DANISH MINISTRY
OF THE ENVIRONMENT
Environmental
Protection Agency

Survey of chemical substances in textile colorants

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Survey of Chemical Substances in Consumer Products, No. 58 2005

The Danish Environmental Protection Agency will, when opportunity offers, publish reports and contributions relating to environmental research and development projects financed via the Danish EPA.

Please note that publication does not signify that the contents of the reports necessarily reflect the views of the Danish EPA.

The reports are, however, published because the Danish EPA finds that the studies represent a valuable contribution to the debate on environmental policy in Denmark.

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Introduction

There is an increasing focus on the chemistry surrounding us. Compounds containing unwanted effects have been identified in commonly used products in several studies. Thus the Danish Environmental Protection Agency has instigated a programme for mapping of chemical compounds in consumer products – including mapping and test of chemical compounds in textile dyes for hobby use.

There are a number of products for decoration and dyeing of textiles for hobby use - fabric colours, colours for e.g. silk printing and batik dyeing, pens, and colour pens for textiles. There is a potential risk of skin contact both at application and following use. In case of volatile compound presence there is a potential risk of breathing at application and following drying. Following wash may imply that the compounds are emitted into the environment. Some compounds can mean an increased consumer environmental strain.

The purpose of the project is to identify the chemical compounds used in textile dyes at dyeing and decoration of household textiles. Furthermore, the project is supposed to identify the extent of private consumers or institutional use of textile dyes enabling an assessment of a potential risk based on the results of this project.

Summary

Textile dyes can be divided into decoration dyes and products for textile dying of which 80% of the total consumption is composed of the latter. The group of decoration dyes includes products as felt-tip pens, pop-up dyes, and transfer dyes. The group of products for textile dying includes textile paint intended for dying or covering textiles in larger proportions. The annual Danish consumption is approximately 30,000 kg. A total of 42 products were identified at the mapping process.

15 products were taken for the initial analyses consisting of X-ray analyses for metals and analyses for volatile compounds. The X-ray analysis detected cupper, antimony, and a single detection of lead in the products.

A specific analysis for cupper, antimony, and lead was performed on the products with metal detection at the X-ray analysis. The level for antimony was 64-84 mg/kg detected in three products and cupper detected levels between 38-2400 mg/kg likewise detected in three products. Lead was not detected above the limit of detection.

Five products were taken for azo-dye analysis. Aromatic amines could not be detected indicating that the products contained no prohibited azo dyes.

The qualitative analysis for volatile compounds detected several glycols and solvents.

The content analysis indicated more glycol compounds in levels from 36 mg/kg to 53,000 mg/kg. Furthermore, other types of solvents as e.g. alcohols were detected in levels from 150 mg/kg to 1300 mg/kg.

1 Mapping

1.1 Definition

In this context textile dyes for hobby use are defined as products used for dyeing and decoration of textiles and textile surfaces not meant for industrial use.

1.2 Purpose

The purpose of this mapping is to identify the textile products sold in Denmark, and the amount to which these products are sold to institutions and private purposes.

1.3 Procedure

The following activities are included in order to map the suppliers of textile dyes in the Danish market:

- Visits to retail
- Contact to trade unions
- Internet search
- Contact to municipalities and institutions

The retail was contacted in order to contact the textile dyes used on the Danish market for hobby use– including Dansk Supermarked (Føtex and A-Z), COOP (Kvikly Xtra), Søstrene Grene, Panduro Hobby, and Stof & Stil.

Members of the Danish Joint Council for Creative and Hobby Materials (FFFH), a union of manufacturers, importers, and distributors of hobby materials in Denmark, have been contacted in writing followed by telephone follow-up if the written inquiry did not result in useable information. Today Joint Council consists of 25 companies equally distributed between manufacturer, importers, and distributors. The members employed with textile dyes are stated as: A.V. Form A/S, Brio A/S BB Institutionssalg, Creative Company, Vestergaard A/S, Nordform, Panduro Hobby A/S, Pébéo Color Scandinavia ApS, and Schjerning's Farver A/S.

