

An Overview of Textiles Processing and Related Environmental Concerns

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Executive Summary

This report presents an overview of the textiles processing industry; highlighting major sources of environmental contamination. Focus is primarily on textiles finishing, identifying chemicals that will be highlighted by the forthcoming REACH legislation and are potential substitution candidates.

The industry has a highly complex chemical consumption pattern, suffering from poor information dissemination. Most approaches to reduce its environmental footprint have focused upon process design rather than chemical substitution. This approach has worth due to the massive loadings of low toxicity substances currently used.

Most of the industries environmental impact occurs during production. The overall content of substances of high concern in finished garments is limited and depends upon specific processing and dyeing techniques employed.

1 Introduction

This report presents an overview of the textiles processing industry; highlighting major sources of environmental contamination.

The research brief was to identify the stages in production that gave greatest cause for concern in relation to the use and release of hazardous chemicals; with a special focus on chemicals that are likely to occur in finished garments and those that will require registration under the proposed REACH legislation. Due to this focus, issues relating to fibre production have been excluded. Major issues of environmental concern include pesticide and defoliant usage on cotton, ectoparasiticides on sheep, and industrial practice and emissions in the case of natural and synthetic fibres (Bunke *et al* 2003).

Much of the focus of scientific research aimed at “greening” the production of textiles focuses on end-of-pipe technologies such as the use of ozonation or advanced Fenton’s oxidation to “clean” dye house effluent. Whilst these approaches may result in lower emissions to the environment they can hardly be considered as part of a green chemistry approach and so are not discussed. Process integration has proved successful in reducing both chemical and energy consumption. Separate processing steps have either been combined or conducted step-wise in the same vessel. This type of approach is central to IPPC recommendations to the industry (IPPC 2003).

The textiles industry in Europe consists largely of SMEs, each concentrating on a limited range of processes. The industry has been hard hit by globalisation and modernisation with an over 40% reduction in workforce between 1980 and 1995 (Stengg 2001). Import penetration has also increased considerably, from 12% in 1990 to 23% in 1999 for textiles, and from 30% in 1990 to 46% in 1999 (Stengg 2001). Concerns have been raised that the ending of the WTO Agreement on Textiles and Clothing, which is due to occur this year, will increase import levels and pressure on domestic producers even further.

Substances	Environmental Load (t/yr)
Salts	200000-250000
Natural fibre impurities (including biocides) and associated material	50000-100000
Sizing agents	80000-100000
Preparation agents (mainly mineral oils, also ester oils)	25000-30000
Surfactants	20000-25000
Carboxylic acids (mainly acetic)	15000-20000
Thickeners	10000-15000
Urea	5000-10000
Complexing agents	<5000

Table 1 Environmental loadings from the EU textiles industry
Source: IPPC 2003 Data extrapolated from studies in Germany and Austria

Much of the industries environmental impact comes in the form of large releases of low toxicity substances such as salts (table 1). The industry has a highly complex chemical consumption pattern and suffers from poor data dissemination. Many finishing mills import pretreated yarns, often not receiving full information about the compounds already applied. Article 6 of REACH (General obligation to register substances in articles) will impact this, though substances present at low concentration may not be affected. The use of pre-formulated products is wide spread; users do not receive a full breakdown of the contents. An example is provided by a UK retailer. Removing alkylphenol ethoxylates from products involved complex paper chains and required textile finishers to actively seek information from formulators. In this climate of poor information dissemination it is especially difficult for the non-industry researcher to gain a true understanding of consumption levels. Many government advisors and published authors in the field all too often have to rely upon existing literature. Independent authors have found industry to not be forthcoming with data; whether this is due to secrecy (for whatever reason) or an inherent lack of information is unclear.

This study has been prepared using information from a range of sources. A basic overview of the industry was gleaned from the IPPC Best Available Techniques document published in 2003. A range of texts and scientific journals have also been searched, industrial, academic and independent advice sought.

In structure, the report follows textiles from fibre to fabric, highlighting environmental concerns as they arise. Information about possible alternatives has also been included in order to present a more complete picture of the state of research.

2 Fibre Preparation

Raw natural fibres require cleaning before entering the fabric production-chain. The process is most intensive in the case of wool. Raw wool can contain 20-40% impurities in the form of wool grease (lanolin), dyed perspiration (suint), dirt and a significant loading of pesticides (IPPC 2003). To remove these impurities the wool is scoured in an energy intensive process requiring large amounts of hot water loaded with non-ionic detergents (namely alcohol ethoxylates and alkylphenol ethoxylates) and builders (inorganic salts) to emulsify the wool grease.

Up to half of the lanolin removed can be recovered and used as an industrial feedstock by the cosmetics industry primarily due to its emollient properties. The lanolin contains high levels of pesticides which must be removed by solvent extraction. In the UK work has been conducted into the potential for composting waste lanolin. This raises concerns about reintroducing pesticides to the environment.

The IPPC document of Best Available Techniques (BAT) for the textile industry recommends the use of an organic-solvent-based wool scouring technique (the Wooltech process). The process is similar to dry-cleaning. Solvent is used to extract impurities; these are then collected by evaporating off the solvent in a collection vessel. The process has significant advantages due to the solvent's low specific heat capacity. Water based scouring techniques employ 10-15 litres of water per kilogramme of greasy wool processed, this must be heated and the cleaned wool dried – requiring far larger amounts of energy. The organic solvent system also allows complete recovery of removed dirt and grease therefore preventing a significant source of heavily loaded waste water. However the solvent employed by the Wooltech process is trichloroethylene.

Trichloroethylene has been classified by International Agency for Research on Cancer in Group 2A (probably carcinogenic to humans) (IARC 1995). Most importantly, an elevated risk for cancer of the liver and biliary tract and a modestly elevated risk for non-Hodgkin's lymphoma were observed. Trichloroethylene has been shown to induce lung and liver tumours in various strains of mice (Fisher & Allen 1993, WHO 1993). The EU Existing Chemicals Bureau risk assessment of trichloroethylene (EU 2004) stated that: "For carcinogenicity and mutagenicity endpoints there is no identifiable threshold exposure level below which the effects would not be expressed, so there are health concerns at all exposure levels".

Though the textiles BAT document (IPPC 2003) recognises that trichloroethylene is persistent and harmful it accounts for the fate of half the solvent used as "uncaptured losses" and still recommends the technique. The document states that only one plant in the EU currently scours with trichloroethylene located in Trieste, Italy. This was not possible to confirm this.

