DANISH MINISTRY
OF THE ENVIRONMENT
Environmental
Protection Agency

Screening for health effects from chemical substances in textile colorants

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Survey of Chemical Substances in Consumer Products, No. 57 2005

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Content

Preface

The present report ”Screening for health effects from chemical substances in textile colorants” is a follow-up of the survey project: ”Survey and analysis of chemical substances in textile colorants for hobby use”.

The purpose of this report is to evaluate the chemical substances detected in the survey project (Survey of chemical substances in textile colorants for hobby use, draft 2004) and which are used in products to dye or decorate textiles for private use. The purpose is furthermore to establish if the consumers by use of textile colorants for hobby uses are exposed to hazardous substances at concentrations that may cause health concern.

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The project is followed by a steering committee consisting of:

Frank Jensen, Danish Environmental Protection Agency and
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The project is performed during autumn 2004.

Sammenfatning og konklusioner

Som et led i Miljøstyrelsens kortlægning af kemiske stoffer i forbrugerprodukter er tekstilfarver til hobbybrug blevet kortlagt og analyseret. På baggrund af analyseresultaterne er der foretaget en vurdering af hvilke kemiske stoffer, der indgik i tekstilfarverne og eventuelle sundhedsskadelige effekter fra stofferne ved anvendelsen af tekstilfarverne.

Tekstilfarver kan inddeles i dekorationsfarver og produkter til indfarvning af tekstiler, hvoraf ca. 80% af det samlede forbrug udgøres af den sidste gruppe. Gruppen af dekorationsfarver omfatter produkter som filtspidspenne, pop-up farver og overføringsfarver (transferfarver). Gruppen af produkter til indfarvning af tekstiler omfatter stoffarver, der enten er beregnet til at indfarve eller dække tekstiler i større omfang. Forbruget er ca. 30.000 kg pr. år i Danmark.

I kortlægningsrapporten er foretaget analyser af 8 tekstilfarveprodukter. Ved den kvalitative analyse for flygtige stoffer blev der påvist flere glycoler og opløsningsmidler. Glycoler anses generelt for ikke-giftige, men undersøgelsen viser, at antagelsen bygger på få eller meget gamle undersøgelsesresultater. Fundet af de mange opløsningsmidler antyder, at det specielt er i anvendelsesfasen af produkterne, at eksponeringen af forbrugeren finder sted. Vurderingerne er derfor koncentreret om denne fase af forbrugerkontakten.

De organiske kemiske stoffer, der enten forekom hyppigt, i store koncentrationer eller havde en alvorlig klassifikation blev udvalgt til nærmere vurdering. I screeningen af klassifikationen blev det fundet, at af de 63 identificerede kemiske stoffer, var 28 stoffer klassificeret i Listen over farlige stoffer, og 5 kunne klassificeres efter Miljøstyrelsens Vejledende liste til selvklassifikation. Et stof var klassificeret Carc.cat.1;R45 (kan fremkalde kræft), 5 stoffer var klassificeret Carc.cat.3;R40 (mulighed for kræftfremkaldende effekt), og 1 stof var klassificeret mutagent Mut.cat.2;R46 (kan forårsage arvelige genetiske skader). 3 stoffer var klassificeret R42 og/eller R43 (kan give overfølsomhed ved indånding og/eller kontakt med huden) og yderligere 2 stoffer var i samme kategori efter Miljøstyrelsens Vejledende liste til selvklassificering. I alt 13 organiske stoffer blev udtaget til nærmere sundhedsmæssig vurdering.

Udvalgte produkter blev yderligere analyseret for 3 metaller, hvoraf kun de to blev fundet i koncentrationer over detektionsgrænsen. De to (antimon og kobber) blev udtaget til nærmere vurdering.

Vurderingen er foretaget på basis af realistiske ”worst case” scenarier efter de metoder, som EU har opstillet for risikovurdering af kemiske stoffer. Det vil sige, at der blev fundet relevante niveauer, hvor der ikke forventes en sundhedsskadelig effekt (NOAEL: no observed adverse effect level) eller en etableret grænseværdi for optagelse, som derefter blev sammenlignet med de estimerede koncentrationer i de valgte scenarier.

Der er i scenarierne foretaget en vurdering baseret på eksponering via indånding (inhalation) af flygtige stoffer under brugen af tekstilfarvestofferne,

ved hudkontakt (dermal kontakt), hvis man får produktet på hænderne eller eksponeret for en tilsvarende mængde fra tøjet efter farvning. Desuden er anført et scenarium for eksponering via munden (oral eksponering), baseret på at fingre, produkt eller tekstil puttes i munden. Sidstnævnte kan næppe undgås, hvis der forefindes småbørn i familien.

To af de vurderede stoffer (1,4-dichlorbenzen og 1,4-dioxan) er klassificeret kræftfremkaldende kategori 3 (R40 Mulighed for kræftfremkaldende effekt). Begge stoffer er blevet vurderet i EUs risikovurderingsprogram. Rapporterne antyder en tærskel for den kræftfremkaldende effekt. De fundne niveauer af stoffet kan derfor være uden betydning, men producent og forbruger bør måske overveje alternativer.

Produktet, der indeholder 3-isocyanatomethyl-3,5,5-trimethyl-cyclohexyl isocyanat (IPDI), er vurderet ikke at udgøre en umiddelbar sundhedsmæssig risiko for forbrugeren af det undersøgte tekstilfarvestof. Der gøres dog opmærksom på, at sikkerhedsmarginen (MOS) er lav, hvilket antyder, at der kan være et potentielt sundhedsmæssigt problem med stoffet, og at længere tids eksponering for produkter med stoffet bør undgås. Det bemærkes også, at stoffet kan være sensibiliserede ved hudkontakt og ved indånding. Opvarmning af farvestof indeholdende dette stof bør foregå under ventilation.

Produkter indeholdende isobutan havde også en meget lav sikkerhedsmargin (MOS), hvilket antyder, at der kan være et potentielt sundhedsmæssigt problem med stoffet, og at længere tids eksponering for produkter med stoffet bør undgås. Anvendelse af produkter med stoffet bør foregå under udluftning/ventilation.

Konklusionen af projektet var, at ingen af de vurderede kemiske stoffer ville give umiddelbar anledning til sundhedsmæssigt skadelige effekter hos forbrugeren ved de estimerede eksponeringer ved inhalation, hudkontakt eller indtagelse via munden.

Vurderingerne er i de fleste tilfælde vurderet ved sammenligninger med data fra langtidsforsøg eller ligefrem kroniske data. Da eksponeringen for tekstilfarvestoffer må antages at være aktuel indenfor kortere perioder, skulle konklusionerne derfor være acceptable.

Det bør dog tilføjes, at forbrugeren er eksponeret for mere end ét af de fundne stoffer på samme tid, og fordi de anvendte effekt data er baseret på forskellige effekter, kan de ikke lægges sammen. Desuden kan forbrugeren blive eksponeret for det samme stof fra andre kilder, som f.eks. andre produkter, fra det omgivende miljø eller fra fødevarer, hvilket samlet kan medføre en total eksponering, som er over de fundne niveauer, hvor der ikke forventes en effekt eller et acceptabelt dagligt indtag. Især for stoffer med en lav sikkerhedsmargin (lav MOS værdi, f.eks. isobutan og IPDI) kan dette blive kritisk.

Summary and conclusions

The Danish Environmental Protection Agency has as a part of the programme on surveys of chemical substances in consumer products performed a survey and analysis of textile colorants for hobby uses. Based on the results of the chemical analysis, an assessment is performed on which chemical substances that were identified in the textile colorant products and the potential adverse effects from these substances when the textile colorant products were used by consumers.

Textile colorants can be divided into decoration colorants and products for textile dying of which 80% of the total consumption is composed of the latter. The group of decoration colorants includes products as felt-tip pens, pop-up dyes, and transfer dyes. The group of products for textile dyeing includes textile dyes intended for dyeing or covering textiles in larger proportions. The annual Danish consumption is approximately 30,000 kg.

In the survey report, analyses were performed on 8 textile dye products. In the qualitative analysis for volatile substances several glycols and solvents were identified. Glycols are generally considered non-toxic but the study showed that the assumption was based on a few or old test results. The identification of many solvents indicated that especially during the use of the products consumers were exposed. The assessments are therefore concerned especially with this phase of the consumer exposure.

The organic chemical substances commonly found, detected at high concentrations or had severe classifications were selected for health assessment. In the screening of classifications, it was observed that of the 63 identified chemical substances, 28 were classified in the List of dangerous substances (Annex I on Directive 67/548/EC). Five substances could be self-classified by the Danish Environmental Protection Agency's Advisory list for self-classification. One substance was classified Carc.cat.1;R45, may cause cancer, 5 substances were classified Carc.cat.3;R40, limited evidence of a carcinogenic effect, 1 substance was classified mutagenic Mut.car.2;R46, may cause heritable genetic damage. Three substances were classified R42 and/or R43, may cause sensitisation by inhalation and/or by skin contact and further 2 substances was placed in the same category according to the Advisory list for self-classification. A total of 13 organic substances were selected for health assessment.

Selected products were analysed for 3 metals of which 2 were found at concentrations above the detection limit. The two substances (antimony and copper) were also selected for health assessment.

The health assessment is performed based on realistic "worst case" scenarios according to the methods developed by EU for risk assessment of chemical substances. This means that relevant levels were identified at which no adverse health effects are expected (NOAEL: no observed adverse effect level) or an established threshold limit value for uptake. This value was then compared to the estimated concentrations or uptakes in the selected scenarios.

In the scenarios, an assessment was performed based on exposure via inhalation of volatile substances during the use of textile dye products, by dermal contact if the consumer gets his hands contaminated or is exposed by an equal amount from the dyed textile. Further, a scenario is included for oral exposure based on mouthing of fingers, product or dyed textiles. The latter may hardly be avoided if the family includes toddlers.

Two of the evaluated substances (1,4-dichlorobenzene and 1,4-dioxane) are classified carcinogenic category 3 (R40 Limited evidence of carcinogenic effect). Both substances have been assessed in the EU risk assessment programme. The reports indicate a threshold to carcinogenic effects. Thus at the determined levels the substance may not be of significance but the manufacturer and the consumer perhaps should consider alternatives.

The product containing 3-isocyanatomethyl-3,5,5-trimethyl-cyclohexyl isocyanate (IPDI) is assessed not to pose an immediate health risk to the consumer of the studied textile colorant. However, the margin of safety (MOS) is low indicating a potential health concern and prolonged exposure should be avoided with products containing this substance. It should be noted also that the substance may cause sensitisation by skin contact and by inhalation. Heating of the colorants containing this substance should be performed under ventilation.

Products containing isobutane also had a very low margin of safety (MOS) indicating a potential health concern. Prolonged exposure should be avoided with products containing this substance. Use of products containing the substance should be performed under aeration or ventilation.

The conclusion of the project is that none of the evaluated chemical substances would cause any immediate adverse health effects to the consumer at the estimated exposure levels by inhalation, dermal or oral contact.

The assessments are in most cases performed by comparing data from long-term studies or even chronic data. As the exposure to textile colorants must be assumed to be actual within shorter periods the conclusions should be acceptable.

However, it should be noted that the consumer is exposed to more than one of the substances simultaneously. Because the effect levels used in the evaluation are based on varying effects they can not be added. Further the consumer may be exposed to the same substances form other sources, e.g. other products, environment or food, which could result in a total exposure above the no-effect levels or tolerable daily intake values. Especially exposure to substances with low MOS values (e.g. isobutane and IPDI) may be critical.

1 Introduction

1.1 Background and prerequisites

A survey and analysis of chemical substances in textile colorants has been performed (Draft dated 20 January 2004, Miljøstyrelsen 2004). The present report contains an evaluation of the detected results.

On the market several products exist that can be used by the common consumer for decorating and dyeing of textiles for hobby use.

Textile products are decorated typically in two principally different ways, by colorants dissolved or dispersed in water, or by insoluble pigments, which like paints are adhered to the substrate by the assistance of a binding agent (adhesive).

Colorants and pigments may contain heavy metals, either incorporated into the molecule and/or as trace elements remaining from the colorant manufacturing.

Furthermore by dyeing and printing of textiles are used several additives that helps the colour to penetrate the textile and to distribute itself evenly and partly to promote/secure the binding to the textile. The additives may be powerful bases or acids, surfactants and reducing or oxidising substances.

The textile colorant products applied in hobby uses may contain significant amounts of volatile substances, especially when using colour pens or Indian inks.

In the survey report the consumption of textile colorants for hobby use was stated to 30 000 kg/year in Denmark (Miljøstyrelsen 2004). 15 products were selected for a preliminary screening of metals and volatile organic components. A separation into 2 use groups was found appropriate. The products were therefore divided into:

- Decoration colorants. Decoration colorants are used on limited textile surfaces and amounted to 20 % of the consumption.
- Products for dyeing. Products for dyeing are made for total dyeing of the textile or added to larger areas of the textile. Products for dyeing amounted to 80% of the consumption.

In the survey report, a quantitative determination of the content of chemical substances in 8 products is performed.

1.2 Health assessment

A health assessment of the identified substances is based on the principles recommended in the European Union (EU) methodology for risk assessment of chemical substances (Technical Guidance Document, TGD, EC 2003). In the TGD exposure to consumers is included. Some data and information are

based on relevant parts of the American “Exposure Handbook” (US-EPA 1997), which contains an extensive data material on American consumers.

The exposure of the consumer varies according to the final use. Still it has been chosen to use as starting point an exposure scenario where the exposure is presumed to be largest. For the use of the product it concerns **inhalation** of solvents from the product when it is applied on textiles, by drying of the colorant. For the use of the coloured/dyed fabric it can be by uses of the textile as clothes worn next to the skin.

A **dermal** exposure can be expected to take place by skin contact during use of the product and of the coloured/dyed textile. The duration of contact exposure of the skin will vary but may cause migration of chemical substances from the textile colorants to the skin, possibly helped by sweat.

The exposure route may also be by **oral** intake if contaminants or residues from the use of the product on hands/fingers or dyed textiles are mouthed.

Scenarios are established for:
- Exposure via inhalation
- Exposure via the skin (dermal exposure)
- Exposure via intake (oral exposure)

1.3 Project progress

The project is divided into two phases:

Phase 1:
Evaluation of the detected chemical substances in textile colorants for hobby use by a screening of immediate available literature on the identified and measured substances. The screening is based on literature information and has the purpose to ensure that the substances focused on by the health assessment are the most relevant substances. In co-operation with the Danish Environmental Protection Agency a number of substances are selected for a further evaluation.

Phase 2:
Establishment of exposure scenarios and evaluation of the selected substances.

Data on the individual substances in form of physical-chemical data, most essential effect data, NOAEL (the level where no adverse effects are observed), LOAEL (the lowest level where adverse effects are observed) or other relevant data are used to the extent they are available. Alternatively are used estimated data based on molecular quantitative structure activity relationship analysis (QSAR data) for the substances where no test data are available.

Exposure scenarios based on the expected exposure of the consumers of ”home coloured textiles” are established. Based on the forwarded analysis results from the survey the primary exposure during the use of textile colorants for hobby use appears to be via inhalation. Since the analysis determines the content of chemical substances in mg/kg product a starting point in a worst case situation is taken with an estimation of the maximum evaporation based on the Law on Ideal gasses. Previous examinations

performed at the Danish Technological Institute have indicated that the actual evaporation was approx. ¼ of the estimated evaporation from solid materials and approx. ½ from textiles.

Another exposure can be expected from dermal contact during use of the product and the dyed textile. The exposed skin areas are primarily the hands during the use of the colorant product and the skin on other parts of the body during the use of the dyed textiles.

The exposure route may also be by oral intake if contaminants or residues from the use of the product on hands or fingers afterwards are mouthed. A *worst case* situation would for instance be if ”unclean” fingers or the textile is mouthed and possible contents of textile colorants migrate to saliva and are taken in orally.

2 Survey and analysis results

2.1 Survey

The survey of the consumption of textile colorants for hobby use has been performed in a previous project: ”Survey and analysis of chemical substances in textile colorants for hobby use” (Miljøstyrelsen 2004). A summary of the results is presented below in an abridged form.

Textile colorants for hobby use is defined in this context as products intended to dye and for decoration of textiles and textile surfaces and that is not intended for industrial use.

Some products for decorating and colouring of textiles for hobby use exist. Fabric printing ink, colorants for e.g. silk screen-printing and batik colouring, Indian ink and colour pens for textiles. There are large possibility for skin contact both during application and subsequent use. For volatile substances a possibility for inhalation during application and subsequent drying exists.

Based on information on production volume and evaluations from the association of manufacturers, importers and distributors of hobby materials in Denmark (The Joint Council for Creative and Hobby Materials) was estimated that in the year 2002 a total of approx. 30,000 kg textile colorant products for hobby use were sold in Denmark.

The study resulted in a separation of textile colorants into two main groups:

- Decoration colorants.
- Products for dyeing.

The two main groups are further separated into five different subgroups divided according to use and effect.

2.1.1 Decoration colorants

This group includes products intended for decoration of the textile. The products are used only on limited areas and thus only in limited amounts. The consumption within this group amounts to less than 20% of the total consumption of textile colorants.

2.1.1.1 Felt-tip pens

The products include pens/crayons with felt-tip (also named textile pens). The felt-tip pens are especially well suited for decoration on T-shirts and cotton fabrics. Different tips are used to obtain different effects and thickness of the lines.

2.1.1.2 Pop-up colorants

The group includes products that after drying ”pop up” by exposure to heat. The colorants are used as contour colours and for smaller motives.

2.1.1.3 Transfer dyes
These dyes are transferred from a carrier of plastic to the textile under the influence of heat. The colour is painted on the carrier medium. When the colour is dry a resistant soft film is formed that can be transferred to most textiles. When the motive is fixed it can be pealed off and relocated or kept for later use.

2.1.2 Products for dyeing of textiles

This group includes products intended to dye or apply to larger areas of the textile. More than 80% of the consumed amount of textile colorants are included in this group.

2.1.2.1 Dyes for hand or machine colouring
The group includes products intended to dye/redye textile fabrics and finished articles in washing machines or by hand dyeing in tub. The number of products for private use within this group is limited.

2.1.2.2 Fabric colorants/dyes
The group includes liquid colour solutions that are applied the textile with pens, brushes or similar, for silk screen paint and textile printing. This subgroup is by far the largest considering the number of different products.

2.2 Ingredients

Generally, there are four basic components in a typical colorant product.

1. Binding agents / Adhesives
2. Solvents
3. Pigments
4. Additives

2.2.1.1 Binding agents/ Adhesives
The adhesives have the purpose to adhere the colour to the surface. The products' contents of adhesives vary considerably. In the study, products are included with an adhesive content from approx. 15 to 98%.

2.2.1.2 Solvents
The solvent keeps the adhesive and pigment liquid and gives the product the correct consistency (build). The solvent must evaporate during drying to make the colorant/dye solid, In products such as textile colorants for hobby use the solvent is typically water. The concentration of solvents in the individual products varies considerably. The content of solvents varied in the study from 20% to more than 80%.

2.2.1.3 Pigments
White pigments such as titanium oxide and calcium carbonate are often used to give bulk to the product where the coloured pigment is giving the product its colour when it is to be everything else than white. Pigments are generally insoluble and most dyes, therefore, are suspensions. Pigments are not soluble in water and are adhered to the surface of the fibres by an adhesive, which encompass the pigment particles and "glue" them to the surface of the fibre.

Reactive dyes are especially well suited to cellulose fibres such as cotton where the dye forms a covalent binding (chemical binding) to the cellulose fibre.

Acid dyes are especially suitable for the dyeing of wool where the reactive group of the acid dyes (sulphonic acid moiety) binds to the amino groups of the wool.

The content of pigments and dyes in colorant products depends of the colour shade. Light shades contain fewer amounts of pigments and colorants than darker shades. The content varies in the current study from less than 5% to more than 65%.

2.2.1.4 Additives

Several types of additives exist. Often solvents are added as *film forming agent* to ensure that the film merges. The substances can be butyl glycol and mineral turpentine, which evaporates quickly, or propylene glycol and butyl diglycol, which evaporates more slowly. The content of film forming agents is typically at a level from a few percentages to more than 10% depending on how glossy the surface of the product is. *Preservatives* shall reduce the risk of growth of microorganisms such as bacteria and fungi. *Surfactants* such as tensides, phosphates and silicones may be added to stabilise the adhesive and pigment dispersion and to wet the textile surfaces. Some colorant products are added *plasticisers* such as phthalates to make the dry product more flexible whereas other products are softened by the structure of the polymer. The formation of certain polymer systems takes place at the presence of a *curing agent*: typically an amine compound. Finally is mentioned that the water-based products may contain a *wetting agent* that is often high boiling polar compounds as e.g. glycols to reduce the surface tension.