The Internet was used to search for further suppliers of textile dyes, however, it did not lead to more suppliers. This was further supplemented with a small survey of textile dye purchase used in textile and design schools, the Danish Design School, and TEKO and local bodies. Thus five larger municipalities were contacted. Please note that this is only a minor test and not a sufficient analysis of the municipalities purchase patterns. Three municipalities could inform that they used a common purchase system for all local schools, bodies etc., which indicates that the municipality has contracted with one or more suppliers to provide all hobby material. Two municipalities informed that they had not contracted to buy hobby material. The National Procurement Ltd. Denmark informed that they had no contract for purchase of hobby material. Contacting the municipalities and purchase bodies provided no further suppliers of textile dyes.

All mapped products are sold both privately and institutionally. Apart from the fact that dyes for hand and machine dying are primarily used in households there are no significant differences on the type of products used in households and institutions.

The mapping provided a total of 42 products mostly sold in different colours. The main part is produced in Denmark, France, Germany, United Kingdom, and the Far East. Based on information regarding production amounts and assessments from FFFH it is estimated that a total of 30,000 kg textile dye products were sold in Denmark for hobby use in 2002. Approximately 80% of the products are sold through FFFH's members.

It proved impossible to gather information on constituents for eleven products within the projects time limit, which means that we were unable to collect the necessary information from the companies within the given time and resource limits. Generally this applies to products from non-member suppliers.

1.4 Products

The test resulted in a division of textile dyes in two main groups:

- Decoration dyes
- Products for dyeing

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

The stated amount distributions mentioned in sections 1.4.1 and 1.4.2 are based on an estimate from the prevailing information on produced amounts to the Danish market and assessments from FFFH.

1.4.1 Decoration dyes

This group includes products meant for decoration of materials. The products are used on limited areas and thus in limited amounts. It is thus assessed that the consumption within this group constitutes less than 20% of the total consumption of textile dyes.

1.4.1.1 Felt-tip pens

The products include pens with felt-tip (also known as textile markers). Felt-tip pens are especially suited for decoration on T-shirts and cotton. Different tips are used to obtain different effects and various types of line thickness.

1.4.1.2 Pop-up colours

This group includes products that pop when heated. The colours are used as contour and minor motives.

1.4.1.3 Transfer colours

These colours are transferred from a subject of plastic to the textile under heat. The colour is painted onto the subject. When the colour dries up it forms a soft resistant film that is transferable to most textiles. When the motive is fixated it may be removed and replaced or stored for later use.

1.4.2 Products for dyeing of textiles

This group includes products meant for dyeing or painting of larger areas. 80% of the used textile dyes are assessed to be in this group.

1.4.2.1 Dye for hand and machine dyeing

The group includes products meant for dyeing/re-dyeing of piece goods and finish goods in washing machine or by hand dyeing. This group differs from the remaining groups because the products are mainly used in households. The number of products within this sub-group is limited.

1.4.2.2 Fabric dyes

This group includes liquid dye solutions for silk or fabric applied with pens, brush, or the likes. This sub-group is far the largest as regards the number of different products.

1.5 Labelling classifications

Products with the CE-label and with the Danish Joint Council for Creative and Hobby Materials' (http://www.fffh.dk/) own labels were found during the mapping. These products are sold to households as well as institutions.

1.5.1 CE Label

The CE label indicates whether the product complies with the European standard. The label is added by the manufacturer or the importer and implies that the product complies with the prevailing safety regulations attached to the product type in question in EU.

Products that may be used as toys or that are recommended for specific types of toys must comply with the toy safety regulations. These regulations are found in the "Regulation no 329 of 23rd May 1995 (http://www.fs.dk/uk/acts/uktoy.htm) on Safety Requirements for Toys and Products, which due to their Appearance could be mistaken for Food", and in the standards referred to in the regulation appendix 3. The regulations on chemicals properties are especially relevant for textile dyes. The regulations indicate that the product in use may not compose a health risk due to ingestion, inhalation, or contact to skin, mucous membranes, or eyes. The product may not contain dangerous compounds. Furthermore, there is a requirement to maximum bioavailability per day of different heavy metals according to CEN-standard no EN71-3 in the Danish directive concerning the security of toys appendix 3.

Two products are CE labelled among the registered textile dyes and one product quotes that the product complies with the regulations for toys according to the standard EN71-3.

