on the market prior to 14 May 2000, the EU-wide collection, categorisation and assessment is under way up to 2010. The goal is to list the active substances in an annex to the Biocide Product Directive. Inclusion in this annex is the precondition for the later authorisation of a biocide product. There are specific regulations for low risk products which merely have to undergo a registration procedure.

Besides possible allergic reactions and a possible impairment of the skin's own bacterial population, resistance development is the biggest problem of textiles with an antibacterial finish. The growing use of biocide substances in the home prompts fears of the selection of resistant germs. There have already been reports in the literature [6] about multiple antibiotic resistance as a consequence of the selection of triclosan, a very frequently used active substance. When it comes to the anti-microbial finish to textiles, the risks and benefits should be carefully weighed up against one another. More particularly no triclosan should be used [7]. Active biocide substances should always be declared.

3.10 Dioxins

In a study [8] the dioxin levels were determined as the sum of chlorinated dibenzodioxins and dibenzofurans in new textiles, mainly cotton products. In one of the samples the maximum levels specified in the Chemical Ban Ordinance for this substance group were exceeded. The main share of the chlorinated benzodioxins and benzofurans found in the respective textiles consisted of higher chlorinated compounds (heptachlorinated and octachlorinated HpCDFs, HpCDDs, OCDF and above all OCDD), which have been assigned a toxicity equivalence factor of only 0.001 (compared with the toxicity equivalence factor 1 assigned to the Seveso dioxin TCDD). Although it was demonstrated that these substances are partly transferred to the skin when wearing contaminated garments, they could only be detected in the outermost layers of the skin. From there the substances are largely eliminated via the scales of the skin. The internal exposure of the consumer wearing these garments is low and there is no health risk. However, the relatively high dioxin levels found in individual garments are technically avoidable. They are not acceptable given the overall objective of minimising dioxin exposure.

In principle there are several possible dioxin sources: organochlorine carriers, certain dyes, some pesticides and pentachlorophenol whereby mention should be made here for instance of their use in layers (substances to treat yarn, in order to improve its properties during weaving and to protect against mechanical stress) and their use as transport preservatives in tropical countries. The use of pentachlorophenol in leather, which also leads to dioxin contamination, should be mentioned too.

4 Dyes

Dyes are the most importance group of substances used in textiles. Textile dyes may be classified by their solubility, chemistry or the dyeing process used. When classification is based on solubility, a distinction is made between two groups: dyes which are deemed to be soluble in the application medium and not readily or insoluble pigments. It is assumed that pigments are not absorbed through the skin as long as they are not readily soluble (solubility < 1 mg/l).

When classification is by colouring groups (chromophores), i.e. from the chemical angle, a distinction is made between azo dyes, anthroquinone dyes, metal complex dyes and others.

The classification of dyes for textiles by the dyeing process is also useful from the health angle (Table 2). Water-soluble direct dyes are bound to the fibres by deposition in cavities. However this binding is not very strong which means that the colour fastness of textiles dyed in this way is only moderate. As a rule, however water-soluble direct dyes are generally characterised by low absorption through the skin. Water-soluble reactive dyes, in contrast, are firmly bound to the fibre by means of a covalent bond which means that there is no significant exposure of the consumer as long as dyeing and after-treatment have been performed properly. Disperse dyes are lipophilic substances which are dissolved in the

chemical fibre. For technical reasons, only small molecules with a required water solubility of approximately 30 mg per litre are suitable. Additional organic solvents (dye accelerators, carriers) are used. If this dyeing is not done in accordance with state of the art, e.g. over-dyeing, wrong textile substrate or incomplete removal of the carriers, there may be higher exposure to dyes and carriers when wearing garments dyed in this way. Given their properties (small molecular size, high lipophilicity) and the fact that disperse dyes and carriers are lipophilic substances, some of them are easily absorbed through the skin which means that health risks cannot be ruled out.

Table 2: Dyes and auxiliaries for dyeing

Name	Chemistry	Dyeing principle, function
Dye		
Reactant-type dyes	Water-soluble	Covalent binding to the fibres
Disperse dyes	Lipophilic azo dyes	Balanced distribution, carriers, chemical fibres
Acid and base dyes		Binding via ion exchange
Mordant agents		Fixation via chromium salts
Direct dyes	Water-soluble	Deposition in cavities
Vat dyes	Anthraquinones	Redox dyeing process, high degree of fastness in use
Sulphur dyes		
Development dyes (naphthols)	Azo dyes	Diazotised amine, coupled on fibre
Pigments	Azo dyes, anthraquinones	Not readily soluble
Dyeing auxiliaries		
Dye accelerators (carriers)	Aromatics	Chemical fibres, disperse dyes
Levelling agents	Surfactants	Uniform coloration
Crease prevention agents	Polyglycol ethers	
After-treatment agents	Surfactants, resins	Colour fastness
Binding agents	Copolymers	Pigment dyeing
Thickening agents	Copolymers	Pigment printing
Dispersing agents	Polymers, surfactants	Pigment dyeing
Fixation accelerators	Oxethylates	Pigment printing

Dyes are the most important group of substances used in textiles when it comes to possible health risks. In a European research project data were compiled on the mutagenic effect of 281 dyes, in some cases from unpublished information sources of the manufacturers. 14 of them were classified as mutagenic; for 25 % (71 textile dyes) the available data were not sufficient in order to assess a possible mutagenic effect. Overall the proportion of problematic substances amongst the textile dyes used is estimated to be 10 % [9].

