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Survey of Selected Allergenic, Disperse Dyes in Clothes

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Survey of Selected Allergenic, Disperse Dyes in Clothes

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Foreword

The project ”Survey of Selected Allergenic, Disperse Dyes in Clothes” was carried out from July 2012 till December 2013.

This report describes the project results and includes a survey, a literature review and results from chemical analyses on a number of selected clothes.

The project was carried out by Danish Technological Institute in cooperation with Force Technology. Participants from Danish Technological Institute were Quality Manager Eva Jacobsen (project manager), Torsten Due Bryld, John Hansen and Eva Pedersen. Pia Brunn Poulsen participated from Force Technology.

A steering group was appointed to evaluate the progress, course and results of the project and it consisted of:

- Lærke Ambo Nielsen, the Danish Environmental Protection Agency (EPA)
- Jette Heltved, the Danish Environmental Protection Agency (DTI)
- Eva Jacobsen, Danish Technological Institute
- Torsten Due Bryld, Danish Technological Institute
- Pia Brunn Poulsen, Force Technology

The project was financed by the Danish Environmental Protection Agency.

Conclusion and Summary

In the textile and clothing industry, a wide range of chemical substances are used to dye clothes. Several of the substances are problematic or their break-down products can be problematic. Some dyes are decomposed to carcinogenic amines and some have proven to be allergenic or to have other undesirable effects. It is important to be aware of chemical substances in clothes that are worn close to the skin and for a longer period of time as direct exposure is in question, and that can give rise to local skin reactions as well as systemic effects by absorption through the skin. Therefore, it is interesting to disclose which dyes are used in textiles for clothes and which undesirable effects the substances might have on human health.

Originally, the objective of this project was to investigate all types of dyes in order to obtain an overview of which dyes typically are used in textiles for children's clothes. That product group was chosen to focus the project and to investigate the content of dye in clothes that are used by one of the most sensitive consumer groups. Focus was on night clothes, underwear, etc., which are in close contact with the skin for a longer period of time. The initial survey showed that companies that produce clothes in general do not have information about which dyes are used in their textiles, as most of them refer to negative lists and to the requirements concerning which dyes are *not* allowed in textiles. The survey also showed that the manufacturers of clothes focus on ensuring that production in as well as outside of the EU follows the guidelines stipulated in REACH and that azo dyes should not be used, as they can degrade to primary aromatic amines that are regulated in appendix 17 in REACH and registered on the candidate list. At the same time, the information collected during the survey showed that the companies do not focus as much on disperse dyes as on azo dyes. In literature, a number of disperse dyes are described as being allergenic.

On the basis of the information from the introductory survey it was decided to change the objective of the project from dealing with the occurrence of dyes in general to focusing on the occurrence of allergenic, disperse dyes in clothes.

A wide range of studies have been carried out concerning contact allergy from disperse dyes. More than 50 studies were found in literature where patch tests had proven contact allergy. The largest investigation was carried out in Germany where 24,980 people were examined and 1.35% showed allergic reactions to disperse dyes. The second largest investigation was carried out on 6,478 people among whom 6.7% had allergic reactions. The different results from the investigations might be due to several factors such as different test conditions and regional differences, including how widely disperse dyes are used and a warmer climate that gives rise to increased perspiration with subsequent increased liberation of dye to the skin.

In the light of a review of the literature on the topic and on the results from previous investigations, it was decided to focus on 23 selected disperse dyes. All dyes were chosen on the basis of their allergenic potential. In addition, two of them are described as being carcinogenic. Disperse dyes are mainly used in synthetic textiles (such as polyester) and inter alia for sportswear. 31 garments were purchased, and they were all examined for content of the 23 dyes.

When the first analyses had been carried out, eight garments were suspected to contain the disperse dyes called Disperse blue 124 or Disperse yellow 49. However, further analyses disclosed that that was not the case and none of the 23 disperse dyes were proven in this investigation.

Only a limited number of samples coming from a very large market were examined, and on the basis of this project it cannot be excluded that disperse dyes exist in other areas of the Danish textile market. However, the 31 garments were purchased according to criteria that should make it easier to identify undesired disperse dyes such as country of production, fibers and shades, and therefore goal-oriented random sampling (and not chance sampling) is in question. At the same time, the results from this investigation confirm previous discoveries made by others. A published investigation comprising 120 garments collected from all over the world only disclosed a content of one or more disperse dyes in three garments. That study only examined the presence of eight disperse dyes, whereas this project examined the presence of 23 dyes. In spite of the difference in number of disperse dyes that were analyzed for, this project arrives at the same result; namely, that the use of disperse dyes, which are known to be allergy causing, is very limited.

Information obtained through interviews with the Danish National Allergy Research Centre and Asthma-Allergy Denmark support the impression that allergic reactions due to disperse dyes in clothes occur, but to a very limited degree. Many of the enquiries received by the National Allergy Research Centre concerning allergy from disperse dyes in clothes have involved the use of new clothes that have not been washed before use.

All in all, it is estimated that this project found no indications that allergenic, disperse dyes constitute a health-related problem in clothes on the Danish market. However, it is important to follow a possible development on the market as these substances are known allergens, and allergic reactions arising from the use of clothes dyed with disperse dyes have been determined, although to a very limited degree.

Konklusion og sammenfatning

I tekstilbranchen anvendes en lang række stoffer til indfarvning af tøj. Flere af disse farvestoffer er enten i sig selv problematiske, eller deres nedbrydningsprodukter kan være det. Nogle farvestoffer nedbrydes til carcinogene aminer, og nogle har vist sig at være allergifremkaldende eller at have andre uønskede virkninger. Det er vigtigt at være opmærksom på kemiske stoffer i tøj, der bæres tæt på kroppen og over længere tid, da der er tale om en meget direkte eksponering, som vil kunne give anledning til både lokale reaktioner på huden eller systemiske virkninger ved absorption gennem huden. Derfor er det interessant at afdække, hvilke farvestoffer der anvendes i tekstiler til tøj, og hvilke uønskede effekter disse stoffer evt. kan have på sundheden.

Oprindeligt var formålet med nærværende projekt at undersøge alle typer farvestoffer for at få overblik over, hvilke farvestoffer, der typisk anvendes i tekstiler til børn. Denne produktgruppe blev valgt for at målrette undersøgelsen og for at undersøge farvestofindhold i tøj, der anvendes af en af de mest følsomme forbrugergrupper. Der blev fokuseret på nattøj, undertøj m.m., som har længerevarende og tæt kontakt med huden. Den indledende kortlægning viste, at virksomheder, der producerer tøj, generelt ikke har informationer om, hvilke farvestoffer, der anvendes i deres tekstiler, idet de fleste arbejder ud fra negativlister og krav til hvilke farvestoffer, der *ikke* må anvendes i tekstilerne. Kortlægningen viste ligeledes, at tøjproducenterne har fokus på, at produktionen både i og uden for EU følger retningslinjerne i REACH, og at man derfor ikke anvender azofarvestoffer, der kan fraspalte primære aromatiske aminer, som er begrænset i bilag 17 i REACH, og som er opført på kandidatlisten. Samtidig tydede de indsamlede informationer fra kortlægningen på, at virksomhederne ikke har samme fokus på gruppen af disperse farvestoffer, som de har på azofarvestoffer. En række disperse farvestoffer er i litteraturen beskrevet som værende allergifremkaldende.

Ud fra disse informationer fra den indledende kortlægning blev det derfor besluttet at ændre projektets formål fra at handle om forekomsten af farvestoffer generelt til at fokusere på forekomsten af allergene, disperse farvestoffer i tøj.

Der er publiceret en lang række undersøgelser om kontaktallergi fra disperse farvestoffer. Der er i litteraturen fundet over 50 studier, hvor der ved hjælp af patch test er påvist kontaktallergi. Den største undersøgelse er foretaget i Tyskland, hvor man undersøgte 24.980 personer, hvoraf 1,35 % udviste allergiske reaktioner på disperse farvestoffer. I Italien blev den næststørste undersøgelse udført på 6.478 personer, og heraf udviste 6,7 % allergi. De forskellige resultater i undersøgelserne kan skyldes flere faktorer, som fx forskellige forsøgsbetingelser og regionale forskelle, herunder udbredelsen af de disperse farvestoffer og et varmere klima, der giver en øget svedproduktion og dermed øget frigivelse af farvestoffer til huden.

På baggrund af en gennemgang af litteraturen om emnet og af resultater fra tidligere undersøgelser blev det besluttet at fokusere på 23 udvalgte disperse farvestoffer Disse farvestoffer er alle valgt på baggrund af, at de har allergifremkaldende potentiale. To af dem er desuden beskrevet som værende carcinogene. Disperse farvestoffer anvendes hovedsageligt i kunststoffer, som fx polyester, og bl.a. til sportstøj. Der blev indkøbt 31 stykker tøj, der alle blev undersøgt for indhold af de 23 farvestoffer.

Efter de første analyser mistænkte man otte tøjstykker for at indeholde de disperse farvestoffer Disperse blue 124 eller Disperse yellow 49. Yderligere analyser afslørede dog, at det ikke var tilfældet, og ingen af de 23 disperse farvestoffer blev således påvist i denne undersøgelse.

Der er tale om et meget begrænset antal prøver på et meget stort marked, så det kan ikke ud fra denne undersøgelse udelukkes, at der findes disperse farvestoffer i andre områder af det danske tekstilmarked. Dog blev de 31 tøjstykker indkøbt ud fra kriterier, som skulle øge sandsynligheden for at identificere uønskede disperse farvestoffer, såsom produktionsland, fibre og farvenuance, og der er således ikke tale om en tilfældig men en målrettet stikprøvekontrol. Samtidig bekræfter resultaterne fra denne undersøgelse tidligere fund gjort af andre. I en publiceret undersøgelse omfattende 120 tøjstykker indsamlet fra hele verden blev der kun fundet indhold af et eller flere disperse farvestoffer i tre stykker tøj. Dette studie undersøgte kun tilstedeværelsen af otte disperse farvestoffer, hvorimod nærværende undersøgelse inkluderede 23. På trods af forskellen i antallet af disperse farvestoffer, der analyseres for, når nærværende undersøgelse frem til det samme resultat, nemlig at udbredelsen af disperse farvestoffer, der er kendt for at være allergifremkaldende, er meget begrænset.

Information opnået gennem interview med Videncenter for Allergi og med Astma-Allergi Danmark underbygger opfattelsen af, at allergiske reaktioner som følge af disperse farvestoffer i tøj forekommer, men i et meget begrænset omfang. Mange af de henvendelser, Videncenteret har fået om allergi fra disperse farvestoffer i tøj, har involveret brug af nyt tøj, der ikke har været vasket inden ibrugtagning.

Samlet set vurderes derfor, at der i denne undersøgelse ikke er fundet indikationer på, at allergene, disperse farvestoffer udgør et sundhedsmæssigt problem i tøj på det danske marked. Dog er det vigtigt at følge en evt. udvikling i markedet, da disse stoffer er kendte allergener, og allergiske reaktioner efter brug af tøj farvet med disperse farvestoffer er påvist, om end i et meget begrænset omfang.

1. Background

1.1 Objective of the Project

In the textile and clothing industry, a wide range of chemical substances are used to dye clothes. Several of the substances are problematic or their break-down products can be problematic. The Danish Environmental Protection Agency has published report No. 534[1] that describes which dyes can be problematic. This report especially points at disperse dyes and azo dyes. Currently, app. 4,000 dyes are listed in the Colour Index[2] and app. half of them are azo dyes. From them app. 500 are made from carcinogenic amines, and around 150 of the azo dyes are still commercially available.

In many cases, dyes in textiles will lead to direct skin contact between the textile and the user with a risk of human exposure. A large amount of the clothes we use in Denmark come from countries outside of the European Union.

Therefore, the objective of this project was to carry out a survey of dyes, used in children's clothes, which have direct contact with the skin for a longer period of time, and which are produced outside of the European Union. In the initial phase of the project, focus was therefore on clothes for children of up to nine years of age.

On the basis of interviews at research centres, with manufacturers and via questionnaires it became clear in the survey phase that it was not possible to procure data about which particular dyes are used.

Focus was, therefore, changed to deal with the general prevalence of allergenic disperse dyes especially in synthetic textiles. This group of dyes was chosen as it in literature is described that disperse dyes can give rise to allergy.

Disperse dyes are mainly used to dye polyester and other synthetic textiles. Polyester-based textiles are used a lot in sports clothes for children as well as for adults. Sports clothes are often tightfitting and therefore increase the risk of allergy. At the same time, the survey showed that clothes made of polyester are only to a smaller degree used in children's clothes that is tightfitting. When choosing products for the chemical analyses, clothes for both adults and children were chosen to obtain a wide variety of clothes that might contain disperse dyes.

It was the original objective of the project to estimate the health-related and environmental aspects of the found dyes and/or their break-down products, but due to the results of the survey and the chemical analyses, where no content of disperse dyes were determined, that part was omitted from the project.

1.2 Legislation

In connection with textiles, there are a number of legal limitations with regard to content of chemical substances. The limitations concern the content of the following substances and fabric groups:

- Azo dyes

[1] Report by the Danish Environmental Protection Agency "Chemicals in Textiles", Survey of chemical substances in consumer products No. 534, 2000
[2] http://www.colour-index.com/

- Brominated flame retardents (penta and octa bromodiphenylether)
- Impregnating agents (Tris (2,3 dibromopropyl)phosphate (TRIS) , Tris(aziridinyl)phosphinoxide (TEPA), Polybrominated biphenyls (PBB) and perfluorooctane suflonic acids (PFOS))
- Bactericides (pentachlorophenol (PCP))
- Fungicides and agents against mould (dimethylformamide (DMF))
- Biocides (organic tin compounds (tributyltin- (TBT), triphenyltin- (TPT), dibutyltin- (DBT) and di-n-octyltin- (DOT) compounds))
- Heavy metals (nickel in metal parts in textiles, mercury for impregnating industrial textiles, lead, cadmium and mercury in general)
- Nonylphenol and nonylphenolethoxylates (for textile processing)

In addition, textiles are subject to the duty to disclose substances on the candidate list under REACH.

In the following, the rules comprising dyes in textiles are described, meaning the rules concerning azo dyes and the Danish rules concerning the limitation of heavy metals (lead, cadmium and mercury), as these heavy metals can be used or previously have been used for dyes. In addition, the rules concerning the duty to disclose substances on the candidate list under REACH are described.

1.2.1 Legislation on Azo Dyes

According to REACH (Regulation No. 1907/2006) enclosure XVII No. 43 azo dyes must not be used in textile or leather articles that for a long duration can come into direct contact with the skin or mouth of humans, if these azo dyes by reductive cleavage of one or several azo groups can release one or more of the 22 aromatic amines that are stated in Annex 8 in the REACH regulation (also stated in Appendix 4 of this report). The limit value is 30 mg/kg (or 0.003% (w/w)) for each of the 22 aromatic amines based on the analysis methods that are described in Annex 10 in the REACH regulation.