Silk and cotton are generally much cleaner fibres and only require dry processing to remove any dirt particles. Production of synthetic fibres, as with all industrial polymer production processes, involves the use of a number of reactive species and is accompanied by a range of environmental concerns. As stated earlier assessing this is generally beyond the scope of this study, though the issue of antimony trioxide is discussed.

2.1 Spinning

During spinning fibres are subjected to various mechanical processes that comb, align and spin them to produce a yarn. In some cases two or more yarns are then twisted together to form a twine. Chemical auxiliaries are used to provide lubrication, allowing high speed processing.

Traditionally mineral oils were used; a source of poly aromatic hydrocarbons (PAHs). PAHs are prevalent pollutants in both terrestrial and aquatic environments that can cause a wide range of toxic effects; some are known human carcinogens (ATSDR 1997). Today they have been largely substituted for synthetic oils (silicone oils, polyglycols) and ester oils (esterified fatty acids) (IPPC 2003). These offer better performance and have more uniform properties. As the oils are applied as aqueous preparations and are not generally water soluble, emulsifiers are required. Generally these are non-ionic surfactants such as alcohol ethoxylates (AEOs) and alkyl phenol ethoxylates (APEOs). The aqueous preparations must be protected from degradation during storage so preservatives such as bactericides and fungicides are also added. As discussed later these end up in finishing plant effluent streams.

Synthetic oils do not contain the same levels of impurities (no metals, PAHs etc) as mineral oils and some biodegrade. Ester oils are also biodegradable and easier to emulsify than mineral oils (therefore a lower surfactant loading is required).

For the spinning of synthetic fibres silicon oils predominate and account for up to 7% of the yarn by weight. Though these are non-toxic and bioeliminable (IPPC 2003) emulsification is difficult and so large amounts of surfactant are employed.

2.2 Weaving

Weaving interlaces two or more perpendicular yarn systems. On a loom weft yarn is woven between taught, parallel warp yarns (the *shed*). The warp yarns are under tension and are subjected to stress during weaving as the weft yarn is inserted between them at great speed.

In order to reduce damage caused by the many abrasive contacts the shed must endure a chemical preparation; size, is applied to warp yarn prior to assembly on the loom. The size forms a film rendering the yarn more slippery, supple and stronger. Thus it reduces friction, the number of free fibre ends that may interfere with the weaving process and the number of warp yarn breakages.

Polysaccharide Based

- Starch
- Starch Derivatives
- Cellulose Derivatives
- Galactomannans

Fully Synthetic

- Polyvinyl alcohols
- Polyacrylates
- Polyvinyl acetate
- Polyester

Figure 1: Size Types (Source: IPPC 2003)

Size preparations fall into two broad classes; natural and synthetic (Figure 1). Natural sizes (of which starch dominates) are currently still the most widely used (UBA 2003). The source of starch varies geographically, in Europe both native and modified starches originate from potatoes, in the US corn starch (from maize) is employed where as in Asia starches originate from rice, sago, maize and tapioca (DEPA 1997). Starch is, increasingly often chemically treated to produce depolymerised derivatives such as carboxymethyl cellulose (CMC). This improves its performance and renders it water soluble (recyclable).

Fibre	Loading(g/kg yarn)	Size Used
Cotton/cotton-polyester	80-200	Starch/ starch derivatives often in combination with others
Polyester	40-60	Mainly polyester also small amounts of PVA
Nylon	20-50	Polyacrylic acid is used
Viscose	40-120	Normally combinations of all types used

Table 2 Size loadings of different fibres (IPPC 2003)

Warp yarns typically account for 60% of the fabric therefore sizing agents represent a significant use of auxiliaries. As can be seen above (Table 2) cotton is the most heavily sized fibre with loads of up to 200 g/kg applied to the warp yarn. This is because starch/starch derivatives are usually employed, for which loadings are significantly higher than for synthetic sizes.

A range of additional agents are generally present in most size preparations for cotton (IPPC 2003). These include:

- **Viscosity Regulators** - agents that interact with the starch to alter its physical properties. For example borax (sodium borate) increases viscosity by complexing (binding to) the starch, whereas peroxy sulphates may be used to chemically cleave the starch macromolecule, reducing viscosity.
- **Antistatic Agents** Phosphoric acid esters may be used, these are water soluble and difficult to degrade resulting in their passage through common waste water systems unscathed.
- **Wetting Agents** - improve size penetration of the yarn.
- **Defoaming Agents** – if PVA size is used it is necessary to add an agent to prevent the formation of foam. Oils (paraffin or silicone) or fatty acid esters are often used.
- **Preservatives** – to prevent degradation of sizes such as starch biocides are often added.

Sizes for fibres other than cotton do not contain such a range of auxiliaries and generally only a preservative is added (as is the case with all aqueous preparations that are stored for long periods of time). It was not possible to find out what percentage of the size additives typically account for.

If garments are not dyed then it is possible that shipment will occur without desizing. In the case of items like shirts the starch may actually be providing a desired effect. High levels of the preservative PCP (pentachlorophenol) in cotton garments was shown to cause elevated levels of certain dioxins in the outer skin layers of wearers (Horstmann and McLachlan

1994). PCP was commonly used as a preservative in starch-based sizes. Its use in the EU is now covered by EU Directive 76/769, it is assumed that use may continue elsewhere.

2.3 Environmental impact of spinning and weaving

Spinning and weaving auxiliary chemicals are generally left on the fabric by producers. Removal is carried out by finishing houses prior to dyeing as an impure fabric would result in poor dye take-up and inconsistent results. For this reason the effects of sizes upon waste water streams shall be discussed in full as part of the pre-treatment section.

Most of the substances are relatively benign in terms of direct environmental toxicity. It is due to the quantity of these substances used that they burden the environment. Noteworthy exceptions are non-ionic surfactants potentially employed (alkyl phenol ethoxylates), borax (although no information of the prevalence of use of this substance could be found) and biocides added to preparations.

3 Pretreatment

Pre-treatment occurs immediately before dyeing/printing in the textile production chain, and prepares the fabric for these processes. The fibres may either be in the form of a yarn or a woven fabric. Pre-treatment normally occurs in the same facility as dyeing, often in the same machine (integrated processing = faster processing). A series of mechanical and wet treatments prepare the fabric in a variety of ways:

- **Removal of foreign material from the fabric.**
Natural impurities present in wool and cotton, production residues in manmade fibres and previously applied processing auxiliaries must be removed. This improves: uniformity, hydrophilicity and fibre affinity for dye stuffs and finishing auxiliaries.
- **Improving the ability to absorb dyes uniformly.**
In the case of cotton a chemical treatment is applied (mercerising) to alter cellulose crystallinity.
- **Relax tensions**
Synthetic fibres are often subjected to a heat treatment relaxing tensions due to upstream processing (Lacasse, Baumann 2004).
- **Bleaching**
To allow light dye shades or to produce white fabrics.