Of the 4,000 or so dyes listed in the Colour Index, about one half are azo dyes. They are, therefore, by far the most important group of dyes. Quite a few of these azo dyes (approximately 500) are manufactured on the basis of carcinogenic amines, and some of them (approximately 150) are still commercially available today. After intake into the human body these azo compounds may be cleaved by means of reduction during metabolism and then form the corresponding aromatic amines from which they had been synthesised. Intestinal bacteria are capable of azo cleaving but the liver also produces corresponding enzymes. Furthermore, there are indications from experiments that azo cleavage may also take place during skin passage and that skin bacteria are capable of cleaving azo dyes [10]. These findings have led to the treatment of all azo dyes in line with the corresponding amine component in occupational health and safety rules. The TRGS 614 (Technical Rules for Dangerous Substances) sets out comprehensive limitations on the use of soluble azo dyes in the application medium, which can be cleaved into carcinogenic aromatic amines.

As far as BfR knows, around 800 dyes are used in textiles. The German industry has long since abandoned the use of azo dyes which can cleave into carcinogenic aromatic amines. However it must be assumed that problematic dyes of this nature may be contained in some imported textiles, particularly from non-EU member states. In such cases the ban on the application of such dyes specified in the Consumer Products Ordinance and European Directive 2002/61/EC applies. This means that no textiles treated with dyes of this kind may be placed on the market if the limit values are exceeded.

5 Allergic reactions to textiles

Intolerance reactions to wool may occur when wearing textiles. However, real allergic reactions are relatively rare [11-14]. In German dermatological clinics contact allergies are attributed in around 1-2% of the cases to textiles. There have been reports of allergic reactions to all groups of textile auxiliaries and dyes. In Germany, however, it is mainly dyes which are of relevance for textile-related contact allergies. Certain disperse dyes in particular have been identified as the trigger. In this context, skin-tight garments made of chemical fibres constitute a special hazard potential. Under the heading "stocking dye allergy", this phenomenon was described in the literature in the 1970s; in the 1990s the so-called "leggings allergy" was described. What is important is the fastness of the dye. Particularly where perspiration fastness is inadequate, the dye may leach during wear. In the case of allergy-triggering dyes, this may cause contact dermatitis.

In conjunction with textile-induced dermatitis 49 dyes are described as contact allergens and about two-thirds of them are disperse dyes [15-19]. After evaluation of the literature on this subject and discussions within the Textiles Working Group, BgVV identified eight dyes at that time which should no longer be used in textiles. They are: Disperse Blue 1 (DB 1), Disperse Blue 35 (DB 35), Disperse Blue 106 (DB 106), Disperse Blue 124 (DB 124), Disperse Yellow 3 (DG 3), Disperse Orange 3 (DB 3), Disperse Orange 37/76 (DO 37) and Disperse Red 1 (DR 1) (see Table 3). Chemically speaking, two of them are anthraquinone dyes (DB 1, DB 35) and the others are azo dyes (DB 106, DB 124, DG 3, DO 3, DO 37, DR 1).

Table 3: Potentially sensitising dyes which should no longer be used in textiles

Colour Index Name	Number
Disperse Blue 1	64500
Disperse Blue 35	-
Disperse Blue 106	-
Disperse Blue 124	-
Disperse Yellow 3	11855
Disperse Orange 3	11005
Disperse Orange 37/76	-
Disperse Red 1	11110

Since then further research findings have become available on contact allergies caused by disperse dyes in textiles. Within the framework of a co-operation project of the Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD) with dermatologists, patients with a textile-induced allergic skin reaction underwent a patch test for twelve disperse dyes. The textiles suspected as being the triggers of the skin reaction were then analysed. In the case of the textiles they were mainly jackets and trousers made of cellulose acetate (CA), in some cases with blends of other fibres (CA blend) or polyester (PES), polyester/cotton blends or elastane/polyamide blend. The colour fastness was between 1 and 5. In 22 out of 27 textile samples a total of 35 different disperse dyes were detected. Nine of them are known contact allergens. The disperse dyes with allergenic potential which were detected most frequently were: Blue 106 (9 samples), Yellow 3

(8 samples), Red 1 (5 samples), Blue 102 (4 samples), Blue 124, Orange 37/76 and Brown 1 (3 samples respectively). Six allergising disperse dyes were detected in CA textiles, four in the CA blend textiles and two in PES textiles. Only Blue 106 was present in all four substance categories. Orange 37/76 could only be detected in PES. There were correlations between analytical detection in the textile and a positive patch test for the disperse dyes Blue 106 (8 cases), Blue 124 (4 cases), Yellow 3 (1 case), Brown 1 and Red 1 (1 case respectively) [20, 21]. All the above dyes are contained in the list of allergenic disperse dyes of the Ökotex Standard 100 and other eco-labels.

It is not possible to make reliable epidemiological statements on the incidence of dye-induced contact allergies on the basis of the available scientific reports. Also the importance of individual dyes is very hard to assess because as a rule only a few selected dyes have been examined by epicutaneous testing in the clinical trials performed. There are frequent reports of cross-reactions with other dyes and also with p-phenylene diamine. One possible explanation is that cleavage products of some azo dyes (aromatic amines) may be structurally related to p-phenylene diamine (DB 124, DB 106, DO 3, see Fig 1).