In addition, according to the REACH regulation Annex XVII No. 43 it is not allowed to use specific azo dyes (stated in Annex 9) as substances or in mixtures in concentrations of more than 0.1% (w/w), if the substance or the mixture is intended for dyeing textile or leather articles. Annex 9 contains (June 2013) a blue azo dye with index No. 611-070-00-2 (it is a mixture of two dyes).

1.2.2 Legislation on Heavy Metals

Several heavy metal compounds can be used (or have previously been used) as dyes or pigments, i.a., nickel, lead, cadmium and mercury compounds. Nickel compounds are not regulated as for the use of dyes, but they are regulated through the liberation of nickel from metal parts that for instance form part of textiles (REACH regulation No. 1907/2006, Annex XVII nr. 27).

Denmark has special legislation regarding the following heavy metals: lead, cadmium and mercury, as described in Executive Order No. 856 (2009), Executive Order No. 858 (2009) and Executive Order No. 627 (2003), respectively. In general it applies that the import, sale and export of products that contain these three heavy metals (in metallic form or in chemical compounds) in higher concentrations than stated below are prohibited:

- Lead – 100 mg/kg (0.01%)
- Cadmium – 75 mg/kg (0.0075%)
- Mercury – 100 mg/kg (0.01%)

The limit values apply to the homogeneous parts of the product. In practice that means that the content of lead, cadmium and mercury in dyed textile must not exceed the above-mentioned values.

1.2.3 Duty to Disclose Substances on the Candidate List under REACH

According to REACH (Regulation No. 1907/2006), article 33, suppliers of articles (including textiles and textile products) are committed to pass on information about content of substances that have been included on the candidate list (as SVHC (Substances of Very High Concern)), if a substance from the candidate list is included in the article in a concentration of more than 0.1% (w/w). If a supplier delivers directly to the consumer, then the same duty to disclose applies to inquiries from consumers.

As at June 2013, the candidate list comprised a total of 138 substances; included are also some specific pigments/dyes. When a supplier sells textile to a non-consumer, the supplier is committed to inform the content of specific substances on the candidate list, if the concentration exceeds 0.1%. As a minimum, information has to be given of the name of the substance and other information that the supplier has at his disposal and that are sufficient for safe use of the textile.

1.3 Outline of Dyes

Generally, dyes are divided into classes that are specific for how the dyes are used, and for which fibres they usually are intended for. How the dyes fix to a textile depends on different stages of the production process (fibres, yarn, piece goods, completed garments) and machine type, e.g., batch machines where pre-treatment, dyeing and after-treatment take place in the same machine, compared to machines that work continuously.

In addition to the dyes, a number of subsidiary materials are used during dyeing to speed up the process. Generally, the subsidiary materials are removed before the textile leaves the dye-works, but in some cases there can still be traces or a minor content of the subsidiary materials in the finished textile.[3]

1.3.1 Fixation of Dyes and Pigments on Textiles

Textiles can be dyed by using dyes or pigments that are applied to textiles in different ways. Dyes are characterised by being soluble in the medium they are in and that the textile is lead through. The dye fixes more or less efficiently to the textile. On the other hand, pigments are insoluble in media that can be used to dye textiles. Pigments are mainly used for printing in the textile industry and in other connections for varnish, paint and cosmetics.

Exhaust dyeing is the process of dissolving dyes and chemicals in water. The fabric is loaded into a machine (batch) and the dye is slowly moved (substantivity) from the solution to the fabric fibres. The substantivity can be influenced by temperature or chemical additives. The process is followed by rinsing to remove any excess dye.

Continuous dyeing is the process of leading textile through a continuous dye bath in a so-called foulard. The textile is pressed through two rolls for constant liquid content. Subsequently, dye application and fixation take place continuously through a dyeing system. Finally, rinsing takes place to remove any excess dye.

Printing is the process of applying dyes or pigments in a very viscous pressure paste to the textile through stencils or through engraved rolls in a certain pattern. There will be a stencil or a roll for each shade in the pattern. When printing with pigments the excess dye is usually not removed by rinsing. When printing with dyes, rinsing takes place at the end of the process to remove any excess dye.

[3] Description of dyes was prepared by Danish Technological Institute, Centre for Textile, general knowledge on dyes and dyeing.

1.3.2 Dyes and Pigments Divided into Classes

Dyes and pigments can be divided into the below classes and at the end of this paragraph they have been summed up in Table 1.1.[4] The English names correspond to the descriptions used in the Colour Index. An important parameter for using dyes is the degree of utilisation that is defined by the amount of dye that fixes to the textile. The part that does not fix to the textile ends in the wastewater. Likewise, wet fastness is a parameter that is important when using dyes. The term comprises the property of the colour to resist changes when the textile becomes wet, e.g., is washed.

Basic dyes

Cationic or basic dyes are mainly applied to acrylic, but can also be used for silk. Most of the basic dyes are azo dyes that are characterized by containing one or more azo compounds (-N=N-). However, methine compounds and triarylmethane compounds also occur. The cationic dyes react with negatively charged functional groups in the acrylic fibres.

The degree of utilisation is high; around 98% of the applied dye fixes to the fabric so only 2% ends in the wastewater.

Acid dyes

Acid dyes are applied to wool, silk and nylon. The majority of acid dyes are azo dyes. Some acid dyes contain complex bound heavy metal atoms (copper, chromium, nickel, cobalt) and are therefore also called metal complex dyes. Anthraquinone compounds, i.e., derived from anthraquinone, also occur. In addition, triarylmethane, phthalocyanine and nitro compounds might occur. Phtalocyanines can also contain heavy metals.

Acid dyes are water-soluble anionic dyes, and they attach to the positively charged amino groups in the fibres. The degree of utilization is high, 95-98%, and only 2 - 5% ends in the wastewater.

Direct dyes

Direct dyes or substantive dyes are applied to cotton and other cellulose fibres. The majority of the direct dyes are azo dyes. They can also contain heavy metals, usually copper. In addition, stilbene and thiazol compounds can occur. Finally, oxazine and phtalocyanine compounds can occur.

Direct dyes are anionic in aqueous solutions, and they show preferential adsorption to the fibres. Rather weak bonds are in question, but the direct dyes have relatively poor wet fastness.

The degree of utilisation is rather high, around 80%, and app. 20% ends in the wastewater. To improve the fastness, after-treatment can be carried out with cationic agents or synthetic resin products. Chromium and copper salts can also be used.

Disperse dyes

Disperse dyes are mainly applied to polyester, but also to nylon and acetate. They can also be used to dye certain acrylic fibres. Also in this case, azo compounds constitute the greater part. Anthraquinone compounds constitute the second largest group. In addition, nitro, methine, amino, ketone and quinolin compounds occur.

Disperse dyes are only slightly soluble in water, but appear as a dispersion. During dyeing the dye molecules are absorbed by the fibres. Dyeing polyester either takes place under high pressure and temperature (130°C), or at 95-100°C by using swelling organic chemicals, the so-called carriers. Acetate and polyamide fibres are dyed at 95-100°C without the use of carriers.

The degree of utilisation is high, around 90%, and therefore app. 10% ends in the wastewater.

[4] Sørensen, T. (1996 (3)). Textilkemi 3. Farvning og Trykning. DTI Beklædning og Textil, april 1996.

Vat dyes
Vat dyes are applied to cotton or other cellulose fibres. Most vat dyes are anthraquinone or indigo compounds. In addition, amino, ketone and sulphur compounds occur.

Vat dyes are insoluble in water, but the reduction in alkaline liquid produces the soluble form (so-called leuco form). The leuco dyes have an affinity for the fibres and will in principle interact with the fibres in the same way as the direct dyes. Subsequent oxidation reforms the original insoluble dye. Sodium dithionite is normally used as reducing agent. Peroxide, dichromate or the air or the water's content of oxygen can be used as oxidizing agent.

The degree of utilisation is high, around 95%, and app. 5% ends in the wastewater.

Sulphur dyes
Sulphur dyes are applied to cotton or other cellulose fibres. They consist of sulphur compounds in the form of thiazole, thiazone or thianthrene compounds.

The sulphur dyes are insoluble just as the vat dyes, but a reduction in alkaline with sodium sulphide produces the soluble form. Glucose can also be used. After dyeing, oxidation to the soluble form takes place by itself during rinsing through the oxygen in the water.

The degree of utilisation is smaller; around 60%, and app. 40% will end in the wastewater.

Azoic dyes
Azoic dyes are applied to cotton and other cellulose fibres. They are all azo dyes, and they are created during the dye process itself. Azoic dyeing is a two-stage process consisting of priming where naphthol is applied, followed by a coupling, where the primed material is treated with a diazo compound.

Reactive dyes
Reactice dyes are applied to dye cotton and other cellulose fibres. However, there is a wide range of reactive dyes for wool that also can be used for nylon and silk.

The majority are azo dyes, some with complex bound metal, most often chromium, copper or cobalt. In addition, anthraquionone and phthalocyanine compounds occur; the last-mentioned often with complex bound metal (copper, cobalt or nickel).

The reactive dyes differ from all other textile dyes as they create covalent bonds with the fibre molecules. Through cellulose, the reaction takes place between the dye molecule and ionised hydroxyl groups, as cellulose in alkaline liquid occurs as a weak acid. The dye can also react with the hydroxyl ions of the water and become a non-reactive hydrolysate.

The degree of utilisation varies a lot, 50-95%, and up to half of it can end in the wastewater.

Mordant dyes
Mordant dyes are mainly applied to wool. They have poor colour fastness, unless they are after-treated (or pre-treated) with a metallic salt, often dichromate. Therefore, this type of dyeing has more or less been phased out in Europe, but it cannot be excluded that it is still used in other parts of the world.

Mordant dyes can be seen as a method where the metal complex dye is created during the dyeing process itself.

Pigments
In principle, pigments are insoluble, but they are nevertheless used in aqueous media by means of disperging agents. Pigments are very often azo compounds; however, many of the above-mentioned compounds also occur. In addition, pigments are special as inorganic compounds often occur, e.g., minerals. Pigments are mainly used in connection with printing, but can also be used for dyeing.

The below table gives an outline of the above-mentioned types of dyes, which type of textile they are used for, how they fix to the fibre and how efficiently they fix to the fibre.

Dye Class	Fibre	Binding Mechanism/ Dye Method	Degree of Utilisation
Basic dyes	Silk Wool	Ionic bond	98%
Acid Dyes	Silk Wool Nylon	Ionic bond	95-98%
Direct dyes	Cotton Cellulose	Ionic bond	app. 80%
Disperse dyes	Cotton Polyester Acetate	Colloidal impregnation in the fibre, adsorption	app. 90%
Vat dyes	Cotton Cellulose	Dye precipitated in the fibre	app. 95%
Sulphur dyes	Cotton Cellulose	Dye precipitated in the fibre	app. 60%
Azoic dyes	Cotton Cellulose		
Reactive dyes	Cotton Cellulose	Covalent binding	50 -95%
Mordant dyes	Silk	Ionic bond	
Pigments		Surface application by means of binding agent Mainly used for printing	app. 100%

TABLE 1.1 OUTLINE OF THE APPLICATION OF DYES FOR VARIOUS FIBRES.

2. Survey

2.1 Objective of the Survey

Originally, the objective of the survey was to identify which dyes are used in clothes produced outside of the EU and then imported to the Danish market, and focus was on clothes with direct skin contact for a longer period of time.

The project was originally limited to dyes used in children's clothes, but the impression from interviews with research centres and questionnaires it became apparent that it was not possible to obtain information about which dyes are used. Therefore, a different approach to the project was necessary, and the decision was made to formulate a new objective. As the feed-back on the questionnaires was sparse, it was necessary to identify a limited group of dyes that could be analysed for. As the questionnaire did not point at obvious groups of substances, inspiration was sought for in literature regarding which dye groups might form a potential health-related problem. Disperse dyes were believed to be interesting as it in literature has been stated that they might constitute an allergy problem. Therefore, the project was prepared once again with the objective to search for selected allergenic, disperse dyes in clothes made from textiles that could be dyed with disperse dyes. As children are not more sensitive to allergy than adults, the samples were extended to also represent clothes for adults.

2.2 Delimitation

The delimitation to children's clothes was originally chosen as children are more sensitive than adults to a number of chemical effects. The survey was also limited to comprise products that have direct skin contact for a longer period of time and on a larger area of the body, e.g., T-shirts. Delimitation was carried out as these types of clothes would have the greatest effect from possible harmful dyes on the person wearing the clothes.

The survey comprises textile companies (dealer/manufacturer/designer), dye products and dye works that are located in Denmark and that are members of the Danish trade association "Dansk Mode og Tekstil", as well as selected larger companies that cover a large part of the Danish market. That was done to obtain information about the Danish textile market. Danish manufacturers were chosen as they form a substantial part of the Danish market, and it would require a lot of work to identify and contact foreign manufacturers.

Dyes in leather and artificial leather products are not comprised by this project as it is anticipated that leather products are not used in the type of children's clothes this project focuses on.

Neither sports clothes nor leisure wear were included in this preliminary survey as short-term exposure is anticipated compared to e.g. night clothes. However, in the course of the project focus was changed (cf. the above) to only comprise disperse, allergenic dyes that, i.e., are used in sports clothes, which therefore were included in the analyses. The project was also expanded to comprise clothes for children as well as adults.

2.3 Procedure

The survey was carried out in the period August-September 2012.
The survey included the following:

- Investigation of labelling schemes for clothes

- Internet search and information retrieval
- Questionnaires
- Telephone interviews
- Enquiries to research centres

2.3.1 Labelling Schemes for Clothes

Relevant labelling rules concerning clothes in the Danish labelling schemes Oeko-Tex®[5] and the European Ecolabel[6] have been studied to determine which chemical compounds form part of their analysis programmes compared to the requirements stated in the EU chemicals legislation called REACH[7].

2.3.2 Internet and Information Search

First of all, an outline was prepared of the dyes that can be expected to be used during the production of clothes. Information from previous surveys for the Danish Environmental Protection Agency has been included in this project.

Searches were carried out in literature and also on the Internet to identify, which dyes can be expected to be used in the production of children's clothes. Searches were also carried out on the websites of selected, larger companies and through general searches by using Google.

Internet searches were carried out to find information about problematic dyes and to find out if a connection has been described between health hazardous dyes in clothes and the production of clothes outside of the EU. In addition, an information search was carried out on Pubmed to find further scientific literature on dyes. When searching on the Internet the following search words were used: textile dyes harmful to health, harmful effects of textile dyes, allergenic textile dyes and mutagenic textile dyes.

Finally, random sampling was carried out on the Internet to clarify if manufacturers of known carcinogenic and allergenic dyes exist.

2.3.3 Questionnaire

Questionnaires were sent to clothing companies (dealers/manufacturers/designers) in Denmark, who are expected to have children's clothes in their product range.

Questionnaires were sent to 79 Danish clothing companies, who are located in Denmark, and who are members of the Danish trade association "Dansk Fashion and Textile", or who are generally known, but not members of the trade association. The questionnaire appears in appendix 2 of this report. The questionnaire was designed to reflect the original delimitation of the survey and therefore it focuses on children's clothes and certain types of clothes as T-shirts, night clothes, tights, underwear etc.