1.5.2 The Danish Joint Council for Creative and Hobby Materials

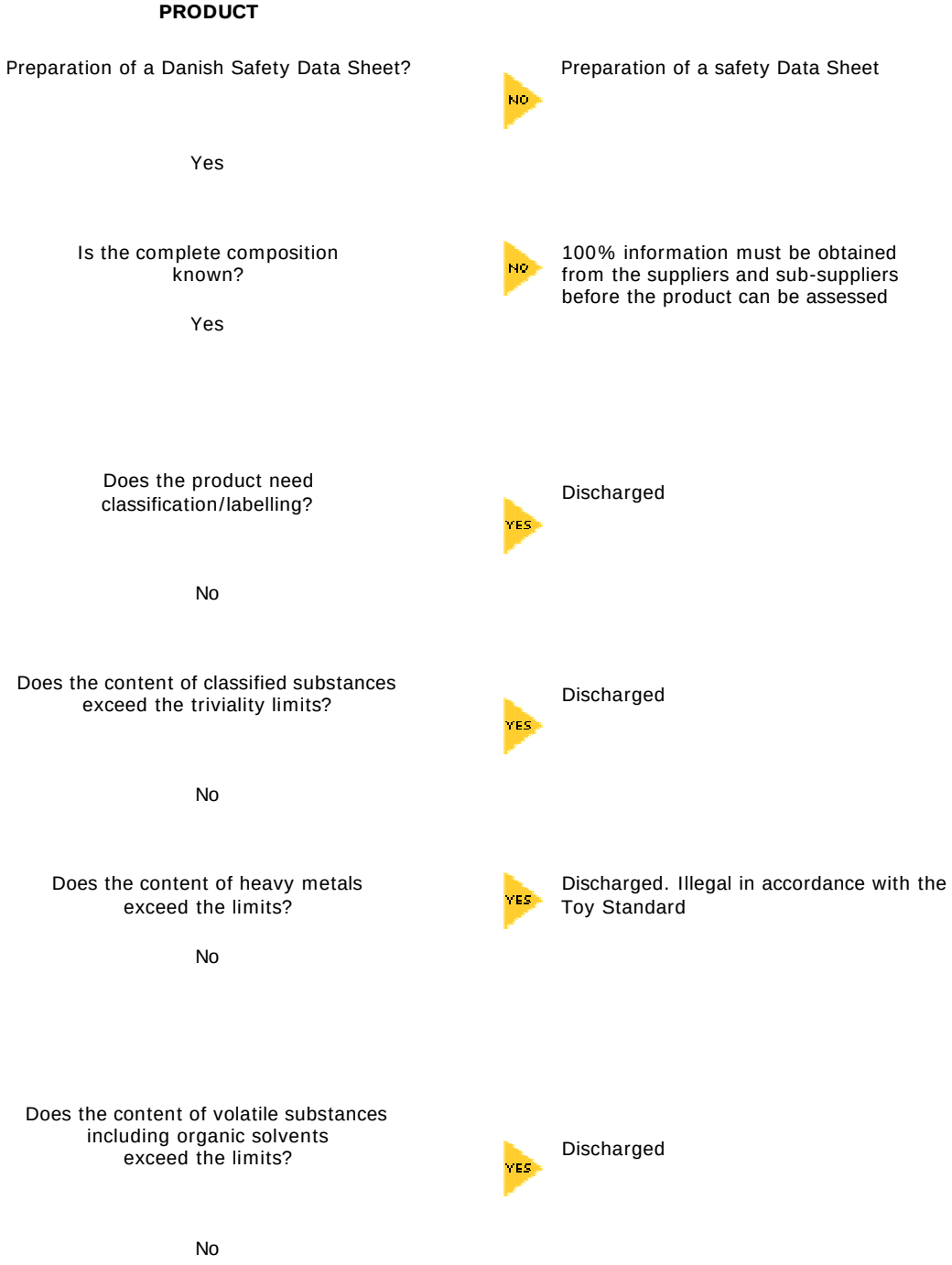
The Danish Joint Council for Creative and Hobby Materials (http://www.fffh.dk/) has prepared a number of requirements for creative and hobby materials to ensure that the materials contain no unwanted substances of environmental effect and thereby unnecessarily influencing children's health and well-being. Simultaneously, the requirements must ensure a solid foundation for assessment of the actual products. Among other things the requirement implies that every product must be accompanied by a Danish