Fig. 1: Structural formulae of Disperse Orange 3 and p-phenylene diamine

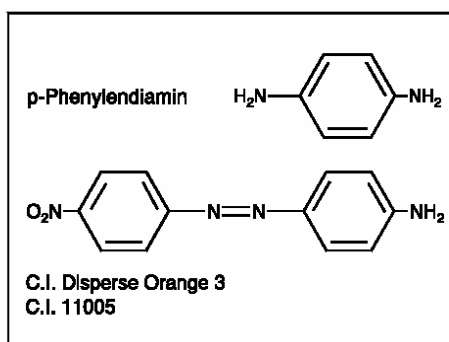


Abb. 1: Strukturformeln von Dispersionsorange 3 und p-Phenyldiamin

6 Test programme for the toxicological assessment of textile chemicals

The Textiles Working Group has drawn up principles for toxicological and allergological testing [22]. On that basis the German industry ran a test programme in which the manufacturers of textile auxiliaries and textile dyes examined the safety of their textiles finished, processed and dyed in this way. In principle, information on mutagenic, carcinogenic and sensitising properties should be available for each substance. The scale of testing should, however, be oriented towards expected exposure. No substances were tested with a molecular weight of more than 700, a water-octanol partition coefficient $\log P_{ow} < -1$ or > 6 or which had been proven to be not bioavailable.

6.1 Tests on the mutagenicity and sensitising properties of textile auxiliaries

The following representatives of large volume ingredients of textile auxiliaries were examined toxicologically from four textile auxiliary groups: levelling agents (benzyl trimethyl ammonium chloride, dimethyl benzyl- C_{12-18} -alkyl ammonium chloride (benzalkonium chloride)), crease prevention agents (sulphated fatty acid dialkylamide), anti-electrostatic agents (di-n-butyl phosphate, alkyl polyglycol ether phosphoric acid ester), water repellents (aluminium oxychloride). Given their high molecular weight no priority for toxicological testing was

attributed to 16 textile auxiliary groups. Data were already available for two groups (conditioning agents, softening agents). The residual contents of these textile auxiliaries after the first wash were in the range of < 0.1 % up to 3.7 %. Migration in the synthetic perspiration solution (DIN 54020) was maximum 1.9 % (aluminium oxychloride). All substances tested negative for mutagenicity in the Ames test and in the micronucleus test. The sensitising effect of benzalkonium chloride is known from positive results from studies in test cohorts and in especially exposed groups. The other substances were not found to be sensitising in animal tests (Magnusson-Kligmann test). For benzalkonium chloride a residual content of 1.4 % and migration of 0.1 % for methodological reasons prior to the first wash were observed. As a rule two to three industrial washes after use of this substance are customary which means that the residual content and migration from textiles should be lower under real conditions [23].

6.2 Dye mutagenicity tests

The test programme did not include pigments or reactive dyes which are not assumed to involve major consumer exposure. Naphthol dyes were not included either because of their partition coefficient ($\log P_{OW} > 6$). Nor were direct dyes with a molecular weight of more than 700 or a partition coefficient $\log P_{OW} > -1$. In the other dye categories it was assumed that at a fastness < 4 relevant migration and, by extension, possible exposure > 1 µg per kilogram bodyweight and day cannot be ruled out. A need for action was, therefore, identified for certain disperse dyes, particularly when used for polyamide and polyacetate, that are also used because of their market importance and for which relevant consumer exposure can be assumed. A total of ten disperse dyes were examined for mutagenicity and sensitising potential. The dyes C.I. Disperse Orange 30, Red 73, Red 167, Red 82, Orange 49, Red 54, Blue 79, Blue 73 and Red 11 were positive in the Ames test but negative in the micronucleus test. A further mutagenicity test was negative for Orange 30, Red 54, Blue 79, Blue 73 (tested in the HGPRT test) and for Red 11 (UDS test). For Red 73, Red 167 and Red 82 it is assumed that they do not have any mutagenic potential either because of their structural similarities to non-mutagenic dyes. Orange 49 did not undergo any further testing as this dye is no longer important. Yellow 211 was negative in all three test systems [23].

6.3 Tests on the sensitising properties of dyes

Orange 30 and Red 82 were sensitising in the Magnusson-Kligmann test. These dyes were then examined in the Local Lymph Node Assay. In this test system the proliferation of T-lymphocytes in the lymph nodes of mice is determined after the dermal application of a test substance by means of the incorporation of radiolabelled thymidine. In the case of these dyes the lymphocyte proliferation was not elevated after the application of concentrations of up to 30 %. It can be assumed that Orange 30 and Red 82 also have a weak sensitising potential. There is no need to assume a hazard to consumers through textiles coloured with these dyes [24, 25].

Studies on the skin penetration of Orange 30 and Red 82 were conducted *in vitro* with human skin and pig skin. For application amounts of 10 µL saturated, synthetic perspiration solution per cm², the absorption rate was below the detection limit of 0.001 µg/cm²/h. Application amounts of 200 µL saturated, synthetic perspiration solution per cm² led in the case of Disperse Orange 30 to absorption rates of 0.004 µg/cm²/h and total uptake of 0.16 µg/cm² in 48 hours (human skin) and 0.022 µg/cm²/h and total intake of 0.86 µg/cm² in 48 hours (pig skin). In the case of Red 82 penetration of this amount also remained below the detection limit. In the case of tests on skin penetration from acetone excretions, the absorption rate was below the detection limit (Orange 30: < 0.05 µg/cm², equivalent to 8 % at

a dose of $0.6 \mu\text{g}/\text{cm}^2$ and 0.8% at $6.0 \mu\text{g}/\text{cm}^2$; Red 82: $< 0.02 \mu\text{g}/\text{cm}^2$ equivalent to 33% at a dose of $0.06 \mu\text{g}/\text{cm}^2$ and 3.3% at $0.6 \mu\text{g}/\text{cm}^2$) when human skin was used. When using pig skin, absorption over 48 hours depending on the receptor liquid was maximum 54% ($0.007 \mu\text{g}/\text{cm}^2/\text{h}$ at a dose of $0.6 \mu\text{g}/\text{cm}^2$) for Orange Red und 79% ($0.002 \mu\text{g}/\text{cm}^2/\text{h}$) for Disperse Red [26].