The reasons for choosing clothing companies in the trade association were that they are registered in the database of the trade association as dealer, manufacturer or designer of clothes for children. In that way, smaller and larger clothing companies were approached, and clothing companies who market themselves as being organic, or who use tests in compliance with one of the Danish labelling schemes, e.g. Oeko-Tex®, the Nordic Ecolabel or GOTS, were included.

[5] http://www.okotex.dk/
[6] http://www.ecolabel.dk/svanenblomsten/omsvanenblomsten/
[7] REACH is the complete chemical legislation of the EU. Annex XVII indeholder en liste over forbud og anvendelsesbegrænsninger. REACH Annex XVII http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:164:0007:0031:da:PDF

2.3.4 Telephone Interviews

Telephone interviews were carried out with the Danish trade association "Dansk Fashion and Textile[8]", two clothing companies, two leading supermarket chains, one dye manufacturer and four dye works on the Danish market. In the interviews, they were asked what they know about dyes used for the production of clothes outside of the EU, and which demands they make on the clothes manufacturers. In addition, they were asked if they have knowledge of health hazardous, e.g., carcinogenic and allergenic dyes or have been informed of allergic reactions. Both of the supermarket chains have implemented policies for test of clothing from their suppliers.

The telephone interviews were carried out in August and September 2012.

2.3.5 Enquiry to Research Centres

Telephone interviews were carried out with the Danish National Allergy Research Centre[9] and Asthma-Allergy Denmark[10] with regard to obtaining information about dyes that can be allergenic and whether or not the centres have registered reports on allergic reactions.

2.4 Result of the Survey

2.4.1 Specification of Labelling Schemes for Clothes

In the textile and clothing industry there are different labelling schemes where participation is voluntary. The intention of the schemes called Oeko-Tex®[11] and the European Ecolabel[12] is to ensure that textiles marked with these labels are made of materials that are not dangerous to human health and that consumers therefore can have confidence in when using.

In Europe and Japan, the Oeko-Tex® scheme is widely used. Currently, the Oeko- Tex® scheme comprises 60 countries and consists of 15 approved certification bodies that deal with research and testing of textiles. In the USA, GOTS[13] (Global Organic Textile Standard) is the leading textile processing standard for organic fibres and it lays down requirements regarding social criteria, manufacturing and active substances in textiles.

The aim of GOTS is to define requirements that ensure the organic status of textiles. The requirements for instance comprise textiles that are made from at least 70% organic, natural fibres. Likewise, GOTS has defined criteria for which chemicals may be used. They are based on the danger classifications under which the chemicals have been grouped.

GOTS places the following requirements on dyes (GOTS, 2008):

- Heavy metals must not exist or be used (according to ETAD rules, i.e., limit values have been made for the content of heavy metals in pigments and dyes); except for iron and copper.
- Chemical substances and products are prohibited if they have one of the following risk sentences: R26, R27, R28, R39, R40, R45, R46, R48, R49, R50, R51, R52, R53, R58, R59, R60, R61, R62, R63 and R68.[14]
- Chemical substances and products are prohibited if oral toxicity LD50<2000mg/kg.
- Chemical substances and products are prohibited if aquatic toxicity LC50, EC50, IC50<1 mg/litre.
- Chemical substances and products must only be used if the connection between biodegradability to aquatic toxicity is <70% and > 100 mg/litre or >70% and 10-100 mg/litre or >95% and 1-10 mg/litre.[15]

[8] http://www.dmogt.dk/
[9] http://www.videncenterforallergi.dk/
[10] http://www.astma-allergi.dk/
[11] http://www.okotex.dk/
[12] http://www.ecolabel.dk/svanenblomsten/omsvanenblomsten/
[13] http://www.global-standard.org/the-standard/gots-version-3.html
[14] GOTS does not yet use GHS labelling, http://www.unece.org/?id=3623

- Chemical substances that according to OECD 302A are bio accumulative and non-biodegradable must not be used.
- Azo dyes that release carcinogenic aromatic amines are prohibited.
- Dyes with heavy metal complex bonds must not be used (except for copper).
- Plastisol printing methods using PVC and phthalates are prohibited.

The labelling schemes Oeko-Tex® and the European Ecolabel give guidelines for the content of a wide range of chemical compounds, including dyes, that are prohibited or that may only be present to a limited extent.[16,17] The guidelines are based on legislation, regulated substances, known harmful substances that are not comprised by legislation and general health criteria based on scientific information. The guidelines for dyes appear in appendix 4.

The guidelines prepared by Oeko-Tex on dyes are based on the below principles:
- Chemical residue with acid or alkaline effect (pH value) as it can irritate the skin.
- The heavy metals chromium, cobalt, nickel, copper, cadmium, antimony, arsenic, lead and mercury that can harm the nervous system and the internal organs must not be extracted above a certain concentration.
- Special dyes that must not be used; some, because they are known to be or are suspected of being carcinogenic, others because they can cause allergy.
- Certain amines (of the type aryl amines) that are known to be or are under the suspicion of being carcinogenic. Such amines can be liberated from special azo dyes and pigments, or they can be found in certain polyurethane (PU) materials.

In addition, there are limitations for:
- Liberation of dye (smudging) through the influence with water, perspiration or rubbing
- For baby clothes also through the influence of saliva
- Evaporation of volatile, organic compounds (also called VOC emission)

An Oeko-Tex® label indicates that the specific textile contains no harmful substances that conflict with the requirements defined by Oeko-Tex®. Moreover, random analyses for selected chemicals in certain textiles will be carried out.

Although only a few manufacturers are registered in the Oeko-Tex® or GOTS scheme, the influence of the associations is far-reaching. The limit values that the associations set up are often referred to in literature, and they are used by large manufacturers as demand values for their own inspections. For instance, Bestseller[18] and H&M[19] have restrictions for the same disperse dyes as those found on the Oeko-Tex® list. Oeko-Tex® prepares its requirements to active substances based on scientifically proven parameters, and they annually revise their requirements on the basis of legislation and research.

[15] Test method [duration]: LC 50 fish: Performing new tests on fish to determine unknown LC50 fish values is prohibited. Instead alternative methods to OECD 203 [96hr] (such as conclusions on analogy, calculation from available data of substances contained, fish egg test, in vitro test) may be used to determine unknown values; EC50 daphnia, OECD 202 [48hr]; algae IC50, OECD 201 [72hr]

[16] https://www.oeko-tex.com/media/init_data/downloads/General%20and%20special%20conditions.pdf

[17] http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:197:0070:0086:EN:PDF

[18] http://www.bestseller.com/~/media/Files/CSR/Bestsellers%20Chemical%20Restrictions%20March%202010.pdf

[19] http://about.hm.com/content/dam/hm/about/documents/en/CSR/Policies/HM%20Chemical%20Restrictions%20May%202013_en.pdf

2.4.2 Result of Internet and Information Search

2.4.2.1 Earlier Relevant Investigations

In the report by the Danish Environmental Protection Agency "Chemicals in Textiles" No. 534[20] from 2000, a survey was carried out on which chemical substances might appear in finished textiles, and so was a screening of how environmentally and health hazardous the chemical substances are. 22 different fabrics on the Danish market were analysed, and i.a. the occurrence of two primary aromatic amines, p-chloroaniline and p-nitroaniline, were observed; they probably originate from azo dyes. In addition, 16 dyes were identified that are potentially allergenic – they have been included in the table in appendix 4.

Chemical/compound	Health risk for the user	Health risk for the shop staff	Water environmental risk
Nicotine	+	-	+
Naphthalene	(-)	+	-
DEHP	(+)	-	+
o-chlorophenol	(+)	+	-
C3-alkylbenzenes	+	-	-
C4-alkylbenzenes	+	-	-
Tetrachlorethylene	+	-	-
p-chloroaniline	+	-	(-)
p-nitroaniline	+	-	-
Toluene diisocyanate	+	+	-
Acridine	(+)	(+)	+
Nitrobenzene	+	-	-
Barium (easy dissolvable)	(+)	(+)	-
Cadmium	(+)	(+)	+
Cobalt	(+)	-	(-)
Chrome	(+)	-	+
Lead	(+)	(+)	+
Arsene	(+)	(+)	-
Mercury	(+)	(+)	-
Tin	(+)	(+)	(-)
Nickel	(+)	-	-
Zinc	-	-	+
Nonylphenolethoxylates	(-)	-	+
2,6-dichloro-4-nitroaniline	-	-	+
2-chloro-4-nitroaniline	(-)	-	+
6-methyl-3-nitroaniline	(-)	-	+
Diphenylamine	(-)	-	+
Copper	-	-	(-)
4-methyl-3-nitroaniline	*	*	(-)
N-butyl sulfonamide	*	*	(-)

+: Risk (+): Small risk (-): Borderline -: No risk *: Not estimated due to lack of data

TABLE 2.1 CHEMICALS IN TEXTILES SELECTED THROUGH RISK ASSESSMENT/SCREENING IN THE REPORT BY THE DANISH ENVIRONMENTAL PROTECTION AGENCY "CHEMICALS IN TEXTILES", SURVEY OF CHEMICAL SUBSTANCES IN CONSUMER PRODUCTS NO. 534, 2000.

[20] Report by the Danish Environmental Protection Agency "Chemical in Textiles", Survey of chemical substances in consumer products No. 534, 2000

In the report by the Danish Environmental Protection Agency "Chemicals in Textile Yard Goods" No. 23[21] from 2003, 20 textile yard goods were examined. The textile samples demonstrated nicotine, naphthalene, DEHP, formaldehyde, nonylphenol ethoxylates and two aromatic amines. The two aromatic amines (p-chloroaniline and o-toluidine) are carcinogenic, but were measured in concentrations substantially below the levels that at that time were regarded to constitute a health hazard. Heavy metals (arsenic, chromium, copper and tin) were also found, and they could give rise to health problems if consumed orally.

The report by the Danish Environmental Protection Agency "Survey of Chemical Substances in Textiles" No. 113[22] from 2011 is based on a search for and study of existing material. Some of the main conclusions in the report were that most (app. 2/3) of the clothes/textiles that are imported to Denmark originate from Asia (mainly China, India, Vietnam and Bangladesh), and the clothes/ textiles can contain a wide range of chemicals in smaller or larger amounts that originate from the production of the textiles, including dyes (azo dyes, other dyes and optical white). However, many of these chemicals can be washed out of the clothes by ordinary washing; however, especially phthalates, some heavy metals and antibacterial agents are not sufficiently removed from the textiles during ordinary washing.

2.4.2.2 Trade Guideline

In the textile and clothing industry, there is increased focus on chemicals in textiles, and in 2011 a cooperation between the Danish Chamber of Commerce, Danish Retail Trade, Danish Sporting Goods Association and Dansk Fashion & Textile led to the publication of "Safe Textiles. A guideline on chemical substances in textiles for companies in the textile trade"[23]. The publication examines legislation on chemicals in textiles and within dyes mainly deals with the requirements of REACH concerning azo dyes.

[21] Report by the Danish Environmental Protection Agency "Chemicals in Textile Yard Goods", Survey of chemical substances in consumer products No. 23, 2003

[22] Report by the Danish Environmental Protection Agency "Survey of chemical substances in textiles", Survey of chemical substances in consumer products No. 113, 2011

[23] http://www.dmogt.dk/~/media/Files/dmt/dokumenter/Teknik%20og%20Miljoe/2012/Vejledning%20-%20sikre%20tekstiler.ashx

2.4.2.3 Investigation of the Use of Azo Dyes in 2011

In 2011, the Laboratory for Chemistry and Microbiology, Danish Technological Institute, investigated 40 textile samples for azo dyes for the Chemical Inspection Service[24], which is a specific unit in the Environmental Protection Agency. In 17 cases, a content of REACH regulated, primary aromatic amines, which are break-down products from azo dyes, was demonstrated. No sample had a content of amines that exceeded the demand values stated in for instance Oeko-Tex® or above the limit values stated in legislation. Therefore, it is the experience of the laboratory that azo dyes (that can release certain carcinogenic primary aromatic amines) were used, but in small amounts.

2.4.2.4 Characterisation of Carcinogenic or Allergenic Dyes

A number of the known problematic dyes mentioned by REACH, Oeko-Tex® and the European Ecolabel have been described in several articles. One article describes dyes that are carcinogenic or allergenic in addition to the ones stated in REACH, Oeko-Tex® and the European Ecolabel[25]. Several articles describe the allergenic effect of Disperse Blue 106 and Disperse Blue 124.[25,26, 27,28] that are classified by Oeko-Tex® as well as by the European Ecolabel. However, one article mentions allergenic reactions from 4 disperse dyes that so far have not been categorised as allergenic, and they are Disperse Orange 6, Disperse Orange 34, Disperse Red 35 and Disperse Red 46, however, in the form of a cross reaction with p-phenylenediamine[29].
One article states that the break-down products of the azo dyes (primary aromatic amines) might be the reason for allergic reactions[26].

The information retrieval did not disclose any new dyes that are described as being potentially carcinogenic. Only four disperse dyes are under suspicion of being allergenic.

2.4.2.5 Use of Carcinogenic and Allergenic Dyes

The original objective of this survey was to obtain a general overview of the use of health hazardous dyes in textiles. In the course of the project, the survey was limited to carcinogenic and allergenic disperse dyes. Other similar investigations have been carried out. One was published in 2012 and attempts to describe the extent of the use of allergenic disperse dyes connected with the dyeing of textiles[27].

Examples of a wide range of tests can be found concerning how patients react to disperse dyes that either are considered as being allergenic or as could be allergenic, but limited data material exists regarding to which extent these dyes are used. In one investigation, dermatologists collected 121 garments from 13 countries – mainly synthetic fibres and primarily in dark, yellow or orange shades. The garments were sent to Swedish researchers and in Sweden they were tested for content of eight different disperse dyes[30]. Indications were found of the content of the following dyes: Disperse Yellow 3, Disperse Blue 124, Disperse Orange 3, Disperse Blue 106 and Disperse Red 1 in 31 garments out of 121, but a subsequent analysis could only confirm their content in three garments. In one garment that was manufactured in Italy Disperse Blue 106, Disperse Blue 124 and Yellow 3 were found, and in the 2 other garments Disperse Orange 1 was found. The article concludes that disperse dyes are used not only outside of the EU, but also in the EU, but the investigation also concludes that the use of the dyes is rather limited. The investigation gives an indication of the use of carcinogenic or allergenic disperse dyes, and this project confirms the same,

[24] Control of azo dyes in textiles and leather products, http://www.mst.dk/Virksomhed_og_myndighed/Kemikalier/kontrol_tilsyn/Fokusomraader/azo.htm
[25] Z Caliskaner, O Kartal, A Baysan, S Yesillik, F Demirel, M Gulec and O Sener; *Human and Experimental Toxicology,* 31(1) 101–103, **2011**
[26] K Ryberg, A Goossens, M Isaksson, B Gruvberger, E Zimerson M Bruze; *Acta Derm Venereol,* 91: 422–427, **2011**
[27] L Malinauskiene, E Zimerson, M Bruze, K Ryberg, M Isaksson; Contact Dermatitis, 67, 130–140, **2012**
[28] L Malinauskiene, E Zimerson, M Bruze, K Ryberg, M Isaksson; Contact Dermatitis, 67, 141–148, **2012**
[29] L LaBerge, M Pratt, B Fong, G Gavigan; Dermatitis, 22, 332-334, **2011**
[30] Malinuauskiene L, Zimerson. E, Bruze M, Ryberg K, Isaksson M (2012) Are allergenic dyes used for dyeing textiles, Contact Dermatitis, 67: 141-148

but the investigation only comprises one screening for a limited selection of disperse dyes (Disperse Red 1, Disperse Red 17, Disperse Blue 106, Disperse Blue 35, Disperse Blue 124, Disperse Yellow 3, Disperse Orange 1 and Disperse Orange 3). Therefore, it cannot be ruled out that other problematic disperse dyes have been present.