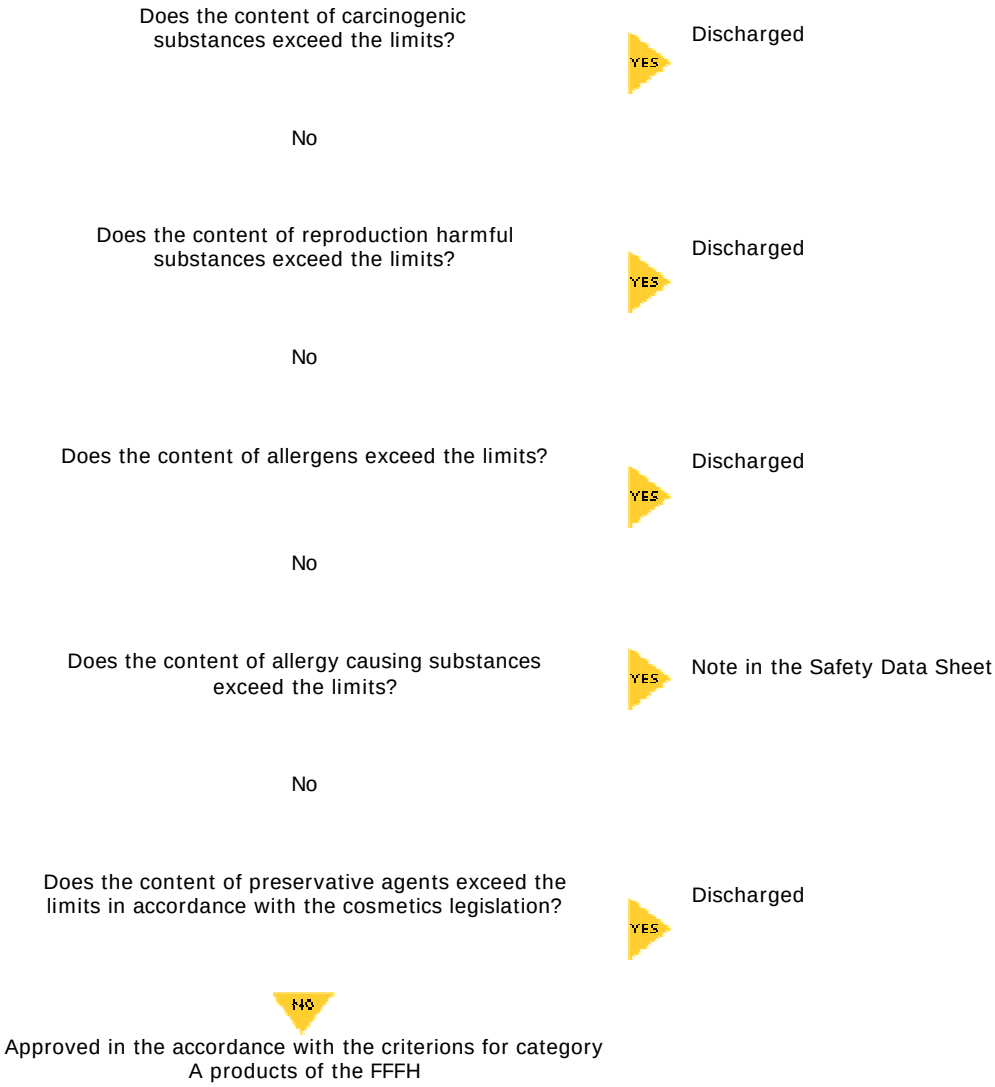
safety data sheet prepared in accordance to the Danish Working Environment Service's regulations (supplier manual).

The products are placed in one of four categories (A, B, C, or D). Category placement must be evident on shelves, in catalogues, and on other material.