7 Exposure

One essential component of any risk assessment is exposure. According to current findings, it is almost impossible to indicate a specific value for textile dyes because the degree of release may vary considerably. In the case of dyes it depends on which dye category, dye content (colour intensity) and fastness are examined on the respective textile substrate. It is also necessary to consider the conditions of wear and dermal absorption.

In order to obtain insight into the release of dyes from textiles, various research was undertaken only recently by both industry and research institutes with a view to creating a database for generally accepted models on the migration of substances from textiles. Textiles and clothing are also one main area of the programme launched by the European Commission: EIS-CHEMRISKS – Risks from chemicals released from consumer products / articles [27].

Until only recently there was only one reliable database on exposure to dyes from textiles, namely a study by the Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD) [28]. This project determined the release of dyes from garments by keeping 500 cm^2 of dyed textile samples in test solutions prepared according to DIN 54020 (Determination of sweat fastness of dyes and prints) at $37 \text{ }^\circ\text{C}$ for four hours. Dermal exposure (external exposure) to dyes during the wearing of textiles was estimated from the amount of dye released. Textiles with varying specific weights and dye content were examined. Between 0.1 and $300 \mu\text{g}$ dye were extracted from 500 cm^2 . For textiles with a high degree of colour fastness releases of $< 1 \mu\text{g}$ per simulated wear event were obtained. When related to the surface area examined or to an equal area of exposed skin, this would mean a surface dose of $< 2 \text{ ng}/\text{cm}^2$. The highest release rate measured was 0.4 mg per simulated wear event.

In this case 0.18% of the dye was released (migration factor 0.18%) on the basis of which a surface-related dose of $0.7 \mu\text{g}$ per cm^2 can be calculated. However, it must be borne in mind in this assessment that under practical conditions the release rates will be lower after repeated washing. On the other hand the samples consisted of textiles which had been dyed in accordance with state of the art and there may be higher release rates from poorly dyed textiles. Furthermore, the mechanical effects which result from the wearing of garments were not considered. The results of a research project supported by the Federal Ministry for Health entitled "Development of practice-oriented models of exposure to chemical substances from textiles" [29] address this aspect. A wear simulator has been developed by the German Wool Research Institute in Aachen (DWI) which was used to examine the release of textile dyes and auxiliaries from textiles under simulated conditions of use. In the wear simulator dynamic processes (friction) were found to have a considerable effect on migration. In a dynamic skin model (1 h, $37 \text{ }^\circ\text{C}$) using an alkaline perspiration solution, a migration factor of 0.26% corresponding to a surface related dose of $1.1 \mu\text{g}$ per cm^2 skin was determined for Palatinenechtmarineblau [29]. In other tests dyed textiles were examined in the wear simulator over a 28-day cycle. Various fibres (wool, cotton, polyamide, acetate) and different dyes (direct dyes and disperse dyes) were compared with and without the addition of textile auxiliaries. In addition, colour fastness was tested according to DIN 54020. It was shown that

the colour fastness of the various types of fibre was dependent on the dyes applied. The volume of dye released during the simulation of wear conditions did not, however, correlate with colour fastness. It was far more the case that the combination of fibre type, dye and test conditions, including the pH value of the elution solution, had a major impact on migration. The migration rate during the first wash cycle for the dye AB158 from wool with acid elution was 0.8 %. By contrast it was 8 % for the dye DB 116 from cotton. Under alkaline elution conditions the elutable proportions were lower. During the last wash cycle only 0.2 up to 0.5 % of the originally applied amounts of dye were released. Dye migration can be reduced through the subsequent treatment of textiles and the use of textile auxiliaries [30].

Another ETAD project sought to determine average exposure to disperse dyes from dyed garments for a typical period of use (50 wash / wear cycles) [31]. In a first extraction, depending on colour intensity, up to 0.43 % of the textile dye migrated to the extraction medium. On this basis, an area dose of up to 0.28 μg per cm^2 was calculated. After five wash cycles the release rates were reduced to about one-third of the initial level. Mean external exposure rates from < 0.005 up to 0.067 μg per cm^2 were calculated from all migration results for the test period. Assuming an exposed surface of 1 m^2 and a bodyweight of 70 kg, mean external exposure rates of < 0.71 to 9.7 μg per kilogram bodyweight can be established. In the case of contact allergies, however, it must be assumed that the decisive factor for risk assessment is not average but peak exposure [32, 33].

In the case of skin penetration it must be borne in mind firstly that there are major differences between dyes and secondly that the penetration rate depends on the concentration. For instance no skin penetration could be demonstrated in an *in vitro* experiment with pig skin and a dose of 0.2 μg per cm^2 whereas at a higher specific dose of 4.2 μg per cm^2 , skin penetration could be measured [34, 35]. From these results it can be concluded that internal exposure to disperse dyes is low in the case of perspiration-resistant dyed textiles. However, when wearing garments whose dye is not perspiration resistant, there may be internal exposure, the level of which will again depend on the ability of the respective dyes to penetrate the skin.