Another investigation[31] analysed clothes that gave rise to allergy reactions, and the clothes were analysed for content of dyes. 27 different samples of clothes were analysed, and disperse dyes were found in 22 of them. The dyes found most frequently were: Disperse blue 106 was found in nine cases, Disperse yellow 3 was found in eight cases and Disperse red 1 was found in five cases.

2.4.2.6 Incidence of Allergy to Disperse Dyes

In addition to being able to determine the use and number of disperse dyes, an important factor was to investigate how many people react to the dyes in order to determine how great a problem allergenic disperse dyes constitute. Several articles have investigated how many people react to patch tests on selected, disperse dyes. These articles were examined and published in 2013[32]. A great challenge when going through the various studies (54 in total) was that the studies have been carried out in different ways, and therefore substantial variations in the results of the investigations might exist. For instance, not necessarily the same dyes form part of all investigations, and the purity of the dyes that were used can vary a lot. If the tested dye contains a lot of impurities, then a possible allergic reaction might be ascribed to the impurities. Likewise, the time and dye concentration people are exposed to can vary a lot. The studies show that people with no known allergic record in general react with allergic reactions to one or several disperse dyes in 0.4% to 6.7% of the cases, while people who have an allergy record react in 5.5% to 100% of the cases. However, it should be stressed that the statistical foundation is substantially lower for the last-mentioned group of people, and the variations in the studies continue to increase. In Germany it is estimated that 1-2% of the patients in dermatological clinics have allergic reactions that are due to textiles.[33] It is also estimated that 2/3 of all allergies originating from textiles are due to disperse dyes.[34, 35]

2.4.2.7 Conclusion of literature studies

A limited number of investigations have been carried out on the use of especially disperse dyes (that can be allergenic) in textiles outside of the EU. However, information retrievals indicate that there is a limited use of dyes that are considered as health hazardous or allergenic.

Disperse dyes constitute 22% of all dyes produced in the whole world.[36] Part of the population reacts with the disperse dyes that are characterized as being allergenic. Therefore, there might be a need to investigate the use of disperse dyes that might be allergenic.

2.4.3 Result of the Questionnaire Study

The questionnaire study consisted of an informative letter and a questionnaire. The questionnaire contains questions related to whether the company sells/makes/designs children's clothes for children under nine years of age; if the clothes have been made within the EU; which type of clothes are made; which materials are used, and questions concerning which colours are used most frequently. In addition, the companies were asked for information about the dyes in their clothes in

[31] 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,
[32] L Malinauskiene, M Bruze, K Ryberg, E Zimerson, M Isakson, *Contact Dermatitis* in press **2013**
[33] Introduction to the problems surrounding garment textiles. BfR Information No. 018/2007, 1 June 2007 http://www.bfr.bund.de/cm/349/introduction_to_the_problems_surrounding_garment_textiles.pdf
[34] Hacth KL, Maibach HI. Textile dye dermatitis. J Am Acad Dermatol 1995, 32:631-639
[35] Lazarov A. Textile dermatitis in patients with contact sensitization in Israel: a 4-year prospective study. J. Eur Acad Dermatol Venereol. 2004, 18:531-537
[36] European Commission. European Commission's 6th Framework Programme: novel sustainable bioprocess for European colour industries 2004. Tilgængelig fra : http://www.sophied.net

the form of data sheets, CAS No. or colour index numbers. Copies of the informative letter and the questionnaire have been enclosed in Appendix 1 and 2.

New contact was taken to the companies that did not respond to the first inquiry.

In total, 34 replies to 79 questionnaires were received, i.e., 43% have replied. Of the 43%, 22 have filled in and returned the questionnaire. The remaining 12 companies informed that they do not produce clothes for children. The number of answers to each question is stated in appendix 3.

Out of the 34 companies that responded, 22 (corresponding to 65%) informed that they sell/make/design children's clothes for children under the age of 9, while the other companies informed that they do not have products for children. Only one company informed which dyes they use.

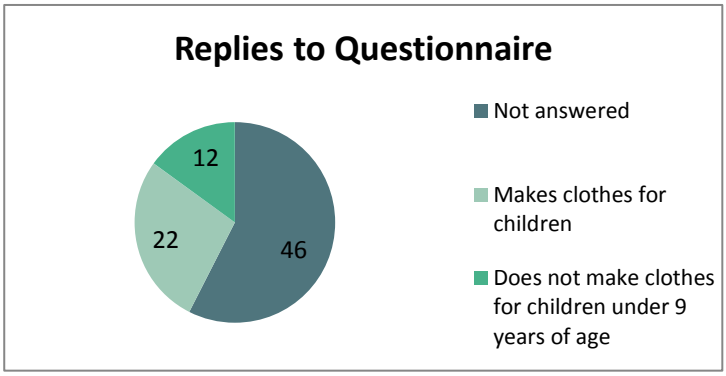


FIGURE 2.1 NUMBER AND TYPE OF REPLIES RECEIVED IN THE QUESTIONNAIRE STUDY

Out of the 22 textile and clothing companies that inform that they sell, make or design children's clothes, four companies (corresponding to 18%) state that the clothes are manufactured within the EU. The other 18 companies (corresponding to 85%) inform that the clothes are manufactured outside of the EU. One company informs that it manufactures clothes within as well as outside of the EU.

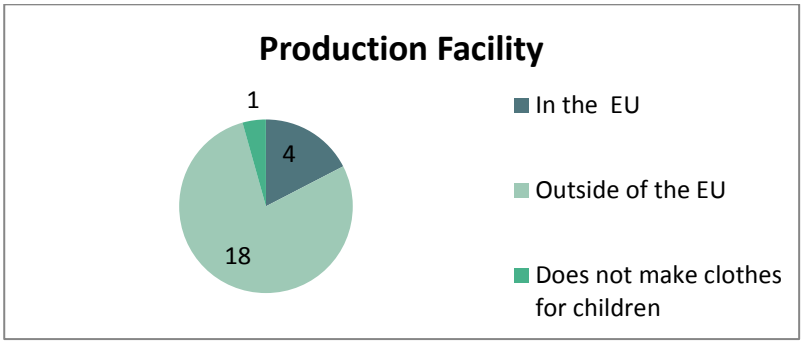


FIGURE 2.2 PRODUCTION FACILITY INFORMED IN THE QUESTIONNAIRE STUDY

In the product categories T-shirts, night clothes, tights and underwear 16 textile companies inform that they have T-shirts in their range, 13 have underwear, 10 have tights and 13 have night clothes. All companies mainly used cotton for their products. In addition, two manufacturers inform that they use regenerated fibres, which is a cross between natural and synthetic fibres, and one uses synthetic fibres for the production of T-shirts.

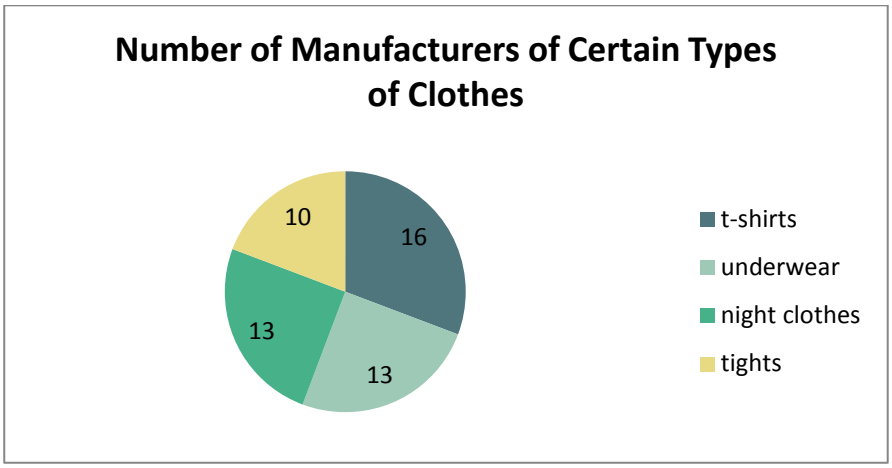


FIGURE 2.3 NUMBER OF MANUFACTURERS OF CERTAIN CLOTHES WITH CLOSE SKIN CONTACT

From the questionnaire study it can be concluded that the main part of the children's clothes that are in focus in this project, e.g. night clothes and underwear, are made of cotton and manufactured outside of the EU.

The questionnaire was sent to presumed children's clothes dealers/manufacturers. The questionnaire study shows that synthetic textiles are used less in this type of products; however, products for children were found in connection with purchase of products for the analyses. The questionnaire was not sent to manufacturers of sports clothes, unless they also make children's clothes, and therefore we do not have information from them on which dyes are used.

However, the impression from the interviews and the questionnaire results is that it hardly would have changed the conclusion that the manufacturers do not have information about dyes; however, they demand that the products must live up to the labelling schemes or valid EU legislation.

2.4.4 Telephone Interviews with Textile Companies, Dye Works and Dye Manufacturers

Telephone enquiries were made to two textile companies, four dye works and one dye manufacturer and two distributors of children's clothes to obtain information about which dyes are used when producing clothes outside of the EU, which demands they place on the manufacturers of clothes, and if they have knowledge of health hazardous dyes or have received reports on allergic reactions.

The dye works agree that they demand that their dye suppliers must meet the REACH regulations or that the dyes have to be approved according to the following labelling schemes: the European Ecolabel, the Nordic Ecolabel, GOTS or Oeko-Tex® Standard 100.

A Danish dye manufacturer informed that they produce pigments for textile prints, but they have no print customers in Denmark. The dye manufacturer is the only one who makes dyes/ pigments for the textile industry.

There is no reliable knowledge of whether or not dyes which are forbidden in the EU are used in other parts of the world, but on the basis of interviews with dye works and general conversations with people who have trade knowledge it is assumed that the use of forbidden dyes might take place.

A larger Danish company, whose textile products continuously are analysed, once in a while finds forbidden primary aromatic amines and rarely finds allergenic dyes. In extremely rare cases,

carcinogenic substances are found. At the same time, the manufacturer has experienced a decline in the number of cases where injurious dyes are found. There are no familiar statistics in that field. Two larger Danish distributors of clothes for children were interviewed by phone. Both had business policies regarding the content of dye in clothes. The policies were in all cases based on present legislation with special focus on azo dyes. The large chains informed that they random sample the clothes they sell themselves, and that they in general do not find azo dyes in the clothes. In one case concerning azo dye found in clothes from one of the market's largest manufacturers, the distributors had intensified their control of the suppliers, which, however, did not lead to the demonstration of use of forbidden dyes.

2.4.5 Result of Interviews with Research Centres

The National Allergy Research Centre and Asthma-Allergy Denmark were contacted by phone.

The National Allergy Research Centre has sent a list of the dyes that are used when testing persons who are suspected of having allergy to textile dyes (patch test). The list comprises the following dyes:

Name of dye	
Acid Yellow 36	Disperse Blue 3*
Acid Yellow 61	Disperse Blue 35*
Acid Red 118	Disperse Blue 85
Acid Red 359	Disperse Blue 106*
Basic Red 46	Disperse Blue 124*
Basic Brown 1 (Bismarck brown R)	Disperse Blue 153
Direct Orange 34	Reactive Red 123
Disperse Yellow 3*	Reactive Red 228
Disperse Yellow 9*	Reactive Red 238
Disperse Red 1	Reactive Orange 107
Disperse Red 11*	Reactive Blue 21
Disperse Red 17*	Reactive Blue 238
Disperse Orange 1*	Reactive Violet 5
Disperse Orange 3*	Reactive Black 5
Disperse Brown 1*	

TABLE 2.2 LIST OF DYES THAT ARE USED FOR ALLERGY TESTING

The list comprises more dyes, than the lists from the European Ecolabel and Oeko-Tex® Standard 100 that only state disperse dyes as allergenic. Dyes that have a * in the list are found in the above-mentioned standards. The National Allergy Research Centre has constructed the list from information retrievals, own experience, experience from doctors and on the basis of information from manufacturers of patch tests for allergy, and it includes more dyes than the environmental labelling schemes carry out tests for. The manufacturers of patch tests are Almirall from Germany, who produce Trolab[37], and ChemoTechnique Diagnostics[38] in Sweden.

[37] http://www.almirall.de/al/en/healthcare-professionals/trolab-patch-test-programme/contact-allergens-database/trolab-database.php

The National Allergy Research Centre informs that allergy related to textile dye is rare. For a period of six months, 1000 Danes at wards for skin diseases were tested, and only two people with allergic eczema caused by dyes were found. In comparison, it is it Italy not unusual that 50 out of 1.000 tested eczema patients have allergy to textile dyes.[39]

Asthma-Allergy in Denmark also confirms in a telephone interview that they only rarely hear of cases of allergic reactions caused by textile dyes, and that the cases largely only are experienced when new, unwashed clothes are in question.

2.4.6 Classification of Surveyed Dyes

Appendix 4 states the dyes that during the survey were registered as carcinogenic or allergenic or as having caused allergy. The information in the survey was collected from different labelling schemes, from literature, from clothes companies and from research centres. The list comprises a total of 60 different dyes and 22 primary aryl amines that are included in REACH. In addition, the list comprises the heavy metals that form part of Oeko-Tex® and that are used for dyes. Some dyes appear several times on the list as they appear under different categories.

If the problematic dyes are classified according to which colour they give to the clothes after dyeing, then especially the colours blue, red, yellow and orange appear.