1.5.2.1 Category A

Useable by children from 3 years of age. FFFH's regulations for group A products are more strict than Danish legislation prescribes. In order for products to enter into category A they must comply with the requirements listed below:




Does the content of carcinogenic substances exceed the limits?
YES
Discharged
No
Does the content of reproduction harmful substances exceed the limits?
YES
Discharged
No
Does the content of allergens exceed the limits?
YES
Discharged
No
Does the content of allergy causing substances exceed the limits?
YES
Note in the Safety Data Sheet
No
Does the content of preservative agents exceed the limits in accordance with the cosmetics legislation?
YES
Discharged
NO
Approved in the accordance with the criterions for category A products of the FFFH

1.5.2.2 Category B
May be used by children from age 3 under expert adult guidance. Very low content of dangerous compounds. The product complies with the requirements in the Danish Toy Regulation.

1.5.2.3 Category C
May not be used by children under age 15. The product does not comply with the requirements in the Danish Toy Regulation.

1.5.2.4 Category D
May only be used by adults. The products are deemed hazardous.

All mapped products are water-based with the exception of one. 24 products are said to be A-classified. The labelling appears on the safety data sheet and/or product information. Four products are informed to be C-classified and one D-classified product. One silk colour is classified as C due to content of ethanol and diethylene glycol. A diluent for this dye is classified as D due to ethanol and butyldiglycol content.

Further two finish products are classified as C (glitter enamel) applied to the textile dyes as final stage (however, not as a necessary part of the process) and a glue agent sold as accessories to textile dye products.

Additionally two products are classified as injurious to health (Xn) and causing local irritation (Xi) respectively, thus they will be classified according to category D following the Danish Joint Council for Creative and Hobby Materials regulations on dye products for hand and machine dye.

The remaining products are insufficient as regards information (see 1.3).

1.6 Constituents

Generally speaking there are four basic components in a typical dye product:

1. Adhesives
2. Solvents
3. Pigments
4. Additives

1.6.1.1 Adhesives
The adhesives is purposed to adhere the dye to the base. It is small polymers (acryl and urethane adhesives for pigment dyeing) in an aqueous suspension (dispersion). Typical use is 3-5 monomers to one products e.g. butyl acrylate and vinyl acetate. The content of residual monomers varies from 0.001% to 0.1%. The products' content of adhesives varies a lot. In the study at hand the products have an adhesive content from approximately 15-98%.

1.6.1.2 Solvents
The solvent must keep the adhesive and the pigment liquid and provide the product with the correct texture. It must evaporate under drying making the colour stable. The solvent in products as textile dyes for hobby use will typically be water. The concentration of the solvent will vary for the single product types. The content varies from 20% to more than 80% in the study in question.

1.6.1.3 Pigments

White pigments such as e.g. titan dioxide and calcium carbonate are often used for filler where the toned pigment provides colour to the product if other than white. There are natural inorganic pigments such as ochre, graphite, and umber together with synthetic inorganic pigments as titan dioxide, zinc oxide, and lead chromate. The pigments are generally insoluble for which reason most colours are suspensions. Organic pigments/dyes are also found in its natural state as e.g. indigo and chlorophyll or as synthetic produced dyes as azo, anthrachinon, and acridin pigments/dyes.

The reactive dyes are especially suitable for cellulose fibres, e.g. cotton where the dye forms a covalent linkage (chemical linkage) to the cellulose fibres. The pigments are insoluble in water and fixed to the fibre surface by means of a binding agent that surrounds the pigment particles and adheres them the fibre surface. Acid dyes are especially suitable for wool dyeing where the acid dye's reactive group (sulphon acid group) is tied to the wool's amino groups.

The content of pigments and dyes in the dye products depends on the shade. Light shades contain minor amounts of pigments and dyes than dark shades. The content varies from <5% to more than 65% in the present study.

1.6.1.4 Additives

There are several types of additives. Solvents will often be added as film formation that ensures that the film merges. This may be compounds as butyl glycol and solvent naphtha (rapid evaporation) or propylene glycol and butyldiglycol that is more slowly evaporating. The content of film formation will typically be on a level from few percents to more than 10% depending on how shinny the surface is.

Preservative agents must reduce the risk of bacterial and fungus growth. It is often a mix of isothiazolons.

Surface active compounds as tensides, phosphates, and silicones may be added to stabilise the additive dispersion and humidify pigments and surfaces. Some colour products are added softener agents as e.g. phthalates to make the dry product more flexible, whereas other products are softened at polymer construction.