Based on the sparse migration data available, it can be concluded by way of summary that the external exposure of consumers to dyes from textiles coloured in accordance with state of the art (fastness between 4-5 and 2-3) is between 1 ng and 1 μg per cm^2 referred to the skin area involved. Where poor dyeing techniques have been used, release rates may however be considerably higher. However, no figures are available on this. In a dose range of 1 μg per cm^2 , allergic reactions to potent allergens like cathone or chromium (VI) cannot be ruled out. For disperse dyes whose sensitising potential is probably much lower, there are not enough quantitative data for a sound risk assessment or the determination of "practically safe surface doses".

The database for textile auxiliaries is even worse.

7.1 Release of substances from textiles (Migration)

General comments on migration measurement

Based on the data compiled by the Working Group Textiles, it was observed that elution is suitable as a simple and practice-driven method for the measurement of dye migration. It supplies values comparable with other methods but it would have to be standardised in terms of sample preparation, elution agent, pH, liquor ratio, temperature, time and mechanical influences (shaking, stirring). There are no comparable studies for auxiliaries or finishing

agents. However, for reasons of simplicity the Working Group Textiles recommends the same methodology. BfR proposes the following procedure [36]:

- 0.5 g unwashed textile fabric is shaken in 25 ml synthetic perspiration (liquor ratio 1:50) for 60 minutes at 40 °C with 90 revolutions per minute.
- According to DIN 54020 both acidic and alkaline perspiration solutions are used.
- The release is quantified with a suitable analytical method and related to 1 g or 1 cm² fabric.
- The higher value is included in the exposure assessment.

This measurement of initial migration helps to estimate the amount of substances released during the first wear of 16 hours from the examined textile. If textiles, as is frequently the case today, are washed prior to wearing, then the value for the first migration will be lower.

The release of substances from textiles changes in the course of wear. Three main results can be derived from the DWI and ETAD studies:

1. The migration values vary considerably depending on the type of fibre, the dye used, the amount applied, colour intensity, extraction agent and after-treatment.
2. Despite the major differences exposure can be estimated in standard procedures whereby a distinction can be made between textile dyes and auxiliaries.
3. The migration rate after 28 hours simulated wash /wear cycles is less than 10 % of the value measured for the first migration.

Very few data are available on migration of textile auxiliaries. Here a distinction must be made between auxiliaries which are added during the production of the textile liquor but which are not meant to remain on the textile and finishing agents which are applied to the textile in line with correct use. The first group includes very hydrophilic substances like surfactants. These are almost completely dissolved during the production process or at the latest during washing of the textile which means that we can assume a low migration rate of any residues. Less hydrophilic substances with a specific fibre affinity are, however, also used. For an ingredient of a water repellent, a migration rate of 1.9 % was determined in experiments. The second group includes hydrophobic substances which are not readily soluble in perspiration. In corresponding studies possible migration almost always remained below the detection level. For levelling agents rates were measured for the first migration of between 0.1 and 0.2 %.

7.2 Exposure assessment model

The basis for the assessment of exposure to textiles are firstly migration data. Secondly, data on the skin penetration of the substances involved are also necessary. In practice, however, given the lack of experimental data for migration and skin penetration, corresponding assessments must be undertaken. As a rule, however, data are available on the levels of substances in textiles.

Based on the studies evaluated the Working Group Textiles recommends the following default values as worst case assumptions when no measurement results are available [36] (Table 4). These default values are based on experimental data determined by way of example for the initial estimation of possible exposure.

Table 4: Recommended default values as the worst case assumption if no other values are available

Substance category	Migration rate	Penetration rate
Dye	0.5 %	1 % ^{*/**}
Hydrophilic textile auxiliary	2 %	5 % [*]
Hydrophobic textile auxiliary	0.1 %	50 % [*]

* Exception molecular weight >700 or log Pow <-1 or >6

** A penetration rate of 2% is used to calculate exposure in perspiration zones

Important parameters which can influence exposure are the area weight of the textile, the size of the exposed skin area, bodyweight, individual wear conditions and washing processes. Exposure calculations are based on the following assumptions:

- Area weight of the textile 100 g/m²
- Exposed skin area 1 m²
- Bodyweight 60 kg

7.2.1 Acute and chronic exposure

It makes sense when estimating exposure to distinguish between acute exposure whilst wearing new textiles with a possibly higher migration rate and chronic exposure during the duration of use. This differentiation not only refers to the release scenario as confirmed by experimental data from the tests with simulated wash / wear cycles but also to toxicity. The data on first migration are used to estimate acute exposure and undertake a risk assessment of acute intoxications and allergic reactions. To determine mean chronic exposure and for the risk assessment of sub-chronic and chronic toxicity, one-tenth of the first migration value can be used alternatively as results from complicated measurements under simulated wear conditions are not normally available. In both instances this is a worst case estimate.