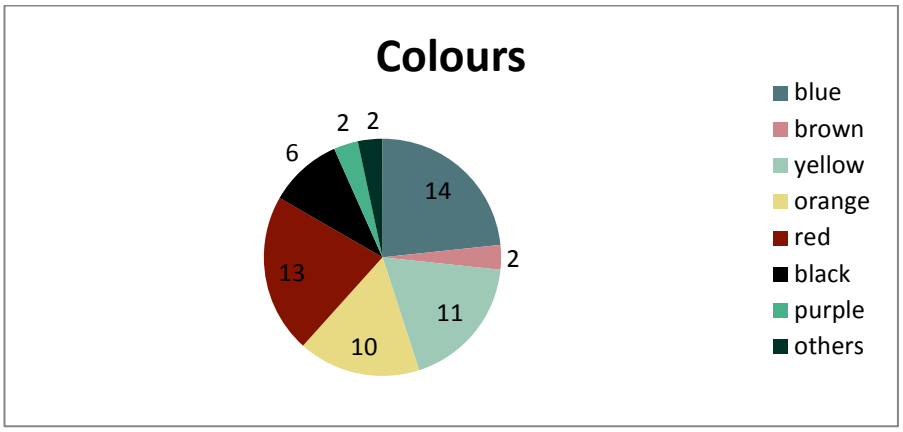


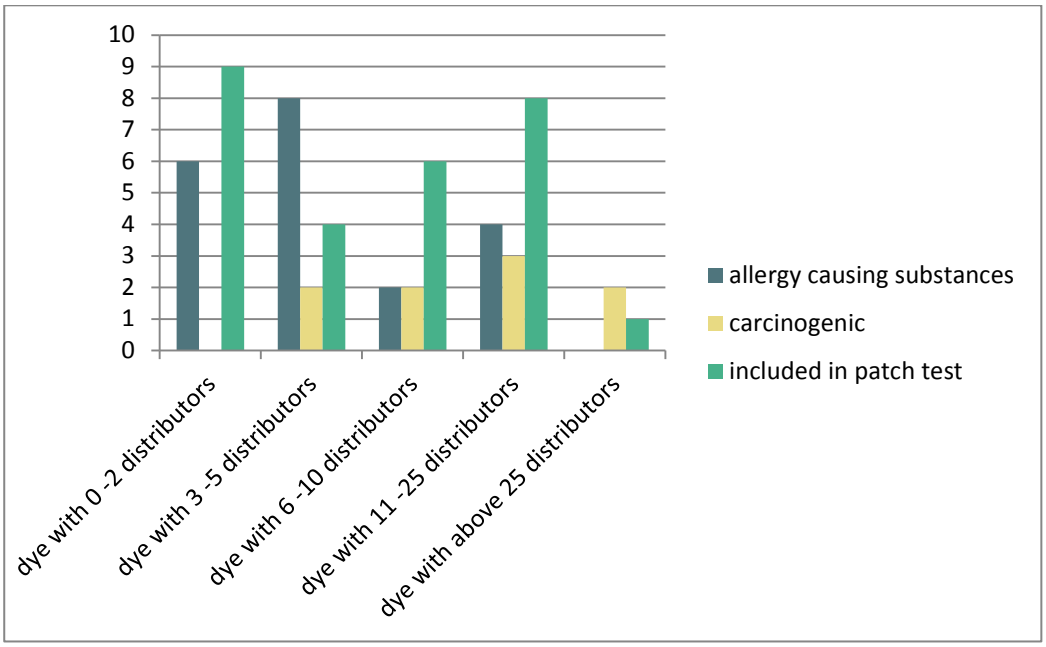
FIGURE 2.4 OUTLINE OF WHICH COLOUR THE PROBLEMATIC DYES GIVE TO THE CLOTHES

Dark and black shades are often a mixture of several dyes, and therefore clothes with such colours often contain several dyes. Other shades can also contain several dyes.

2.4.7 Commercial Use of Harmful Dyes

No statistics are available on how many of the surveyed dyes stated in appendix 4 actually are in use. Information searches and interviews indicate that the use is limited. However, it is possible to obtain an indication of the use by carrying out a rough investigation of how many distributors exist. That was done by searching on http://www.lookchem.com/ on the colour index name.

[38] http://www.chemotechnique.se/res/Catalogue/Patch-Test-Products-and-Reference-Manual-2013-For-digital-distribution.pdf side 63
[39] http://www.videncenterforallergi.dk/tekstilfarve-hyppighed.html



FIGUER 2.5 NUMBER OF PROBLEMATIC DYES COMPARED TO NUMBER OF DISTRIBUTORS

The diagramme shows how many distributors were found on lookchem.com of each individual dye. It appears from the diagramme that distributors exist of the majority of the harmful dyes. Some substances, of which two (Basic Violet 14 and Direct Red 28) have been suspected as carcinogenic substances by IARC, are distributed by up to 44 distributors. The majority of the distributors are located in China and India. The investigation of the dyes did not demonstrate if they are used for textiles, but only that they exist on the market and are intended for textiles.

2.5 Summary of the Survey

The survey put forward the following results:

- The literature search disclosed articles that describe dyes that are considered as carcinogenic or allergenic, and in addition four disperse dyes that are allergenic are described. No literature was found in which other dyes that are suspected of having health hazardous effects are mentioned.
- During the information search it was not possible to obtain data that gave an outline of the distribution of health-related problematic dyes in clothes on the European market.
- In general, neither importers nor manufacturers turned out to have general knowledge of which dyes are used in the clothes they sell. On the other hand, the companies demand that their suppliers have to meet various standards of Oeko-Tex®, GOTS, the European Ecolabel or the Nordic Ecolabel which have a number of black lists. That means that it is only possible for the companies to point out which dyes they do not want to find in their clothes, but not which dyes actually are used. Only one single clothes company has informed which dyes they use.
- The National Allergy Research Centre and Asthma-Allergy Denmark inform that they rarely are contacted about cases concerning allergic reactions caused by textile dyes, and that the reactions by and large only are experienced in connection with new, unwashed clothes.
- The questionnaires disclose that children's clothes, e.g., night clothes and underwear are made of cotton and mainly outside of the EU.
- If the problematic dyes are classified according to which colour they give to the clothes when dyed, especially the colours blue, red, yellow and orange are in question. Dark and black shades are often a mixture of several dyes.

- Interviews with companies and an investigation carried out in 2011 by the Chemical Inspection Service, the Danish Environmental Protection Agency, in cooperation with Danish Technological Institute indicate that azo dyes can be decomposed so the primary aromatic amines mentioned in REACH are not used and so the dissemination of the most well-known carcinogenic dyes becomes limited.
- Distributors exist of most of the carcinogenic and allergenic dyes, and two carcinogenic substances are distributed by more than 25 distributors.
- An outline of known carcinogenic or allergenic substances has been prepared, see appendix 4.

2.6 Discussion

When the clothing companies order clothes from the manufacturers in Asia (mainly China, India, Vietnam and Bangladesh), they typically make heavy demands to shades and colour fastness, and the manufacturer sends a sample to the clothing company for approval before final production.

The survey in this project indicates that the clothing companies do not necessarily ask for information about which dyes are used and no legal requirements exist on that point. Instead, the companies often make demands to what must not be used, e.g., according to the rules in REACH or one or several of the labelling schemes. Therefore, it is very likely that mainly the manufacturers in Asia know which dyes are used in the clothes.

It is striking that only 34 out of 79 companies have answered the questionnaire even after reminders were forwarded. 22 of the companies that answered the questionnaire stated that they manufacture children's clothes, and of the companies that answered the question regarding whether or not they have information about combinations and contents in the dyes that are used only 5 answered that they have. Only in one case, the information they have regards specific dyes; otherwise it is stated that the manufacturer lives up to Oeko-Tex® and/or GOTS. The conclusion from the questionnaire study is that the clothing companies have very limited knowledge of which dyes are used to dye their textiles. This missing knowledge might be one of the reasons why only a limited number of companies have answered the questionnaire. That could have been avoided by carrying out interviews where it was stressed that all information would be treated confidentially. This presumption was substantiated by the interviews that were carried out with many actors on the Danish market. However, such an investigation would require a lot of time, so it was only used on selected actors. It could also be considered if the questionnaire was addressed to the right contact person in the organisation.

The survey also disclosed by means of literature studies and interviews that the problematic azo dyes are not widespread as dye in textiles, and that gives the clear impression that dye works in the manufacturing countries do not use such dyes.

Finally, it appears that several dyes that are regarded as being problematic, i.e., carcinogenic and allergenic, have several distributors. That does not necessarily mean that the dyes are used in textiles, but it indicates that they still are used to a certain degree.

3. Choice of Analyses and Criteria for Purchase

3.1 Choice of Dyes for Chemical Analysis

The survey showed that it is not possible to procure information about which dyes are used for the production of clothes outside of the EU, but only information about which dyes the companies do not want the suppliers to use is available.

Enquiries to the National Allergy Research Centre and Asthma-Allergy Denmark, respectively, indicate that there are few cases of allergy that are suspected of being caused by dyes in clothes. The survey also discloses that examples of the use of azo dyes only rarely arise, and it was not possible to obtain information about which other dyes are used. Studies in literature show that especially disperse dyes can give allergic reactions and the use of these dyes is unknown. A number of disperse dyes are not covered by REACH and they do not get the same attention as the dyes that are covered by REACH. A goal-oriented investigation of the use of disperse dyes on the Danish market would therefore give new knowledge. Disperse dyes are mainly used to dye polyester, and in consultation with the Danish Environmental Protection Agency it was decided to focus on disperse dyes that can cause allergy. They are primarily found in clothes made of polyester.

3.2 Criteria for Purchase of Clothes

In consultation with the Danish Environmental Protection Agency the following criteria were chosen for the clothes that were to be purchased and analysed (prioritised order):

- Manufactured outside of Europe
- Made of synthetic textiles, mainly polyester
- Made in dark or luminous colours
- The garment should have close skin contact
- It was agreed to purchase children's clothes as well as clothes for adults

31 different garments were purchased in physical shops from October-December 2012. None of the clothes that were purchased are comprised by the common labelling schemes such as the Nordic Ecolabel or Oeko-Tex®.

Some of the clothes contain different dyes and are made of different materials, and analyses were carried out of the different materials and dyes (e.g., separate analysis of collar material and the main fabric the blouse is made of). Therefore, 54 subsamples made from the 31 garments were analysed for disperse dyes. More subsamples were analysed than the number of garments as a piece of clothing can consist of different materials; a sweater can for instance have a collar that is made of a material that is different from the rest of the sweater and therefore subsamples were made of cut-outs of the collar and cut-outs of the other material. Information about the purchased clothes appears in appendix 5.

4. Analysis for Disperse Dyes

4.1 Outline of Selected Disperse Dyes for Analysis

On the basis of information about expected constituents in polyester material and the classification of the dyes, it was in cooperation with the Danish Environmental Protection Agency decided that the clothes should be analysed for the disperse dyes stated in Table 4.1. The list (in the column on the right-hand side) states which labelling scheme or other source has registered the substances as being problematic. In addition, the chemical fundamental structure each dye is stated.[40]

Name	CAS no.	Chemical structure	Reference
Disperse Blue 1*	2475-45-8	Anthraquinone	European Ecolabel / Oeko-Tex®
Disperse Blue 3	2475-46-9	Anthraquinone	European Ecolabel/ Oeko-Tex®, Nat. Allergy Research Centre
Disperse Blue 7	3179-90-6	Anthraquinone	European Ecolabel/ Oeko-Tex®
Disperse Blue 26	3860-63-7	Anthraquinone	European Ecolabel/ Oeko-Tex®
Disperse Blue 35	12222-75-2	Anthraquinone	European Ecolabel/ Oeko-Tex®, Nat. Allergy Research Centre
Disperse Blue 102	12222-97-8	Azo	European Ecolabel/ Oeko-Tex®,
Disperse Blue 106	12223-01-7	Azo	European Ecolabel/ Oeko-Tex®, Nat. Allergy Research Centre
Disperse Blue 124	61951-51-7	Azo	European Ecolabel/ Oeko-Tex®, Nat. Allergy Research Centre
Disperse Brown 1	12236-00-9	Azo	European Ecolabel/ Oeko-Tex®, Nat. Allergy Research Centre
Disperse Orange 1	2581-69-3	Azo	European Ecolabel/ Oeko-Tex®, Nat. Allergy Research Centre
Disperse Orange 3	730-40-5	Azo	European Ecolabel/ Oeko-Tex®, Nat. Allergy Research Centre
Disperse Orange 37	13301-61-6	Azo	European Ecolabel/ Oeko-Tex®
Disperse Orange 76	13301-61-6	Azo	European Ecolabel/ Oeko-Tex®

[40] http://www.worlddyevariety.com

Name	CAS no.	Chemical structure	Reference
Disperse Red 1	2872-52-8	Azo	European Ecolabel/ Oeko-Tex®, Nat. Allergy Research Centre
Disperse Red 11	2872-48-2	Anthraquinone	European Ecolabel/ Oeko-Tex®, Nat. Allergy Research Centre
Disperse Red 17	3179-89-3	Azo	European Ecolabel/ Oeko-Tex®,
Disperse Yellow 1	119-15-3	Nitrodiamine	European Ecolabel/ Oeko-Tex®,
Disperse Yellow 3*	2832-40-8	Azo	European Ecolabel/ Oeko-Tex®, Nat. Allergy Research Centre
Disperse Yellow 9	6373-73-5	Nitrodiamine	European Ecolabel/ Oeko-Tex®, Nat. Allergy Research Centre
Disperse Yellow 39	12236-29-2	Methine	European Ecolabel/ Oeko-Tex®,
Disperse Yellow 49	54824-37-2	Methine	European Ecolabel/ Oeko-Tex®,
Disperse Orange 13	6253-10-7	Double azo	Environ. project No. 534, 2000
Disperse Yellow 54	12223-85-7	Quinoline	Environ. project No. 534, 2000

TABLE 4.1 SELECTED DISPERSE DYES FOR ANALYSIS

All dyes in the list are stated as being allergenic; however, Disperse Blue 1 and Disperse Yellow 3 are also stated as being carcinogenic.

4.1.1 Analysis Method for Determination of Disperse Dyes

The clothes were separated into subsamples (described under chapter 3.2). Two representative subsample amounts were made of each subsample, and they were analysed separately (analysis in duplicate). The dyes were removed from the subsample amounts by the extraction method called ASE (accelerated solvent extraction). That method utilizes an organic solvent (in this case acetone) and increased temperature and pressure. The treatment results in an extract of the dyes. The amount and type of dyes is determined by liquid chromatography followed by a mass spectrometric (LC-MS) analysis against reference substances of the selected disperse dyes. The analysis method is an Oeko-Tex® standard method[41] that refers to a DIN standard[42].
The conditions of the LC-MS analysis are as follows:

Equipment	Agilent LC-MS
Column	Zorbax solvent saver plus, SB-C18, 3.5 µm. 150 x 3.0 mm
Solvent A	2 mM Ammonium acetate I 80 % H_2O/ 19.9% acetonitrile
Solvent B	99% acetonitrile/0.1% formic acid
Flow	0.1 ml/min.
Mass spectrometer	Scan mode

TABLE 4.2 LC-MS CONDITIONS

[41] Oeko-Tex® Standard 201 M-4 Determination of banned Disperse Dyes
[42] DIN 54231:2005-11 Textilien – Nachweis von Dispersionsfarbstoffen

The method has a detection limit from 0.2 to 2 µg/g depending on the dye, and the analysis uncertainty of the method is max. 13%.

LC-MS is a very accurate and sensitive analysis method; LC (liquid chromatography) separates the components that are found in the solution. The separation takes place according to the nature of the substances, first and foremost their affinity between water and oil (polarity). It can be said that the greater affinity a substance has towards water, the shorter time the substance remains in the column. The time a substance remains in a column is called retention time, in short, R_t.