2.3 Analysis results

2.3.1 Sample preparation

The samples consisted of felt-tip pens, liquid products and powder products. For the liquid products and powder products, the samples are weighed and used directly. For felt-tip pens the cartridge was removed and used as sample in itself. The content in the colour mixture will be considerably higher than in the cartridge.

2.3.2 Analysis results for organic substances

2.3.2.1 Analysis method for quantitative determination of volatile and semi-volatile compounds

A subsample of the product is extracted using dichloromethane added internal standards. The mixture is shaken for 2 hours and left standing for approx. 16 hours. To detect the very volatile components an extraction of a subsample using dimethylformamide was also performed. The mixture was also shaken for 2 hours and left standing for approx. 16 hours. A subsample of the extracts was taken and analysed directly by combined gaschromatography and mass spectrometry (GC/MS) by scanning over a wider mass area. Detected components were identified using NIST library on mass spectra and manual evaluation of the spectra. The components that were uncertain for identification are marked with * in the table (table 1). The components that could only be identified to a group are designated a group name. Finally the components that could not be identified are presented as unidentified.

For the components that were detected by the qualitative analysis for volatile substances, the content was calculated quantitatively against external

standards when possible. The remaining components were calculated semiquantitatively against external standards.

The analysis uncertainty to components calculated quantitatively (external standard) are 15 to 20% RSD and for components calculated semiquantitatively (internal standard) the analysis uncertainty are estimated to 50 to 200%. The reporting limit: 10-50 mg/kg.

2.3.2.2 Analysis results for organic substances

The results of the semiquantitative analysis of volatile and semivolatile organic substances are based on the product types:

Felt-tip pen	Product no. 1
Pop-up colorant	Product no. 4 and 5
Transfer colorant	Product no. 6 and 7
Fabric dye	Product no. 9, 10 and 12

In co-operation with the Danish Environmental Protection Agency, 8 products were selected for analysis of content of extractable organic substances (GC/MS screening). The table below presents the result of the analysis. The substances marked with # after the name are calculated against external standard (analysis uncertainty 15-20% RSD) whereas all remaining components are calculated against internal standard (analysis uncertainty of 50-200% RSD).

Table 1. Analysis results of organic substances in textile colorants (mg/kg)

Name	CAS no.	1	4	5	6	7	9	10	12
Acetone	67-64-1	-	45	-	-	-	-	-	25
Alcohol	64-17-5	-	-	150	-	-	-	-	-
Azacyclotridecan-2-one (=Dodecan-12-lactam)	947-04-6	-	-	-	-	51	-	-	-
Benzaldehyde	100-52-7	-	3.6	-	-	-	-	-	-
Benzophenone	119-61-9	-	-	-	-	-	8.6	-	-
1-Butanol #	71-36-3	150	650	690	-	77	190	-	620
2-(2-Butoxyethoxy)-ethanol #	112-34-5	-	-	-	-	460	-	-	-
2-Butylamine	13952-84-6	-	-	-	-	53	-	-	-
Butyleret hydroxytoluene (BHT)	128-37-0	-	-	-	-	16	-	-	-
n-Butylether #	142-96-1	-	110	11	-	-	-	-	19
Caprolactam #	105-60-2	-	-	-	-	1100	-	-	-
5-Chlor-2,4-dimethoxy-benzenamine, (=5-Chlor-2,4-dimethoxy-aniline)	97-50-7	-	20	-	-	-	-	-	-
2-Chloro-4-dimethylamino-6-t-butylpyrimidine		-	23	-	-	-	-	-	-
Cyanocyclohexene (=Cyclohexencarbonitrile)	1855-63-6 100-45-8	-	-	-	-	-	-	110	-
1,3,5-Cycloheptatriene	544-25-2	-	6.5	-	-	-	-	-	-
Cyclopropane, nonyl *	74663-85-7	-	-	10	-	-	-	-	-
1,4-Dichlorobenzene	106-46-7	9.9	-	-	-	-	-	-	-
1,2-Dichlorethene	540-59-0	-	-	14	-	-	-	-	-
Diethylene glycol # (isomere compounds)	111-46-6	53000	-	6200	-	-	-	-	-
2,4-Diisocyanato-1-methyl-benzene (=toluendiisocyanate, = 2,4-diisocyanatotoluene)	584-84-9	-	3.2	-	-	-	-	-	-
Diisopropylenglycol #	110-98-5	2300	-	5000	3100	5100	390	-	4900

Name	CAS no.	1	4	5	6	7	9	10	12
1,3-Dimethyl-benzene (= m-xylene)	108-38-3	-	12	-	-	-	-	-	-
4-(1,1-Dimethylethyl)-cyclohexanol, (isomere compounds) (=4-tert-Butylcyclohexanol)	98-52-2	-	48	-	-	-	-	-	-
4,4-Dimethyl oxazolidine *	51200-87-4	-	-	-	-	-	200	150	-
1,4-Dioxane	123-91-1	11	-	-	-	-	4.7	-	-
2-(2-Ethoxyethoxy)-ethanol # (=diethylenglycol-monobutyl ether)	111-90-0	590	-	-	-	-	-	-	-
Ethylbenzene	100-41-4	-	19	-	-	-	-	-	-
2-Ethyl-1,3-cyclopentanedione, =2-Ethylcyclopentan-1,3-dion	823-36-9	-	-	-	-	-	-	98	-
Glycerin ** (=1,2,3-propanetriol)	56-81-5	-	-	11000	27000	-	-	-	-
Hexa(methoxymethyl)melamine	3089-11-0	-	-	-	-	-	-	73	67
Hexamethylentetramine # (= Methenamine)	100-97-0	-	49	800	-	11	22	570	860
2-Ethyl-hexanol	104-76-7	-	20	-	-	-	-	-	-
Hexanoic acid	142-62-1	-	4.1	-	-	-	-	-	-
Isobutane	75-28-5	-	3500	2000	-	-	-	-	-
3-Isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate	4098-71-9	-	-	-	-	270	-	-	-
Isopropyl alcohol	67-63-0	1300	-	-	-	-	-	-	-
1-(2-Methoxy-1-methylethoxy)-2-propanol, (isomere compounds)	34590-94-8	-	220	-	-	-	-	190	180
1-(2-Methoxypropoxy)-2-propanol	34590-94-8	-	210	-	-	-	-	-	100
Methylene chloride	75-09-2	-	-	62	-	130	-	-	-
1-Methyl-2-pyrrolidione #	872-50-4	-	-	-	-	740	-	-	-
7-Nitro-1,3,5-triazadamantane		-	-	53	-	-	-	-	-
Nonanoic acid	112-05-0	-	-	14	-	-	-	-	-
Octanol, butyl	3913-02-8	-	-	-	-	11	-	-	-
Octanoic acid	124-07-2	-	-	-	-	-	-	7.1	-
2-Oxepanone	24980-41-4	-	6.4	-	-	-	-	-	-
Parabenes (sum)		-	-	-	-	-	-	600	-
2-Phenoxy-ethanol, #	122-99-6	-	460	-	-	-	-	4900	-
Phthalate		9.8	-	5.2	-	-	7.8	-	-
2-Propenoic acid, 2-methyl - methyl ester (=Methylmethacrylate)	80-62-6	-	8.9	-	-	-	-	-	-
Propanoic acid, butyl ester # (=Butylpropionate)	590-01-2	-	44	-	-	-	-	-	15
1-Propen-1,2,3-tricarboxylic acid, tributylester (isomere compounds) *	7568-58-3	-	-	-	-	1500	-	-	-
Propyleneglycol # (=1,2-Propanediol)	57-55-6	370	2300	36	-	3300	-	7100	-
Styrene	100-42-5	-	6.6	-	-	-	-	3.8	-
Sulfo succinate-bis-2-ethylhexyl ester (=dioctylsulfosuccinate, Na-salt)	577-11-7	-	150	-	-	-	-	-	-
1,1,3,3 Tetramethylbutyl phenol (=4-(1,1,3,3-tetramethyl-butyl)-phenol or 4-tert-octylphenol)	140-66-9	-	-	-	-	-	-	-	24
Tetrasiloxane, decamethyl	141-62-8	-	-	-	-	6.8	-	-	-
Tributyl acetylcitrate	77-90-7	-	29	-	-	-	-	-	-

Name	CAS no.	1	4	5	6	7	9	10	12
Tributyl citrate (isomere compounds)	77-94-1	-	-	-	-	13000	-	-	-
Tributyl phosphate	126-73-8	-	-	-	-	-	-	-	63
Triethylamin #	121-44-8	-	-	-	-	2100	-	-	-
2,4,4-Trimethyloxazolidine *	75673-43-7	-	-	-	-	-	28	24	-
Urea *	57-13-6	-	200	-	-	-	-	-	-
Sum of groups									
Alkanes		-	22	-	-	1600	7.3	8000	3900
Alkenes		-	-	14	-	-	-	18	150
Chloralkanes		-	-	34	-	4.2	-	190	-
Cyclic ethers		-	26	-	-	-	-	-	-
Esters		-	8.9	-	-	-	-	-	-
Ethers		11	-	-	-	-	8.5	-	-
Unidentified		75	-	-	3900	33	23	1100	1600

-: Means not detected (below detection limit).
*: Means best suggestion for identification.
**: Overestimated due to interference from other substances:
#: Means determined against external standard.

Most dominating are the content of very volatile solvents such as alcohols (e.g. ethanol, butanol, ethylhexanol and methylpropanols), ketones (e.g. acetone), ethers (e.g. n-butylether), esters (e.g. ethylacetate and butylpropanate), and aliphatic and aromatic hydrocarbons (e.g. C_8-C_9 alkanes, xylene and methylstyrene). Most products contain these substance types and it is characteristic that they are also contained in water based products. The substances may either be added to the product to optimise the solubility of one or more of the additives or introduced with one of the raw materials of the product, e.g. as solvent.

A number of other – and less volatile – substances is detected also in some products at moderate to large amounts. That concerns for instance phthalates (e.g. diethyl-phthalate), high boiling aromatic and aliphatic hydrocarbons (e.g. cyclohexane-derivatives, C_{16}-C_{17} aromatics and pentamethylheptane), alcohols (e.g. phenoxy-ethanol) and 4-cyano-cyclohexene. The purpose of the presence of these substances varies considerably and may be as surfactants, preservative, dispersants, etc.

In the products, several types of glycol compounds have been detected such as diisopropylene glycol, diethylene glycol, propylene glycol, 2-propanol, 2-(2-butoxyethoxy)ethanol and 2-(2-ethoxyethoxy)ethanol. Typically, these glycols are used as solvents. Caprolactam may be used as solvent in polymers.

Tributyl citrate can be used as emollient in e.g. toners/pigments. Glycerine can be used as solvent but may also be used as wetting agent, i.e. as a component that can retain the water and thus prolong the drying period. Hexamethylene tetramine is used as curing agent in certain products.

Isobutane is detected in the 2 pop-up products. Isobutane is probably used as blowing agent.

2.3.3 Analysis results for metals

Quantitative determination of metals (ICP) was performed by removal of approx. 0.25 g of sample and dissolution with sulphuric acid and nitric acid in a microwave oven at an effect increasing from 250 W to 650 W over 34 minutes. The extract was filtered and the dissolved metals determined

subsequently by Inductively Coupled Plasma (ICP) analysis. The uncertainty of the analysis was 10% RSD. Detection limit: 1-2 mg/kg.

The results of the quantitative analysis of the selected metals in selected products are based on the product types:

Felt-tip pen Product no. 1, 2 and 3
Fabric dye Product no. 12 and 14

Table 2. Results of the metal analyses. The results are presented in mg/kg.

	DL	1	2	3	12	14
Antimony	1	78	64	84	*	*
Copper	2	2400	170	38	54	*
Lead	1	*	*	*	*	-

DL: Means detection limit.
-: Means below detection limit.
*: Means not analysed.

2.4 Selection of chemical substances for evaluation

From the detected substances, based on classification and detection were selected a number of substances for further evaluation of a potential health risk to the consumers.

Of the 63 identified substances, 28 are classified in the List of dangerous substances (Miljøministeriet 2002), further 5 substances could be self-classified according to the Danish Environmental Protection Agency's Advisory list for self-classification (Miljøstyrelsen 2001). Of the classified substances, 1 substance is classified as possibly carcinogenic (Carc.cat.1;R45 May cause cancer), 5 substances are classified as potential carcinogenic (Carc.cat.3;R40 Limited evidence of carcinogenic effect), and 1 substance as possibly mutagenic (Mut.cat.2;R46 May cause heritable genetic damage). Three substances are classified R42 and/or R43 (May cause sensitisation by inhalation and/or by skin contact) and further 2 substances are in the same category according to the Danish Environmental Protection Agency's Advisory list for self-classification.

The exact classifications are presented in the table below (table 3).

Table 3. Classification of the identified substances

Name	CAS no.	EINECS no.	Classification	
Acetone	67-64-1	200-662-2	F;R11 Xi;36 R66 R67	Highly flammable. Irritating to eyes. Repeated exposure may cause skin dryness or cracking. Vapours may cause drowsiness and dizziness.
Alcohol	64-17-5	200-578-6	F;R11	Highly flammable.
Azacyclotridecan-2-one (=Dodecan-12-lactam)	947-04-6	213-424-8		
Benzaldehyde	100-52-7	202-860-4	Xn;R22	Harmful if swallowed
Benzophenone	119-61-9	204-337-6		
1-Butanol	71-36-3	200-751-6	R10 Xn;R22 Xi;R37/38-41 R67	Flammable. Harmful if swallowed. Irritating to respiratory system and skin. Risk of serious damage to eyes. Vapours may cause drowsiness and dizziness.
2-(2-Butoxyethoxy)-ethanol	112-34-5	203-961-6	Xi;R36	Irritating to eyes.
2-Butylamine (= sec-butylamine)	13952-84-6	237-732-7	F;R11 Xn;R20/22 C;R35 N;R50	Highly flammable. Harmful by inhalation and if swallowed. Causes severe burns. Very toxic to aquatic organisms.
Butylated hydroxytoluene (BHT) (= 2,6-di-tert-butyl-p-cresol)	128-37-0	204-881-4	Self-class.: Xn;R22 N;R50/53	 Harmful if swallowed Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
n-Butylether	142-96-1	205-575-3	R10 Xi;R36/37/38 R52/53	Flammable. Irritating to eyes, respiratory system and skin. Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment. Conc.>=10%: Xi;R36/37/38
Caprolactam (= *epsilon*-caprolactam)	105-60-2	203-313-2	Xn;R20/22 Xi;R36/37/38	Harmful by inhalation and if swallowed. Irritating to eyes, respiratory system and skin.
5-Chloro-2,4-dimethoxy-benzenamine, (=5-Chlor-2,4-dimethoxyaniline)	97-50-7	202-586-5		
2-Chloro-4-dimethylamino-6-t-butylpyrimidine				
Cyanocyclohexene (=Cyclohexencarbonitrile)	1855-63-6 100-45-8	217-454-2	Self-class.: Xn;R22	 Harmful if swallowed
1,3,5-Cycloheptatriene	544-25-2	208-866-3		
Cyclopropane, nonyl	74663-85-7			
1,4-Dichlorbenzene	106-46-7	203-400-5	Xi;R36 N;R50/53 29ATP+ Carc.Cat.3;R40	Irritating to eyes. Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. Limited evidence of carcinogenic effect.
1,2-Dichlorethene	540-59-0	208-750-2	F;R11 Xn;R20 R52/53	Highly flammable. Harmful by inhalation. Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment. Conc.>=12.5%: Xn;R20
Diethylene glycol (isomere compounds)	111-46-6	203-872-2	Xn;R22	Harmful if swallowed
2,4-Diisocyanato-1-methyl-benzen (= toluendiisocyanate, = 2,4-diisocyanatotoluene =4-methyl-m-phenylendiisocyanate)	584-84-9	209-544-5	Tx;R26 Xi;R36/37/38 Carc3;R40 R42/43 R52/53	Very toxic by inhalation. Irritating to eyes, respiratory system and skin. Limited evidence of carcinogenic effect. May cause sensitization by inhalation and skin contact. Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment. Conc.>=20%: Tx;R26 Xi;R36/37/38 Carc3;R40 R42/43 7%<=conc.<20% : Tx;R26 Carc3;R40 R42/43 1%<=conc.<7%: T;R23 Carc3;R40 R42/43 0,1%<=conc.<1%: Xn;R20 R42
Diisopropylene glycol (= 1,1'-oxydipropan-2-ol)	110-98-5	203-821-4		

Name	CAS no.	EINECS no.	Classification	
1,3-Dimethyl-benzene (= m-xylene)	108-38-3	203-576-3	R10 Xn;R20/21 Xi;R38	Flammable Harmful by inhalation and in contact with skin. Irritating to skin.
4-(1,1-Dimethylethyl)-cyclohexanol (isomere compounds) (=4-tert-Butylcyclohexanol)	98-52-2	202-676-4		
4,4-Dimethyl oxazolidine	51200-87-4	257-048-2		
1,4-Dioxane	123-91-1	204-661-8	F;R11-19 Xi;R36/37 Carc3;R40 R66	Highly flammable. May form explosive peroxides. Irritating to eyes and respiratory system. Limited evidence of carcinogenic effect. Repeated exposure may cause skin dryness or cracking.
2-(2-Ethoxyethoxy)-ethanol (=diethyleneglycol-monobutyl ether)	111-90-0	203-919-7		
Ethylbenzene	100-41-4	202-849-4	F;R11 Xn;R20	Highly flammable. Harmful by inhalation. Conc.>=25%: Xn;R20
2-Ethyl-1,3-cyclopentanedione (= 2-Ethylcyclopentan-1,3-dion)	823-36-9	212-512-3		
2-Ethyl-hexanol	104-76-7	203-234-3		
Glycerine (=1,2,3-propanetriol)	56-81-5	200-289-5		
Hexa(methoxymethyl)melamine	3089-11-0	221-422-3		
Hexamethylentetramine (= methenamine)	100-97-0	202-905-8	F;R11 R42/43	Highly flammable. May cause sensitization by inhalation and skin contact
Hexanoic acid	142-62-1	205-550-7		
Isobutane	75-28-5	200-857-2	Fx;R12 Carc1;R45 Mut2;R46	Extremely flammable. if containing >= 0.1 % butadiene (203-450-8) also: May cause cancer. May cause heritable genetic damage.
3-Isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate (=5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethyl-cyclohexane (CA)	4098-71-9	223-861-6	T;R23 Xi;R36/37/38 R42/43 N;R51/53	Toxic by inhalation. Irritating to eyes, respiratory system and skin. May cause sensitization by inhalation and skin contact. Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. Conc.>=20%: T;R23 Xi;R36/37/38 R42/43 2%<=conc.<20%: T;R23 R42/43 0.5%<=conc.<2%: Xn;R20 R42/43
Isopropyl alcohol	67-63-0	200-661-7	F;R11 Xi;R36 R67	Highly flammable. Irritating to eyes. Vapours may cause drowsiness and dizziness.
1-(2-Methoxy-1-methylethoxy)-2-propanol, (isomere compounds) = 2-Methoxymethylethoxy)propanol	34590-94-8	252-104-2		
1-(2-Methoxypropoxy)-2-propanol	34590-94-8	252-104-2		
Methylen chloride (= dichlormethane)	75-09-2	200-838-9	Carc3;R40	Limited evidence of carcinogenic effect.
1-Methyl-2-pyrrolidone	872-50-4	212-828-1	Xi;R36/38	Irritating to eyes and skin. Conc. >=10%: Xi;R36/38
7-Nitro-1,3,5-triazadamantane				
Nonanoic acid	112-05-0	203-931-2	C;R34	Causes burns.
Octanol, butyl	3913-02-8	223-470-0		
Octanoic acid	124-07-2	204-677-5		
2-Oxepanone	24980-41-4			
Parabenes (sum)				
2-Phenoxyethanol,	122-99-6	204-589-7	Xn;R22 Xi;R36	Harmful if swallowed. Irritating to eyes.
Phthalate				

Name	CAS no.	EINECS no.	Classification	
2-Propenoic acid, 2-methyl methyl ester (=Methylmethacrylate)	80-62-6	201-297-1	F;R11 Xi;R37/38 R43	Highly flammable. Irritating to respiratory system and skin. May cause sensitization by skin contact.
Propanoic acid, butyl ester (=Butylpropionate)	590-01-2	209-669-5	R10	Flammable.
1-Propen-1,2,3-tricarboxylic acid, tributylester (isomere compounds) (=Tributylprop-1-en-1,2,3-tricarboxylate)	7568-58-3	231-468-6	Self-class.: R43	May cause sensitization by skin contact.
Propylene glycol (=1,2-Propanediol)	57-55-6	200-338-0		
Styrene	100-42-5	202-851-5	R10 Xn;R20 Xi;R36/38	Flammable. Harmful by inhalation. Irritating to eyes and skin. Conc.>=12.5%: Xn;R20 Xi;R36/38
Sulfosuccinate-bis-2-ethylhexyl ester (=dioctylsulfosuccinate, Na-salt =bis(ethylhexyl)-sulfosuccinate, NA-salt = Docusate sodium	577-11-7	209-406-4		
1,1,3,3 Tetramethylbutyl phenol (=4-(1,1,3,3-tetramethylbutyl)phenol or 4-tert-octylphenol)	140-66-9	205-426-2	Self-class.: R43 N;R50/53	May cause sensitization by skin contact. Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
Tetrasiloxane, decamethyl (= Decamethyltetrasiloxane)	141-62-8	205-491-7		
Tributyl acetylcitrate	77-90-7	201-067-0		
Tributyl citrat (isomere compounds)	77-94-1	201-071-2		
Tributyl phosphate	126-73-8	204-800-2	Xn;R22 Xi;R38 Carc.Cat.3;R40	Harmful if swallowed. ATP29 + Irritating to skin. Limited evidence of carcinogenic effect.
Triethylamine	121-44-8	204-469-4	F;R11 Xn;R20/21/22 C;R35	Highly flammable. Harmful by inhalation, in contact with skin and if swallowed. Causes severe burns. Conc.>=25%: Xn;R20/21/22 C;R35 10%<=conc.<25%: C;R35 5%<=conc.<10%: C;R34 1%<=conc.<5%: Xi;R36/37/38
2,4,4-Trimethyloxazolidine	75673-43-7			
Urea	57-13-6	200-315-5		
Metals				
Antimony	7440-36-0	231-146-5		Antimony organic compounds: various classifications !!
Lead	7439-92-1	231-100-4		organic compounds: various classifications !!
Copper	7440-50-8	231-159-6		organic compounds: various classifications !!