The nature and number of pre-treatment stages depends upon both the fibre and the required end result. Natural fibres generally contain more impurities and so are subjected to more intense processes.

The type of environmental pollution resulting from pre-treatment depends upon process ordering; if heat processing precedes wet then the off gas contains a higher proportion of the removed impurities and vice versa.

3.1 Singeing

Singeing is carried out on both yarns and fabrics. The material is exposed to a gas flame to burn off protruding fibres that cause non-uniform dye uptake. No chemical agents are required except for a water bath that is used to quench any sparks (in integrated systems this is often the desizing vat). The process has a low environmental impact; however dust and volatile organic compounds (VOCs) are produced (UBA 2003).

3.2 Desizing

The complete removal of size is required for all woven fabrics prior to dyeing. The nature of this process depends upon the type of size applied. Water soluble size may simply be washed out, whereas water insoluble size must first be subjected to chemical or enzymatic

degradation. This prevents size recovery and so a large burden is placed on waste water streams.

3.2.1 Removal of water insoluble size

Removal of starch and starch derivatives (with the exception of carboxymethyl cellulose) requires agents that degrade the size and render it water soluble. This is accomplished by employing either enzymes or oxidizing agents.

Enzymatic methods generally employ amylases with a surfactant and small amounts of complexing agent. Oxidative desizing can be achieved with hydrogen peroxide in the presence of sodium hydroxide, surfactants and stabilisers (complexing agents). This method allows for integrated desizing, bleaching and scouring thus, reducing chemical consumption. However cotton fibres differ only slightly from starch and so unless conditions are tightly monitored the fibres may be damaged, not a concern with enzymatic desizing.

3.2.3 Removal of water soluble size

Theoretically only hot water is required to remove water soluble sizes such as PVA and CMC. However efficiency is usually increased by the addition of a combination of non- and ionic surfactants. This prevents size recycling. Often dye houses do not know what blend of sizes has been applied, in this case an oxidative desizing liquor is applied as it will remove both water soluble, and insoluble size.

3.2.3 Environmental considerations

Synthetic size and CMC can be recovered from the desizing liquor by ultra-filtration and recycled. Starch size is degraded during desizing; losing its adhesive and film-forming properties and so may not be recycled. As a result desizing liquors can account for up to 70% of the COD (chemical oxygen demand) load of a mill finishing woven fabric.

Due to the general industry problem of a lack of information dissemination it is often not clear what blend of size has been applied. This prevents widespread size recovery. Also sizing and desizing do not usually occur on the same site raising questions of whether long distance transportation of bulk chemicals can be justified, as environmental gains may potentially be offset. Also starch sizes are from a renewable resource therefore it isn't clear which is better for the environment.

3.4 Scouring

Natural impurities such as waxes, pectins and proteins must be removed. Raw cotton may contain between 4 and 12% of these impurities by weight (Karapinar and Sariisik 2004). Hot sodium hydroxide, a complexing agent and a surfactant (act as wetting agents) are generally used though enzyme based approaches exist (Karapinar and Sariisik 2004). The process can take from six to twelve hours making it energy intensive. As stated earlier wool may be scoured with organic solvents or aqueous solutions of detergents.

In the case of synthetics processing oils must be removed with detergents, again, enzyme based alternatives exist. Waste streams are rich in residues from the polymers production, such as un-reacted monomers, low molecular weight oligomers and residual catalysts. The resultant environmental burden is discussed later.

3.5 Mercerisation

Mercerisation is a treatment specific to cotton. It improves tensile strength, lustre, and ability to take up dyes. Baths containing very concentrated solutions of sodium hydroxide (20- 30%) are used (UBA 2003). These may either be reused or the NaOH recovered and employed in other pre-treatment steps (IPPC 2003). If discharge is required then the alkali is neutralized, leading to the discharge of large quantities of salt.

3.6 Carbonising

Wool may still contain impurities of plant origin that cannot be removed by mechanical means. A treatment known as carbonisation is used to remove them, usually in the scouring mill. The wool is soaked in a solution of sulphuric acid, heated to concentrate the acid and baked to carbonise the impurities. These are then crushed between rollers to aid removal. Wool – polyester blends are treated with gaseous hydrochloric acid (or source thereof) as the polymer is sensitive to sulphuric acid. In this form HCl presents a risk to the respiratory systems of workers (Stringer and Johnston 2001).

3.7 Bleaching

Bleaching is used to destroy natural impurities in fibres when either a white finish is desired or if a light dye is to be applied. Two alternative chemical routes may be employed to achieve a whiter fabric. Both attack colour producing compounds, destroying them.

3.7.1 Oxidative Bleaching

Cellulose fibres are bleached almost exclusively by oxidative methods. The most common; chlorine-based and hydrogen peroxide, can either be used in combination or individually. It is claimed that it is not possible to attain high levels of whiteness by the exclusive application of hydrogen peroxide. However this argument appears to be (at least) partially based on economic considerations. Reports indicate that through the use of carefully controlled conditions H_2O_2 can achieve a high degree of whiteness (Lacasse and Baumann 2004). There are indications that this technique costs two to six times as an equivalent chlorine based process.

Sodium hypochlorite ($NaOCl$) bleaching is conducted at an alkaline pH. Due to high reactivity milder conditions are required than for hydrogen peroxide. An anti-chlorine treatment follows to remove excess $NaOCl$. Bleaching with sodium hypochlorite causes a number of subsidiary reactions leading to the production of a range of AOX (absorbable

organic halogens) including trichloromethane (Lacasse and Baumann 2004) and dioxin precursors (Stringer and Johnston 2001). Bleaching with hypochlorite is not permitted in Germany (UBA 2003) and has been to a large extent, substituted throughout the rest of Europe. World wide use is still large, not only for bleaching but also for the cleaning of dyeing machines and for stripping faulty dyed goods (Lacasse and Baumann 2004).

An alternative, highly effective, chlorine-based bleaching agent is sodium chlorite (NaClO_2). Much lower levels of AOX are produced compared with hypochlorite. The active bleaching agent; ClO_2 gas, is hydrophobic thus preventing damage to cellulose fibres. However the substance is associated with handling difficulties. Chlorine dioxide is highly toxic, attacks stainless steel and is unstable. Though levels of AOX are lower, complete substitution of chlorine based bleaches is the only way to avoid evolution of hazardous substances (Stringer and Johnston 2001).