These components are then detected with MS (mass spectrometer). The MS measures the weight of the molecule and fragments of the molecule. The fragmentation is determined by the structure of the molecule. The mass spectrometer is set for scan mode as that is sufficient to obtain the desired specificity and detection limit, and it gives information about the content in the sample.

4.2 Results of Quantitative Analyses for Disperse Dyes

31 garments were purchased and 54 subsamples were made from them for analysis for selected disperse dyes, see Table 4.1.

The main part of the purchased clothes showed no sign of content of the selected dyes. However, eight pieces of clothes (nine subsamples) showed a content of 2 different disperse dyes. The average results of the analyses of the two disperse dyes were proven to be above the detection limit and they are stated in Table 4.3.

The dyes called Disperse Blue 124 and Disperse Yellow 49 are in question. Eight of the samples contained the dye Disperse Blue 124 and the ninth sample contained Disperse Yellow 49. Five of the garments allegedly contained more than 100 mg/kg. Closer analyses showed that they were false positive. The following chapter describes the analyses that demonstrated that false positive results were in question and therefore they are not the two dyes in the subsamples.

Article clothing	4B	8	16B	16C	24	25	26 A	27	29
Description	Blouse ribbing	Women's leggings	Blouse ribbing	Pattern on blouse	Children's thermo tights	Adult thermo leggings	Blouse	Tights	Child gloves
Disperse Blue 124	840	105	310	66	60	240	64		250
Disperse Yellow 49								33	

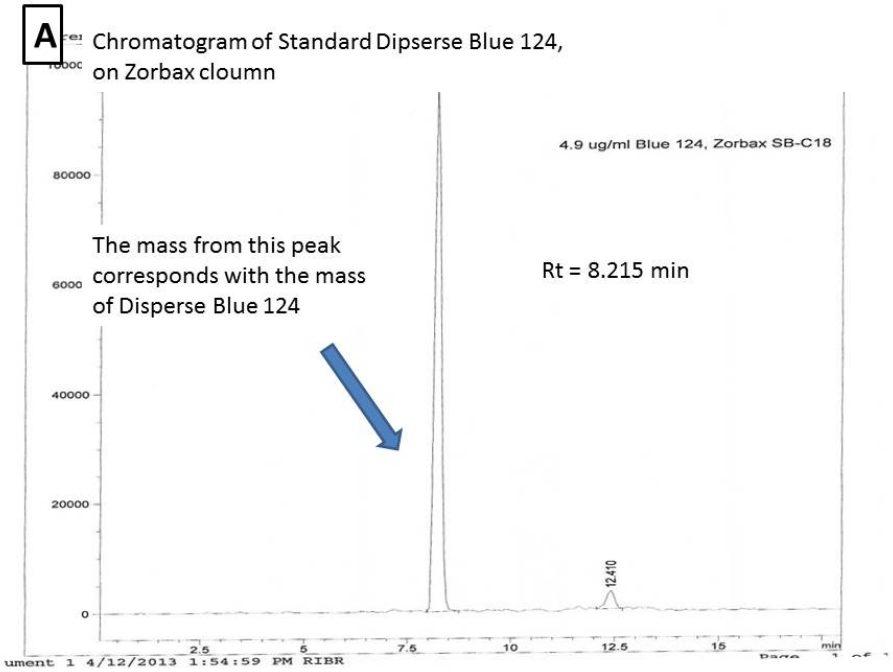
TABLE 4.3 RESULTS OF ANALYSES FOR CONTENT OF SELECTED DYES (MG/KG)

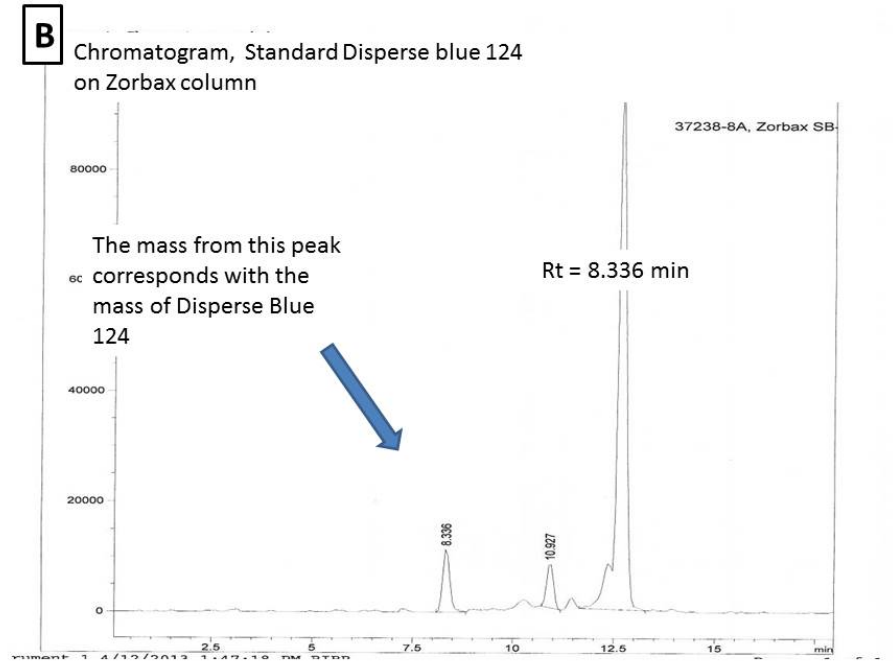
4.2.1 Discussion of Results

The applied method comes from Oeko-Tex® and refers to a DIN standard. Therefore, it is anticipated that the method is well-tested and reliable.

The Danish Environmental Protection Agency demands recovery tests for analysis methods that are not accredited. In connection with recovery tests, a known amount of the substance that is analysed

for is added to a subsample, and subsequently it is investigated if there is an increased content of the substance in question that corresponds to the amount that has been added. That was also carried out in connection with this method. Likewise, a sample of clean dye (called standard) was analysed to investigate how the chemical substance reacts to the conditions the dye is exposed to. A chromatogram is then obtained showing how much is discharged from the device compared to the time that has passed. Only chemical substances with the desired weight are analysed. Below is an example with sample no. 8.





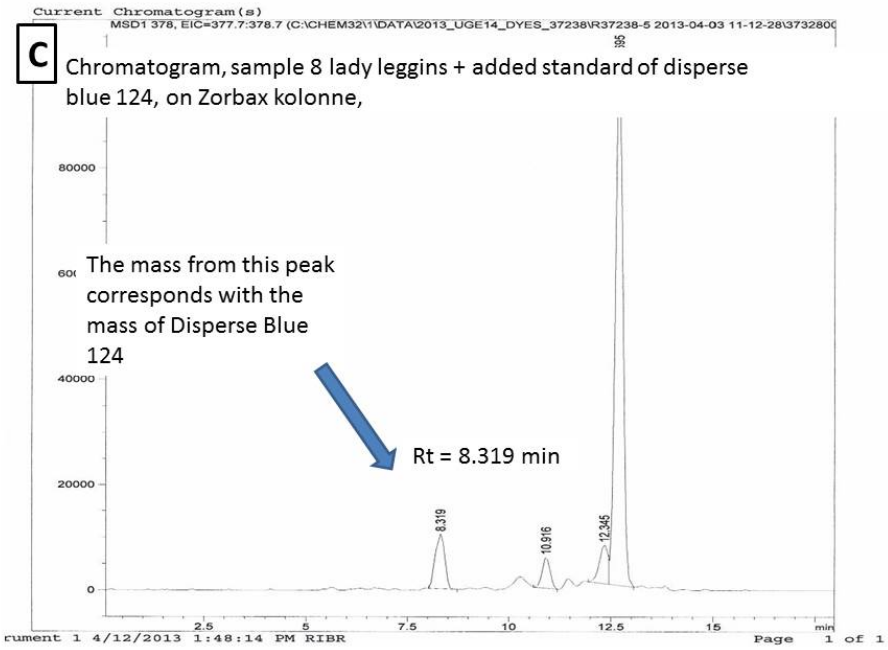


FIGURE 4.1 CHROMATOGRAMS FROM LC-MS FOR ANALYSIS OF DISPERSE BLUE 124 A) STANDARD OF DISPERSE BLUE 124, B) EXTRACT FROM SAMPLE NO. 8 C) STANDARD OF DISPERSE BLUE 124 AND EXTRACT FROM SAMPLE 8

A peak appeared when the standard Disperse Blue 124 and the extract from the garment were mixed and the weight of the molecule from the sample extract corresponds with the weight of Disperse Blue 124. The first time it was therefore concluded that Disperse Blue 124 exists in the clothes. However, it also appears that the peak from the clothes extract appears marginally later than the peak from the standard. Such shifts are normal, but it is worth noting that the shift is consistent, see Table 4.4.

Content of sample	Rt
Standard of Disperse Blue 124	8.215 min.
Sample no. 8 lady leggings	8.336 min.
Sample no. 8 lady leggings + Standard of Disperse Blue 124	8.319 min.
Standard of Disperse Blue added to blank sample	8.204 min.

TABLE 4.4 RETENTION TIMES FOR ANALYSES FOR CONTENT OF DISPERSE BLUE 124

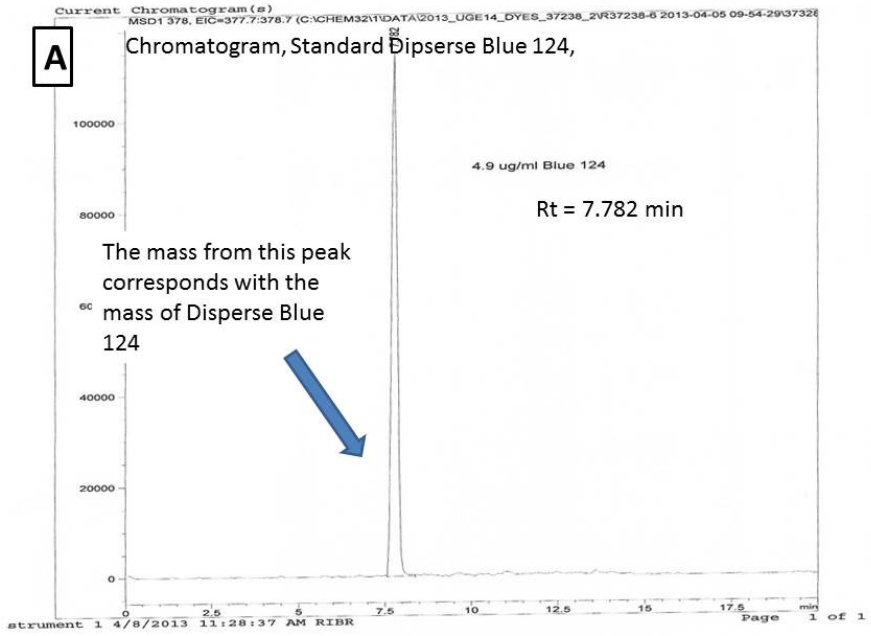
The shift in retention times encourages a more thorough analysis. Therefore, it was decided to develop a method optimized for analysis of Disperse Blue 124. For the new analysis the following conditions were used:

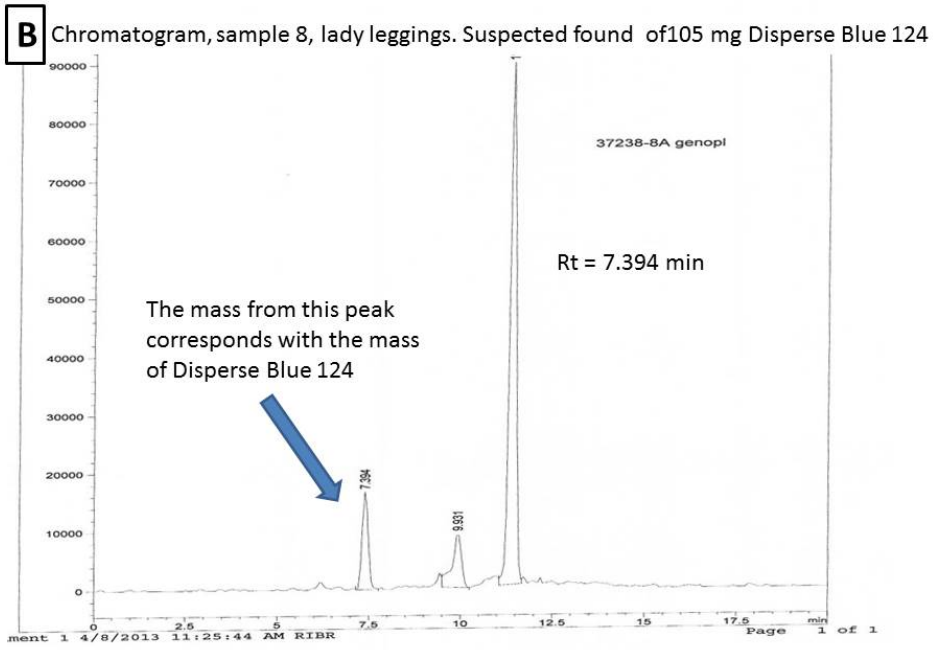
Equipment	Agilent LC-MS
Column	Kinetex C18, 2.6 µm. 100 x 3.0 mm
Solvent A	2 mM Ammonium acetate I 80 % H_2O/ 19,9 % acetonitrile
Solvent B	99 % acetonitrile/0.1 % formic acid
Flow	0.1 ml/min.
Mass spectrometer	Scan mode

TABLE 4.5 LC-MS CONDITIONS FOR ANALYSIS OF DISPERSE BLUE 124.

This method resulted in clearly different retention times for the standard of Disperse Blue 124 and the extract from the pieces of clothes, and when the two are mixed, two separate peaks are obtained in the chromatogram (see Figure 4.2).

In the light of the optimised analysis method it can be concluded that there is no Disperse Blue 124 in sample 8. By using the same method for the other samples that are suspected to have a content of Disperse Blue 124 it was ascertained that they do not contain Disperse Blue 124. The same process was used for Yellow 49. It can be ascertained that none of the purchased products contain the mentioned disperse dyes.