The formation of certain polymer systems occurs under presence of a hardener – typically an amine-compound.

Finally the water-based products may contain *surface-active agents* often high-boiling polar compounds as e.g. glycols to reduce the surface tension.

1.6.2 Constituents in products

The main part of the mapped products is water-soluble and therefore required classified according to the Danish Environmental Protection Agency's labelling regulations. However, there is a frequent content of compounds listed in the Statutory Order no 439 of 3 June 2002, "The list of dangerous substances", however, in minor amounts requiring no labelling.

The main part of the textile dyes are based on reactive colour dyes and pigments – a few are on acid colour dyes.

The study has mapped the use of the following preservative agents: 5-chlor-2-methyl-4-isothiazolin-3-on/2-methyl-4-isothiazolin-3-on (CMI/MI), phenoxyethanol, and parabens. Preservative agents are added in amounts ranging from 9 up to 2000 ppm.

Single products are solvent-based applying solvents as ethanol, diethylene glycol, and 2-amino-2-methylpropanol.

1.6.3 Selection of products and analyses

15 products were selected in co-operation with the Danish Environmental Protection Agency from the view of including products from the different product groups (section 1.4), Danish and foreign goods, products from different sales areas (mail order, specialist shops, and supermarkets), and products sold in large amounts.

The principle used for analyses selection is an initial qualitative screening of a larger number of products. A qualitative analysis is performed on selected products based on the analytical results. The initial qualitative analyses include X-ray analysis for metals and GC/MS screening analysis for volatile and semi-volatile compounds.

The quantitative analyses were selected from experience with dyes. The most critical chemical compounds were expected to be on the following compound list:

- Organic solvents (solvents)
- Heavy metals (pigments)
- Azo compounds (dyes)
- Amines (impurities from azo dye production)
- Phthalates and adipates (softener and fixation agents)
- Biocides (preservative agents)

The GC/MS screening for content of extractable organic compounds will include solvents, phthalates, and adipates and a part of preservative agents and amines. The ICP analysis for metals will include the selected metals. An analysis for aromatic amines will detect a potential presence of prohibited azo dyes.

The table states the preformed analyses for each product.

Table 1 Products selected for further analysis

Product no	Product group	Water based	Metals	Volatile and semi-volatile compounds	Azo dyes	Volatile and semi-volatile compounds	Selected metals
			Qualitative screening	Qualitative screening	Quantitative	Quantitative screening	Quantitative
1	Felt-tip pen	X	x	x	x	x	x
2	Felt-tip pen	X	x	x			x
3	Felt-tip pen	X	x	x			x
4	Pop-up dye	X	x	x	x	x	
5	Pop-up dye	X	x	x		x	
6	Transfer dye	X	x	x			
7	Transfer dye	X	x	x		x	
8	Machine dye	X	x	x			
9	Fabric dye	X	x	x		x	
10	Fabric dye	X	x	x	x	x	
11	Fabric dye	X	x	x	x		
12	Fabric dye	X	x	x	x	x	x
13	Fabric dye	X	x	x			
14	Fabric dye	X	x	x			x
15	Fabric dye	X	x	x			

The products selected for analyses for specific metals and the quantitative screening are based on the results from the initial screenings.

The products for analyses for azo dyes are selected based on criteria to represent different manufacturers (five different) and product groups (three different). Moreover, the Danish Environmental Protection Agency has requested red or blue shades.

2 Analytical methods

2.1 Sample preparation

The samples consisted of pens, liquid products, and powder products.

The liquid and powder products are weighed and used directly. The cartridge was removed from the pens used as sample. The content in the colour mixture will therefore be significantly larger than in the cartridge.

2.2 Qualitative determination of volatile and semi-volatile compounds (GC/MS screening)

1 g sample was weighed in a 50 ml membrane glass. The sample was incubated in heat cupboard at 50°C ± 2°C for 2 hours. A part sample of the gas phase was injected directly and analysed at gas chromatography with mass spectrometric detection (GC/MS). Identified components were identified using a NIST library over mass spectra and manual evaluation of the spectra. The content of the identified components are quantified relative, thus a release of 1-4 crosses indicate the amount of the components in the products. The semi-quantitative release of the content refers to the amount of the component in the product and not in the gas phase. Uncertainty: 15-20% RSD. Estimated limit of detection: 10-50 mg/kg.