This procedure is illustrated below using a simple example for a dye (dye content 1 %). According to the above assumptions the following applies:

Exposed area 1 m ²	Surface weight 100 g/m ²	Dye content 10 g/kg	Migration share 0.5/100
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This leads to an external individual dose of 5 mg. The following exposure scenarios can be considered:

Scenario A: Acute exposure

External body dose	5 mg/60	= 83 µg/kg bodyweight
Internal body dose (penetration rate 1 %)	83 µg/100	= 0.83 µg/kg bodyweight
External surface dose (exposed area 1 m ²)	5 mg/10.000	= 0.5 µg/cm ² body area

Scenario B: Mean chronic exposure

External body dose	5 mg/60/10	= 8.3 µg/kg bodyweight
Internal body dose (penetration rate 1 %)	8,3 µg/100	= 83 ng/kg bodyweight
External surface dose (exposed area 1 m ²)	5 mg/10.000/10	= 0,05 µg/cm ² body area

7.2.1.1 Special exposure calculations

The assumptions in the exposure model described are only applicable to textiles which were dyed in line with state of the art. In the case of textiles which were not produced in line with

state of the art, there may be higher migration rates and, by extension, higher exposure. If data on individual parameters are available in the case to be considered, the corresponding calculation model can be adjusted. This will lead to a more realistic estimate of exposure. A corresponding correction can be undertaken of the following parameters:

- Exposure area particularly for textiles which only come into contact with specific parts of the body
- Surface weight
- Migration rate after experimental determination
- Penetration rate after experimental determination
- Wear behaviour
- Bodyweight, e.g. in order to estimate the exposure for children
- Consideration of perspiration zones, e.g. in sports wear. Here however for the dyes a worst case skin penetration rate of 2 % can be used and, if appropriate, a correspondingly smaller relevant body area.

8 Detergent residues and additives

Data on detergent residues on textiles are available in particular from the commercial sector. When examining complaints, the frequency of which is given as approximately $1:10^7$, it was shown that the residual contents of surfactants do not exceed 100 ppm in most cases whilst organic and inorganic encrustations are mainly below 1 % (10,000 ppm). The pH values in the majority of the samples examined were between pH 6 and pH 8; pH 10 was not exceeded. From wash experiments with branded detergents in household washing machines it can be determined that residual contents of soaps and surfactants of > 1,000 ppm are to be expected depending on the type of fabric and the composition of the detergent. Residual zeolite contents (phosphate substitutes) were found in one case of almost 37,000 ppm. Also after the switch to phosphate substitutes, there were not any signs from the environmental medical angle of a health threat to consumers from detergent residues in textiles aside from individual cases of intolerance reactions.

For the purposes of the ecological optimisation of household laundry (energy and water savings) water consumption was reduced by 50 % in modern household washing machines. The German associations of detergent and washing machine manufacturing industries set up a working group "Dermatological Aspects of Washing" to collect the latest data on detergent residues and their dermatological relevance.

Besides the primary wash effect, dirt removal, secondary wash effects also play a role like preventing discoloration, bleeding or encrustations on the fabric or washing machine parts. As a rule these effects are achieved by applying corresponding additives. Encrustations and greying are prevented by the use of polymers like polycarboxylates which disperse calcium and magnesium compounds. Other polymers are applied as a protective coating to fibres and remain on the textile after washing. To inhibit colour carryover polyvinyl polypyrrolidones (PVPPs) are used which complex anionic azo dyes. "Colour care" additives fix the dyes in the fabric. These are special additives which contain a cationic polymer amongst other things. It forms a water-insoluble complex with the anionic dye molecules on the fabric. Fragrances are also of importance; they are added to detergents, softening agents and ironing aids. Allergic reactions are possible. It is estimated that 10 % of patients with contact eczemas and between 1 and 2 % of the total population react positively in patch tests to fragrances [37]. The Scientific Committee on Cosmetics and Non-Food Products of the EU (SCCNFP) is of the opinion that the same requirements should apply to perfumes in detergents and household chemicals that apply to cosmetics [38]. The SCCNFP has listed

perfume ingredients with a known allergenic effect [39] and also a number of fragrances which may not be contained in cosmetics [40]. The European Regulation on Detergents (648/2004/EC) envisages the mandatory declaration of allergenic fragrances in detergents from a concentration of 0.01 % upwards.

The use of nitromusk compounds and polycyclic musk compounds is viewed critically from the ecological and toxicological angle. Musk xylene has not been used in any new products since 1994 because of a voluntary undertaking by the German Cosmetic, Toiletry, Perfumery and Detergent Association (IKW) in Germany. It is gradually being replaced in products which were already on the market prior to 1994. Major constraints on the use of musk ambrette had already been imposed in 1983 by IFRA (International Fragrance Association). The other nitromusk compounds have not been subject so far to any constraints on use in detergents; however in some cases manufacturers are voluntarily refraining from using them.

The use of substances with antibacterial or disinfectant effects is also proving popular in detergents. Products of this kind are covered by the Biocide Directive since it came into force in 2005. Sanitary cleaning agents, which are used like softening agents after washing and are not rinsed out, are enriched with a concentration of around 7 % benzalkonium chloride. Benzalkonium chloride has a sensitising potential. The use of isothiazolinones for the preservation of liquid starch must also be viewed as problematic as these substances are contact allergens and skin contact must be assumed.

9 Nanotechnology in textiles

Textile production and finishing is also seen as an important future area of use for nanotechnology. "Nano" finishing is the term used to describe the application of particles (between 10 nm and 100 nm in size) and also the application of oligomer or polymer substances which form a thin layer (web). The particles may be compact (crystalline or amorphous) or cavities (globules or tubules). They, in turn, may contain specific active substances. Nano particles may be integrated into synthetic fibres or applied to the surface of fibres (free or bound) during final finishing. Furthermore, the applied layers may freely coat the fibres or be covalently bound to the fibre material.