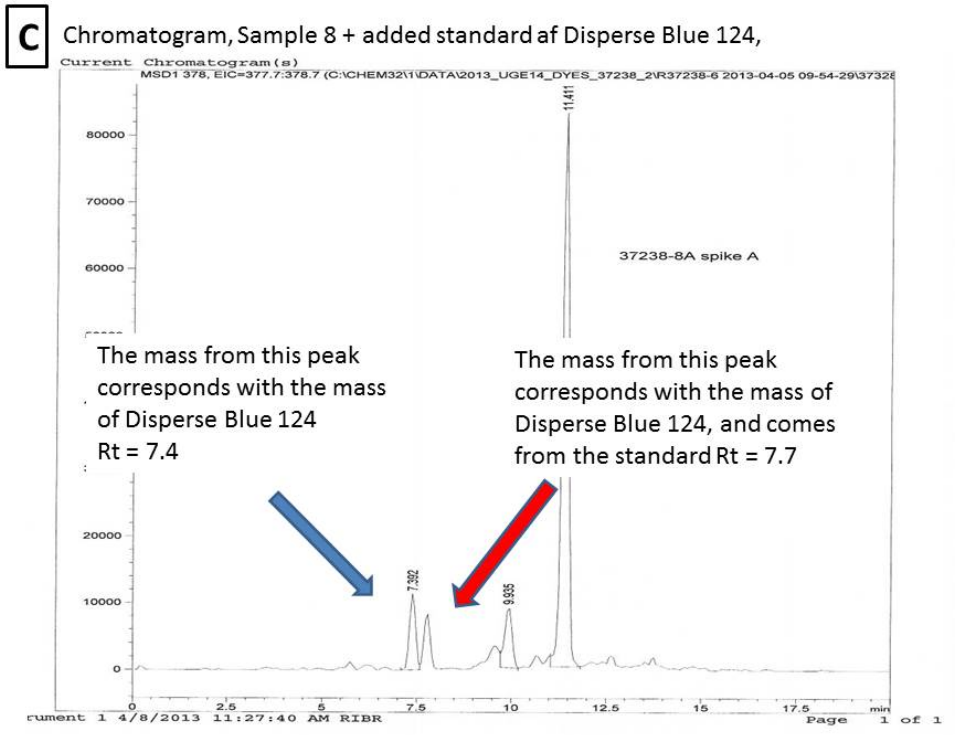


FIGURE 4.2 CHROMATOGRAMS FROM LC-MS FOR OPTIMISED ANALYSIS OF "DISPERSE BLUE 124" STANDARD AND EXTRACT.

5. Conclusion

In the preliminary phase of the project it was decided to focus on dyes that might have a health hazardous effect on children. The greatest risk of exposure is assumed to originate from long-term and close contact with skin. Such exposure arises when using night clothes, underwear, etc. Therefore, it was during the survey chosen to focus on that type of clothing. The survey disclosed that such clothes mainly are made of cotton. Known problematic dyes that are used to dye cotton are azo dyes, and they are comprised by REACH and included on the candidate list.

During the survey it was only in one case possible to procure information about which dyes are used. That indicates that the Danish clothes companies do not necessarily ask for information about which dyes are used, and there are no legal requirements in that respect.

In connection with the survey, interviews and questionnaires disclosed that larger clothes manufacturers mainly focus on ensuring that production in the EU and outside the EU follows the guidelines in REACH and that the azo dyes stated on the candidate list are not used. It was also disclosed that several of the larger actors on the Danish market follow guidelines that are very close to the guidelines used by the labelling organisations such as Oeko-Tex® and GOTS.

As no clear picture arose of which dyes are used, but rather of which dyes are not used, it was necessary to reformulate the objectives of the project. It was interesting to continue the investigation of disperse dyes as they in literature are believed to have an allergy potential and a few of them are considered as carcinogenic. In that way, the project changed from merely focusing on children's clothes to also comprising other types of clothing.

Disperse dyes are mainly used in synthetic textiles such as polyester and, i.a., for sports clothes. Sports clothes were not included in the questionnaire as children's clothes were in focus at the beginning of the project, and synthetic textiles are only used to a limited degree in children's clothes. However, the questionnaire did disclose that only one company informed which dyes were used in the production of clothes, and therefore it was assessed that forwarding questionnaires to manufacturers of sports clothes would not contribute to additional information.

A wide range of studies concerning human allergic reactions to dyes that are suspected of being allergenic have been published. Primarily, patch tests are used in at least 54 different studies to investigate possible exposure, and it has been proven that a substantial part of the population reacts to disperse dyes with allergy. The largest investigation was carried out in Germany, where 24,980 people were examined and 1.35% showed allergic reactions. The next largest investigation was carried out in Italy on 6,478 persons and 6.7% showed allergic reactions. The different results in the investigations can be due to several things, such as test conditions and regional differences, the use of disperse dyes and a warmer climate that makes perspiration increase and subsequently liberates dye to the skin.

In the light of a review of the literature on the subject and of results from previous investigations, 23 disperse dyes were selected; they might be problematic in relation to health as they either have been reported to have an allergenic potential or they have been considered as carcinogenic.

In literature or from their classification, the selected disperse dyes are known to be either carcinogenic or allergenic or both. 31 garments were purchased and all of them were investigated for content of dyes. After the first analyses, eight pieces of clothing were suspected to contain the following disperse dyes: Disperse blue 124 or Disperse yellow 49. However, further analyses disclosed that that was not the case and none of the selected allergy-causing or carcinogenic disperse dyes were found in the samples in these analyses. The 31 garments were purchased on the basis of criteria that were to increase the probability of identifying unwanted disperse dyes such as land of origin, fibres and shades and chance random sampling was therefore not question, but goal-oriented random sampling was.

In comparison, another investigation that comprised 120 pieces of clothing, collected from the entire world, disclosed three garments that contained one or several disperse dyes. In the project it appeared to be difficult with certainty to identify disperse dyes. The study that was published only investigated the presence of eight allergenic disperse dyes, whereas this project included 23 dyes. Despite the difference in the number of disperse dyes that were analysed for, this project reaches the same result, meaning that the use of disperse dyes known to be allergy-causing is very limited. However, this project has a limitation as only 31 pieces of clothing have been investigated and it cannot be excluded that there might be areas in the Danish textile market where the use of disperse dyes is larger.

Information obtained through interviews with the National Allergy Research Centre and Asthma-Allergy Denmark support the impression that allergic reactions due to disperse dyes in clothes are very rare. They are only contacted by few people who have experienced allergic reactions caused by clothes, and the enquiries they receive usually involve reactions that arise after having worn new clothes that have not been washed prior to use. The allergic reactions can also be due to other things, for instance other chemical components in the clothes.

There are currently many dealers of the selected problematic dyes, so a market must exist for the dyes. Disperse dyes are mainly used for dyeing polyester and other synthetic textiles so it seems unlikely that these dyes are not used to dye clothes. Of course, it might be the case that clothes dyed with these dyes do not reach the European or Danish markets because the clothes manufacturers in these countries demand that the rules in REACH and the labelling schemes such as Oeko-Tex® and GOTS have to be met. However, it would be remarkable if it is possible to clearly separate clothes intended for different markets. So, indications seem to point in different directions.

The conclusion of this investigation and the results from literature support each other. Limited knowledge exists on the use of health hazardous dyes in clothes. In addition, the knowledge of which dyes are used in clothes very likely mainly lies with the manufacturers in Asia (mainly China, India, Vietnam and Bangladesh) and not with the Danish manufacturers/dealers/importers.

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- http://www.dmogt.dk/
- http://www.videncenterforallergi.dk/
- http://www.astma-allergi.dk/
- http://www.okotex.dk/
- http://www.ecolabel.dk/svanenblomsten/omsvanenblomsten/
- http://www.global-standard.org/the-standard/gots-version-3.html
- GOTS does not yet use GHS labelling, http://www.unece.org/?id=3623
- Test method [duration]: LC 50 fish: Performing new tests on fish to determine unknown LC50 fish values is prohibited. Instead alternative methods to OECD 203 [96hr] (such as conclusions on analogy, calculation from available data of substances contained, fish egg test, in vitro test) may be used to determine unknown values; EC50 daphnia, OECD 202 [48hr]; algae IC50, OECD 201 [72hr]
- https://www.oeko-tex.com/media/init_data/downloads/General%20and%20special%20conditions.pdf
- http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:197:0070:0086:EN:PDF
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Appendix 1: General information to companies that might be possible manufacturers of children's clothes

Enquiry on Dyes in Clothes for Children

On behalf of the Danish Environmental Protection Agency, Danish Technological Institute is carrying out a survey of the Danish market regarding dyes in children's clothes that are manufactured outside the EU and aimed at children of up to 9 years of age.

Dyes can have very different chemical compositions depending on which colour is desired and which material is going to be dyed. This project focuses on dyes that are used for the production of children's clothes outside the EU.



In that connection, we would like to know if your company sells/makes clothes for children, and if the production of clothes takes place outside of the EU. We would like to know which products are manufactured and which dyes are used.

If you do not sell/make this type of clothes, then it is nevertheless important that you return the questionnaire out of regard for the statistical preparation of the results.

For the sake of clearness, we have collected our questions in the enclosed questionnaire, and we hope that you will spare the time to help us by answering the questions.

Unfortunately, we have a very tight time schedule and would therefore appreciate your quick response and preferably by Friday 31 August 2012 at the latest.

For the sake of good order we would like to mention that Danish Technological Institute is bound by professional secrecy and therefore respects the confidentiality of any company-specific information you may give us.

If you have any questions to the above, then please do not hesitate to contact us.

Best regards

Torsten Due Bryld, tel. +45 72 20 29 17, email tsb@teknologisk.dk
Eva Jacobsen, tel. +45 72 20 18 93, email evj@teknologisk.dk

Appendix 2: Questionnaire sent to Danish Clothing Companies

The questions relate to clothing for children under 9 years of age and clothing that is manufactured outside the EU

Please state the name and address of your company as well as relevant phone number and e-mail address:

	Yes	No	Don't know
Does your company sell/manufacture/design textile products for children under the age of 9?			
Are the clothes manufactured/dyed outside the EU?			

If yes to both questions, then please tick off which products

Trousers	[ ]	Underwear	[ ]
Blouses	[ ]	Socks	[ ]
T-shirts	[ ]	Tights	[ ]
Underwear	[ ]	Dresses/skirts	[ ]
Night clothes	[ ]	Shirts	[ ]

Please mark with an X, which of your products mainly contain natural fibres (cotton etc.)

Trousers	[ ]	Underwear	[ ]
Blouses	[ ]	Socks	[ ]
T-shirts	[ ]	Tights	[ ]
Underwear	[ ]	Dresses/skirts	[ ]
Night clothes	[ ]	Shirts	[ ]

Please mark with an X, which of your products mainly contain synthetic fibres (polyester, nylon, polypropylene, acrylic etc.)

Trousers	[ ]	Underwear	[ ]
Blouses	[ ]	Socks	[ ]
T-shirts	[ ]	Tights	[ ]
Underwear	[ ]	Dresses/skirts	[ ]
Night clothes	[ ]	Shirts	[ ]

Please mark with an X, which of your products mainly contain regenerated fibres (viscose, acetate, lyocel etc.)

Trousers	[ ]	Underwear	[ ]
Blouses	[ ]	Socks	[ ]
T-shirts	[ ]	Tights	[ ]
Underwear	[ ]	Dresses/skirts	[ ]
Night clothes	[ ]	Shirts	[ ]

	Yes	No	Don't know
Are any colours used more than others, e.g., black?			

If yes, then please state the three colours that are used the most (e.g. black, red or blue) and please include information about the manufacturer's/importer's name of the colour, e.g., colour index No. or the like.

	Yes	No	Don't know
Do you have written information about the composition and content in the dyes the manufacturer/dye works uses?			
If yes, then please send the information with the questionnaire, e.g., in the form of a copy/pdf of outline of colour index No., safety data sheets, test reports or other information from the manufacturer/dye work/importer/supplier. Oeko-tex standard 5 GOTS: 3			
	Yes	**No**	**Don't know**
Have you experienced complaints on health-related problems (e.g., itchy skin) or other inconveniences that you suspect being caused by dyes?			
Please state which problems, type of clothes and colours (state the name of the colour, e.g., the colour index No.) The textile will be examined for azo dyes that cannot be found.			

Please return the questionnaire as letter or pdf to:
Danish Technological Institute, attn.: Torsten Due Bryld, Gregersensvej 1, DK - 2630 Taastrup
or e-mail: tsb@teknologisk.dk

Thank you in advance.

Appendix 3: Total Number of Replies to Questionnaire Sent to Danish Clothing Companies

The questions relate to clothing for children under 9 years of age and clothing that is manufactured outside the EU

Please state the name and address of your company as well as relevant phone number and e-mail address:

	Yes	No	Don't know
Does your company sell/manufacture/design textile products for children under the age of 9?	**21**		
Are the clothes manufactured/dyed outside the EU?	**18**	**4**	

If yes to both questions, then please tick off which products

Trousers	[14]	Underwear	[13]
Blouses	[14]	Socks	[11]
T-shirts	[16]	Tights	[10]
Underwear	[13]	Dresses/Skirts	[13]
Night clothes	[13]	Shirts	[11]

Please mark with an X, which or your products mainly contain natural fibres (cotton etc.)

Trousers	[14]	Underwear	[13]
Blouses	[14]	Socks	[12]
T-shirts	[16]	Tights	[11]
Underwear	[13]	Dresses/Skirts	[13]
Night clothes	[13]	Shirts	[11]

Please mark with an X, which of your products mainly contain synthetic fibres (polyester, nylon, polypropylene, acrylic etc.)

Trousers	[1]	Underwear	[ ]
Blouses	[1]	Socks	[ ]
T-shirts	[1]	Tights	[ ]
Underwear	[ ]	Dresses/skirts	[3]
Night clothes	[ ]	Shirts	[1]
		Coats	[1]

Please mark with an X, which of your products mainly contain regenerated fibres (viscose, acetate, lyocel etc.)

Trousers	[1]	Underwear	[ ]
Blouses	[3]	Socks	[ ]
T-shirts	[2]	Tights	[ ]
Underwear	[ ]	Dresses/skirts	[2]
Night clothes	[ ]	Shirts	[ ]

	Yes	No	Don't know
Are any colours used more than others, e.g., black?	1	16	2

If yes, then please state the three colours that are used the most (e.g. black, red or blue) and please include information about the manufacturer's/importer's name of the colour, e.g., colour index No. or the like.

Black: 3
Blue: 1
White: 1
Off-white: 1
Red: 1

	Yes	No	Don't know
Do you have written information about the composition and content in the dyes the manufacturer/dye works uses?	**5**	**13**	

If yes, then please send the information with the questionnaire, e.g., in the form of a copy/pdf of the outline of colour index No., safety data sheets, test reports or other information from the manufacturer/dye work/importer/supplier.

Oeko-tex standard 5
GOTS: 3

	Yes	No	Don't know
Have you experienced complaints on health-related problems (e.g., itchy skin) or other inconveniences that you suspect are caused by dyes?	**1**	**17**	

Please state which problems, type of clothes and colours (state the name of the colour, e.g., the colour index No.)
The textile will be examined for azo dyes that cannot be found.

Please return the questionnaire as letter or pdf to:
Danish Technological Institute, attn.: Torsten Due Bryld, Gregersensvej 1, DK - 2630 Taastrup
or e-mail: tsb@teknologisk.dk

Thank you in advance.