Below is mentioned the substances that had the most rigorous classification and selected substances with a less rigorous classification. Besides, commonly detected substances are included with or without classification. A possible reason for the selection of the substance for an actual health evaluation is presented.

Acetone, CAS no. 67-64-1, is classified F;R11 Xi;36 R66 R67, i.e. Highly flammable, Irritating to eyes, Repeated exposure may cause skin dryness or cracking and Vapours may cause drowsiness and dizziness. Acetone was quantified in 2 out of 8 samples at 25 and 45 mg/kg (0.0025 and 0.0045%, cf. table 1).

Benzaldehyde, CAS no. 100-52-7, is classified Xn;R22, i.e. Harmful if swallowed. Benzaldehyde was detected in 1 sample at 3.6 mg/kg (0.0004%).

Benzophenone, CAS no. 119-61-9, is not classified in the List of dangerous substances. The substance was detected in 1 sample at 8.6 mg/kg (0.0009%).

1-Butanol, CAS no. 71-36-3, is classified R10 Xn;R22 Xi;R37/38-41 R67, i.e. Flammable, Harmful if swallowed, Irritating to respiratory system and skin, Risk of serious damage to eyes, Vapours may cause drowsiness and dizziness. Butanol was detected in 6 out of 8 samples at 77-690 mg/kg (0.008-0.069%). Based on classification and frequency the substance was selected for further evaluation.

2-(2-Butoxyethoxy)-ethanol, CAS no. 112-34-5, is classified Xi;R36, i.e. Irritating to eyes. The substance was detected in1 sample at 460 mg/kg (0.046%).

2-Butylamine, CAS no. 13952-84-6, is classified F;R11 Xn;R20/22 C;R35 N;R50, i.e. Highly flammable, Harmful by inhalation and if swallowed, Causes severe burns and Very toxic to aquatic organisms. The substance was detected in 1 out of 8 samples at 53 mg/kg (0.0053%).

Butylated hydroxytoluene (BHT) (= 2,6-Di-*tert*-butyl-*p*-cresol), CAS no. 128-37-0, is not adopted on the List of dangerous substances but found on the Danish Environmental Protection Agency's Advisory list for self-classification with Xn;R22 N;R50/53, i.e. Harmful if swallowed and Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. The substance was detected in 1 out of 8 samples at 16 mg/kg (0.0016%).

n-Butylether, CAS no. 142-96-1, is classified R10 Xi;R36/37/38 and later added R52/53 (EC 2004), i.e. Flammable, Irritating to eyes, respiratory system and skin, and Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment. The classification is depending on concentration as concentrations >=10%: Xi;R36/37/38. n-Butylether was detected in 3 out of 8 samples at 11-110 mg/kg (0.0011-0.011%).

Caprolactam, CAS no. 105-60-2, is classified Xn;R20/22 Xi;R36/37/38, i.e. Harmful by inhalation and if swallowed, and Irritating to eyes, respiratory system and skin. Caprolactam was detected in 1 sample but as the concentration appears high (1100 mg/kg, 0.11%) the substance is selected for further evaluation.

Cyanocyclohexene (= Cyclohexenecarbonitrile), CAS no. 1855-63-6 and 100-45-8, is not adopted on the List of dangerous substances but found on the Danish Environmental Protection Agency's Advisory list for self-classification with Xn;R22, i.e. Harmful if swallowed. The substance is detected in 1 sample at 110 mg/kg (0.011%).

1,4-Dichlorbenzene, CAS no. 106-46-7, is classified Xi;R36 N;R50/53 with the addition of Carc.Cat.3;R40 in Directive 2004/73/EC (EC 2004), i.e. Irritating to eyes, Limited evidence of carcinogenic effects and Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. The substance is detected in 1 sample at 9,9 mg/kg (0.001%). Based on the added classification it is selected for further evaluation.

1,2-Dichlorethene, CAS no. 540-59-0, is classified F;R11 Xn;R20 R52/53, i.e. Highly flammable, Harmful by inhalation and Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment. The classification is depending on the concentration as concentrations in the product >=12.5% is classified Xn;R20. The substance is detected in 1 sample at 14 mg/kg (0.0014%).

Diethylene glycol (isomere compounds), CAS no. 111-46-6, is classified Xn;R22, i.e. Harmful if swallowed. The substance is detected in 2 out of 8 samples but at high concentrations of 53000 and 6200 mg/kg (5.3% and 0.62%). Therefore the substance is selected for further evaluation.

2,4-Diisocyanato-1-methyl-benzene (= toluendiisocyanate or = 2,4-diisocyanatotoluene), CAS no. 584-84-9, is classified Tx;R26 Xi;R36/37/38 Carc3;R40 R42/43 R52/53, i.e. Very toxic by inhalation, Irritating to eyes, respiratory system and skin, Limited evidence of carcinogenic effects, May cause sensitization by inhalation and skin contact, and Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment. The classification is depending on the concentration in the product as:
Conc.>=20%: Tx;R26 Xi;R36/37/38 Carc3;R40 R42/43
7%<=conc.<20%: Tx;R26 Carc3;R40 R42/43
1%<=conc.<7%: T;R23 Carc3;R40 R42/43
0,1%<=conc.<1%: Xn;R20 R42.
The substance was detected in 1 sample at low concentration close to the detection limit (3.2 mg/kg or 0.0003%). Thus despite of the rigorous classification the substance is not selected for further evaluation.

Diisopropylene glycol (=1,1'-oxydipropan-2-ol), CAS no. 110-98-5, is not adopted on the List of dangerous substances. However, as diisopropylene glycol is detected in 6 out of 8 samples at 390-5000 mg/kg (0.04-0.5%) the substance is selected for further evaluation.

1,3-Dimethyl-benzene (= m-xylene), CAS no. 108-38-3, is classified R10 Xn;R20/21 Xi;R38, i.e. Flammable, Harmful by inhalation and in contact with skin, and Irritating to skin. The substance was detected in 1 sample at 12 mg/kg (0.0012%).

1,4-Dioxane, CAS no. 123-91-1, is classified F;R11-19 Xi;R36/37 Carc3;R40 R66, i.e. Highly flammable, May form explosive peroxides, Irritating to eyes and respiratory system, Limited evidence of carcinogenic effects, and Repeated exposure may cause skin dryness or cracking. The substance was detected in 2 products. The substance occurred at low concentration 4.7 and 11 mg/kg (i.e. <0.0011%) but due to the rigorous classification the substance was selected for further evaluation.

Ethylbenzene, CAS no. 100-41-4, is classified F;R11 Xn;R20, i.e. Highly flammable and Harmful by inhalation. The classification is depending on the concentration in the product as concentrations >=25%: Xn;R20. The substance was detected in 1 sample at 19 mg/kg (0.0019%).

Glycerine (=1,2,3-propanetriol), CAS no. 56-81-5, is not adopted on the List of dangerous substances. As glycerine occurs in 2 samples at high concentrations of 11000 and 27000 mg/kg (1.1 and 2.7%) the substance is included for further evaluation.

Hexamethylentetramine (= Methenamine), CAS no. 100-97-0, is classified F;R11 R42/43, i.e. Highly flammable and May cause sensitization by inhalation and skin contact. The substance was detected in 6 out of 8 samples at 11-860 mg/kg (0.001-0.086%). Due to frequency and classification the substance is selected for further evaluation.

Isobutane, CAS no. 75-28-5, is classified Fx;R12, i.e. Extremely flammable. With a content >= 0.1 % butadiene (203-450-8) also Carc1;R45 Mut2;R46, i.e. May cause cancer and May cause heritable genetic damage. The substance was detected in 2 samples at 2000 and 3500 mg/kg (0.2 and 0.35%). Butadiene was not detected.

3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate, CAS no. 4098-71-9, is classified T;R23 Xi;R36/37/38 R42/43 N;R51/53, i.e. Toxic by inhalation, Irritating to eyes, respiratory system and skin, May cause sensitization by inhalation and skin contact, and Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. The classification is depending on the concentration in the product as:
Concentrations >=20%: T;R23 Xi;R36/37/38 R42/43
2%<=conc.<20%: T;R23 R42/43
0.5%<=conc.<2%: Xn;R20 R42/43.
The substance was detected in 1 sample at a low concentration of 270 mg/kg (0.027%) but due to the classification it is included for further evaluation.

Isopropyl alcohol, CAS no. 67-63-0, is classified F;R11 Xi;R36 R67, i.e. Highly flammable, Irritating to eyes, and Vapours may cause drowsiness and dizziness. The substance is detected in 1 sample at 1300 mg/kg (0.13%).

Methylene chloride (= dichloromethane), CAS no. 75-09-2, is classified Carc3;R40, i.e. Limited evidence of carcinogenic effects. The substance is detected in 2 samples at 62 and 130 mg/kg (0.0062 and 0.013%).

1-Methyl-2-pyrrolidione, CAS no. 872-50-4, is classified Xi;R36/38, i.e. Irritating to eyes and skin. The classification is depending on the concentration in the product as concentration >=10%: Xi;R36/38. The substance is detected in 1 sample at 740 mg/kg (0.074%).

Parabenes (sum). The parabenes are given as sum. As they are not specified further they can not be evaluated individually. The group is detected in 1 sample at 600 mg/kg (0.06%).

2-Phenoxyethanol, CAS no. 122-99-6, is classified Xn;R22 Xi;R36, i.e. Harmful if swallowed and Irritating to eyes. The substance is detected in 2 samples at 460 and 4900 mg/kg (0.046 and 0.49%).

Phthalate. Phthalate is given unspecified. As they are not specified further they can not be evaluated individually. An evaluation would be strongly dependent on which phthalate referred to. Phthalate is stated as detected in 3 samples at low concentrations (5.2-9.8 mg/kg i.e. <0.001%).

2-Propenoic acid, 2-methyl- methyl ester (= Methylmethacrylate), CAS no. 80-62-6, is classified F;R11 Xi;R37/38 R43, i.e. Highly flammable, Irritating to respiratory system and skin, and May cause sensitization by skin contact. The substance is detected in 1 sample at 8.9 mg/kg (0.0009%).

1-Propen-1,2,3-tricarboxylic acid, tributylester (isomer compounds) (=Tributylprop-1-en-1,2,3-tricarboxylate), CAS no. 7568-58-3, is not adopted on the List of dangerous substances but to be found on the Danish Environmental Protection Agency's Advisory list for self-classification with R43, i.e. May cause sensitization by skin contact. The substance is detected in 1 sample at 1500 mg/kg (0.15%).

Propylene glycol (=1,2-Propanediol), CAS no. 57-55-6, is not adopted on the List of dangerous substances but is detected in 5 out of 8 samples at 36 to 7100 mg/kg (0.004-0.71%) and therefore selected for a further evaluation.

Styrene, CAS no. 100-42-5, is classified R10 Xn;R20 Xi;R36/38, i.e. Flammable, Harmful by inhalation and Irritating to eyes and skin. The classification is depending on the concentration in the product as concentration >=12.5%: Xn;R20 Xi;R36/38. The substance is detected in 1 sample at 6.6 mg/kg (0.0007%).

1,1,3,3-Tetramethylbutyl phenol (= 4-(1,1,3,3-tetramethylbutyl)phenol or 4-tert-octylphenol), CAS no. 140-66-9, is not adopted on the List of dangerous substances but to be found on the Danish Environmental Protection Agency's Advisory list for self-classification with R43 N;R50/53, i.e. May cause sensitization by skin contact and Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. The substance is detected in 1 sample at 24 mg/kg (0.0024%).

Tributyl phosphate, CAS no. 126-73-8, is classified Xn;R22, Harmful if swallowed. The classification is made more rigorous in Directive 2004/73/EC with Xi;R38 Carc.Cat.3;R40, i.e. Irritating to skin and Limited evidence of carcinogenic effects. The substance is detected in 1 sample at 63 mg/kg (0.0063%).

Triethylamine, CAS no. 121-44-8, is classified F;R11 Xn;R20/21/22 C;R35, i.e. Highly flammable, Harmful by inhalation, in contact with skin and if swallowed, and Causes severe burns. The classification is depending on the concentration in the product as:
Concentration >=25%: Xn;R20/21/22 C;R35
10%<=conc.<25%: C;R35
5%<=conc.<10%: C;R34
1%<=conc.<5%: Xi;R36/37/38.
The substance is detected in 1 sample at 2100 mg/kg (0.21%).

Metals
For quantitative metal analyses, samples were taken to analysis for 3 metals. As the analysis was performed as elemental analysis the nature of the metal compound (organic or inorganic) is unknown.

Antimony, CAS no. 7440-36-0, is not adopted on the List of dangerous substances in itself but organic antimony compounds have several classifications. Antimony is quantitatively determined as element and not further identified. Because the substance is detected in 3 out of 5 examined products at 64-84 mg/kg (0.006-0.008%) it has been selected for further evaluation.

Lead, CAS no. 7439-92-1, is contained in several organic compounds that are classified. The substance is not detected above the detection limit.

Copper, CAS no. 7440-50-8, is not adopted on the List of dangerous substances in itself but organic compounds have several classifications Copper is quantified as element and not further identified. Because the substance is detected in 4 out of 5 examined products at 38-2400 mg/kg (0.0034-0.24%) it has been selected for further evaluation.

Summary of selected substances
For evaluation of individual substances the below mentioned chemical substances are selected.

Of organic substances:

1-Butanol
Caprolactam
1,4-Dichlorobenzene
Diethylene glycol
Diisopropyl glycol
1,4-Dioxane
Glycerine
Hexamethylentetramine (Methenamine)
Isobutane
3-Isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate
1-Methyl-2-pyrrolidone
2-Phenoxyethanol
Propylene glycol

Of metals:

Antimony
Copper

3 Health assessment

3.1 Assessment method

For the chemical substances detected by the analyses, an evaluation of which substances appeared immediate to be the most interesting was performed. The selection is performed in agreement with the Danish Environmental Protection Agency. Data on the individual substances then are retrieved from available sources in order to perform a health hazard evaluation based on known information from previous prepared Danish or foreign monographs, etc. The obtained data for toxicity are then compared with the concentrations estimated in the used scenarios described below.

The methods used are approximately the same as recommended in connection with risk assessment of chemical substances in the European Union (EU) and described in the Technical Guidance Document, TGD (EC 2003). In the TGD the potential risk to the consumer is estimated as the ratio between the concentration where no adverse effect is expected (No Observed Adverse Effect level, NOAEL) and the predicted exposure concentration, i.e. NOAEL / the estimated uptake in the exposed consumers. NOAEL is based on mammalian data: typically rats, mice and rabbits. Therefore, it is necessary to introduce a safety factor (SF) to cover potential differences when extrapolating from these mammals to humans.

The safety factor is interpreted as a margin of safety applied to a NOAEL to produce a value below which exposures are presumed to be without significant health risk. The safety factor is traditionally composed of a factor 10 for extrapolation between species (animal to human, interspecies variation), a factor 10 to protect the most sensitive individuals of the population such as e.g. children (intraspecies variation). A third factor is applied depending on the data and may vary. For instance 10 is used if LOAEL (Lowest Observed Adverse Effect Level) is used instead of NOAEL or using subchronic data instead of chronic data. The total safety factor is a result from multiplication of the three factors.

In the EU risk assessment, the risk of health effect is expressed by NOAEL dicided with the exposure, i.e. by expressing the margin of safety (MOS) to reflect whether the distance from the level where no adverse effect is expected to the estimated exposure level is sufficient. Typically MOS is preferred to be above 100.

The classification authorised in Denmark (Miljøministeriet 2002), which is an implementation of the European Union classification (28th amendment to EU directive 67/548/EEC), is used in the evaluation. The amendments performed in the 29th amendment and adopted in Directive 2004/73/EC (EC 2004) and not yet implemented in Denmark are included, however, as the implementation may be expected within the near future.

For the evaluation of the individual substances is used the threshold limit values derived and evaluated by the authorities or recognised institutions. The

limit values thus contain an evaluation of the data used including a safety factor that qualified persons have evaluated as acceptable.

Of relevant limit values included in the health evaluation if available are:

ADI: Acceptable Daily Intake. A value calculated from NOAEL by an official authority as an acceptable daily intake (mg/kg body weight/day. ADI is usually based on chemical substances in food.

C-value: Contribution value: The C-value is defined as the total maximal allowed contribution to the air pollution from an enterprise to the environment outside the production site. The C-value usually is derived from NOAEL levels and includes safety factors (Miljøstyrelsen 2002).

RfC: Reference concentration. RfC is an inhalation reference concentration based on the assumption that a threshold limit value for certain toxic effects exists. The value is based on NOAEC from inhalation studies of subchronic or chronic character and includes safety factors. The value is given in mg/m^3.

RfD: Reference dosis. RfD is an oral reference dosis based on the assumption that a threshold limit for certain toxic effects exists. The value is based on NOAEL from subchronic or chronic studies using oral administration and includes safety factors. The value is given in mg/kg body weight/day.
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TLV: Threshold Limit Value in force for the working environment is set by the Danish Working Environment Authority (Arbejdstilsynet, AT 2002). The threshold limit values of the Danish Working Environment Authority is valid where the chemical substances are used in the production. The threshold limit values are based on 8-hour time-weighted average (a working day). It is important to note that the threshold limit value does not include the consumer at home.

TDI: Tolerable Daily Intake. Almost identical to ADI but usually based on chemical pollutants.

3.2 Assessment scenarios

Scenarios for the assessment of textile colorants are based on the products used by the consumer for decoration or dyeing of textiles at home.

The exposure of the consumer therefore varies according to the end use. Nevertheless it is chosen to use as starting point the exposure scenarios where the exposure is presumed to be the highest.

The highest primary exposure takes place when using the product, i.e. when the consumer decorates or dyes the textile. The exposure route will be by inhalation of volatile substances that evaporate during use and dermal exposure by contact to the product or the non-dried textile.

A further exposure may occur by contact next to the skin of the coloured textile (e.g. clothes and bed linen). The direct exposure from the coloured textile will be lower and to a higher degree of another character such as e.g. inhalation of evaporated substances or substances adsorbed to detached fibres as dust. The contact exposure is in the current evaluation assumed to be included in the used scenarios.

The oral exposure of the consumer may occur if for instance a child puts fingers with colours or the product into the mouth or if the coloured/dyed textile is mouthed.

Scenarios are presented for:

- Exposure via inhalation
- Dermal exposure
- Oral exposure

3.2.1 Exposure via inhalation

Exposure to the substance via inhalation of volatile substances may be direct exposure to evaporated substances from the use of the colorant product, either directly from the ”source” or after its application to the textile. Further inhalation may occur of dust from fibres that contain the chemical substance or dust to which the chemical substance is absorbed

The exposure period theoretically may extend from the use of the colour product until it is completely dry. However, it is considered likely that the consumer leaves the spot where the dyeing has taken place following the use and therefore not necessarily is so highly exposed during the actual drying period.