2.3 Qualitative determination of metals (X-ray)

A part sample of the products was tested at X-ray technique for content of all metals. Uncertainty: 10% RSD. Limit of detection: 5-10 mg/kg.

2.4 Quantitative determination of metals (ICP)

Approximately 0.25 g sample was opened with sulphuric acid and nitric acid in microwave oven with increasing effect from 250 W to 650 W during 34 minutes. The extract was filtered and the dissolved metals were determined accordingly at Inductively Coupled Plasma (ICP).

Uncertainty: 10% RSD. Limit of detection: 1-2 mg/kg.

2.5 Quantitative determination of volatile and semi-volatile compounds (GC/MS screening)

A part sample of the product is extracted with dichloromethane added internal standards. The mixture is shaken for 2 hours and left for approximately 16 hours. In order to detect the very volatile compounds an extraction of a part sample with demethyl formamide was performed. Equally the mixture was shaken for 2 hours and left for approximately 16 hours. A part sample of the extracts were taken and analysed directly at combined gas chromatography and mass spectrometry (GC/MS) by scanning over a larger mass area. The determined components were identified using NIST library over mass spectra and manual evaluation of the spectra. The uncertain components in the identification are stated with * in the table and the components that were solely identified to a group are stated with a group designation. Finally the components that were not identified are stated under unidentified.

The content of the components determined at the qualitative analysis for volatile compounds (section 2.2) was calculated quantitatively to external standards if possible. The other determined components were calculated semi-quantitatively to internal standards.

Uncertainty for components calculated quantitatively (external standard) is 15-20% RSD, and 50-200% for components calculated semi-quantitatively (internal standard). The reporting limit: 10-50 mg/kg.

2.6 Quantitative determination of azo dyes

The products selected for azo dye analysis were all in the red or blue shades.

The samples are extracted with an aqueous buffer and reduced with dithionite, where the amine part is split of the azo dye.

The reaction products are extracted with t-Butylmethylether followed by analysis using high liquid chromatography with Diode-Array Detection (HPLC/DAD).

The analysis includes the following aromatic amines:
2,4-Diaminoanisol, 2,4-Toluylenediamine, o-Toluidine, 4,4-Oxydianiline, Benzidine, p-Chloraniline, p-Cresidine, 4,4'-Methylenedianiline, 2-Naphthylamine, 4,4-Thiodianiline, 3,3-Dimethoxybenzidine, 4-Chlor-o-toluidine, 2,4,5-Trimethylaniline, 3,3-Dimethylbenzidine (= o-Tolidine), 3,3-Dimethyl-4,4-diaminodiphenyl methane, 4-Aminodiphenyl, 3,3-Dichlorobenzidine, and 4,4-Methylene-bis(2-chlor-aniline)

Limit of detection: 30 mg/kg. Uncertainty: 15%RSD.

3 Results

3.1 Qualitative determination of metals (X-ray)

The results of the X-ray analyses are given in table 1. The analyses solely include metals with mass from element 19 (potassium). The metals not included in the table could not be determined at the analysis. All results are given with a number of + corresponding to the determined amount of metal in the product:

+	trace amounts (more than 5-10 mg/kg)
++	minor amounts
+++	moderate amounts
++++	large amounts.

Table 2 Results of the X-ray analyses. The results are given with a number of + for the amount of determined metal.

	1	2	3	4	5	6	7	8
Potassium	++	++	+	-	-	+	-	++
Calcium	++	++	++	-	+	++	++	++
Titanium	+++	+++	+++	-	++	-	++++	-
Iron	-	-	-	-	-	++	-	++
Copper	+++	++	++	-	-	-	-	-
Zinc	+	-	-	-	-	-	-	-
Strontium	-	-	-	-	-	-	-	-
Antimony	++	++	++	-	-	-	-	-
Lead	-	-	-	-	-	-	-	-

	9	10	11	12	13	14	15	
Potassium	-	-	-	++++	++	-	-	
Calcium	++	++	++	+	++++	-	++	
Titanium	-	-	-	++++	++	-	++++	
Iron	++	-	-	++	++	-	-	
Copper	-	-	-	++	-	-	-	
Zinc	-	-	-	-	-	-	+++	
Strontium	-	-	-	-	++	-	-	
Antimony	-	-	-	-	-	-	-	
Lead	-	-	-	-	-	+	-	

Previously metals such as cadmium, chromium, and lead could occur in colour products. Cadmium and chromium were not determined in the analyses and lead was only determined in one product.