Hydrogen peroxide is the most common bleaching agent (IPPC 2003). Alkaline conditions are required to generate the active bleaching agent (the dioxide radical). Complexing agents are required to sequester any metal ions present. These catalyse the decomposition of hydrogen peroxide, forming hydroxide radicals that attack cellulose. Other common additives include sodium silicate, a pH buffer and H_2O_2 stabiliser, Mg salts: also stabilisers and surfactants to act as wetting agents.

Use of the most common complexing agent, EDTA has given rise to concern. EDTA is non-toxic to mammals at environmental concentrations. (Kari 1996), and exhibits low aquatic toxicity to fish though algae prove to be more sensitive. The largest concern relating to many chelating agents (especially EDTA) is their slow environmental decomposition. The resulting persistence in the environment (Nowack 2002) has led to a background level being present in European waters. Persistence allows chelating agent's effect upon metal ion chemistry to continue beyond the point of application. Chelation lowers metal ion affinity for surfaces, leading to passage through wastewater systems and an enhancement of mobility in aquatic systems (Bedsworth 1999). Remobilisation of metal ions from sediments potentially leads to contamination of ground and drinking water (Nowack 2002).

The issue has been given different levels of attention by different nations depending upon the basis of their environmental policy. For though the persistence of EDTA is definite toxicological issues arising from this are still unclear. Germany, concerned by rising EDTA levels in rivers entered into a legally non-binding agreement with industry to halve consumption in the 1990's. This sparked the search for environmentally benign alternatives which provided the same level of performance.

Two currently available are ethylenediaminedisuccinate (EDDS) and iminodisuccinic acid (IDA). Both are structurally very similar to EDTA yet biodegrade rapidly. EDDS appears to slightly out perform IDA (marketed as BaypureCX) produced by Bayer (Tandy 2004).

3.7.2 Reductive bleaching

Oxidative bleaching isn't suitable for polyamides as H_2O_2 attacks the polymer, instead reductive dyeing using sodium hydrosulphite is used. Though the bleaching of wool is uncommon (IPPC 2003) sodium hydrosulphite is also used in a two stage process following H_2O_2 (wool is sensitive to chlorine based agents). Sodium hydrosulphite is an EU high

production volume chemical which is toxic and an irritant (Lewis 2004) though will not be a substance of high concern under REACH.

3.8 Optical Brightening

Application of optical brighteners may occur after bleaching to hide any coloration still present (and may be considered as a form of dyeing itself). The agents are also components of many detergent formulations. Historically blue dyes were applied to counter the natural yellow colour of cotton and wool. Latterly optical brightening agents that absorb U.V light and emit visible wavelengths have been developed allowing “whiter than white” fabrics.

A number of these agents are listed as high and low production volume substances and so will be subject to REACH. For example C.I. Fluorescent Brightener 220 (used on cellulose fibers) is a high production volume chemical. A general observation that these substances persist has been made; though bioaccumulation has not been shown. A literature survey indicated that, when reported at all, low or no toxicity is associated with these substances. The BGVV conducted a health assessment of specific stilbene derived optical brightening agents (BGVV 2002) following concerns of potential health risks to the public. It was found that there is a general lack of information on toxicity and a need for studies into dermal absorption and the release of these substances from clothes.

4 Dyeing and printing

Arranged by dye type, an overview of dyeing methods is presented highlighting major chemical auxiliaries employed.

4.1 Reactive Dyes

One third of dyes used for cellulose are reactive and an increasing amount is used on wool and nylon (IPPC 2003). The dyes contain chemical groups that covalently bind to the fabric. For cellulose these are typically pyrimidine groups, triazine groups or sulphones, reaction occurs with hydroxyl groups of the cellulose by either nucleophilic substitution or addition.

For dyeing cotton a pH of 9.5-11 is used (IPPC 2003), achieved with NaCO_3 and/or NaOH . Up to 40% (Blackburn 2002) of the dyestuff may be hydrolysed by water, rendering it inert. This leads to the presence of reacted (inert) dye in waste water streams that is difficult to isolate (water soluble). Salt (NaCl) is used to increase dye bath exhaustion. The electrolyte suppresses negative charge build-up on the fabric caused by the use of anionic dyes and, hence, promotes increased dye uptake (Ahmed 2005). Quantities of up to 100g/l of dye liquor may be used, though required loadings vary with dyestuff (Ahmed 2005). Urea has traditionally been used as an additional solvent but use was already in decline by early 1990s (IPPC 2003). Modern dyes that don't require urea to achieve high fixation rates have been developed.

Poor dye fixation has been a longstanding problem with reactive dyes. Use has continued as shade reproducibility and colour fastness is excellent. Work is being undertaken to alleviate the environmental impact of reactive dyeing. The use of either cationic dyes or a cationic polymer based pre-treatment for the fabric alleviates the need for an electrolyte and reduces water consumption (Burkinshaw et al 2000) (Ahmed 2005) (Blackburn 2002). After dyeing the fabric is repeatedly washed with surfactants to remove excess/unfixed dyestuff.

4.2 Direct Dyes

Direct dyes are long planer molecules that can align with fibre macromolecules. These are held in place by Van der Waals (electrostatic) interactions and hydrogen bonds. 75% of consumption is for the dyeing of cellulose fibres (IPPC 2003).

Similar auxiliaries are used as with reactive dyes. Electrolytes (sodium chloride or sodium sulphate) are applied to favour the aggregation of dye molecules on the fibre. Wetting agents (usually non-ionic surfactants) aid uniform and thorough dye uptake. In order to achieve good colourfastness after-treatment is important; hydrophilic groups on the dye molecule are blocked resulting in reduced water solubility. This is referred to as "enlargement of the molecule" (IPPC 2003). Quaternary ammonium compounds with long hydrocarbon chains predominate; these form salt-like compounds with the dye molecule. Quaternary ammonium compounds are often toxic to aquatic organisms.

Agents based on formaldehyde condensation products can also be used (IPPC 2003). These form sparingly soluble adducts with the dyestuffs. As discussed later in more detail release of free-formaldehyde presents ecological and toxicological concerns.

4.3 Vat Dyes

Vat dyes are water insoluble compounds, generally based around anthraquinone or indigo. Excellent colour fastness and UV stability is displayed and so these expensive dyes are often used for fabrics that must withstand frequent, harsh washing such as military uniforms and hospital textiles or those continuously exposed to daylight such as furnishings.