The exposure via inhalation is expressed as the concentration of the chemical substance in the air in the breathing zone and is given as an average concentration over a reference period, e.g. 8 hours for the working environment. For the consumer of textile colorants the exposure duration may be from a few minutes to a few hours at the home. In the assessment is used an exposure duration of 30 minutes (half an hour).

For the estimation of exposure via inhalation you have to know the inhalation rate, the size of the breathing zone or the room, and the release rate of the substance to the room or the concentration in the breathing zone or the room.

The inhalation rates for a child and adult by sedentary activities are 0.4 and 0.5 m^3/hour, respectively, by exposure for a short period (TGD, EC 2003). By prolonged exposure which is assumed only to apply to adults is used an inhalation rate of 15.2 m^3/day (standard in TGD, EC 2003). The exposure by dyeing is assumed rarely to comprise a whole day. As young humans are considered the most sensitive group in this context an inhalation rate of 0.4 m^3/hour is used in the assessment.

The concentration in the breathing zone is based on an estimate of the concentration in 1 m^3 of air right around the consumer during the use of the colorant product to colour/dye the textile. This concentration will be somewhat diluted relative to the consumer sitting with the head close to the product when working intensely with decorating colours. On the other hand

the exposure is assessed as a repeated exposure which is assumed to compensate for the dilution.

The concentration in closed rooms is assumed to be higher than by outdoor use of the textile colorants. For the calculation of the concentration in the room is used an equation for volatile substances and airborne particles where it is assumed that the substance is released instantaneously to the breathing zone or the entire room and distributed homogeneously. It is assumed that the consumer is in a room where the ventilation is too small to contribute further to the dilution already used (immediate breathing zone of 1 m^3).

For the calculation of the theoretical maximum concentration of the substance in the air is used the Law on ideal gasses in an adapted form (EC 2003):

$$C_{air,\max} = C_{tex} \times \frac{MW}{22.4} \times \frac{273}{TEMP_a} \times \frac{P_a}{101325} \quad (mg/m^3)$$

Where

$C_{air,\ max}$	Maximum concentration obtainable in air	mg/m^3
C_{tex}	Concentration of the substance in product	mg/kg
MW	Molecular weight	g/mol
22.4	The volume that 1 mol of a substance occupies in gaseous form at 0ºC and 1 atm	l
273	Temperature 0ºC in ºK	ºK
$TEMP_a$	Actual temperature in ºK	ºK
P_a	Vapour pressure of the substance in Pascal	Pa
101325	Standard normal atmospheric pressure	Pa

The same equation is used in the EASE model designed for the working environment (EC 2003).

The concentration in inhaled air then can be calculated according to the equation:

$$C_{inh} = \frac{Q_{prod} \times C_{air,\max}}{V_{room}} \quad (mg/m^3)$$

C_{inh}	Concentration in inhaled air	mg/m^3	
Q_{prod}	Amount of product used	kg	0.005 kg
$C_{air,\ max}$	Maximum concentration obtainable in the room	mg/m^3	
V_{room}	Volume of the room / breathing zone	m^3	Used: 1 m^3

The amount of inhaled substance is then (EC 2003):

$$I_{inh} = \frac{F_{resp} \times C_{inh} \times Q_{inh} \times T_{contact}}{BW} \times N_{event} \quad (mg/kgBW/day)$$

I_{inh}	Amount of substance inhaled	mg	mg/kg bw/day
F_{resp}	Inhalable or respirable fraction of the substance		(e.g. 1 (i.e. 100%))
C_{inh}	Concentration in air	mg/m^3	
Q_{inh}	Inhalation rate	m^3/hour	0.4 m^3/hour
$T_{contact}$	Duration of exposure	hours	0.5
N_{event}	Number of events	day^{-1}	1
BW	Body weight	kg	Used: 20 kg

The consumers in this case are assumed to be children 7 to 10 years old. According to realistic worst case the body weight is set to the 5 percentile body weight (AUH 1995) of children 7 to 8 years of age which is approx. 20 kg (AUH 1995, US-EPA 2002).

As starting point is used a scenario where the highest exposure is expected. The consumer is a child of 20 kg body weight decorating/dyeing a piece of textile for 30 minutes. The respiration rate is 0.4 m^3/hour. The exposure is directly to the breathing zone set to 1 m^3.

In professional dyeing mills, a large number of dyes are used and the consumption varies from 2 to more than 80 g/kg of textile with an average of 20 g/kg according to the required depth of colour (Laursen *et al.* 1997). The TGD indicates that commercial dye factories use 10 kg dye/ton of textiles, i.e. 1% (ECB 2003). The Swedish Chemicals Inspectorate indicates that for both dyeing and printing 500 to 30000 ppm dyes or pigments, i.e. up to 3%, may be used (KemI 1997). OECD presents data indicating that the consumption of dyestuff in the textile finishing industry varies between 11 and 88 g/kg textile (OECD 2004).

Assuming that the coloured textile weights approx. 100-200 gram, that decorations may occupy a smaller area than total dyeing of the textile but using more colorant/area, and that home dyeing consumers probably use a little more colorant than the professionals the used amount is set to 5 g.

For the organic substances is assumed that the maximum obtainable concentration is reached in the breathing of 1 m^3 by the use of 5 g of the colour product.

3.2.2 Dermal exposure

Before uptake via the skin the chemical compound has to migrate from the colour in or on the textile to the skin or directly from skin contact with the colorant from the product (pen, powder etc.). When the substance has reached the skin the substance may be absorbed percutaneous to the blood stream and then distributed throughout the body.

The uptake after contact may be from ”free” chemical substances released from the colour in/on the textile or from degradation products. The degradation of the substance may take place in the textile or via bacteria or enzymes on the skin or in the gastro-intestinal-tract after absorption.

The exposure can be expressed shortly by the equation (EC 2003) which is modified to the used exposure scenario:

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

Where:

U_{derm}	Potential uptake of the chemical substance	µg/kg bw/day
Q_{prod}	Amount of product	g
Fc_{prod}	Weight fraction of chemical substance	µg/g
$F_{area,\ derm}$	Fraction of exposed skin	
N_{event}	Number of exposure events	per day
BW	Body weight	kg

For the evaluation of dermal exposure is used a scenario with skin contact during the use of the colorant and the coloured textile. The exposed skin area such as hands is assumed to be the palm of the hand for 30 minutes (half an hour) which is assumed to be the period used to decorate or dyeing the textile. The palm of the hands varies as humans grow but assuming that the ratio between hands and the body surface is reasonably constant the exposed surface may be estimated. Both hands constitute approx. 5% of the total body surface (US-EPA 1997). It is assumed that maximum 1/5 of the hands are exposed thus 1% of the body may directly get into contact with the colorant during the use.

Skin contact with the textile after the application is assumed less relevant for solvents where the main part is expected to evaporate. Besides in the assessment is used a repeated exposure and in total the assessment is assumed to involve both exposure routes.

As in the scenario on inhalation the exposure is assumed to be 5 gram of colorant and a body weight of 20 kg.

Absorption
After exposure to the skin the chemical compound has to pass the skin before actual absorption is taking place. Only a few data of percutaneous absorption of the studied compounds have been found. The dermal absorption is therefore estimated.

Depending on the exposure and/or the compound's lipophilicity the dermal penetration is assumed to be insignificant for very lipophilic compounds with a log Kow more than 5 (OECD 1993).

Dermal penetration is considered very small for compounds with a log Kow less than -1 (i.e. very hydrophilic) and for compounds with a molecular weight above 700 (Vermeire *et al.* 1993). According to a Dutch model the dermal absorption is estimated to 10% for compounds with a molecular weight above 500 g/mol and a log Kow <-1 or >4 (De Heer 1999). The latter values are also included in the TGD (EC 2003).

In standard assessments or when no informations are available a typical dermal absorption of 100% is used (EC 2003). This has been performed with all organic compounds. If information on absorption was available the information has been used in refining of the estimates. It has been performed by multiplying the dermal exposure (U_{derm}) with the absorption factor (F_{abs}):

$$A_{derm} = U_{derm} \acute{} F_{abs}$$

3.2.3 Oral exposure

Oral exposure may take place by chewing or sucking on fingers that have been in contact with colorant or the dyed textile (children). By oral exposure the absorption takes place after intake by uptake over the epithelium in the mouth cavity or the gastro-intestinal-tract.

The oral intake can be estimated by the equation (OECD 1993, EC 2003):

$$I_{oral} = \frac{V_{oral} \times C_{oral} \times F_{orl} \times N_{event}}{BW}$$

Where

I_{oral}	Intake of the compound	µg/kg bw/day
V_{prod}	Weight of product mouthed	kg
C_{oral}	Concentration of substance in the product	mg/kg
N_{event}	Number of events per day	assumed 1 time/day
BW	Body weight	kg
F_{oral}	Fraction absorbed (bioavailable part)	

As starting point is chosen that the consumer in the current case a child sucks/chews on textile corresponding to 10×10 cm = 100 cm^2 textile. In the TGD (EC 2003) is assumed use of 0.5 g/m^2 by total dyeing. In the remaining scenarios are assumed a use of 5 g of colorant for decorating that will be dispersed unevenly.

It is therefore assumed that maximum 1/10 of the coloured material might be mouthed. This may be set high but it also includes other sources such as contaminants on hands or felt-pens, which are then mouthed, getting into contact with food or in other ways bring the substance in indirect contact with the mouth.

This is assumed in total to be included in the selected parameters that is then a total oral exposure to textile with 0.5 g colorant.

The body weight is set to 20 kg as in the other scenarios.

3.3 Assessment of individual substances

3.3.1 1-Butanol

Identification:

Name	1-Butanol
CAS no.	71-36-3
EINECS no.	200-751-6
Molecular formula	$C_4H_{10}O$
Molecular structure	
Molecular weight	74.12 g/mol
Synonyms	Butan-1-ol
	n-Butanol
	Butylalcohol
	1-Hydroxybutane
	Propylcarbinol

The melting point is –89.8ºC. The boiling point is 117.7ºC. The water solubility is 70000 mg/l at 25ºC. The vapour pressure is 640 Pa at 20ºC and 910 Pa at 25ºC (6.7 mmHg, Boublik *et al.* 1984). The octanol/water partition coefficient is measured to log Kow 0.88 (Hansch *et al.* 1995).

Classification

1-Butanol is adopted on the List of dangerous substances (Miljøministeriet 2002) and classified:

R10	Flammable.
Xn;R22	Harmful if swallowed.
Xi;R37/38-41	Irritating to respiratory system and skin. Risk of serious damage to eyes.
R67	Vapours may cause drowsiness and dizziness.

Use
1-Butanol is used among others as additive in the paint and lacquers industry, especially as solvent.

Effects on health
Some data have been found on acute toxicity. Of those can be mentioned:

Acute oral, rat	LD_{50}	790 mg/kg	IUCLID 2000
Acute oral, mouse	LD_{50}	2680 mg/kg	IUCLID 2000
Acute dermal, rabbit	LD_{50}	3400 mg/kg	IUCLID 2000
Acute inhalation, rat	LC_{50}, 4 h	>24000 mg/m^3	IUCLID 2000
Acute inhalation, mouse	RD_{50}, 1 min	11696 ppm	IUCLID 2000

Data on acute exposure to 1-butanol show a low toxicity. On the other hand several data on irritation exist. In a study on humans was observed that vapours at a concentration of 50 ppm (150 mg/m^3) resulted in eye irritation in most test persons while 25 ppm (75 mg/m^3) caused irritation of the nose and throat in the test persons (IPCS 1987). Irritation of skin and respiratory system is observed in several tests on test animals (IUCLID 2000).

In a 92 days inhalation study, rats were continuously exposed to 0.03 and 7.02 ppm. Based on changes in blood parameters at the high dose NOAEL was set to 0.03 ppm corresponding to 0.09 mg/m^3 (IPCS 1987).

Of studies with prolonged exposure duration is found a 13 weeks rat study where the rats daily were administered 1-butanol directly into the stomach by gavage with the doses 0, 30, 125 and 500 mg/kg bw/day. Based on observed effects on the central nervous system such as ataxia and hypoactivity at 500 mg/kg bw/day the NOAEL was set to 125 mg/kg bw/day (IRIS 2004).

Threshold limit values
The threshold limit value for the working environment is 50 ppm corresponding to 150 mg/m^3 with notation LH. L indicates that the threshold limit value is a ceiling value that at no time must be exceeded. H means that the substance may penetrate the skin (AT 2002).

The C-value is 0.2 mg/m^3 (Miljøstyrelsen 2002).

The oral RfD value is 0.1 mg/kg bw/day. The value is based on a subchronic rat study where a NOAEL of 125 mg/kg bw/day was set and with the application of a safety factor of 1000: 10 for interspecies, 10 for intraspecies differences and 10 for subchronic to chronic extrapolation (IRIS 2004).

Absorption
Descriptions indicating readily absorption by oral intake and via inhalation have been found. No values were found for dermal absorption. Therefore 100% absorption is assumed.

Assessment
Exposure by inhalation was based on a child of 20 kg using the textile colour product for 30 minutes/day. The consumption is set to 5 g/event, 1 time/day.

Calculation example (only performed for the first substance, for further information cf. the section on methods):

Cair, max =690 × (74.12/22.4) × (273/298) × (910/101325) = 18.785 mg/m^3
C inhalation = 18.785 × 0.005 (kg/kg) / 1 (m^3) × 1000 = 93.9 µg/m^3
Uptake = 93.9 × 1 (100% abs.)× 0.4 (resp. rate) × 0.5 (h) / 20 (kg) = 0.939 µg/kg bw/day.

Table 4. Uptake via inhalation

Prod.no.	Content in prod. mg/kg	C air, max mg/m^3	C inh µg/m^3	Uptake via inhalation µg/kg bw/day
1	150	4.084	20.418	0.204
4	650	17.696	88.479	0885
5	690	18.785	93.924	0.939
7	77	2.096	10.481	0.105
9	190	5.173	25.863	0.259
12	620	16.879	84.396	0.844

Uptake through skin (dermal uptake) is estimated assuming that both palms are exposed to 5 g of the product 1 time per day. The skin area on both hands is approx. 5% of the total body skin area (US EPA 1997). It is assumed that maximum 1/5 of the hands is exposed thus 1% is used in the calculations:
Dermal uptake = 690 × 0.005 × 0.01 ($F_{AREA, derm}$) × 1 (F abs) × 1 (d^{-1}) / 20 (kg) × 1000 = 1.725 µg/kg bw/day

Oral uptake assuming an exposure to 0.5 g product
Oral uptake = 690 × 0.0005 (kg prod) × 1 (F orl) × 1 (d^{-1}) / 20 (kg) × 1000 = 17.25 µg/kg bw/day

Table 5. Dermal and oral uptake, and total uptake

Prod.no.	Content in prod. mg/kg	Dermal uptake µg/kg bw/day	Oral uptake µg/kg bw/day	Total uptake (inhalation + dermal + oral) µg/kg bw/day
1	150	0.375	3.75	4.3
4	650	1.63	16.25	18.8
5	690	1.73	17.25	19.9
7	77	0.19	1.93	2.2
9	190	0.48	4.75	5.4
12	620	1.55	15.50	17.9

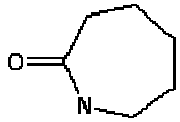
Based on observed effects on the central nervous system such as ataxia and hypoactivity with a NOAEL of 125 mg/kg bw/day the margin of safety (MOS) for total exposure is: ≥ 125 / 0.0199 = 6280.
The distance to the RfD value is a factor of: 0.1/0.0199 = ≥ 5.

Conclusion
The content of the products of 1-butanol is assessed not to pose a health risk to the consumer of the studied textile colorants.

However, the possibility of irritation of nose and throat mucous membranes can not be excluded during the use of the products. The estimated maximum concentrations in air are approx. 1/3 of the concentration where irritation is reported (75 mg/m^3).

3.3.2 Caprolactam

Identification:

Name	Caprolactam
CAS no.	105-60-2
EINECS no.	203-313-2
Molecular formula	$C_6H_{11}NO$
Molecular structure	
Molecular weight	113.16 g/mol
Synonyms	epsilon-caprolactam (EINECS name) 2-Oxohexamethylenimin (AT name and C-value name) 2-Azacycloheptanone Hexahydro-2H-azepin-2-one (CA)

The melting point is 69.2ºC. The boiling point is 270ºC. The water solubility is 772000 mg/l at 25ºC (Yalkowsky and Dannenfelser 1992). The vapour pressure is 0.21 Pa at 25ºC (0.0016 mmHg). The octanol/water partition coefficient is measured to log Kow 0.12 (IUCLID 2000).

Classification
Caprolactam is adopted on the List of dangerous substances and classified (Miljøministeriet 2002):

Xn;R20/22	Harmful by inhalation and if swallowed.
Xi;R36/37/38	Irritating to eyes, respiratory system and skin.

Use
Caprolactam has several uses within the chemical industry in the production of other chemical compounds, polymers and in the production of paints and lacquers. The use as solvent in polymers may explain the presence.

Effects on health
Some data on acute toxicity have been available. Of these can be mentioned:

Acute oral, rat	LD_{50}	1210 mg/kg	HSDB 2004
Acute oral, mouse	LD_{50}	930 mg/kg	HSDB 2004
Acute dermal, rat	LD_{50}	>2000 mg/kg	IUCLID 2000
Acute inhalation, rat	LC_{50}, 2 h	300 mg/m^3	HSDB 2004
Acute inhalation, mouse	LC_{50}, 2 h	450 mg/m^3	HSDB 2004

Of studies using prolonged exposure duration some references have been found. Only two studies on exposure via inhalation and dietary toxicity with the lowest levels are mentioned.

In a 13 weeks inhalation study rats were exposed to 0, 23, 66 and 244 mg/m^3, 6 hours/day, and 5 days/week. A NOEL was set to 70 mg/m^3 for the upper respiratory tract and a NOEL of 243 mg/m^3 for the lower respiratory tract, systemic and neurotoxic effect (HSDB 2004).

In an inhalation study rats were exposed via inhalation to 0.06, 0.6 and 6 mg/m^3 caprolactam in the breathing air for 24 hours/day over 82 days. At the highest concentration was observed reduced body weight gain and changes in clinical-chemical parameters. Similar observations but to a lesser extent were also observed at 0.6 mg/m^3. NOAEL was set to 0.06 mg/m^3 (IUCLID 2000).

In a 90 days study with oral administration, rats were dosed caprolactam at the dosages 0.05, 0.1, 0.25, 0.5 and 1% in the diet (41.7, 83.3, 208.3 and 833.3 mg/kg) for 90 days. Based on degeneration of the kidneys a NOAEL was set to 41.7 mg/kg bw/day (IUCLID 2000).

In a 3-generation reproduction study, rats were dosed with 0, 1000, 5000 or 10000 ppm in the diet. The body weight in offspring and parental animals was reduced at 5000 and 1000 ppm including certain effects on the kidneys. NOAEL was set to 1000 ppm in the diet corresponding to 50 mg/kg bw/day (Serota *et al.* 1984 in IRIS 2004).

Threshold limit values
The threshold limit value for the working environment is 2 ppm corresponding to 10 mg/m^3 (AT 2002).

The C-value is 0.01 mg/m^3 (Miljøstyrelsen 2002).

The oral RfD value is 0.5 mg/kg bw/day.
The value is based on a 3-generation rat study. The NOAEL of 50 mg/kg bw/day was divided with a safety factor of 100 (10 for interspecies and 10 for intraspecies variability).

Absorption
Indications on readily absorption of the substance are found but no values are available (IUCLID 2004). Therefore, 100% absorption is assumed.

Assessment
Uptake via inhalation was based on a child of 20 kg using the textile colour product for 30 minutes/day. The consumption is set to 5 g/event, 1 time/day.

Table 6. Uptake via inhalation

Prod.no.	Content in prod. mg/kg	C air, max mg/m^3	C inh µg/m^3	Uptake via inhalation µg/kg bw/day
7	1100	0.0106	0.053	0.00053

Dermal uptake is estimated assuming that 1% of the skin area is exposed to 5 g of the product 1 time/day.

Oral uptake is assuming an exposure to 0.5 g product.

Table 7. Dermal and oral uptake, and total uptake

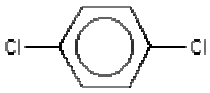
Prod.no.	Content in prod. mg/kg	Dermal uptake µg/kg bw/day	Oral uptake µg/kg bw/day	Total uptake (inhalation + dermal + oral) µg/kg bw/day
7	1100	2.75	27.50	30.25

For the assessment is used the 3-generation reproduction study because the threshold for the most sensitive reproductive effect, reduced body weight of offspring, was clearly identified. In this study NOAEL for kidney effects in rats, another critical effect in the most sensitive species, was also 50 mg/kg bw/day.
Based on NOAEL of 50 mg/kg bw/day the margin of safety (MOS) for total exposure is: ≥ 50 / 0.03025 = 1650.
The distance to the RfD value is 0.5/0.03025 = 17.