Nanotechnology is used in order to give the fibres new functional properties. From the array of possible applications, however, only few have been used in textile products available on the market. Examples for the use of nano particles are the biocide finishing of fibres using silver particles and sunscreen finishing with titanium dioxide or zinc oxide. A dirt-repellent effect can also be achieved through surface structuring (lotus effect) with the help of silica or a hydrophobic and oleophobic finish. Particularly in the case of the last examples there are demarcation problems between "nanotechnological" and "normal" finishing.

Cosmetic textiles are securing growing market shares particularly in ladies' tights. In most cases, these are nano capsules filled with cosmetic agents which are released when exposed to mechanical and/or thermal friction. The difficulty so far has been in finishing the textiles in such a way that the desired function is maintained over a longer period, if possible, permanently and also survives the mechanical and thermal stress of washing. Another problem with a nanotechnological finish is maintaining the fabric's haptic properties (grip, flexibility). Furthermore, a nano finish is a by no means insignificant cost factor.

When it comes to possible hazard potential, the focus in the case of textiles is on nano particle abrasion and inhalational or oral exposure. Given the size of the particles it is not assumed that there is any uptake of textile material through the skin. At the present time

there are no specific legal requirements for the use of nano particles. The production and use of nano particles are governed by general chemical law requirements. Textiles which come under the provisions of the Consumer Products Ordinance must comply with them. In the case of cosmetic textiles, the provisions of the Cosmetics Ordinance also apply to the active substances.

10 Summary

- No systemic toxic effects from chemical substances are expected from the wearing of textiles (exception contact allergies).
- There are only health risks from textile dyes in the case of poorly dyed, non-colour fast products. Given that everyone has close skin contact with textiles 24 hours a day, the documented cases of contact allergies triggered by textiles are rare. Textile-related contact allergies probably account for around 1-2 % of cases.
- In the case of disperse dyes with a sensitising potential in textiles, there is a risk of a contact allergy when perspiration resistance is < 4 and there is intensive skin contact, particularly in perspiration zones. Another risk factor is already damaged skin with an inadequate barrier function.
- On precautionary grounds the following dyes should no longer be used in textiles: Disperse Blue 1, Disperse Blue 35, Disperse Blue 106, Disperse Blue 124, Disperse Yellow 3, Disperse Orange 3, Disperse Orange 37/76 und Disperse Red 1. Other dyes with allergenic potential have since been identified and should at least be declared.
- For precautionary reasons certain azo dyes, that can be cleaved into carcinogenic aromatic amines, were banned in the Consumer Products Ordinance. It can be assumed that these dyes are present particularly in imported textiles.
- The use of 1,2,4-trichlorobenzene as a dye accelerator (carrier) in textiles is not safe and should be banned.
- There are hardly any data on exposure to textile auxiliaries.
- Exposure to dyes, related to skin area, is between 1 ng and 1 μg pro cm^2 depending on colour fastness.
- Exposure can be estimated using suitable models.
- The risk assessment for finishing with fluorine polymers revealed that there is no worrying exposure to fluorine surfactants from textiles.
- When it comes to the anti-microbial finishing of textiles, the risks and benefits should be carefully weighed up against one another. BfR recommends in particular that triclosan should not be used. Active biocidal substances should always be declared.

11 References

- [1] Textilhilfsmittelkatalog 2000, Konradin Verlag Leinfelden-Echterdingen
- [2] Stilbenderivate als Textilhilfsmittel. Stellungnahme des BgVV. 2001.
<http://www.bfr.bund.de>
- [3] Gaikem, FJ, Alberts, PJ (1999) Gaschromatografische bepaling van residuen van organotinverbindingen in textielproducten. De Ware-Chemicus 29: 23-33
- [4] Appel, KE, Böhme, C, Platzek, T, Schmidt, E, Stinchcombe, S (2000) Organozinnverbindungen in verbrauchernahen Produkten. Umweltmed Forsch Prax 5: 67-77

- [5] Washburn ST, Bingman TS, Braithwaite SK, Buck RC, Buxton LW, Clewell HJ, Haroun LA, Kester JE, Rickard RW, Shipp AM (2005) Exposure assessment and risk characterization for perfluorooctanoate in selected consumer articles. *Environmental Science & Technology* 39: 3904-3910
- [6] Schuster A, Daschner F (2002) Antibakterielle Produkte im Haushalt: Chance oder Risiko? *Dtsch Med Wochenschr* 127: 2340-2344
- [7] Bundesinstitut für Risikobewertung (BfR) (2006) Triclosan nur im ärztlichen Bereich anwenden, um Resistenzbildungen vorzubeugen. Stellungnahme Nr. 030/2006 des BfR vom 08. Mai 2006.
http://www.bfr.bund.de/cm/217/triclosan_nur_im_aerztlichen_bereich_anwenden_um_resistenzbildungen_vorzubeugen.pdf
- [8] Horstmann M, McLachlan MS (1994) Textiles as a source of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) in human skin and sewage sludge. *Environmental Science and Pollution Research* 1: 15-20
- [9] Schneider K, Hafner C, Jäger I (2004) Mutagenicity of Textile Dye Products. *J Appl Toxicol* 24: 83-91
- [10] Platzek T, Lang C, Grohmann G, Gi US, Baltes W (1999) Formation of a carcinogenic aromatic amine from an azo dye by human skin bacteria in vitro. *Human and Experimental Toxicology* 18: 552-559
- [11] Feinman SE, Doyle EA (1988) Sensitization to dyes in textiles and other consumer products. *J Toxicol Cut Ocul Toxicol* 7: 195-222
- [12] Hornstein OP (1989) Textilverträglichkeit bei Hautkrankheiten. *Melliand Textilberichte* 3: 222-227
- [13] Klaschka F (1994) Textilien und die menschliche Haut, Fakten und Fiktionen - eine Situationsbeschreibung aus dermatologischer Sicht. *Melliand Textilberichte* 3: 193-202
- [14] Maurer S, Seubert A, Seubert S, Fuchs TH (1995) Kontaktallergie auf Textilien. *Dermatosen* 43: 63-68
- [15] Hatch KL (1984) Chemicals and textiles Part I: Dermatological problems related to fiber content and dyes. *Textile Research Journal* 54: 664-682
- [16] Hatch KL (1984) Chemical and textiles Part II: Dermatological problems related to finishes. *Textile Research Journal* 54: 721-732
- [17] Hatch KL, Maibach HI (1985) Textile dye dermatitis. *J Amer Acad Dermatol* 12: 1079-1092
- [18] Hatch KL, Maibach HI (1995) Textile dye dermatitis. *J Amer Acad Dermatol* 32: 631-639
- [19] Hatch KL (1995) Textile dye contact allergens. In: *Current Problems in Dermatology*. Surber, Elsner, Bircher (eds) 22: 8-16