Appendix 4: Outline of Surveyed Dyes

Name	CAS no.	C.I. Structure No.	Limit values mg/kg*	Reference	Potentially carcinogenic	Potentially allergenic	Type of dye	Degradation product of azo dyes
4-Aminobiphenyl	92-67-1		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
Benzidine	92-87-5		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
4-Chloro-o-toluidine	95-69-2		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
2-Naphthylamine	91-59-8		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
o-Aminoazotoluene	97-56-3		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
2-Amino-4-nitrotoluene	99-55-8		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
p-Chloroaniline	106-47-8		30 / 20	REACH / Oeko-Tex®	x			Primary aromatic amine
2,4-Diaminoanisole	615-05-4		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
4,4'-Diaminobiphenyl-methane	101-77-9		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
3,3'-Dichloro-benzidine	91-94-1		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
3,3'-Dimethoxy-benzidine	119-90-4		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
3,3'-Dimethyl-benzidine	119-93-7		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
3,3'-Dimethyl-4,4'-diaminobiphenyl-methane	838-88-0		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine

Name	CAS no.	C.I. Structure No.	Limit values mg/kg*	Reference	Potentially carcinogenic	Potentially allergenic	Type of dye	Degradation product of azo dyes
p-Cresidine	120-71-8		30 / 20	REACH / Oeko-Tex®	x			Primary aromatic amine
4,4'-Methylene-bis-(2-chloroaniline)	101-14-4		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
4,4'-Oxydianiline	101-80-4		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
4,4'-Thiodianiline	139-65-1		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
o-Toluidine	95-53-4		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
2,4-Toluendiamine	95-80-7		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
2,4,5-Trimethyl-aniline	137-17-7		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
o-Anisidin (2-Methoxyaniline)	90-04-0		30 / 20	REACH	x			Primary aromatic amine
4-Aminoazobenzene	60-09-3		30 / 20	REACH / Oeko-Tex®	X			Primary aromatic amine
2,4-Xylidine	95-68-1		20	Oeko-Tex®	X			Primary aromatic amine
2,6-Xylidine	87-62-7		20	Oeko-Tex®	X			Primary aromatic amine
Acid Black 48	1328-24-1	65 005		Environ. project no. 534, 2000		x	Acid / anthrax-quinone	
Acid red 118	12217-35-5; 83027-46-7	170540		National Allergy Research Centre		X	Acid / azo	
Acid Red 26	3761-53-3	16 150		EU Ecolabel Oeko-Tex®	X		Acid / Azo	

Name	CAS no.	C.I. Structure No.	Limit values mg/kg*	Reference	Potentially carcinogenic	Potentially allergenic	Type of dye	Degradation product of azo dyes
Acid red 359	61814-65-1			National Allergy Research Centre		X	Acid / azo / metal complex	
Acid yellow 36	587-98-4	13 065		National Allergy Research Centre		X	Acid / azo	
Acid yellow 61	12217-38-8	18 968		National Allergy Research Centre		X	Acid / azo	
Basic Black 1	2229967	50 431		Environ. project no. 534, 2000		X	cationic / azine	
Basic Brown 1	8005-77-4	21 000		Environ. project no. 534, 2000 / National Allergy Research Centre		x	cationic/ azo	
Basic Green 1	633-03-4	42 040		Environ. project no. 534, 2000		X	cationic/ methane	
Basic Red 46	12221-69-1	110825		Environ. project no. 534, 2000 / National Allergy Research Centre		x	cationic/ azo	
Basic Red 9	25620-78-4	42 500		EU Ecolabel Oeko-Tex®	X		cationic/ triarylmethane	
Basic Violet 14	632-99-5	42 510		EU Ecolabel Oeko-Tex®	X		cationic/ triarylmethane	
Direct Black 38	1937-37-7	30 235		EU Ecolabel Oeko-Tex®	X		Direct / azo	
Direct Blue 6	2602-46-2	22 610		EU Ecolabel Oeko-Tex®	X		Direct / azo	
Direct Orange 14	5859-00-7	16 100		Environ. project no.		x	Direct / azo	

Name	CAS no.	C.I. Structure No.	Limit values mg/kg*	Reference	Potentially carcinogenic	Potentially allergenic	Type of dye	Degradation product of azo dyes
				534, 2000				
Direct orange 34	12222-37-6	40 215; 40 220		National Allergy Research Centre		X	Direct / azo	
Direct Orange 8	2429-79-0	22 130		Environ. project no. 534, 2000		x	Direct / azo	
Direct Red 28	573-58-0	22 120		EU Ecolabel Oeko-Tex®	X		Direct / azo	
Disperse Black 1	6054-48-4	11 365		World Dye Variety		X	Disperse / azo	
Disperse Blue 1	2475-45-8	64 500		EU Ecolabel Oeko-Tex®	x	X	Disperse / anthraquinone	
Disperse Blue 102	12222-97-8			EU Ecolabel Oeko-Tex®		X	Disperse / azo	
Disperse Blue 106	12223-01-7	11 935		EU Ecolabel Oeko-Tex® / National Allergy Research Centre		X	Disperse /azo	
Disperse Blue 124	61951-51-7	111938		EU Ecolabel Oeko-Tex® / National Allergy Research Centre		X	Disperse / azo	
Disperse Blue 153				Environ. project no.534, 2000 / National Allergy Research Centre		x	Disperse / anthraquinone	
Disperse Blue 26	3860-63-7	63 305		EU Ecolabel Oeko-Tex®		X	Disperse / anthraquinone	
Disperse Blue 3	2475-46-9	61 505		EU Ecolabel Oeko-Tex®		X	Disperse / anthraquinone	
Disperse Blue 35	12222-75-2			EU Ecolabel Oeko-Tex®		X	Disperse / anthraquinone	

Name	CAS no.	C.I. Structure No.	Limit values mg/kg*	Reference	Potentially carcinogenic	Potentially allergenic	Type of dye	Degradation product of azo dyes
Disperse Blue 7	3179-90-6	62 500		EU Ecolabel Oeko-Tex®		X	Disperse / anthraquinone	
Disperse Blue 85	12222-83-2	11 370		Environ. project no.534, 2000 / National Allergy Research Centre		x	Disperse / azo	
Disperse Brown 1	23355-64-8	11 152		World Dye Variety / EU Ecolabel Oeko-Tex® / National Allergy Research Centre		X	Disperse / azo	
Disperse Orange 1	2581-69-3	11 080		EU Ecolabel Oeko-Tex® / National Allergy Research Centre		X	Disperse / azo	
Disperse Orange 11	82-28-0	60 700		EU Ecolabel Oeko-Tex®	X		Disperse / anthrax-quinone	
Disperse Orange 13	1590182	11 080		Environ. project no.534, 2000		x	Disperse / azo	
Disperse Orange 3	730-40-5	11 005		EU Ecolabel Oeko-Tex® / National Allergy Research Centre		x	Disperse / azo	
Disperse Orange 37	12223-33-5; 13301-61-6	11 132		World Dye Variety / EU Ecolabel Oeko-Tex®		X	Disperse / azo	
Disperse Orange 76	51811-42-8/13301-61-6	11 132		World Dye Variety / EU Ecolabel		X	Disperse / azo	

Name	CAS no.	C.I. Structure No.	Limit values mg/kg*	Reference	Potentially carcinogenic	Potentially allergenic	Type of dye	Degradation product of azo dyes
				Oeko-Tex®				
Disperse Red 1	2872-52-8	11 110		EU Ecolabel Oeko-Tex® / National Allergy Research Centre		X	Disperse / azo	
Disperse Red 11	2872-48-2	62 015		EU Ecolabel Oeko-Tex® / National Allergy Research Centre		X	Disperse	
Disperse Red 17	3179-89-3	11 210		EU Ecolabel Oeko-Tex® / National Allergy Research Centre		X	Disperse / anthrax-quinone	
Disperse Yellow 1	119-15-3	10 345		EU Ecolabel Oeko-Tex®		X	Disperse / aromatic amine	
Disperse Yellow 3	2832-40-8	11 855		EU Ecolabel Oeko-Tex® / National Allergy Research Centre	X	x	Disperse / azo	
Disperse Yellow 39	12236-29-2	480095		World Dye Variety / EU Ecolabel Oeko-Tex®		X	Disperse / aromatic amine	
Disperse Yellow 49	54824-37-2	11 855		World Dye Variety / ChemNet / EU Ecolabel Oeko-Tex®		X	Disperse / aromatic amine	
Disperse Yellow 54	12223-85-7	47 020		Environ. project no.534, 2000		X	Disperse / methane	
Disperse Yellow 9	6373-73-5	10 375		EU Ecolabel Oeko-Tex® National		x	Disperse / aromatic amine	

Name	CAS no.	C.I. Structure No.	Limit values mg/kg*	Reference	Potentially carcinogenic	Potentially allergenic	Type of dye	Degradation product of azo dyes
				Allergy Research Centre				
Neutrichrome Red (acid dye)				Environ. project no.534, 2000			Acid / metal complex	
Reactive black 5	61969-31-1	179085		National Allergy Research Centre		X	Reactive / azo	
Reactive blue 21	164578-12-5	205055		National Allergy Research Centre		X	Reactive / metal complex	
Reactive blue 238	12226-38-9	18 097		National Allergy Research Centre		X	Reactive / azo	
Reactive orange 107	12236-86-1; 73049-92-0			National Allergy Research Centre		X	Reactive / azo	
Reactive red 123	140876-11-5			National Allergy Research Centre		X	Reactive / azo	
Reactive red 228	173995-81-8			National Allergy Research Centre		X	Reactive / azo	
Reactive red 238	90597-79-8; 12220-08-5			National Allergy Research Centre		X	Reactive / azo	
Reactive violet 5	12225-25-1/17095-24-8	20 505		National Allergy Research Centre		X	Reactive / azo	
Supramine Yellow G (acid dye)		19300		Environ. project no.534, 2000			Acid / azo	

Name	CAS no.	C.I. Structure No.	Limit values mg/kg*	Reference	Potentially carcinogenic	Potentially allergenic	Type of dye	Degradation product of azo dyes
Supramine Yellow S (acid dye)		18930		Environ. project no.534, 2000			Acid / azo	
Turquoise Reactive (basic dye)		42 035; 42 036; 42 037		Environ. project no.534, 2000		x	cationic / methine	
Heavy metals								
Antimone (Sb)	7440-36-0		30	Oeko-Tex®				
Arsene (As)	7440-38-2		0,2	Oeko-Tex®				
Lead (Pb)	7439-92-1		0,2	Oeko-Tex®				
Cadmium (Cd)	7440-43-9		0,1	Oeko-Tex®				
Chrome (Cr)	7440-47-3		1,0	Oeko-Tex®				
Chrome (Cr VI)	18540-29-9		0,5	Oeko-Tex®				
Cobalt (Co)	7440-48-4		1,0	Oeko-Tex®				
Cupper (Cu)	7440-50-8		25,0	Oeko-Tex®				
Mercury (Hg)	7439-97-6		0,02	Oeko-Tex®				
Nickel (Ni)	7440-02-0		1,0	Oeko-Tex®				

Appendix 5: Outline of Clothes for Analysis

No.	Clothes type	Shop type	Material	Subsample description	Colour	Country of origin
1a	Aertex blouse	Sports chain	100% polyester	Blouse material	Neon green	Taiwan
1b				Collar	Neon green	
1c				Edging at the neck	Neon green	
2a	T-shirt, red	Sports chain	100% polyester	Blouse material	Red	the Philippines
2b				Edge at neck	Red	
2c				Edging at the neck	Orange	
3a	T-shirt, black	Sports chain	100% polyester	Blouse material	Black	the Philippines
3b				Edge at neck	Black	
3c				Edging at neck	Orange	
4a	Hooded blouse	Fashion shop	55% polyester 45% cotton	Blouse material	Black	China
4b				Ribbing at sleeve	Black	
4c				Ribbon on sleeve	Orange/ black	
5a	Black blouse, child	Super-market	100% polyester	Ribbing	Black	China
5b				Blouse material	Black	
6	Purple gloves, child	Super-market	97% polyester 3% elastane		Purple	China
7a	Black gloves, child	Super-market	73% acrylic 25% polyester 1% elastodiene 1% elastane	Mitten	Black	China
7b				Fingertip with touch effect	Black	
8	Blue leggings	Super-market	95% polyester 5% elastane		Blue	China

No.	Clothes type	Shop type	Material	Subsample description	Colour	Country of origin
9	Blue scarf with glitter	Department store	53% acrylic 47% polyester		Blue	China
10	Sort ladies' blouse	Fashion shop	55% polyester 45% viscose		Black	China
11	Ladies' jeans	Fashion shop	59% polyester 38% cotton 3% elastane		Bordeaux	Bangladesh
12	Black knit scarf	Fashion shop	100% acrylic		Black	China
13	Black ski underwear	Super-market	100% polyester		Black	China
14a	Grey duvet vest	Super-market	100% polyester	Outer material	Grey	China
14b				Lining	Grey	
15a	Neon vest for running	Super-market	100% polyester	Outer material – neon yellow	Neon yellow	China
15b				Net material	Neon yellow	
15c				Edging	Black	
16a	Black/white Sweatshirt	Super-market	100% polyester	Blouse material	Black	China
16b				Rib	Black	
16c				Pattern	Black	
17a	Red girl's dress	Super-market	95% polyester 5% spandex	Dress	Red	Ukraine
17b				Sløjfe	Red	
18a	Striped children's bathrobe	Fashion shop	100 % polyester	Stribe	Turquoise	China
18b				Stripe	Navy blue	
18c				Neck edging	Navy blue	
19a	Children's sports pants	Fashion shop	87% polyester 13% elestane	Trouser material	Black	Indonesia
	19b			Hem	Pink	

No.	Clothes type	Shop type	Material	Subsample description	Colour	Country of origin
20a	Pink children's skirt	Fashion shop	100% polyester	Skirt	Pink	Vietnam
20b				Bow	Pink	
21	Blue blouse	Fashion shop	100% polyester		Blue	
22a	Neon Yellow skirt	Fashion shop	100% polyester	Outer material	Neon yellow	India
22b				Lining	Neon yellow	
23	Mauve fleece trousers for children	Super-market	100% polyester		Mauve	China
24	Thermo tights for children	Super-market	95% polyester 5% elastane		Black	China
25	Ladies' thermo leggings	Discount shop	92% polyester 8% elastane		Black	China
26a	Black ladies' blouse Sort coated jersey	Fashion shop	95% polyester 5% spandex	Blouse material	Black	China
26b				Edge	Black	
27	Black ladies' sock	Discount shop	100% polyester		Black	China
28	Mauve ladies' socks	Discount shop	100% polyester		Mauve	China
29	Pink children's gloves	Discount shop	100% polyester		Pink	China
30	Black fleece	Sports chain	100% polyester		Black	China
31a	Green track shirt	Sports chain	100% polyester	Light green	Light green	China
31b				Dark green	Dark green	China

Kortlægning og sundhedsmæssig af farvestoffer i tøj

In the textile and clothing industry, a wide range of chemical substances are used to dye clothes. Several of the substances are problematic or their break-down products can be problematic. Some of the problematic dyes, such as azo dyes, are regulated in REACH and registered on the candidate list. Other dyes, such as disperse dyes, which can give rise to allergy and cancer, are not regulated by REACH or other legislation. The Danish Environmental Protection Agency has therefor investigated manufacturers' knowledge of which dyes are used in textiles in Denmark. Further the occurrence of 23 selected allergenic, disperse dyes in textiles were examined in a goal-oriented random sampling.

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Environmental Protection Agency

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