Conclusion
The product's content of caprolactam is assessed not to pose a health risk to the consumer of the studied textile colorant.

3.3.3 1,4-Dichlorobenzene

Identification:

Name	1,4-Dichlorobenzene
CAS no.	106-46-7
EINECS no.	203-400-5
Molecular formula	$C_6H_4Cl_2$
Molecular structure	
Molecular weight	147.0 g/mol
Synonym	p-Dichlorobenzene

The melting point is 52.7ºC. The boiling point is 174ºC. The water solubility is 81.3 mg/l at 25ºC (Yalkowsky and Dannenfelser 1992). The vapour pressure is 232 Pa at 25ºC (1.74 mmHg). The octanol/water partition coefficient is measured to log Kow 3.44 (Hansch *et al.* 1995).

Classification
1,4-Dichlorobenzene is classified in the List of dangerous substances (Miljøministeriet 2002) with Xi;R39 and N;R50/53. By the addition of Carc.cat.3 in the 29th ATP (Directive 2004/73/EC, EC 2004) that will be implemented by the next revision of the Statutory Order on dangerous substances, the new classification is:

Xi;R36	Irritating to eyes.
	29th ATP addition:
Carc.Cat.3;R40	Limited evidence of a carcinogenic effect.
N;R50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

Use
1,4-Dichlorobenzene is most known as air freshener in lavatories/rest rooms. The substance is used as carrier in textile dyes and in the production of

colorants and pigments via the tranformation to 1,4-dichloro-2-nitrobenzene (ECB 2004a).

Effects on health
Some data on acute toxicity have been recovered. Of these are mentioned:

Acute oral, rat	LD_{50}	500 mg/kg	ECB 2004a
Acute oral, rat	LD_{50}	>2000 mg/kg	ECB 2004a
Acute oral, mouse	LD_{50}	3000 mg/kg	ECB 2004a
Acute dermal, rat	LD_{50}	>2000 mg/kg	ECB 2004a
Acute inhalation, rat	LC_{50}, 4 h	5070 mg/m^3	ECB 2004a

The acute toxicity thus appears low regardless of exposure route (ECB 2004a).
Irritation after inhalation that resulted in a 50% decrease of the respiration rate in mice (RD_{50}) was 270 ppm for males and 245 ppm for females (Wilson 1990, ECB 2004a). The concentrations correspond to 1620 and 1470 mg/m^3, respectively.

Of studies with prolonged exposure duration was found a 2-generation reproduction study where rats were exposed to 1,4-dichlorobenzene vapour at the concentrations of 0, 50, 150, or 450 ppm (0, 301, 902, 2705 mg/m^3) for 10 weeks, 6 hours/day, 7 days/week, then the rats were mated. Next generation was exposed in the same way. Based on significant increase in liver weights of P1, parental males, NOAEC was set to 50 ppm corresponding to 300 mg/m^3 (IRIS 2004).

In a two-generation oral study conducted on rats the substance was administered by gavage at 0, 30, 90, 270 mg/kg bw/day, 7 days/week. At 270 mg/kg bw/day was observed serious damages to kidneys. At 90 mg/kg/day, statistically significant ($p < 0.05$) reversible reduced mean body weight in foetuses was observed. Thus, the NOAEL for these developmental effects is set at 30 mg/kg/day (ECB 2004).

In a 1-year oral toxicity study on Beagle dogs were administered gelatine capsules with the substance at the doses of 0, 10, 50 and 150 mg/kg bw/day. In the liver was observed absolute and relative increase of the liver weight. NOAEL was set to 10 mg/kg bw/day (Naylor 1996 in ECB 2004a).

The carcinogenic potential of 1,4-dichlorobenzene has been demonstrated in mice which are of very high sensitivity towards hepatotoxic chemicals but the mechanism by which these hepatic tumours form, has not been clearly identified. A threshold mechanism for carcinogenicity of 1,4-dichlorobenzene is proposed in view of the liver tumours from the highest doses tested (oral and inhalation route in two species of mice). For carcinogenicity, a NOAEC of 75 ppm following inhalation exposure was obtained in mice (6 hours/day, 5 days/week for 13 weeks), equivalent to 13 ppm or 80 mg /m^3, for continuous exposure. A NOAEL of 300 mg/kg/day was identified in mice following oral administration (ECB 2004).

With regard to mutagenicity, even if 1,4-dichlorobenzene has been investigated in a large number of *in vitro* and *in vivo* tests, data do not provide a coherent view of the genotoxicity of 1,4-dichlorobenzene. The so-called standard tests for genotoxicity do not suggest that 1,4-dichlorobenzene has any such potential; the evidence pointing in this direction comes from non-standard tests. The overall weight of evidence from the most reliable studies indicates that it does not have any significant genotoxic potential. According to the EU criteria for classification

and labelling of dangerous substances, 1,4 dichlorobenzene is not considered as a genotoxic agent (ECB 2004).

Threshold limit values
The threshold limit value for the working environment is 10 ppm corresponding to 60 mg/m^3 with notation K. K means that the substance is adopted on the list of substances considered to be carcinogenic (AT 2002).

The inhalation reference concentration value (RfC) is by US-EPA set to 0.8 mg/m^3. The value is based on NOAEL of 300 mg/m^3 recalculated from an exposure of 6 hours/day to 24 hours and applying a safety factor of 100 (IRIS 2004).

The TDI value is 107 µg/kg bw/day according to WHO (1993, 2004). The value is derived from a LOAEL of 150 mg/kg bw/day for kidney damages in a 2-year rat study with oral administration. A correction for 5 days/week and a safety factor of 1000 was applied (10 for interspecies, 10 for intraspecies variability and 10 for the use of LOAEL.

Absorption
The absorption of the substance after inhalation takes place readily. In rats were found that after inhalation they excrete 73% via urine and 2.5% via faeces and after oral administration 87% are excreted via urine and 2% via faeces. The dermal absorption is the lowest with 41% excreted via urine and 0.1% via faeces. The remaining amounts are assumed excreted via the exhaled air. The values vary to a large extent though depending on animal species and whether the exposure is repeated. Therefore 100% absorption is assumed in this assessment.

Assessment
Uptake via inhalation was based on a child of 20 kg using the textile colour product for 30 minutes/day. The consumption is set to 5 g/event, 1 time/day.

Table 8. Uptake via inhalation

Prod.no.	Content in prod. mg/kg	C air, max mg/m^3	C inh µg/m^3	Uptake via inhalation µg/kg bw/day
1	9.9	0.136	0.681	0.0068

Dermal uptake is estimated assuming that 1% of the skin area is exposed to 5 g of the product 1 time/day.

Oral uptake is assuming an exposure to 0.5 g product.

Table 9. Dermal and oral uptake, and total uptake

Prod.no.	Content in prod. mg/kg	Dermal uptake µg/kg bw/day	Oral uptake µg/kg bw/day	Total uptake (inhalation + dermal + oral) µg/kg bw/day
1	9.9	0.025	0.25	0.28

General systemic repeated-dose toxicity, carcinogenicity and the developmental toxicity are the critical end points for humans. As 1,4-dichlorobenzene is considered to be a non-genotoxic carcinogen, a threshold approach is appropriate.

The lowest and relevant NOAEL of 10 mg/kg/day was found in a chronic oral study on dogs with the critical effects on liver (significant increase of liver weight).

Based on NOAEL of 10 mg/kg bw/day the margin of safety (MOS) for total exposure is: 10 / 0.00028 = 35710.
The distance to the TDI value is a factor of 107/0.28 = 382.

Conclusion
The product's content of 1,4-dichlorobenzene is assessed not to pose an immediate health risk to the consumer of the studied textile colorant.

It should be noted that 1,4-dichlorobenzene is classified carcinogenic (category 3; R40 Limited evidence of carcinogenic effect). The assessment performed in the EU risk assessment report indicates a threshold to carcinogenic effects. Thus at the determined levels the substance may not be of significance but the manufacturer and the consumer perhaps should consider alternatives.

3.3.4 Diethylene glycol

Identification:

Name	Diethylene glycol
CAS no.	111-46-6
EINECS no.	203-872-2
Molecular formula	$C_4H_{10}O_3$
Molecular structure	
Molecular weight	106.12 g/mol
Synonyms	2,2'-Oxydiethanol 2,2' –Oxybisethanol 2,2' –Dihydroxyethylether 3-Oxapentane-1,5-diol

The melting point is -8ºC. The boiling point is 245ºC. The water solubility is high (miscible with water at 25ºC). The vapour pressure is 1.04 Pa at 25ºC (Daubert and Danner 1989). The octanol/water partition coefficient is measured to log Kow 1 (IUCLID 2000).

Classification
Diethylene glycol is adopted on the List of dangerous substances and classified (Miljøministeriet 2002):

Xn;R22	Harmful if swallowed

Use
Among several uses the substance is used also as solvent in colorants and adhesives.

Effects on health
Some data on acute toxicity has been available. Of these can be mentioned:

Acute oral, rat	LD_{50}	15600 mg/kg	Clayton and Clayton 1982
Acute oral, mouse	LD_{50}	13000 mg/kg	Clayton and Clayton 1982
Acute dermal, rabbit	LD_{50}	11890 mg/kg	IUCLID 2000
Acute inhalation, rat	LC_{LO}, 4 h	4500 mg/m^3	IUCLID 2000
Acute inhalation, mouse	LC_{LO}, 2 h	130 mg/m^3	IUCLID 2000

Studies with acute exposure indicate a low acute toxicity (IUCLID 2000).

Of studies with prolonged exposure duration some are available but most are of older date or only available as insufficient references in RTECS.

For exposure via inhalation a study is found where rats were exposed 5 days/week for 6 months. LOAEL was 0.02 - 0.03 mg/l corresponding to 20 - 30 mg/m^3 (IUCLID 2000).

In a 90 days oral study, rats were administered daily the substance in the drinking water at the doses 0, 200, 700, and 8000 mg/kg/day. Based on effects on the kidney a NOAEL was set to 200 mg/kg bw/day (Freundt and Weis 1989).

In a 225 days oral study, rats were administered daily the substance in the diet at the doses 0, 0.085, 0.17, 0.4 or 2% corresponding to 0, 64, 128, 300 or 1500 mg/kg bw). Based on functional disorders of the kidneys a NOAEL was set to 64 mg/kg bw/day (IUCLID 2000).

References on several poisonings of humans in 1937 with more than 100 deaths from the use of the substance as solvent in a sulphanilamide ”elixir” (pharmaceutical preparation). The mixture contained 72% diethylene glycol. Pathological examination showed effects on kidneys and to a lesser extent on liver. The lowest lethal dosis (LD_{LO}) was set to 1 ml/kg or approx. 1000 mg/kg bw/day (IUCLID 2000).

Threshold limit values
The threshold limit for the working environment is 2.5 ppm corresponding to 11 mg/m^3 (AT 2002).

Absorption
No values on absorption were available. Therefore, 100% absorption is assumed.

Assessment
Uptake via inhalation was based on a child of 20 kg using the textile colour product for 30 minutes/day. The consumption is set to 5 g/event, 1 time/day.

Table 10. Uptake via inhalation

Prod.no.	Content in prod. mg/kg	C air, max mg/m^3	C inh µg/m^3	Uptake via inhalation µg/kg bw/day
1	53000	1.725	8.627	0.086
5	6200	0.202	1.009	0.010

Dermal uptake is estimated assuming that 1% of the skin area is exposed to 5 g of the product 1 time/day.

Oral uptake is assuming an exposure to 0.5 g product.

Table 11. Dermal and oral uptake, and total uptake

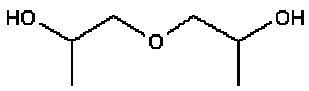
Prod.no.	Content in prod. mg/kg	Dermal uptake µg/kg bw/day	Oral uptake µg/kg bw/day	Total uptake (inhalation + dermal + oral) µg/kg bw/day
1	53000	132.5	1325	1457
5	6200	15.5	155	170

The critical effect is functional disorders of the kidneys. The lowest available NOAEL for this effects is therefore used in the assessment.
Based on a NOAEL of 64 mg/kg bw/day the margin of safety (MOS) for total exposure is: ≥ 64 / 1.475 = ≥ 43.

Conclusion
The products' content of diethylene glycol are assessed not to pose a health risk to the consumer of the studied textile colorants.

3.3.5 Diisopropylene glycol

Identification:

Name	Diisopropylene glycol
CAS no.	110-98-5
EINECS no.	203-821-4
Molecular formula	$C_6H_{14}O_3$
Molecular structure	
Molecular weight	134.18 g/mol
Synonyms	1,1'-oxydipropan-2-ol (EINECS name) 1,1'-oxydi-2-propanol (CA name) Dipropylene glycol

The melting point is 6ºC. The boiling point is 230ºC. The water solubility is high (miscible with water at 25ºC). The vapour pressure is 4.3 Pa at 25ºC (0.032 mmHg, Daubert and Danner 1989). The octanol/water partition coefficient is estimated to log Kow -0,64 (EPI).

Classification
Dipropylene glycol is not classified in the List of dangerous substances (Miljøministeriet 2002).

Use
The substance is used as solvent and plasticiser in resins and printing inks (HSDB 2004).

Effects on health
Only few data on acute toxicity were available. Of these are mentioned:

Acute oral, rat	LD_{50}	14800 mg/kg	HSDB 2004
Acute inhalation, rat	LC_{50}, 8 h	>6000 mg/m^{3*}	IUCLID 2000
Acute dermal, rabbit	LD_{50}	>20600 mg/kg	IUCLID 2000

*: Saturated air, aerosol. None out of 6 animals died.

Dipropylene glycol is observed to be slightly irritating to skin (IUCLID 2000).

Very few useful data is found available on acute and chronic exposure of test animals (IUCLID 2000). The data available are often insufficiently described.

Of tests a study was found where rats were exposed orally via drinking water containing 5% dipropylene glycol (approx. 3100 mg/kg bw/day) for 77 days without any effects were observed. At 10% few animals died. In these degeneration of the kidney epithelium and liver parenchyma were observed (IUCLID 2000).

In a teratogenicity study, rats were exposed orally via gavage at the doses 800, 2000, and 5000 mg/kg/day in days 6 to 15 of the gestation period. Toxic effects and deaths were observed in the maternal animals at 2000 and 5000 mg/kg bw/day (mortality rate 4% and 9%, respectively). A NOAEL was set for maternal toxicity to 800 mg/kg bw/day. No differences between exposed foetuses and control animals were observed (NTP 1992, ref. in IUCLID 2000).

Sufficient data to establish the dosis-response relationship for dipropylene glycol were not available. Data to identify the critical effect are not available though doses close to lethal dose have effects on the central nervous system and the kidney epithelium (Lundberg 1993).

Threshold limit values
No threshold limit values for the working environment were found for Denmark or other countries.

Absorption
No values for absorption were available and, therefore, 100% absorption is assumed.

Assessment
Uptake via inhalation was based on a child of 20 kg using the textile colour product for 30 minutes/day. The consumption is set to 5 g/event, 1 time/day.

Table 12. Uptake via inhalation

Prod.no.	Content in prod. mg/kg	C air, max mg/m^3	C inh µg/m^3	Uptake via inhalation µg/kg bw/day
1	2300	0.536	2.68	0.027
5	5000	1.164	5.82	0.058
6	3100	0.722	3.61	0.048
7	5100	1.188	5.94	0.036
9	390	0.091	0.45	0.059
12	4900	1.141	5.71	0.057

Dermal uptake is estimated assuming that 1% of the skin area is exposed to 5 g of the product 1 time/day.

Oral uptake is assuming an exposure to 0.5 g product.

Table 13. Dermal and oral uptake, and total uptake

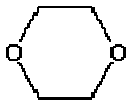
Prod.no.	Content in prod. mg/kg	Dermal uptake, µg/kg bw/day	Oral uptake µg/kg bw/day	Total uptake (inhalation + dermal + oral) µg/kg bw/day
1	2300	5.7	57.5	63.3
5	5000	12.5	125.0	137.6
6	3100	7.8	77.5	85.3
7	5100	12.7	127.5	140.3
9	390	0.98	9.8	10.7
12	4900	12.3	122.5	134.8

No NOEL values after repeated exposure studies were available. Based on the apparent low toxicity of the substance NOEL may be expected to be around the gram/kg bw/day level. The assessment is therefore based on the analogous glycol: diethylene glycol, which appears to have a similar acute toxicity and long-term effects on the kidneys. The assessment is thus based on the same NOAEL of 64 mg/kg bw/day. The margin of safety (MOS) for total exposure is then: ≥ 64 / 0.140 = ≥ 456.

Conclusion
The products' content of diisopropylene glycol is assessed not to pose a health risk to the consumer of the studied textile colorants.

3.3.6 1,4-Dioxane

Identification:

Name	1,4-Dioxane
CAS no.	123-91-1
EINECS no.	204-661-8
Molecular formula	$C_4H_8O_2$
Molecular structure	
Molecular weight	88.11 g/mol
Synonyms	1,4-dioxacyclohexane Diethylene ether Glycolethylene ether

The melting point is 11.8ºC. The boiling point is 101.5ºC. The water solubility is high (miscible with water at 25ºC, Riddick *et al.* 1986). The vapour pressure is 5080 Pa at 25ºC (38.1 mmHg, Daubert and Danner 1989). The octanol/water partition coefficient is measured to log Kow -0.27 (Hansch *et al.* 1995).

Classification
1,4-Dioxane is adopted on the List of dangerous substances and classified (Miljøministeriet 2002):

F;R11-19	Highly flammable. May form explosive peroxides.
Xi;R36/37	Irritating to eyes and respiratory system
Carc3;R40	Limited evidence of carcinogenic effects
R66	Repeated exposure may cause skin dryness or cracking.

Use
1,4-Dioxane has many uses but in this context it is used as solvent in colorants and adhesives (ECB 2002).

Effects on health
Some data on acute toxicity are available. Of these are mentioned:

Acute oral, rat	LD_{50}	5170 mg/kg	ECB 2002
Acute oral, mouse	LD_{50}	5850 mg/kg	ECB 2002
Acute dermal, rabbit	LD_{50}	7855 mg/kg	RTECS 1995
Acute inhalation, rat	LC_{50}, 2 h	46000 mg/m^3	ECB 2002
Acute inhalation, mouse	LC_{50}, 2 h	37000 mg/m^3	ECB 2002

Following acute oral administration to different mammals were observed narcotic effects, coma, irritation of gastro-intestinal mucous membranes and damages to liver and kidneys (ECB 2002).

By dermal exposure similar effects are observed, i.e. the substance can be absorbed via the skin (ECB 2002).

In a 2-year rat toxicity study the rats were exposed to a concentration in the breathing air of 400 mg 1,4-dioxane vapour/m^3 for 7 hours/day, 5 days/week for 104 weeks. Based on 100% absorption, 240 ml inhaled air, a body weight of 400 g and 7 hours exposure/day an exposure of 108 mg/kg bw/day was calculated. No clinical effects, effects on body weight or mortality were observed. NOAEL for toxic effects was set thus to 400 mg/m^3 (Torkelson *et al.* 1974).

Of studies with prolonged exposure duration, several are mentioned in the EU risk assessment report (ECB 2002). Common to the studies on oral exposure via the drinking water of rats and mice for 2 to 13 weeks are a description of serious effects on liver, kidney and nose (liver and nasal tumours and organ damage) with a LOAEL of 16 mg/kg bw/day and NOAEL of 10 mg/kg bw/day.

Despite the fact that the substance is a carcinogen in two species (rats and mice), with some indication for a third species (guinea pigs), the substance is a low potent carcinogen and the available data indicate a non-genotoxic mechanism. For both liver and nasal tumours, cytotoxic effects and organ damage are considered to be involved, which are subject to non-linear kinetics, implicating a threshold (ECB 2002).

In studies on the carcinogenicity were observed that 1,4-dioxane showed inadequate evidence for the carcinogenicity in humans but sufficient evidence for the carcinogenicity in experimental animals. The conclusion was that dioxane was placed in class 2B, i.e. possibly carcinogenic to humans (IARC 1999).

Threshold limit values
The threshold limit value for the working environment is 30 ppm corresponding to 36 mg/m3 with notations HK. L indicates that the substance may penetrate the skin. K means that the substance is adopted on the list on substances that is considered carcinogenic (AT 2002).

The C-value is 0.01 – 0.1 mg/m^3 (Miljøstyrelsen 2002).