- [20] Hatch KL, Motschi H, Maibach HI (2003) Identifying the source of textile-dye allergic contact dermatitis – a guideline. *Exog. Dermatology* 2: 240-245
- [21] Hatch KL, Motschi H, Maibach HI (2003) Disperse dyes in fabrics of patients patch-test positive to disperse dyes. *Am. J. Contact Dermatits* 14: 205-212,
- [22] Aus dem Arbeitskreis „Gesundheitliche Bewertung von Textilhilfsmitteln und –farbmitteln“ der Arbeitsgruppe „Textilien“ des BgVV. 1996 Bundesgesundheitsblatt 11: 430
- [23] Krätke R, Platzek T, Arbeitsgruppe "Textilien" beim BfR, Bericht über die 11. Sitzung des Arbeitskreises "Gesundheitliche Bewertung von Textilhilfsmitteln und -farbmitteln" der Arbeitsgruppe "Textilien" des Bundesinstituts für Risikobewertung (BfR) am 16.12.2003 in Berlin. *Bundesgesundheitsbl.* 48, 120-124, 2005
- [24] ETAD, C.I. Disperse Red 82: Local Lymph Node Assay, Forschungsbericht, 2003
- [25] ETAD, C.I. Disperse Orange 30: Local Lymph Node Assay, Forschungsbericht, 2003
- [26] ETAD, In vitro absorption of two disperse dyes through human and pig epidermal membranes, Forschungsbericht, 2001
- [27] Schneider K, Platzek T, Heinemeyer G, Doser M, Lahaniatis M, Papameletiou D (2007) Chemtest phase I project: evaluation of exposure data for consumer products. *Naunyn-Schmiedeberg Arch Pharmacol* 375: S1 R519
- [28] ETAD, Final report on extractability of dyestuffs from textiles. Project A 4007 (1983)
- [29] Höcker H (1996) Entwicklung praxisgerechter Modelle für die Exposition mit chemischen Stoffen aus Textilien. Abschlußbericht
- [30] Heine H, Heinemann M, Thomas H, Höcker H (2000) Freisetzung von Textilhilfsmitteln und –farbstoffen aus textilen Bedarfsgegenständen und Übergang auf die Haut. Abschlußbericht
- [31] ETAD, Extractibility of dyestuffs from textiles over a normal lifetime of use. Project G 1033 (1997)
- [32] White SI, Friedmann PS, Moss C, Simpson JM (1986) The effect of altering area of application and dose per unit area on sensitization by DNCB. *Brit J Dermatol* 115, 663-668
- [33] ETAD, Risk assessment of contact sensitizing disperse dyes in representative textiles. Project G 1033/1041 (1996)
- [34] ETAD, In vitro absorption of various dyes through human and pig epidermis. Project T 2030, Part 1 (1994)
- [35] ETAD, In vitro absorption of two disperse dyes from synthetic perspiration and five formulations. Project T 2030, Part 2 (1995)

- [36] Krätke R, Platzek T (2004) Migrationsverfahren und Modelle zur Abschätzung einer möglichen Exposition mit Textilhilfsmitteln und –farbstoffen aus Bekleidungstextilien unter Anwendungsbedingungen. Bundesgesundheitsbl – Gesundheitsforsch – Gesundheitsschutz 47: 810-813
- [37] The Scientific Committee on Cosmetic Products and Non-Food Products intended for Consumers (SCCNFP): Opinion concerning the interim position on fragrance allergy, adopted 23.06.1999
- [38] The Scientific Committee on Cosmetic Products and Non-Food Products intended for Consumers (SCCNFP): Position statement concerning fragrance chemicals in detergents and other household products, adopted 04.06.2002
- [39] The Scientific Committee on Cosmetic Products and Non-Food Products intended for Consumers (SCCNFP): Opinion concerning fragrance allergy in consumers, adopted 08.12.1999
- [40] The Scientific Committee on Cosmetic Products and Non-Food Products intended for Consumers (SCCNFP): Opinion concerning an initial list of perfumery materials which must not form part of fragrances compounds used in cosmetic products. Adopted 03.05.2000