The dyes are water insoluble, REDOX chemistry is employed to allow fixation. Firstly the dye stuff is reduced to a water soluble form using sodium dithionite (sodium hydrosulphite); resulting in sulphur salts in the waste water. Substitutes are available such as acetol (hydroxyacetone) though this is generally not as effective and so cannot reduce some dyes (Lacasse and Baumann 2004). The dyes may also be supplied in a pre-reduced form. Dispersants are often present in the dye mixture (IPPC 2003) such as naphthalenesulfonic acid-formaldehyde condensate (Figure 2).

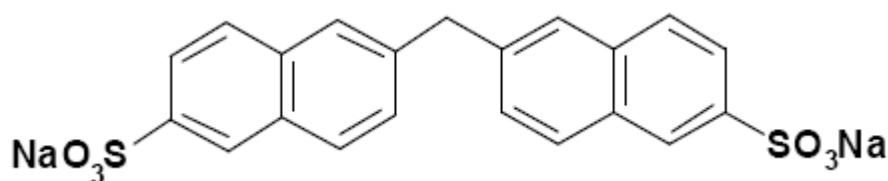


Figure 2 A naphthalenesulfonic acid-formaldehyde condensation product

These are not biodegradable as their molecular structure is too large for take-up by whole bacteria cells (Reiger et al 2002). Free formaldehyde contamination is also a problem with all such polymers though industrial literature (product information sheets) often states “low formaldehyde content” and acceptable levels have been set. Formaldehyde is very soluble in water (Merk Index 1999) this results in low concentrations in finished garments. Any contamination present reduces quickly due to washing (DEPA 2003).

Once absorption into the fabric has occurred an oxidising agent (often hydrogen peroxide or perborate) is added to reform the water insoluble dye. An after-treatment of mildly alkaline (NaOH, or NaSO₄) soap solution removes excess pigment and chemically alters dye particles.

Vat dyes are only very sparingly soluble therefore excess/waste can be regarded as highly eliminable from waste streams (IPPC 2003). Therefore it is assumed that water course contamination is not associated with vat dyes. Heavy metal impurities may be present due to production processes (IPPC2003).

4.4 Sulphur Dyes.

Mainly used for dyeing cellulose fabrics (including blends) to dark (and generally dull) shades, these are cheap and well established. Water insoluble, high molecular weight dye compounds are formed by reacting sulphurous compounds with amines and phenols. Many dyes contain sulphur groups, but only those that become water soluble after reaction with sodium sulphide in alkaline conditions are classified as sulphur dyes.

The use of sulphide and sodium hydrosulphide to produce a water soluble form of the dye gives rise to environmental concerns. (Lacasse and Baumann 2004). Their use is reported to be in decline (IPPC 2003). Alternative methods exist; either the dye is marketed in a pre-reduced form or alternative reducing agents are used. Sugar based systems exist; glucose can be effective either on its own or in combination with sodium dithionite or hydroxyacetone.

As with vat dyeing, dispersing agents are employed such as naphthalenesulphonic acid-formaldehyde condensates and sulphonated oils.

After rinsing the dye is oxidized to fix it. For this H_2O_2 can be used, the IPPC reports that halogenated compounds are also employed (iodate, chlorate, bromate). Literature also suggests that dichromate is used; though this is likely to be the historically employed method.

4.5 Naphthol dyes

Over half of all dyes currently used contain azo groups. Naphthol dyes are distinguished by their method of fixation. The azo bond is synthesised on the fabric forming an insoluble dye molecule from two water soluble fragments; a naphtholate and a diazotized compound.

A naphthol based compound is reacted with sodium hydroxide resulting in a naphtholate, this is an electron-rich species capable of coupling. The other coupling component, a diazotized aromatic compound, is either prepared from an aromatic amine in the dye house (by reaction with sodium nitrite and hydrochloric acid) or is supplied as a stabilized salt. The diazo developing agent is applied to the naphthol-impregnated fibre. The resulting coupling reaction forms an insoluble dye stuff.

Azo compounds exhibit a high degree of aromaticity and are vividly coloured. A degree of “mixing and matching” is possible, different combinations of coupling component and diazotic base result in different colours. This is possibly the most complex dye application process requiring skilled technicians and precise chemistry. As a result most dye houses no longer use it, opting for simpler processes.

4.6 Wool dyeing

Wool only accounts for approximately 4% of textile fibre use, but because dark shades predominate 8% of total dye consumption is for wool (Lacasse and Baumann 2004). The following dyestuffs may be used:

- Acid (metal free) dyes

- Chrome (mordant) dyes
- 1:1 and 1:2 metal complex dyes
- Reactive dyes
- (and more recently) temporarily solubilised disperse dyes.

Currently more than 65% of wool is dyed with chrome or metal-complex dyes.

4.7 Acid dyes

Acid dyes are generally bright with a variable fastness to washing. Structurally the dye molecules vary greatly and include some metal complexes (for example C.I acid blue 249 is centred around a copper ion). The defining feature of the group is the presence of sulphonate groups, these provide water-solubility. Bonding to wool occurs partially due to interaction between these sulphonate groups and ammonium groups on the wool fibre. Additional bonding interaction is provided by Van der Waals forces. The degree of interaction, and hence, the degree of colour fastness varies directly with dye molecule size.

The dyes are generally applied under acidic conditions (using formic or acetic acid) with the degree of acidity depending upon individual dye properties. The use of levelling agents is also governed by dye affinity for the fibre. Those that exhibit a high degree of affinity require chemical regulation so that even dyeing can be achieved. Sulphate salts (ammonium or sodium) compete with dye molecules for binding sites on the fibre, this controls the rate of dye uptake producing a more even result. A wide range of surfactants are also used as levelling agents, these may be non-ionic, anionic, cationic or amphoteric. Commercially available products contain synergistic mixtures of different types of surfactants (Lacasse and Baumann 2004).

4.8 Chrome (mordant) dyes

This dyeing method uses chrome ions to 'attach' dyestuffs to the fibre. The chrome forms a complex with both the dye and groups present on the fibre, acting as a bridge. This very strong bond supplemented by ionic interactions between dyestuff and fibre results in excellent wash fastness. The dyes are mainly used to achieve dark shades.

The most common technique used is now *after chroming* (IPPC 2003). Dye stuff is first applied to the fibre and then, in a separate step, a chrome salt is added. Chrome (VI) salts, which are water-soluble are used (generally dichromate $\text{Cr}_2\text{O}_7^{2-}$). The chrome is reduced to form a water-insoluble Cr (III) complex by groups on the fibre. Organic acids or thiosulphate may be added to increase the degree of fixation.