The TDI value is 16 µg/kg bw/day according to WHO (2004). The value is based on a NOAEL of 16 mg/kg bw/day for hepatocellular tumours observed in a long-term study where rats were exposed via the drinking water. A safety factor of 1000 is used (100 for inter and intraspecies differences and 10 for non-genotoxic carcinogenicity (WHO 2004).

Absorption
Radioactive labelled 1,4-dioxane is absorbed readily and almost completely after oral administration and exposure via inhalation in rats. Dermal absorption is less, especially since the substance is volatile. In the EU risk assessment is used 100% absorption for oral intake or exposure via inhalation and 50% by dermal exposure (ECB 2002).

Assessment
Uptake via inhalation was based on a child of 20 kg using the textile colour product for 30 minutes/day. The consumption is set to 5 g/event, 1 time/day.

Table 14. Uptake via inhalation

Prod.no.	Content in prod. mg/kg	C air, max mg/m^3	C inh µg/m^3	Uptake via inhalation µg/kg bw/day
1	11	0.0020	0.010	0.000098
9	4.7	0.0008	0.004	0.000042

Dermal uptake is estimated assuming that 1% of the skin area is exposed to 5 g of the product 1 time/day.

Oral uptake is assuming an exposure to 0.5 g product.

Table 15. Dermal and oral uptake, and total uptake

Prod.no.	Content in prod. mg/kg	Dermal uptake, µg/kg bw/day	Oral uptake µg/kg bw/day	Total uptake (inhalation + dermal + oral) µg/kg bw/day
1	11	0.028	0.275	0.303
9	4.7	0.012	0.118	0.129

The starting point for the risk assessment are the exposure estimates and the overall NOAEL for oral repeated exposure of 10 mg/kg bw/day from the 2-year drinking water study in rats. As 1,4-dioxane is considered to be a non-genotoxic carcinogen, a threshold approach is appropriate.

Based on a NOAEL of 10 mg/kg bw/day the margin of safety (MOS) for total exposure is: ≥ 10 / 0.00030 = 33000.

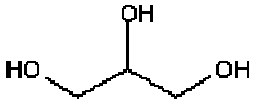
Conclusion
The products' content of 1,4-dioxane is assessed not to pose an immediate health risk to the consumer of the examined textile colorants.

Based on all data it can be concluded that 1,4-dioxane is irritating to the eye and the respiratory tract, but not to the skin. However, being a fat solvent, 1,4-dioxane can cause eczema upon prolonged or repeated contact.

It should also be noted that 1,4-dioxane is classified carcinogenic (category 3;R40 Limited evidence of carcinogenic effect). The assessment performed in the EU risk assessment report indicates a threshold to carcinogenic effects. The report also states that 1,4-dioxane has tumour promoter but not initiator properties. Thus at the determined levels the substance may not be of significance but the manufacturer and the consumer perhaps should consider alternatives.

3.3.7 Glycerine

Identification:

Name	Glycerine
CAS no.	56-81-5
EINECS no.	200-289-5
Molecular formula	$C_3H_8O_3$
Molecular structure	
Molecular weight	92.09 g/mol
Synonyms	Glycerol 1,2,3-Propanetriol 1,2,3-Trihydroxypropane

The melting point is 18.2ºC. The boiling point is 290ºC. The water solubility is high (miscible with water at 25ºC). The vapour pressure is 0.022 Pa at 25ºC ($1.68x10^{-4}$ mmHg, Daubert and Danner 1989). The octanol/water partition coefficient is measured to log Kow –1.76 (Hansch *et al.* 1995).

Classification
Glycerine is not classified in the List of dangerous substances (Miljøministeriet 2002).

Use
Glycerine is used as solvent, thickener and softener in a series of products, among others printing inks. Glycerine may also be used as humectant i.e. retains the water and thus increase the drying period and provide time for curing of the colorant.

Effects on health
Few data on acute toxicity are available. Of these are mentioned:

Acute oral, rat	LD_{50}	12600 mg/kg	IUCLID 2000
Acute oral, mouse	LD_{50}	4090 mg/kg	IUCLID 2000
Acute dermal, rat	LD_{50}, >0.3 h	>21900 mg/kg	IUCLID 2000

Based on the few available data glycerine is not acute toxic.

Of studies with prolonged exposure duration a 13 weeks rat study is found where rats were exposed via inhalation for 6 hours/day, 5 days/week at the doses 0, 0.033, 0.167, 0.662 mg/l air. Based on damages to the nose epithelium a NOAEL was set to 0.167 mg/l air corresponding to 167 mg/m^3 (Renne *et al.* 1992).

Of oral studies a study was found where rats were exposed to diet containing concentrations of 0, 1, 3, 6, 10, 15, 20, 30, 40, 50 or 60% (corresponding to 0, 1000, 3000, 6000, 10 000, 15 000, 20 000, 30 000, 40 000, 50 000, or 60 000 mg/kg bw/day) for 20 weeks. A reduced body weight gain at doses above 40% glycerine in the diet and tissue pathological changes in liver cells at doses above 10% were observed. NOEL was set to 5% glycerine in the diet corresponding to 5000 mg/kg bw/day (Guerrant *et al.* 1947).

In a 2-year study where rats were administered glycerine in the diet at concentrations of 0, 5, 10 or 20% (corresponding to 0, 2500, 5000 or 10 000 mg/kg bw/day) no significant changes in body weight or histopathological changes were observed. NOEL was thus 10 000 mg/kg bw/day (JECFA 2001).

Threshold limit values
No threshold limit value for the working environment is available for Denmark (AT 2002).
For glycerine mist a threshold limit value for 8 hours time weighted average (TLV – TWA) of 10 mg/m^3 was found (ACGIH 2002).

The ADI value is not specified because the Joint FAO/WHO Expert Committee on Food Additives found that due to the low toxicity it was not necessary (JECFA 2001).

Absorption
Following oral administration glycerine is readily absorbed from the gastro-intestinal tract. The main part is distributed to the body fat and only 7-14% is excreted unchanged in the urine (HSDB 2004). Therefore, 100% absorption is assumed.

Assessment
Uptake via inhalation was based on a child of 20 kg using the textile colour product for 30 minutes/day. The consumption is set to 5 g/event, 1 time/day.

Table 16. Uptake via inhalation

Prod.no.	Content in prod. mg/kg	C air, max mg/m^3	C inh µg/m^3	Uptake via inhalation µg/kg bw/day
5	11000	0.009	0.045	0.00045
6	27000	0.022	0.110	0.00110

Dermal uptake is estimated assuming that 1% of the skin area is exposed to 5 g of the product 1 time/day.

Oral uptake is assuming an exposure to 0.5 g product.

Table 17. Dermal and oral uptake, and total uptake

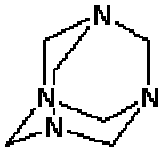
Prod.no.	Content in prod. mg/kg	Dermal uptake, µg/kg bw/day	Oral uptake µg/kg bw/day	Total uptake (inhalation + dermal + oral) µg/kg bw/day
5	11000	27.5	275	302.5
6	27000	67.5	675	742.5

Toxic effects appear to take place at high doses and thus the lowest available NOAEL is used in the assessment.
By a comparison to NOAEL 5000 mg/kg bw/day the margin of safety (MOS) for total uptake is: 5000/0.7425 = >6730.

Conclusion
The products' content of glycerine is assessed not to pose a health risk to the consumer of the examined textile colorants.

3.3.8 Hexamethylentetramine (methenamine)

Identification:

Name	Hexamethylentetramine (= methenamine)
CAS no.	100-97-0
EINECS no.	202-905-8
Molecular formula	$C_6H_{12}N_4$
Molecular structure	
Molecular weight	140.19 g/mol
Synonyms	Methenamine (EINECS name) 1,3,5,7-Tetraazatricyclo-3.1.1.1^{3,7}-decane (IUPAC name)

The melting point is >250ºC. The boiling point is unknown. The water solubility is 667000 mg/l at 25ºC (Merck Index). The vapour pressure is 0.05 Pa at 25ºC (0.004 mmHg). The octanol/water partition coefficient is estimated to log Kow –4.15 (EU RAR draft 2005, ECB 2005).

Classification
Methenamine is adopted on the List of dangerous substances and classified (Miljøministeriet 2002):

F;R11	Highly flammable.
R42/43	May cause sensitization by inhalation and skin contact.

Use
Methenamine is added as curative agent in resins used as binder in different products among other textile colorants. Methenamine is also used as preservative in cosmetics.

Effects on health
Methenamine is in the process of EU risk assessment but the report is not finalised (ECB 2005). Germany is rapporteur country.

Only a few data on acute toxicity have been available. Of these are mentioned:

Acute oral, rat	LD_{50}	>10000 mg/kg	Della Porta 1966, ECB 2005
Acute dermal, rat	LD_{50}	>2000 mg/kg	ECB 2005

Based on the few data methenamine is not acute toxic by oral or dermal exposure.

Of studies with prolonged exposure duration several studies are available using oral administration of the substance via the diet or drinking water. Almost all studies, which last from 2 to 104 weeks, use 1 dose for the duration (limit tests). Apparently the NOAEL is about 5000 mg/kg bw/day and the highest NOAEL for systemic effects is 2500 mg/kg bw/day from a 60 weeks study on mice with exposure via drinking water (Della Porta 1968).

The developmental toxicity of methenamine was studied in dogs. Methenamine was given at dietary levels of 600 or 1250 ppm (corresponding to doses of 15 and 31 mg/kg bw/day) at days 4 to 54 after mating. Growth retardation and higher mortality was observed in the high dosage group. The NOAEL was set to 15 mg/kg bw/day (ECB 2005).

In humans where methenamine has been used in the treatment of urinary tract inflammation is observed that a dose of 2-4 g/day over 3 to 4 weeks does not affect the patient while 8 g/day resulted in side-effects such as bladder irritation and blood in the urine. Based on a body weight of 70 kg this corresponds to a LOAEL of 57 mg/kg bw/day and NOAEL 27 mg/kg bw/day. This value is used in risk characterisation in the EU risk assessment report (ECB 2005).

In a dermal study where 1.3 mg/kg bw/day was applied to the skin of rabbits 5 days/week for 6 weeks no visible effects were observed (ECB 2005).

The substance is shown to be skin sensitising to humans. Allergic symptoms such as asthma are observed by exposure though with simultaneously exposure to other irritating and sensitising substances (ECB 2005).

Because no data on effects by exposure via inhalation a recalculation has been performed based on the NOAEL value for oral administration of 57 mg/kg bw/day. The absorption in both exposure routes is assumed to be 100% and the respiration rate 20 m^3/dag. NOAEC for inhalation then becomes: 57/20 = approx. 3 mg/m^3.

Threshold limit values
No threshold limit values for the working environment is available (AT 2002).

The ADI value is set to 0.15 mg/kg bw by WHO (1974).

According to the Statutory Order on cosmetics the maximum allowed concentration of methenamine in cosmetic products is 0.15%.

Absorption
Methenamine is readily absorbed after oral intake and is distributed to the whole body. The substance may penetrate the placenta and has been detected in mother's milk. No values are available for absorption through the skin or after inhalation (ECB 2005). Therefore, 100% absorption is assumed.

Assessment
Uptake via inhalation was based on a child of 20 kg using the textile colour product for 30 minutes/day. The consumption is set to 5 g/event, 1 time/day.

Table 18. Uptake via inhalation

Prod.no.	Content in prod. mg/kg	C air, max mg/m^3	C inh $\mu g/m^3$	Uptake via inhalation µg/kg bw/day
4	49	0.00014	0.00069	0.0000069
5	800	0.0023	0.01132	0.0001132
7	11	0.000031	0.00016	0.0000016
9	22	0.000062	0.00031	0.0000031
10	570	0.0016	0.00806	0.0000806
12	860	0.0024	0.01217	0.0001217

Dermal uptake is estimated assuming that 1% of the skin area is exposed to 5 g of the product 1 time/day.

Oral uptake is assuming an exposure to 0.5 g product.

Table 19. Dermal and oral uptake, and total uptake

Prod.no.	Content in prod. mg/kg	Dermal uptake µg/kg bw/day	Oral uptake µg/kg bw/day	Total uptake (inhalation + dermal + oral) µg/kg bw/day
4	49	0.123	1.23	1.35
5	800	2.000	20.0	22.00
7	11	0.028	0.28	0.30
9	22	0.055	0.55	0.61
10	570	1.425	14.3	15.68
12	860	2.150	21.5	23.65

As human data exist and are considered more reliable than the study on dogs the human NOAEL of 27 mg/kg bw/day are used in the assessment.
Based on a NOAEL of 27 mg/kg bw/day The margin of safety (MOS) for total uptake is: ≥ 27 / 0.024 = ≥ 1125.

The ADI value of 0.15 mg/kg bw/day is not exceeded. The distance is at least 6.

The maximum concentration of methenamine allowed in cosmetic products according to the Statutory Order on cosmetics of 0.15% (1500 mg/kg) is not exceeded.

Conclusion
The products' content of methenamine is assessed not to pose a health risk to the consumers of the examined textile colorants.

However, it should be noted that methenamine has demonstrated skin sensitising properties in humans and may cause sensitisation by inhalation.

3.3.9 Isobutane

Identification:

Name	Isobutane
CAS no.	75-28-5
EINECS no.	200-857-2
Molecular formula	C_4H_{10}
Molecular structure	
Molecular weight	58.12 g/mol
Synonyms	2-Methyl-propane 1,1-Dimethylethane Trimethylmethane

The melting point is –138.3ºC. The boiling point is –11.7ºC. The water solubility is 48.8 mg/l at 25ºC (Riddick *et al.* 1986). The vapour pressure is 348000 Pa at 25ºC (2610 mmHg). The octanol/water partition coefficient is measured to log Kow 2.76 (Hansch *et al.* 1995).

Classification
Isobutane is adopted on the List of dangerous substances and classified (Miljøministeriet 2002):

Fx;R12 Extremely flammable
if >= 0.1% 1,3-butadien (CAS no. 106-99-0, EINECS no. 203-450-8, then also:
Carc.cat.1;R45 May cause cancer
Mut.cat.2;R46 May cause heritable genetic damage
NB: 1,3 butadiene was not detected in the analysis.

Use
Isobutane is a gas detected in the 2 ”pop-up” textile colorants where the substance is used as blowing agent of the colour when heated.

Effects on health
Few data on acute toxicity are available. Sine the substance is a gas the data only comes from studies with exposure via inhalation. Of these are mentioned:

Acute inhalation, rat	LC_{50}, 15 min.	570000 ppm, 1375000 mg/m^3	IUCLID 2000
Acute inhalation, rat	LC_{50}, 4 h	658000 mg/m^3	IUCLID 2000

Acute exposure primary takes place via inhalation since the substance is very volatile. The mortalities recorded during the inhalation studies happened during and not after the studies. The test animals that survived the studies appeared normal within 10 minutes. The effects are caused by stimulation of the central nervous system (IUCLID 2000).

Of studies with prolonged exposure duration a 90 days rat study was available where the rats were exposed via inhalation for 6 hours/day, 5 days/week to 0, 1000 or 5000 ppm with a gas mixture comprising 50% butane and 50% pentane. At the highest dose no effects on kidneys or body weight were observed, and no effects were evident from haematological or biochemical

parameters or from histopathology. Of clinical observations were noted hunched posture, lethargy and intermittent tremor (IUCLID 2000).

Threshold limit values
A threshold limit value for the working environment is not available for Denmark but matching values from other countries are found. For instance for Germany was found a MAK(Maksimaler Arbeitsplatz Konzentration) value of 2350 mg/m^3, for USA a TLV (TWA) value of 1780 mg/m^3 and for United Kingdom an OES (Occupational Exposure Standard) value of 1430 mg/m^3 (IUCLID 2000).

Absorption
No values on absorption are available and, therefore, 100% absorption is assumed.

Assessment
Uptake via inhalation was based on a child of 20 kg using the textile colour product for 30 minutes/day. The consumption is set to 5 g/event, 1 time/day.

Table 20. Uptake via inhalation

Prod.no.	Content in prod. mg/kg	C air, max mg/m^3	C inh µg/m^3	Uptake via inhalation µg/kg bw/day
4	3500	28572	142865	1428
5	2000	16327	81637	816

Dermal uptake is estimated assuming that 1% of the skin area is exposed to 5 g of the product 1 time/day.

Oral uptake is assuming an exposure to 0.5 g product.

Table 21. Dermal and oral uptake, and total uptake

Prod.no.	Content in prod. mg/kg	Dermal uptake, µg/kg bw/day	Oral uptake µg/kg bw/day	Total uptake (inhalation + dermal + oral) µg/kg bw/day
4	49	8.75	87.5	1525
5	800	5.0	50.0	871

Isobutane is a gas. The estimates also indicate that the primary exposure takes place via inhalation with a maximum exposure in the breathing zone of 143 mg/m^3. The estimated concentration is approx. 1/10 of the lowest available value for the working environment of 1430 mg/m^3. This distance seems to be small when addressing exposure at home and not at work.

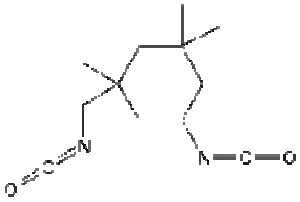
An attempt to recalculate to oral exposure based on the lowest found threshold limit value for the working environment resulted in: 1430 × 10/20 m^3 × 5/7 days = 510 (mg/m^3/day) / 70 kg = 7.3 mg/kg bw/day. The margin of safety is then 7.3/1.5 = 4.8, which is considered low. On the other hand, the value of the used safety factor is unknown

Conclusion
The products' content of isobutane though is assessed not to pose an immediate health risk to the consumer of the examined textile colorants as the exposure is presumed to be of a short duration. However, aeration or forced ventilation should be recommended when using the products.

1,3-Butadiene was not detected in the analysis and thus the classifications as carcinogenic and mutagenic is not warranted for the analysed products.

3.3.10 3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate

Identification:

Name	3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate
CAS no.	4098-71-9
EINECS no.	223-861-6
Molecular formula	$C_{12}H_{18}N_2O_2$
Molecular structure	
Molecular weight	222.29 g/mol
Synonyms	5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethyl-cyclohexane Isophorone diamine diisocyanate Isophoronediisocyanate IPDI

The melting point is -60ºC. The boiling point is 158ºC. The water solubility is estimated to 3 mg/l at 25ºC (EPI). The vapour pressure is 0.04 Pa at 20ºC (0.0003 mmHg, Lewis 1997, HSDB). The octanol/water partition coefficient is estimated to log Kow 4.75 (EPI).

Classification

3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI) is adopted in the List of dangerous substances (Miljøministeriet 2002) and classified:

T;R23	Toxic by inhalation.
Xi;R36/37/38	Irritating to eyes, respiratory system and skin
R42/43	May cause sensitization by inhalation and skin contact
N;R51/53	Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

The classification is depending on the concentration in the product (cf. table 3).

Use

IPDI yields polyurethanes with high stability, resistance to light discoloration and chemical resistance (HSDB). IPDI is used in colorants as hardener, binding agent and adhesive.

Effects on health

Some data on acute toxicity have been recovered. Of these are mentioned:

Acute oral, rat	LD_{50}	1270 mg/kg	IUCLID 2000
Acute oral, mouse	LD_{50}	>2500 mg/kg	IUCLID 2000
Acute dermal, rat	LD_{50}	1060 mg/kg	HSDB
Acute inhalation, rat	LC_{50}, 4 h	123 mg/m^3	IUCLID 2000

The acute oral toxicity thus appears low but IPDI is toxic by skin absorption.

IPDI is a severe irritant, irritating to eyes, skin and the respiratory system. Irritation after inhalation for 1 hour that resulted in a 50% decrease of the respiration rate in mice (RD_{50}) was 1.2 ppm corresponding to 0.01 mg/m^3 (IUCLID 2000).

Of studies with prolonged exposure duration was found a repeated dose toxicity study where rats were exposed to IPDI via inhalation at the concentrations of 0, 0.25, 0.64 or 1.37 mg/m^3 for 4 hours/day, 5 days/week over 28 days. At the highest dose group was observed reduced weight gain and slightly oedematous lungs. At the other dose groups no symptoms and no pathological findings were observed. Thus, NOAEL was set to 0.64 mg/m^3. In a similar study using 0, 0.525, 0.84, 3.57 and 33 mg/m^3 a NOAEL 0.525 mg/m^3 was found, but without reported effects except mortality at the 2 highest concentrations: 1 and 4 out of 20 animals/group, respectively (IUCLID).