Whereas chromium (III) is an essential nutrient (in low doses), chromium (VI) is non-essential and toxic (ATSDR 2000, Goyer 1996). Compounds are corrosive, and allergic skin reactions readily occur following exposure, independent of dose. Short-term exposure to high levels can result in ulceration through skin contact, perforations of respiratory surfaces through inhalation and irritation of the gastrointestinal tract through ingestion. Damage to the kidney and liver have also been reported (ATSDR 2000)

The aquatic toxicology of chromium is also dependent upon speciation, with chromium (III) far less biologically available and toxic than chromium (VI). Negative effects have been observed in aquatic organisms exposed to dissolved chromium (VI) at concentrations below 40 µg/l. Furthermore, both chromium (III) and chromium (VI) have been shown to accumulate in many aquatic species, especially in bottom-feeding fish, bivalves, mussels and clams (Kimbrough *et al.* 1999).

Chromium levels in dye house effluent are related to industrial practice. Improper application of dichromate or in complete reduction could lead to the presence of chromium (VI) salts. As this is water soluble it is more likely to reach waterways than chromium (III) species which are more likely to precipitate or be absorbed into sludge. The environmental life of chromium (VI) species will be short; instability of the oxidation state will cause rapid reduction.

4.9 Metal-complex dyes

Rather than being a separate application-class, metal-complex dyes are simply grouped by a common structural feature: the presence of a metal ion. Labels 1:1 and 1:2 express the ratio of metal ion to dye molecule. As with mordant dyes an excellent wet fastness is exhibited. Application occurs under acidic conditions with required acidity varying with dyestuff. High levels of acidity are provided by sulphuric acid, for milder conditions acetic acid is used. If levelling is required either sulphate salts or surfactants are employed (IPPC 2003).

4.10 Disperse dyes - Polyester Dyeing

Polyester is dyed exclusively with disperse dyes; of which more than 50% are azo compounds and another 25% anthraquinones (IPPC 2003). As the fibre is hydrophobic water-soluble dyes do not attach. Instead disperse dyes can be characterised by the lack of polar groups and are generally small molecules (these penetrate into the fibre more readily). The dye molecules are not bound to the fibre, instead a variety of electrostatic interactions (dipole-dipole, Van der Waals, and hydrogen bonds) increase affinity for the fibre, resulting in fixation. The lack of a strong chemical bond permits a degree of migration out of the fibre, this accounts for the high incidence of contact dermatitis associated with disperse dye stuffs.

Aqueous liquors are the industrially favoured method of applying dye stuffs. For polyester the water insoluble dye is applied as an aqueous dispersion. The dye does not readily penetrate the fibres and so some kind of forcing conditions are required. In the case of pure polyester (or blends with cellulose fibres) heat is used. One method (batch dyeing) is conducted under pressure at 125-135°C at an acidic pH (acetic acid). Levelling agents (generally carboxylic esters, ethoxylates, or combinations of other hydrocarbons) are added to prohibit too rapid dye uptake (Lacasse and Baumann 2004). An important method of dyeing polyester/cellulose blends; the Themosol process, involves padding the dye at 140°C and then fixing briefly at over 200 °C.

Dyeing of wool/polyester blends must occur at lower temperatures; in this case chemical agents (carriers) are employed to aid dye penetration. Compounds used include:

- halogenated benzenes including di- and tri- chlorinated benzenes and dichlorotoluene.
- aromatic hydrocarbons (including biphenyls such as 2-phenylphenol).
- carboxylic acids, including phthalates (DMP, dibutyl phthalate, DEHP) and benzoates.
- alkyl phthalimides for example, N-butylphthalimide.

The carrier content of finished garments may be very low (<0.2%) if state of the art dyeing practices are used otherwise contents of up to 2.7% may occur (Platzek 2002). Toxicological issues are associated with most carriers (Lacasse and Baumann 2004). Halogenated benzenes (e.g. 1,2,4-trichlorobenzene), dibutyl phthalate and diethylhexyl phthalate fall under the OSPAR convention, are bioaccumulatory (Smith *et al* 1990) (Sanders *et al* 1973) and toxic (OSPAR). These substances will also be subjected to restrictions due to REACH. Though usage information was not obtained it appears that the most commonly applied substances in the EU are carboxylic acid esters and alkylphthalimides. It is suspected that chlorinated species are still in use (IPPC 2003).

Subjecting polyester to high temperatures can cause species to migrate out of fibres into the dye liquor. The release of antimony oxides (PET production catalysts present as an impurity) is known to occur. Antimony trioxide is listed as a category 2b substance by IARC (possibly carcinogenic to humans). Evidence is based primarily on inhalation studies with rats. It is recorded as a poison by intravenous and subcutaneous routes (Lewis 2004). The substance carries the risk phrase “possible risk of irreversible effects”. As an EU substance of high concern it is subject to risk assessment under Council Regulation (EEC) 793/93, currently no draft risk assessment is available. A lack of comprehensive toxicological information for this substance is clear from searching various resources. This substance provides a clear example of the need for REACH.

Alternative catalysts exist, notably systems based around titanium dioxide. Sachtleben Chemie GmbH and others have been marketing such a system for at least three years. Patents have been filed by other companies including a number by DOW. Titanium dioxide is a registered food additive. The substance is more expensive though this is offset by greater catalytic activity. There are indications that some of the alternative systems feature cobalt oxides, these too have been shown exhibit toxic effects and so must be avoided.

4.11 Nylon Dyeing

Nylon may be dyed with a variety of dye classes: due to the fibre’s hydrophilic nature disperse dyes may be used, whilst the presence of polar groups allows the use of metal-complex, acid and reactive dye stuffs.

4.12 Acrylic Dyeing

Hydrophobic acrylic may be dyed easily with disperse dyes without the need for carriers, whilst the presence of anionic groups allows for the use of cationic dyestuffs.

4.13 Printing

Whereas dying conveys a uniform colour, printing allows a range of different colours to be applied. Usually between 5 and 10 pastes are required for a single pattern. Colour may be supplied by either pigments or dyes.

Pigment printing is gaining popularity (IPPC 2003). As the pigment has no natural affinity for the fabric it must be attached with a binding system generally some form of self-cross linking polymer such as acrylates.

Plastisol printing is commonly used for tee-shirts. The colour is applied in a paste of PVC and plasticizer, forming a noticeably tactile layer. One example of application is football shirts. The printed label areas (often with a fibrous content) are based on PVC/phthalate pastes. These are used due to their versatility, production is conducted in small batches and the shirts are re-designed often. Therefore the paste formulators need a base that can withstand different pigment/additive mixtures.