IPDI is shown to provoke allergic dermatitis in human. One hour exposure to IPDI caused eczema in 3 of 4 workers of which only 1 had pervious contact to the substance. The others had previous contact to toluene diisocyanate and methyldiisocyanate, suggesting cross-sensitisation (ACGIH 1991 in HSDB)

Several studies on test animals and humans have confirmed the sensitisation potential of IPDI. One of the studies indicates a threshold to be present (cf. below).

The allergic contact hypersensitivity sensitising potential of IPDI was studied in female mice. The mice were sensitised with 0.1, 0.3, and 1.0% IPDI and challenged with 3.0% IPDI. Doses of IPDI were selected from assays for primary irritancy. Mice received 20 microliters by direct dermal application for 5 days to sites prepared by shaving, dermabrading, and in some cases, with intradermal injection of Freund's complete adjuvant (FCA). The rest period was 7 days. Measurement of contact hypersensitivity response in mice was by radioisotopic assay. A statistically significant hypersensitivity response was elicited in mice using a sensitising concentration of 1.0% and a challenge concentration of 3.0%, with or without pretreatment with Freund's complete adjuvant (NTP 1990).

Very little direct information on the health effects associated with exposure to IPDI has been available, except for numerous studies on exposure via inhalation causing irritation of the respiratory tract and decreases in pulmonary function, and dermal exposure causing skin sensitisation (allergy, eczema).

The isocyanates: methylenediphenyl diisocyanate (several CAS nos.) and 1,3-diisocyanatomethylbenzene (toluenediisocyanate) (several CAS nos.) are included on the List of undesirable substances (Miljøstyrelsen 2004b).

Threshold limit values
The threshold limit value for the working environment is 0.005 ppm corresponding to 0.045 mg/m^3 with skin notation H. H means that the substance may penetrate the skin (AT 2002).

Absorption
No information was available on absorption. Therefore 100% absorption is assumed.

Assessment
Uptake via inhalation was based on a child of 20 kg using the textile colour product for 30 minutes/day. The consumption is set to 5 g/event, 1 time/day.

Table 22. Uptake via inhalation

Prod.no.	Content in prod. mg/kg	C air, max mg/m^3	C inh µg/m^3	Uptake via inhalation µg/kg bw/day
7	270	0.0010	0.0048	0.000048

Dermal uptake is estimated assuming that 1% of the skin area is exposed to 5 g of the product 1 time/day.

Oral uptake is assuming an exposure to 0.5 g product.

Table 23. Dermal and oral uptake, and total uptake

Prod.no.	Content in prod. mg/kg	Dermal uptake µg/kg bw/day	Oral uptake µg/kg bw/day	Total uptake (inhalation + dermal + oral) µg/kg bw/day
7	270	0.675	6.75	7.43

Because no NOAEL value on repeated exposures by oral administration was available a transformation of the inhalation data is performed:
NOAEL (in mg/kg/d) = NOAEL inh (mg/m^3) × 1/bw (kg) × inhalation rate (m^3/d).
Using rat body weight 0.3 kg and inhalation rate, rat = 0.0144 m^3/h then:
NOAEL = 0.0525 × 1/0.3 × 0.0144 × 24/4 (h) × 7/5 (d) =0.021 mg/kg/day.

Based on the estimated NOAEL of 0.021 mg/kg bw/day the margin of safety (MOS) for total exposure is: 0.021 / 0.00743 = 2.8.

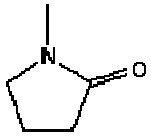
Conclusion
The product's content of IPDI is assessed not to pose an immediate health risk to the consumer of the studied textile colorant.

However, the MOS is low indicating a potential health concern and prolonged exposure should be avoided with products containing this substance. It should be noted also that the substance may cause sensitisation by skin contact and may cause problems by inhalation. Heating of the colorants should be performed under ventilation.

3.3.11 N-Methyl-2-pyrrolidone

Identification:

Name	N-Methyl-2-pyrrolidone
CAS no.	872-50-4
EINECS no.	212-828-1
Molecular formula	C_5H_9NO
Molecular structure	



Molecular weight	99.13 g/mol
Synonyms	N-Methylpyrrolidinone
	1-Methyl-2-pyrrolidone

The melting point is -24ºC. The boiling point is 202ºC. The water solubility is high at 25ºC (miscible with water). The vapour pressure is 25.3 Pa at 25ºC (Riddick *et al.* 1986). The octanol/water partition coefficient is measured to log Kow –0.46 (IUCLID 2000).

Classification
N-Methyl-2-pyrrolidone is adopted on the List of dangerous substances and classified (Miljøministeriet 2002):

Xi;R36/38	Irritating to eyes and skin.

Use
The substance has several uses within the chemical industry among others in paints, dyes and lacquers. The substance is used as solvent and in the production of pigment and printing inks (IUCLID 2000, CICAD 2001).

Effects on health
N-Methyl-2-pyrrolidone has a low acute toxicity.

Some data on acute toxicity have been found. Of those are mentioned:

Acute oral, rat	LD_{50}	3084 mg/kg	IUCLID 2000
Acute oral, mouse	LD_{50}	4050 mg/kg	IUCLID 2000
Acute dermal, rat	LD_{50}	7000 mg/kg	IUCLID 2000
Acute inhalation, rat	LC_{50}, 4 h	5100 mg/m^3	IUCLID 2000

Uptake of acute toxic doses by oral intake, dermal exposure or exposure via inhalation causes functional disorders and affects the central nervous system. Irritations of the respiratory system by exposure via inhalation and of the gastro-intestinal tract after oral administration have been observed (IUCLID 2000, CICAD 2001).

N-Methyl-2-pyrrolidone has a potential for skin irritation and eye irritation in rabbits. The effects are dependent of the concentration (IUCLID 2000).

In a 13 week study with exposure via inhalation, rats were exposed to 0, 500, 1000 and 3000 mg/m^3 for 6 hours/day, 5 days/week. Nasal irritation and crust formations on nasal edges were observed at 1000 mg/m^3. At 3000 mg/m^3,

decreased body weight and decreased relative weight of testis were observed. The NOAEL was then set to 500 mg/m^3 (CICAD 2001).

Of studies with prolonged duration of oral exposure, a 28-day study was found where rats were orally administered (via gavage) the doses 0, 257, 514, 1028 and 2060 mg/kg bw/day. A dose-dependent increase in relative liver and kidney weights was observed at 1028 mg/kg bw/day. Thus, the NOAEL was 514 mg/kg bw/day (CICAD 2001).

In a 90-day study, rats were administered the substance in the diet at the doses 0, 3000, 7500, and 18 000 mg/kg diet/day corresponding to 0, 169, 433 and 1057 mg/kg bw/day in males and 0, 217, 565 and 1344 mg/kg bw/day in females. A dose-related decrease in body weight and effects on the central nervous system was observed at 433 and 565 mg/kg bw/day in males and females, respectively. The NOAEL was 169 mg/kg bw/day in males and 217 mg/kg bw/day in females (CICAD 2001).

Threshold limit values
The threshold limit value for the working environment is 5 ppm corresponding to 20 mg/m^3 (AT 2002).

The C-value is 0.5 mg/m^3 (Miljøstyrelsen 2002).

The TDI value is 0.6 mg/kg bw/day. The value is derived from the 90-day oral study with a NOAEL of 169 mg/kg bw/day divided with a safety factor of 300 (10 for interspecies and 10 for intraspecies variation and 3 for adjusting from a 90 day subchronic to chronic) (CICAD 2001).

Absorption
N-Methyl-2-pyrrolidone is absorbed easily after inhalation, oral or dermal exposure and is distributed to the whole body. Approximately 80% of the administered dosis are excreted via the urine within 24 hours (Åkesson and Paulsson 1997). Therefore, absorption of 100% is assumed.

Assessment
Uptake via inhalation was based on a child of 20 kg using the textile colour product for 30 minutes/day. The consumption is set to 5 g/event, 1 time/day.

Table 24. Uptake via inhalation

Prod.no.	Content in prod. mg/kg	C air, max mg/m^3	C inh µg/m^3	Uptake via inhalation µg/kg bw/day
7	740	0.749	3.745	0.037

The uptake via skin (dermal uptake) is estimated assuming that 1% of the skin area is exposed to 5 g of the product, 1 time per day.

Oral uptake assumes an exposure to 0.5 g product.

Table 25. Dermal and oral uptake, and total uptake

Prod.no.	Content in prod. mg/kg	Dermal uptake µg/kg bw/day	Oral uptake µg/kg bw/day	Total uptake (inhalation + dermal + oral) µg/kg bw/day
7	740	1.85	18.5	20.4

As systemic effects appear to be the most sensitive endpoint, the lowest NOAEL available is used in the assessment.
Based on NOAEL of 169 mg/kg bw/day the margin of safety (MOS) to total uptake is: 169/0.0204 = 8284.

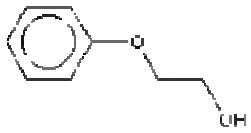
The estimated uptake does not exceed the TDI value of 600 µg/kg bw/day. The distance is approx. a factor 30.

Conclusion
The product's content of N-methyl-2-pyrrolidone is assessed not to pose an immediate health risk to the consumer of the examined textile colorant.

The substance is classified as irritating to eyes and skin. Data from IUCLID indicate that the effects are depending on the exposure concentration and at higher levels than detected.

3.3.12 2-Phenoxyethanol

Identification

Name	2-Phenoxyethanol
CAS no.	122-99-6
EINECS no.	204-589-7
Molecular formula	$C_8 H_{10} O_2$
Molecular structure	
Molecular weight	138.17 g/mol

The melting point is 14ºC. The boiling point is 245ºC (Budavari 1996). The vapour pressure is 0.93 Pa at 25ºC (0.007 mmHg, Dow 1990) or 4 Pa at 20ºC (IUCLID 2000). The water solubility is 26700 mg/l at 20ºC (Yalkowsky and Dannenfelser 1992). The partition coefficient log Kow is measured to 1.16 (Hansch *et al.* 1995).

Use
2-Phenoxyethanol is used in many industrial products as solvent and/or as preservative.

Classification
2-Phenoxyethanol is adopted on the List of dangerous substances and classified (Miljøministeriet 2002):

Xn;R22	Harmful. Harmful if swallowed
Xi;R36	Irritant: Irritating to eyes

Effects on health
Some data on acute toxicity have been found. Of those are mentioned:

Acute oral, rat	LD_{50}	1260 mg/kg	IUCLID 2000
Acute oral, rat	LD_{50}	2740 mg/kg	IUCLID 2000
Acute inhalation, rat	LC_{50} (8 h)	>saturated atmosphere	IUCLID 2000
Acute dermal, rat	LD_{50}	14422 mg/kg bw	IUCLID 2000
Acute dermal, rabbit	LD_{50}	3660 mg/kg bw	IUCLID 2000

The substance was not irritating to skin in tests on humans in 48 hours closed patch tests and 24 hours tests 3 times/week for 3 weeks. The substance is found irritating to eyes in rabbits (IUCLID 2000). The substance is not sensitising in maximisation tests on guinea pigs and in patch tests on humans (IUCLID 2000).

2-Phenoxyethanol is studied in a repeated dose toxicity test for 13 weeks on rats using oral administration of 2-phenoxyethanol in the diet at the concentrations 0, 50, 100, 200 and 500 mg/kg bw. At the highest concentration was observed a significant decrease in body weight gain and an alteration in blood parameters. Thus, NOAEL is set to 200 mg/kg bw/day (IUCLID 2000).

Threshold limit values
The threshold limit value for working environment (TLV) is 20 ppm corresponding to 110 mg/m^3 with skin notation (H), i.e. the substance may penetrate the skin (DF 2001).

The C-value is 0.1 mg/m^3 (Miljøstyrelsen 2002).

Absorption
Because no value on absorption is available the absorption is set to 100%.

Assessment
Uptake via inhalation was based on a child of 20 kg using the textile colour product for 30 minutes/day. The consumption is set to 5 g/event, 1 time/day.

Table 26. Uptake via inhalation

Prod.no.	Content in prod. mg/kg	C air, max mg/m^3	C inh µg/m^3	Uptake via inhalation µg/kg bw/day
4	460	0.024	0.12	0.0012
10	4900	0.254	1.27	0.013

The uptake via skin (dermal uptake) is estimated assuming that 1% of the skin area is exposed to 5 g of the product, 1 time per day.

Oral uptake assumes an exposure to 0.5 g product.

Table 27. Dermal and oral uptake, and total uptake

Prod.no.	Content in prod. mg/kg	Dermal uptake µg/kg bw/day	Oral uptake µg/kg bw/day	Total uptake (inhalation + dermal + oral) µg/kg bw/day
4	460	1.15	11.5	12.7
10	4900	12.3	122.5	134.8

The lowest NOAEL from a long-term repeated dose toxicity test is used in the assessment.

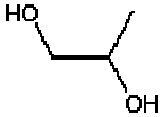
Based on NOAEL of 200 mg/kg bw/day the margin of safety (MOS) to total uptake is at least: 200/0.135 = 1480.

Conclusion
The products' content of 2-phenoxyethanol is assessed not to pose an immediate health risk to the consumer of the examined textile colorants.

The substance is classified irritating to eyes but if the colorant gets in contact with the eyes the irritation may also be caused by other components.

3.3.13 Propylene glycol

Identification:

Name	Propylene glycol
CAS no.	57-55-6
EINECS no.	200-338-0
Molecular formula	$C_3H_8O_2$
Molecular structure	
Molecular weight	76.10 g/mol
Synonyms	1,2-Propanediol Propan-1,2-diol (EINECS name) Methylethylene glycol

The melting point is -60ºC. The boiling point is 187.6ºC. The water solubility is high (miscible with water at 25ºC). The vapour pressure is 17 Pa at 25ºC (0.129 mmHg, Daubert and Danner 1989). The octanol/water partition coefficient is measured to log Kow –0.92 (Hansch *et al.* 1995).

Classification
Propylene glycol is not classified in the List of dangerous substances (Miljøministeriet 2002).

Use
The substance is contained in several products within several industries among other the paint and lacquers industry and the textile manufacturing industry. The substance is mostly used as solvent (IUCLID 2000).

Effects on health
Some data on acute toxicity have been found. Of these are mentioned:

Acute oral, rat	LD_{50}	20300 mg/kg	IUCLID 2000
Acute oral, mouse	LD_{50}	23900 mg/kg	Ruddick 1972
Acute dermal, rabbit	LD_{50}	20800 mg/kg	IUCLID 2000

Data from studies using single dose exposures indicate that propylene glycol has a low toxicity by acute exposure.

Of studies with prolonged exposure duration a 90 days inhalation study has been found where rats were exposed for 6 hours/day, 5 days/week to 0, 0.16, 1 and 2.2 mg/l air. In the second week, nose bleeding was observed as a result of dehydration effect from propylene glycol on the nose mucous membranes.

At the highest doses reduced body weight and diet intake were observed. NOAEL was set to 1 mg/l corresponding to 1000 mg/m^3 (IUCLID 2000).

For oral intake a 2-year study was found where rats were administered daily to 0, 6250, 12500 and 50000 ppm in the diet. Because no damaging effects were observed NOAEL was set to 50000 ppm in the diet corresponding to 2500 mg/kg bw/day (IUCLID 2000).

A further 2-year oral study is available where rats were administered propylene glycol in the diet at the concentration 0, 310, 630, 1300 or 2500 mg/kg bw/day for 2 years. No adverse effects on weight gain of body or organs, haematological or clinic-chemical parameters were observed. NOAEL was 1300 mg/kg bw/day (Gaunt *et al.* 1972).

Threshold limit values
Threshold limit values for the working environment is not available for Denmark (AT 2002) but for the United Kingdom was found an OES value of 474 mg/m^3 and for Germany an AIHA Workplace Exposure Limit Guide value of 10 mg/m^3 (IUCLID 2000).

The C-value is 1 mg/m^3 (Miljøstyrelsen 2002).

An ADI value of 25 mg/kg bw/day is proposed for humans based on a 2-year oral rat study with a NOAEL of 2500 mg/kg bw/day and a safety factor of 100 (10 for interspecies and 10 for intraspecies differences) (Gaunt *et al.* 1972).

Absorption
Propylene glycol administered orally is absorbed rapidly (Hanzlik *et al.* 1939, Yu *et al.* 1985, JECFA 2001). No values have been available, therefore, 100% absorption is assumed.

Assessment
Uptake via inhalation was based on a child of 20 kg using the textile colour product for 30 minutes/day. The consumption is set to 5 g/event, 1 time/day.

Table 28. Uptake via inhalation

Prod.no.	Content in prod. mg/kg	C air, max mg/m^3	C inh µg/m^3	Uptake via inhalation µg/kg bw/day
1	370	0.193	0.97	0.010
4	2300	1.201	6.01	0.060
5	36	0.019	0.094	0.0009
7	3300	1.723	8.62	0.086
10	7100	3.707	18.54	0.185

Dermal uptake is estimated assuming that 1% of the skin area is exposed to 5 g of the product 1 time/day.

Oral uptake is assuming an exposure to 0.5 g product.

Table 29. Dermal and oral uptake, and total uptake

Prod.no.	Content in prod. mg/kg	Dermal uptake µg/kg bw/day	Oral uptake µg/kg bw/day	Total uptake (inhalation + dermal + oral) µg/kg bw/day
1	370	0.93	9.25	10.2
4	2300	5.75	57.5	63.3
5	36	0.09	0.90	0.99
7	3300	8.25	82.5	90.8
10	7100	17.75	177.5	195.4

Propylene glycol is apparently not very toxic except for the dehydrating effect on mucous membranes. For the assessment the lowest available NOAEL of 1300 mg/kg bw/day from the 2-year rat study is used.
Based on NOAEL 1300 mg/kg bw/day the margin of safety (MOS) for total uptake is at least 1300/0.1954 = 6650.

The estimated uptake does not exceed the ADI value of 25 mg/kg bw/day. The distance is more than a factor of 128.

Conclusion
The products' content of propylenglycol is assessed not to pose an immediate health risk to the consumer of the examined textile colorants.

3.3.14 Antimony

Identification

Name	Antimony
CAS no.	7440-36-0
EINECS no.	231-146-5
Molecular formula	Sb
Atomic weight	121.75 g/mol
Synonym	Stibium (Sb)

The melting point of antimony is 630ºC. The boiling point is 1635ºC. (Budavari 1989). The vapour pressure is 1 mmHg at 885ºC (ATSDR 1992).

Classification
Antimony compounds are classified under several index numbers.
Antimony trioxide (CAS no.: 1309-64-4, EINECS no.: 215-175-0) is classified:

Carc3;R40; Harmful. Limited evidence of carcinogenic effects.

Antimony compounds, other than antimony chlorides, oxides and sulphides, are classified:

Xn;R20/22 Harmful by inhalation and if swallowed.
N;R51/53 Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

Use
Antimony is typically present in textile colorants for two reasons. Firstly antimony is used as component in certain colorants or pigments and secondly antimony is used as synergist to flame retardants. Since antimony trioxide is used as white pigment in colours and as synergist to flame retardants in

textiles the substance detected is probably antimony trioxide. However, as the analysis was performed as an element analysis it is unknown. Other antimony compounds such as antimony trisulphide and pentasulphide may alsobe detected in textile colorants (Lindell 2000).

Effects on health
Antimony trioxide is in the process of EU risk assessment with Sweden as rapporteur country.

Some data on acute toxicity have been available. Most data are derived from studies using antimony compounds such as antimony trioxide, antimony trichloride, etc. Of these can be mentioned:

Acute oral, rat	LD_{50}	100 mg Sb/kg	Sax 1989
Acute oral, mouse	LD_{50}	550 mg Sb/kg	Sax 1989

Antimony and its compounds have been reported to cause dermatitis, keratitis, conjunctivitis and nasal septal ulceration by contact, fumes or dust (Budavari 1989).

In Sloof *et al.* (1992) the results from several subacute studies using different antimony compounds are presented in tabular form. Many of the tests are performed as limit tests i.e. using only one concentration. Since effects were observed in most studies at the used concentrations they can not be used to establish a NOAEL. Besides, the results clearly indicate that the observed values on toxicity depend on which antimony compound that is used in the study. For instance the water solubility and lipid solubility of the used antimony compound will be decisive for bioavailability/absorption and thus the test result.

The currently best results and evaluations are therefore found in the EU draft on a risk assessment of antimony trioxide (ECB 2004b). Because the detected antimony probably are a result of the use of antimony trioxide in colorants this is considered acceptable for this assessment.

For exposure via inhalation the EU risk assessment draft uses a 1-year rat study where rats were exposed to antimony trioxide at the doses 0, 1.9 and 5 mg Sb_2O_3/m^3 for 6 hours/day, 5 days/week over 52 weeks corresponding to 1.6 and 4.2 mg Sb/m^3. Based on numerous harmful effects to the lungs a LOAEC was set to 1.9 mg antimony trioxide/m^3 corresponding to 1.6 mg Sb/m^3 (EU draft 2004, ECB 2004b).