The most commonly used plasticizers for this application are phthalates, namely DEHP (di-ethylhexyl phthalate), BBP (benzylbutylphthalate), DINP (diisononyl phthalate) and DHP (diheptyl phthalate) (Greenpeace 2004). These substances have been subject to concerns relating to their toxicity to the environment and humans for a number of years. They have been identified as components of household dust (Santillo et al. 2003) and presence in human blood has been detected (Colon et al. 2000, Blount et al. 2000). DEHP is a reproductive toxin and has been listed as such under EU Directive 76/769. It has been shown to cause morphological changes in the testis, including apoptosis, necrosis, and loss of spermatogenic cells, resulting in testicular atrophy (Park *et al.* 2002). The use of phthalates in PVC children's toys is now controlled by emergency EU legislation. Both phthalate free and (more importantly) phthalate *and* PVC free printing pastes are available and have been for at least two years. Despite this the products are still in use and are found in high street brands (Greenpeace 2004, DEPA 2003).

Dye printing pastes are of a more variable composition, dependant upon the type of dye used (IPPC 2003). Environmental issues are similar to the equivalent wet dyeing technique except for an additional COD loading due to the use of thickeners.

4.14 Dyes Derived From Nature

Utilisation of modern technology has reduced the amount of dyestuff entering the environment considerably. However a return to natural dyestuffs has been proposed as a more fundamental method of reducing the environmental burden. It has been shown that natural dyes can provide a wide range of shades and that acceptable levels of colourfastness can be obtained (Bechtold *et al* 2002). The dyes tend to be inherently biodegradable and a lower chemical loading to waste streams is associated with their use.

Traditionally the dyes have been applied by craftsmen; this expertise is now being lost and certainly is not of a form that allows direct transference to modern dye houses. Problems of colour variation are often cited (Slater 2004). This problem may be solved by the application of modern extraction methods.

4.15 Toxic Dyes and Pigments

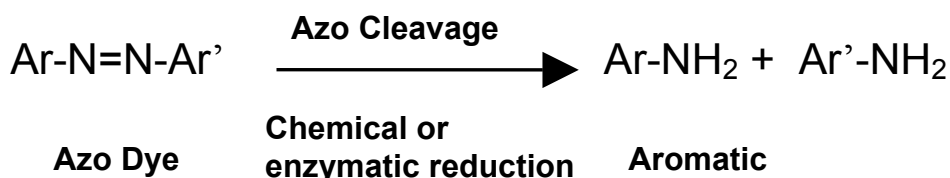
Many dyes are persistent substances. As many of the most important dyes have been on the market for years they come under the existing chemicals directive and are not fully (if at all) tested for potential health effects. So REACH will definitely cause an impact.

4.15.1 Carcinogenicity and Mutagenicity

Over half of the dyes used contain azo bonds. This chemical bond, in combination with large aromatic groups endows the molecule with its colour. Azo bonds can cleave, under reductive conditions, to form amines. Some of these aromatic amines have been shown to be carcinogenic and 22 are covered by EU directive 2002/61/EC. The legislation is based on a German Consumer Goods Ordinance and bans the use of dyes that can release any of the amines at concentrations greater than 30ppm from finished garments. However more than 100 dyes with the potential to release carcinogenic amines are still on the market (IPPC 2003)

Azo dyes released from textiles may either be exposed to chemical reducing agents or reductive enzymes. In the human organism, these could be intestinal bacteria or azo reductase in the liver (Oh et.al 1997).

Azo pigments may also release amines. These may not be covered by the legislation, as pigments are generally water insoluble it is assumed that they pose no threat to health. The German Consumer Goods Ordinance differentiates between types of azo pigments testing some and not others.



Hazards arising from azo dye derivatives have been recognised for years. This is not the case for textile dyes generally. Toxicological information is scarce as most were placed on the market before 1983 (Schneider 2004). Recent studies funded under an EU CRAFT initiative show there is just reason for concern. 14 out of 281 dye products tested were shown to be mutagenic, for a further 16 there is a suspicion of mutagenicity (Schneider 2004). The paper reveals the scale of the problem, for 93 of the substances evaluated it was not possible to find any mutagenicity data (access to industrial information was available). It is also noted that dyes of concern came from all chemical classes represented, indicating the need for evaluation of dyes on a case-by-case basis. This paper and others indicate that many dyes would be chemicals of concern under REACH. An example is C.I Basic Blue 3 this substance has been shown to have potential carcinogenic properties (CCRIS online) yet is still widely used for dyeing polyacrylic fibres.

4.15.2 Contact Dermatitis

Dyes have been linked with contact dermatitis (Hatch 1999). The problem is known to occur with disperse, acid and reactive dyes. It is especially associated with disperse dyes; as these are not chemically bound to the fibres there is a higher chance of them coming into direct contact with the skin. The Öko-tex eco label lists 21 dyestuffs classified as allergens, all are disperse dyes.

4.15.3 Heavy Metal content

Dyes are a very important source of metals in finished textiles. Typically transition metals such as chrome, copper, nickel and cobalt are used. These are able to form multiple bonds with organic dyestuffs and/or fibres. If the metal is intentionally used in dyeing it may be detected in the finished garment at high concentrations. Copper concentrations of up to 300 ppm are not uncommon (Rybicki *et al* 2004, DEPA 2003).

Many heavy metals are present at ppm levels as impurities in raw fibres (Rybicki *et al* 2004), and may also be present as impurities in dyestuffs as a result of their use as catalysts in dye synthesis (Lacasse and Baumann 2004). The availability of metals, and thus the potential health concerns arising are difficult to assess. Metals bound in water-insoluble dye-complexes are unlikely to be released and as these complexes are not water soluble are unlikely to be bioavailable. Eco-labels (Öko-tex 100) set limits upon the levels of metals allowed in fabrics but detection methods do not take into account availability or oxidation state (factors that have great effect upon toxicity and bioavailability).

5 Finishing

Textile finishing represents the most variable area in the production process. A wide and ever growing range of finishes are now available; these either improve the properties of the garment, for example imparting crease-resistance or provide “performance” properties, including antimicrobial agents to prevent sports and undergarments developing odours. Finishes now include the (questionably) superfluous, such as a “wellness” finish produced by CHT R. Beitlich GmbH which releases the antioxidant vitamin E.

5.1 Easy-care

Easy care finishes are the most common and are perceived to be necessary in order to allow cellulose fibres to compete with modern synthetics. Cross-links between the fibres prevent wrinkling after wetting and reduce shrinkage due to laundering.