For oral exposure the EU draft on antimony trioxide (ECB 2004b) uses a 90 days rat study where the rats were administered diet containing 0, 1000, 5000 or 20000 ppm antimony trioxide. Based on effects on the liver a NOAEL was set to 5000 ppm in the diet corresponding to 421 mg Sb_2O_3/kg bw/day for male rats and 494 mg Sb_2O_3/kg bw/day for female rats (Hext *et al.* 1999). Recalculated to antimony on the basis of molecular weight this corresponds to the lowest NOAEL being $421\times(2\times121.75)/291.52 = 351$ mg Sb/kg bw/day.

In the EU risk assessment scenarios for consumers are included. From exposure to antimony trioxide the most essential effects are mutagenic and carcinogenic effects. It is assessed that a potential possibility of health problems exists. To the risk assessment of effects to the reproduction and development is used a NOAEL from inhalation of 6.3 mg/m^3 recalculated to

oral exposure assuming that the rat weighs 250 g and has an inhalation rate of 0.0144 m^3/h to: 6.3 mg/m^3× 0.0144 m^3/h × 6 h/day / 0.25 kg = 2.2 mg/kg bw/day (ECB 2004b). Recalculated to antimony this corresponds to 1.8 mg Sb/kg bw/day.

The study that WHO (1996) has used to derive ADI is a long-term study where rats for the duration of their lives were exposed to antimony in the drinking water at 5 ml Sb/l corresponding to 0.43 mg/kg bw/day. Based on 15% reduction of lifetime and changed blood chemistry a LOAEL was set to 0.43 mg Sb/kg bw/day (Schröder *et al.* 1970).

However, WHO has later revised the antimony studies due to newer studies and severe criticism. WHO now bases its TDI value on a 90-day rat study where the rats were administered potassium antimony tartrate in the drinking water. Based on decreased body weight gain and reduced food intake a NOAEL was set to 6 mg Sb/kg bw/day (WHO 2004, 2004b).

Antimony may migrate out of the colorant in or on the textile even at low temperatures to liquids such as sweat, saliva and synthetic blood (Hansen *et al.* 2002).

Threshold limit values
The threshold limit for air in the working environment is 0.5 mg Sb/m^3 (AT 2002).

The C-value for antimony compounds is 0.001 mg Sb/m^3 (Miljøstyrelsen 2002).

US-EPA derives an inhalation RfC of 0.2 µg/m^3 for antimony trioxide (IRIS 2002).

Of oral limit values is found that ATSDR (1992) has calculated an oral RfD to 0.4 µg Sb/kg bw/day based on a LOAEL 0.35 mg Sb/kg/day from a chronic rat study (IRIS 2002).

An acceptable daily intake (ADI) is derived by WHO to 8.6×10^{-4} mg Sb/kg bw/day (WHO 1996). The value is based on a LOAEL of 0.43 mg Sb/kg bw/day and a safety factor of 500 (10 for interspecies, 10 for intraspecies differences and 5 for LOAEL to NOAEL), i.e. ADI = 430/500 = 0.86 µg Sb/kg bw/day.

Based on the same study as WHO 1996 (LOAEL 0.43 mg Sb/kg bw/day) but using a safety factor of 1000 (used factor 10 for LOAEL to NOAEL) A TDI value can be set to 0.43 µg Sb/kg bw/day. This value is found in several references.

The revised TDI value 6 µg Sb/kg bw/day is given in WHO (2004). This TDI value is based on a NOAEL of 6 mg/kg bw/day from a 90-day rat study. A safety factor of 1000 was applied (100 for inter and intraspecies differences and 10 for subchronic to chronic) (WHO 2004c).

Absorption
The bioavailability by inhalation is not available and therefore set to 100%.

The bioavailability by dermal uptake is unknown but for other metals it is assumed to be about 1-5% (ECB 2004b-draft antimony trioxide). The value is in this report set to 10%.
The bioavailability by oral intake is estimated to 10%. The value is based on uptake from gastro-intestinal tract has been found to 2-7% (Miljøstyrelsen 2002).

Assessment
Exposure via inhalation is based on that antimony as metalloid has a very low vapour pressure. The release from the use of textile colorant products is therefore assumed to be very low and insignificant in relation to other sources of antimony exposure in the indoor climate (dust from clothes of polyester containing antimony, the releases from electronic equipment, plastic, etc. where antimony is used as flame retardant, Laursen *et al.* 2003).

Dermal uptake is estimated assuming that 1% of the skin area is exposed to 5 g of the product 1 time/day. The absorption is set to 10%.

Oral uptake is assuming an exposure to 0.5 g product and absorption of 10%.

Table 30. Dermal and oral uptake, and total uptake

Prod.no.	Content in prod. mg/kg	Dermal uptake, µg/kg bw/day	Oral uptake µg/kg bw/day	Total uptake (inhalation + dermal + oral) µg/kg bw/day
1	78	0.020	0.195	0.215
2	64	0.016	0.160	0.176
3	84	0.021	0.210	0.231

Based on a LOAEL of 0.43 mg Sb/kg bw/day the margin of safety (MOS) for total uptake is at least 0.43/0.000231 = 1861.

Using a NOAEL of 6 mg Sb/kg bw/day the margin of safety (MOS) for total uptake is at least 6/0,00023 = 26000.

The estimated uptake does not exceed the ADI value of 0.86 µg/kg bw/day and not at all the revised TDI value of 6 µg/kg bw/day (WHO 2004).

However, it should be noted that other sources to antimony exposure also exist from the environment and in food. This means that during the exposure period (the use period of the textile colorant product) exceeding of an acceptable daily intake of antimony may occur. As antimony relatively fast is excreted and not accumulated in the body exceeding of short duration are considered acceptable.

Conclusion
The products' content of antimony is assessed not to pose a health risk to the consumer of the examined textile colorants.

However, it should be noted that antimony trioxide is classified carcinogenic (category 3; R40 Limited evidence of carcinogenic effect). The assessment to be performed in the EU risk assessment programme is not yet finalised. The determined levels the substance may not be of significance but the manufacturer and the consumer perhaps should consider alternatives until this is clarified.

3.3.15 Copper

Identification

Name	Copper
CAS no.	7440-50-8
EINECS no.	231-159-6
Molecular formula	Cu
Atomic weight	63.55 g/mol

The melting point is 1083ºC. The boiling point is approx. 2590ºC (Budavari 1989).

Copper may occur at two valences: copper(I) and copper(II). The two forms may each be included in several different chemical compounds.

Classification
Copper compounds are classified differently depending on the specific compound. Most copper compounds are classified Harmful if swallowed as copper may cause liver damages (Larsen *et al.* 2000).

Certain compounds such as copper(I)chloride and copper sulphate are classified Dangerous to the environment and Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. Other compounds are classified Irritants but not with risk of sensitisation (Miljøministeriet 2002).

Use
The detection is probably caused by the application of copper compounds in different colour pigments.

Effects on health
Copper belongs to the essential metals i.e. a certain minimum uptake is necessary not to retrieve deficiency diseases. It is estimated that copper is necessary at a level of normally 1 to 5 mg Cu/adult person/day corresponding to 20 to 80 µg/kg bw/day (WHO 1996b). The need of copper is usually regulated by the organism so accurately that the body's content of copper in adults is constantly about 100 to 150 mg (Scheinberg 1983).

WHO states that the daily need of copper is covered by food and drinking water at an exposure to 1 to 5 mg/day. All other intakes (via inhalation and the skin) are considered insignificant compared to the oral exposure route. For instance inhalation is assessed to contribute with an uptake of 0.3 to 2.0 µg/day from dust and smoke (IPCS 1998).

Few data on acute toxicity have been available. Of these are mentioned:

Acute oral, mouse	LD_{50}	0.7 mg/kg	IUCLID 2000
Acute oral, human	TD_{LO}	0.12 mg/kg	IUCLID 2000
Acute inhalation, human	TC_{LO}	1 mg/m^3	IUCLID 2000

Several data exist on organic and inorganic copper compounds. Because it is unknown, which copper compounds that may be contained in the products, these data are not included in this context.

A study of 13 weeks exposure of rats and mice showed no harmful effects besides dose related decrease in body weight gain following administration of 138 mg Cu/kg bw/day for rats and 1000 mg Cu/kg bw/day for mice. NOAEL was 17 mg Cu/kg bw/day for rats and 44 and 126 mg Cu/kg bw/day for male and female mice, respectively. The effects included inflammation of liver and degeneration of kidney epithelium (Hébert *et al.* 1993).

In a reproduction study on rats the effect level for effects on testicles, semen quality, etc. was studied. NOAEL was set to 8000 mg copper sulphate/kg diet corresponding to 140 mg Cu/kg bw/day for males and 134 mg Cu/kg bw/day for females (Hébert *et al.* 1993).

Because copper is essential a ”window” exists between the necessary intake and the limit of toxicity: the acceptable range of oral intake (AROI). The lower limit for AROI is set to 20 µg Cu/kg bw/day for adults and 50 µg Cu/kg bw/day for children. The upper limit for AROI is not set but lies apparently around 2-3 mg/day based on studies of the gastro-intestinal tract following intake of copper contaminated drinking water (IPCS 1998, WHO 2004c).

Effects following inhalation of copper is not well studied. A study was available with exposure of rabbits to copper chloride for 6 hours/day, 5 days/week over 6 weeks. Based on effects to the respiratory and immune system a NOAEC was set to 0.6 mg Cu/m^3.

Effects following dermal exposure is insufficiently studied but effects have been reported such as contact dermatitis in patch tests using copper (Baars *et al.* 2001).

Threshold limit values
The threshold limit value for the working environment is 10 mg Cu/m^3 based on copper as powder and dust (AT 2002).

The C-value for copper as inorganic dust is 0.01 mg Cu/m^3 (Miljøstyrelsen 2002).

In the available data on acceptable daily intake/concentration, no distinction is made on which copper compound it concerns. The different forms are therefore considered as one in the following text.

Copper is mainly harmful if swallowed. The acceptable daily intake (TDI) is set to 0.14 mg/kg bw/day based on estimated maximum daily intake in the Dutch population (Vermeire *et al.* 1991, Baars *et al.* 2001).

The tolerable concentration in air by inhalation (TCA) is calculated to 1×10^{-3} mg/m^3. The value is based on a subacute rabbit study where NOAEC was recalculated to continuous exposure ($0.6 \times 6/24$ hours $\times$ 5/7 days) = 0.1 mg Cu/m^3. Applying a safety factor of 100 (for inter and intraspecies differences) the value is calculated to $0.1/100 = 1\times10^{-3}$ mg/m^3 = 1 µg Cu/m^3 (Baars *et al.* 2001).

WHO has suggested a preliminary TDI value of 0.5 mg/kg bw/day based on a study on dogs where a NOAEL of 5 mg/kg bw/day was found. Applying a safety factor of 10, which is chosen as copper is an essential metal (WHO 1996, 1998).

WHO has suggested a preliminary drinking water criteria value of 2 mg Cu/l (WHO 1996, 1998). The value is later set as established to 2 mg/l since several studies have demonstrated the level to be acceptable (WHO 2004c).

Absorption
Merian (1991) states that approx. 50% is absorbed in the gastro-intestinal tract. Apparently the absorption is inverse proportional to the concentration in the diet in a study from 1989 on 11 young men where an absorption was observed varying from 67% at 0.38 mg/day to 12% at 7.53 mg/day (WHO 2004c). The bioavailability by inhalation is determined to 50% and the bioavailability by oral intake is estimated to 50% (Baars *et al.* 2001).

Assessment
Exposure via inhalation is based on copper as a metal having a very low vapour pressure. The release from the use of textile colorants is therefore assumed very low and insignificant in relation to other sources of copper exposure in the indoor environment such as dust, food etc.

Dermal uptake is estimated assuming that 1% of the skin area is exposed to 5 g of the product 1 time/day. The absorption is set to 50%.

Oral uptake is assuming an exposure to 0.5 g product and absorption of 50%.

Table 31. Dermal and oral uptake, and total uptake

Prod.no.	Content in prod. mg/kg	Dermal uptake µg/kg bw/day	Oral uptake µg/kg bw/day	Total uptake (inhalation + dermal + oral) µg/kg bw/day
1	2400	0.600	30.0	30.60
2	170	0.043	2.125	2.17
3	38	0.010	0.475	0.48
12	54	0.014	0.675	0.69

Based on a NOAEL of 17 mg/kg bw/day the margin of safety (MOS) for total uptake is at least 17/0.0306 = 556.

The estimated uptake does exceed the Dutch TDI value of 0.14 mg/kg bw/day. The distance is at least a factor 4.6.

Using the WHO guideline value for drinking water of 2 mg/l it can be recalculated assuming an intake of 2 l/day and a weight of 70 kg and an absorption of 50% to: $2 \times 2/70 \times 0.5 = 0.12$ mg/kg bw/day. This value is close to the Dutch value.

The WHO temporary TDI of 0.5 mg/kg bw/day is not exceeded. The distance is at least a factor of 16.

However, it should be noted that other sources to copper exposure also exist from the environment and in food. This means that during the exposure period (the use period of the textile colorant product) exceeding of an acceptable daily intake of copper may occur. As copper contained in the body apparently is relatively constant indicating that copper relatively fast is excreted and not accumulated in the body an exceeding of short duration are considered acceptable.

Conclusion
The products' content of copper is assessed not to pose a health risk to the consumer of the examined textile colorants.

4 Conclusion

From the substances that were identified in the survey report (Miljøstyrelsen 2004) a number was selected for further evaluation of a potential health risk to the consumers based on classification and frequency. The consumers are in this context defined as children at the age around 7-8 years with a body weight of 20 kg.

The table below summarises the results of the assessment of the individual substances and the determined concentrations.

Table 32. Summary of conclusions

Chemical substance	Measured concentrations in products	Total uptake (inh+derm+oral) µg/kg bw/day	Reference value mg/kg bw/day	MOS	Conclusion
1-Butanol	Detected in 6 samples. The concentrations were between 77 and 690 mg/kg	2.2 - 19.9	NOAEL: 125 RfD: 0.5	>6280	No health risk from any of the samples.
Caprolactam	Detected in 1 sample. The concentration was 1100 mg/kg	30.3	NOAEL: 50	1650	No health risk from the sample.
1,4-Dichlorobenzene	Detected in 1 sample. The concentration was 9.9 mg/kg	0.28	NOAEL: 10 ADI: 0.107	35710	No health risk from the sample. (NB carcinogenic)
Diethylene glycol	Detected in 2 samples. The concentrations were 6200 and 53000 mg/kg	170 and 1457	NOAEL: 64	>43	No health risk from any of the samples.
Diisopropylene glycol	Detected in 6 samples. The concentrations were between 390 and 5100 mg/kg	11 – 140	NOAEL: - (used analogous NOAEL: 64)	>456	No health risk from any of the samples.
1,4-Dioxane	Detected in 2 samples. The concentrations were 4.7 and 11 mg/kg	0.13 and 0.30	NOAEL: 10	>33000	No health risk from any of the samples. (NB carcinogenic)
Glycerine	Detected in 2 samples. The concentrations were 11000 and 27000 mg/kg	303 and 743	NOAEL: 5000	>6730	No health risk from any of the samples.
Hexamethylentetramine (=methenamine)	Detected in 6 samples. The concentrations were between 11 and 860 mg/kg	0.3 – 24	NOAEL: 27	>1125	No health risk from any of the samples.
Isobutane	Detected in 2 samples. The concentrations were 2000 and 3500 mg/kg	871 and 1525	NOAEL: - est. NOAEL: 7.3	- 4.8	No health risks from any of the samples if short term exposure and ventilation is presumed.
3-Isocyanatomethyl-3,5,5-trimethyl-cyclohexyl isocyanate (IPDI)	Detected in 1 saple. The concentration was 270 mg/kg	7.4	est. NOAEL 0.021	2.8	No health risks if short term exposure and ventilation is presumed. (NB allergenic)
N-Methyl-2-pyrrolidone	Detected in 1 sample. The concentration was 740 mg/kg	20.4	NOAEL: 169 TDI: 0.6	8250	No health risk from the sample.

Chemical substance	Measured concentrations in products	Total uptake (inh+derm+oral) µg/kg bw/day	Reference value mg/kg bw/day	MOS	Conclusion
2-Phenoxyethanol	Detected in 2 samples. The concentrations were 460 and 4900 mg/kg	12.7 and 135	NOAEL: 200	>1480	No health risk from any of the samples.
Propylene glycol	Detected in 5 samples. The concentrations were between 36 and 7100 mg/kg	1.0 – 195	NOAEL: 1300 ADI: 25	>6650	No health risk from any of the samples.
Antimony	Detected in 3 samples. The concentrations were between 64 and 84 mg/kg	0.18 – 0.23	LOAEL: 0.43 NOAEL: 6	>1860 >26000	No health risk from any of the samples. (NB antimony trioxide carcinogenic)
Copper	Detected in 4 samples. The concentrations were between 38 and 2400 mg/kg	0.5 – 30.6	NOAEL: 17 TDI: 0.43	>556	No health risk from any of the samples.

In spite of none of the identified substances could be assessed to pose an immediate health risk to the consumer it should be pointed out that the classification of some of the identified substances was of a serious character.

In the screening of the classification was found that out of the 63 identified chemical substances 28 substances were classified in the List of dangerous substances and 5 could be classified according to the Danish Environmental Protection Agency's Advisory list for self-classification. One substance was classified Carc.cat.1 (May cause cancer), 5 substances were classified Carc.cat.3;R40 (Limited evidence of carcinogenic effects), and 1 substance was classified mutagenic Mut.cat.2;R46 (May cause heritable genetic damage). Three substances were classified R42 and/or R43 (May cause sensitization by inhalation and/or by skin contact), and further 2 substances were in the same category according to the Danish EPA's Advisory list for self-classification. In total 13 organic substances were selected for a further health assessment.

Selected products were further analysed for 3 metals of which 2 were found at concentrations above the detection limit. The two substances (antimony and copper) were selected for further evaluation.

The health assessment is performed based on realistic "worst case" scenarios according to the methods developed by EU for risk assessment of chemical substances. This means that relevant levels were identified at which no adverse health effects are expected (NOAEL: no observed adverse effect level) or an established threshold limit value for uptake. This value was then compared with the estimated concentrations or uptakes in the selected scenarios.

In the scenarios, an assessment was performed based on exposure via inhalation of volatile substances during the use of textile colorants, by dermal contact if the consumer gets his hands contaminated or is exposed by an equal amount from the dyed textile. Further, a scenario is included for oral exposure based on mouthing of fingers, product or dyed textiles. The latter may hardly be avoided if the family includes toddlers.

Two of the evaluated substances (1,4-dichlorobenzene and 1,4-dioxane) are classified carcinogenic category 3 (R40 Limited evidence of carcinogenic effect). Both substances have been assessed in the EU risk assessment programme. The reports indicate a threshold to carcinogenic effects. Thus at the determined levels the substance may not be of significance but the manufacturer and the consumer perhaps should consider alternatives.

Antimony trioxide has the same classification. The EU risk assessment is not finalised and whether it actually is antimony trioxide or another antimony compound that is contained in the products is unknown.

The product containing 3-isocyanatomethyl-3,5,5-trimethyl-cyclohexyl isocyanate is assessed not to pose an immediate health risk to the consumer of the studied textile colorant. However, the MOS is low indicating a potential health concern and prolonged exposure should be avoided with products containing this substance. It should be noted also that the substance may be allergenic (may cause sensitisation by skin contact and by inhalation). Heating of the colorants should be performed under forced ventilation.

Products containing isobutane also had a very low margin of safety (MOS) indicating a potential health concern. Prolonged exposure should be avoided with products containing this substance. Use of products containing the substance should be performed under aeration or ventilation.

Substances classified as irritants were detected at concentrations below the reported irritating concentrations.

The conclusion of the project is that none of the evaluated chemical substances would cause any immediate adverse health effects to the consumer at the estimated exposure levels by inhalation, dermal or oral contact.

The assessments are in most cases performed by comparing data from long-term studies or even chronic data. As the exposure to textile colorants must be assumed to be actually within shorter periods the conclusions should be acceptable.

However, it should be noted that the consumer is exposed to more than one of the substances simultaneously. Because the effect levels used in the evaluation are based on varying effects they can not be added. Further the consumer may be exposed to the same substances form other sources, e.g. other products, environment or food, which could result in a total exposure above the no-effect levels or tolerable daily intake values. Especially exposure to substances with low margins of safety (low MOS values e.g. isobutane and 3-isocyanatomethyl-3,5,5-trimethyl-cyclohexyl isocyanate) may be critical.

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