Cross-linking agents are the main source of formaldehyde releases from finished garments (IPPC 2003). Industry has worked at developing “low” and “very low” formaldehyde products. Some formaldehyde free substitutes now exist. A Danish EPA study of chemicals in clothes found free-formaldehyde in three out of ten garments tested. Levels were shown to fall markedly after one launder at a low temperature. This indicates that the greatest exposure to this carcinogen is likely to be to industry employees including retail staff (DEPA 2003).

5.2 Water-repellent Finishes

Water repellent properties may be imparted to fabrics in a variety of ways. Paraffin wax based methods have been used for a large number of years. Despite comparative costs fluoropolymer based solutions have gained popularity due to performance (IPPC 2003), silicon and resin based treatments also exist.

Paraffin wax is applied in combination with aluminium or zirconium salts, these generally exhibit lower toxicity to many other metals. It is noted that high levels of VOCs are released during heat treatments.

Fluoropolymers based products are repellent to both oil and water. Short-chain fluorinated compounds, the building blocks of finishes, have attracted much concern due to their proliferation throughout the environment (Boulanger *et al* 2004, So *et al* 2004, Martin *et al* 2004). The substances persist due to the inherent strength of carbon-fluorine bonds. PFOS (perfluorooctanyl sulphonate) is starting material for many finishes. 3M voluntarily withdrew some of its fluorocarbon based products (including Scotchguard) in 2000 due to environmental concerns over PFOS (ENDS 2000). The substance has been detected in human blood (Kannan 2004) and is likely to meet the criteria for a POP (ENDS 2004 a).

5.3 Flame retardants

A wide range of chemical flame retardant systems exist. As application is mainly to non-apparel fabrics discussion here is restricted to highlighting a few current issues..

Halogenated flame retardants have come under close scrutiny in recent years. The polybrominated diphenolethers have received much attention. PBDEs are persistent, lipophilic, and bioaccumulating chemicals of anthropogenic origin (Jakobsson *et al* 2002). Exponential increases in concentrations of PBDEs in arctic wildlife have been observed using archived tissues over the period 1981-2000 (Ikonomou *et al.* 2002).

Whilst the use of two lesser substituted substances penta- and octa-PDE is being phased out due to EU directive 2003/11/EC it has generally been assumed that the most substituted PBDE (Deca-PDE) does not pose a risk. As production levels of the lesser substituted PDBEs were much lower regulatory action did not affect industry much. Decabromodiphenylether came out of the EU risk assessment process relatively unscathed. The substance is very versatile and is employed both in textiles and polymers. However the risk assessment summary (ECJRC 2003) concluded that:

- further studies were required to fully assess the effect of deca-BDE on the environment.
- *“[An] aspect of the concern for secondary poisoning is that although the substance is persistent, there is evidence that it can degrade under some conditions to more toxic and bioaccumulative compounds.”*
- *“There is a high level of uncertainty associated with the suitability of the current risk assessment approach for secondary poisoning and the debromination issue. The combination of uncertainties raises a concern about the possibility of long-term environmental effects that cannot easily be predicted. It is not possible to say whether or not on a scientific basis there is a current or future risk to the environment. However, given the persistent nature of the substance, it would be of concern if, once the further information had been gathered, the analysis indicated a risk to predators, since it could then be difficult to reduce exposure.”*
- *“A number of technical experts from EU member states consider that this uncertainty is sufficient to warrant risk reduction measures directly ... based on the information currently provided in this assessment.”*

Numerous studies have now been published indicating the risk posed by deca-PDE. It has also been shown that deca-PDE can debrominate in the environment forming the congeners that have been shown to be more toxic (Tysklindet *al.*, 2001). Environmental agencies and pressure groups had hoped that a voluntary initiative involving industry group the BSEF (Bromine Science and Environmental Forum) would monitor and reduce emission levels. However at the task force's first meeting the BSEF announced that monitoring deca-BDE levels would prove too expensive (ENDS 2004 b). This evidence combined with a technical assessment of alternatives in textile applications concluding that the technology for substitution already exists (KEMI 2004) presents a very strong case for substitution.

5.4 Bactericidal and fungicidal Agents

The application of antibacterial products is increasing; in apparel triclosan is most commonly applied (DEPA 2004). The substance has raised concerns amongst dermatologists due to potential risks to the natural fauna of the skin. A positive n-octanol-water partition coefficient indicates the potential for bioaccumulation. The bioaccumulation factor of the main metabolite, methyl-triclosan, has been estimated to be 2000-5200 (Balmer *et al* 2004) sufficient to reach the persistent, and possibly very persistent thresholds of REACH. NOEC for rainbow trout has been determined to be 34×10^{-6} g/L (Orvos *et al* 2002) above the required REACH limit for classification as toxic. The same source states the value for algae *scenedesmus subspicatus* as $0.5 \times 34 \times 10^{-6}$ g/L; below the threshold. Bioaccumulation data is scarce though it appears that conversion to methyl-triclosan occurs (Singer *et al* 2002).

A study conducted by the Danish EPA of antibacterial clothes found triclosan at levels of 7-195 ppm (l.o.d: 5 ppm) and concluded that emission to waterways through from clothes washing was likely to be much lower than from other domestic sources (DEPA 2004).

Substitution of antibacterial components involves user-practice substitution: infrequent washing by more frequent.

6 Conclusions

As far as possible the terms of reference have been fulfilled and an overview of the main sources of emission of chemicals of concern identified. Most of the environmental footprint of textiles occurs during production, largely due to amount of chemical auxiliaries required to produce finished fabrics. Finished garments may contain a limited amount of residual processing chemicals. The overall content of toxic substances within finished garments tends to be limited. An extensive study conducted by the Danish EPA found no great causes for concern (DEPA 2003).

The main chemicals of concern identified in finished garments which may be of particular interest are: phthalates in Plastisol printed garments and antimony trioxide in polyester fabrics. Certain dyes give cause for concern, though due to the specific nature of their application these are probably not suitable for exposure. Issues relating to the use of fluoropolymers may, likewise, deserve attention. However at the time of writing a number of questions remain unanswered and no studies could be found linking garments to emissions. Antibacterial additives have also received much attention. A separate DEPA study looking at antibacterial agents in garments found only limited concentrations of triclosan and no other agents.

The textiles industry and its products give rise to a wide range of environmental and toxicological impacts. However, due to the complexity and range of chemistry involved and the lack of available data an accurate assessment of this impact is difficult. Efforts have been made in Europe at least to avoid chemicals of high concern, unfortunately this cannot be taken for granted world wide.

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