The determined titanium in two products could e.g. be due to a content of titan dioxide applied as white pigment and filler. This also applies to calcium, which could be attributed to a content of calcium carbonate equally used as filler or white pigment.

Samples 1, 2, and 3 are all felt-tip pens. Sample 3 is analysed in one colour, whereas the results for samples 1 and 2 provide an average value for several colours. Subsequently during the project, samples 1 and 2 were analysed for more colours separately in order to identify a potential difference between the single colours. The colours that detected the largest content of cupper and lead were taken for further analysis at ICP (2.3).

The remaining products that contained copper, antimony, and lead were further analysed for these metals at ICP (2.3).

3.2 Qualitative determination of volatile and semi-volatile compounds (GC/MS screening)

The following pages provide the results of the semi-quantitative analyses for volatile and semi-volatile compounds. The number of crosses indicates the compound amount present in the product:

+	minor amounts
++	moderate amounts
+++	large amounts.

Table 3 Results of the headspace analyses. The results are semi-quantitative

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Acetaldehyde						+							+	++	
Acetone				+++	+++		++	+	++	++	+++	+++	++	+++	
Alkane mix incl. cyclohexanes	+++								++	++++	++++	++++			+++
C8-C9 alkanes	++	+												++	
C16 aromates								++							
C17 aromates								+++							
Butanal						++								+	
Butanamine							+								
1-Butanol	+++	++			++++	++	++		+++		+++	+++	+++	++	++
2-Butanol												+			
2-Butanon												+	+		
Butyric acid, butylester					++							++		++	
Butenal						++								+	
Butoxyethanol		++													
2-(2-Butoxyethoxy)-ethanol							++								
Butylacetate	++			++	++						+++	++	+		+
n-Butylether	++			+++	++						+++	++	++	++	
Butylpropanate	++			++	++						+++	++	++	++	
4-Cyanocyclohexene										++++					
Cyclopentanon															++
Dichloromethane								+							
Diethylphthalate			+++				++								
Dimethoxy methane										++					
1,4-Dioxane	+				++				++		+				
Di-tert-butyl peroxide														++	
Acetic acid								+		++					
Ethanol					+++		+		++			++	++		+
Ethylacetate	+													++	++
Ethylbenzene				++	+		++				++				
2-Ethyl-1-hexanol		++	++	++		+			++					+	

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
2-Ethylhexylacetate		++													
Heptanon												++			
Hexane		+													
Isopropylbenzene				+											
Kodaflex								++							
1-(2-Methoxy-1-methylethoxy), 2-propanol				++											
Methyl cyclopentane		+													
3-Methyl 4-heptanon												++			
Methylmetacrylate				+											
2-Methyl-1-propanol			++	+										+++	
2-Methyl-2-propanol				+++	+++		++		+++		+++	+++		+++	
n-Methyl-pyrrolidon							++								++
Methylstyrene	++														
2,2,4,6,6-Pentamethyl heptane															+++
Phenol	+					+		+					(+)		
2-Phenoxy-ethanol														+++	
Phthalic acid hydride															+
2-Propanol	++++	++													++
Propyl acetate														+	
Propylene glycol						+	+			++			++	+++	
Pyridine											+				
Styrene	+	++								++	++				
Texanol (isomer)		++											+++		
Texanol (isomer)		++											+++		
Triethylamins							+++								++
Trimethylsilanol															++
Trishydroxymethyl-propantrimeth-acrylats			+												
Xylene (all isomers)				++	++	++	++				++				

The screenings for volatile solvents indicate that the products contain a large and varying number of compounds.

The content of volatile solvents is dominating i.e. alcohols (e.g. ethanol, butanol, ethylhexanol, and methyl-propanoles), ketones (e.g. acetone), ether (e.g. n-butylether), ester (e.g. ethyl acetate and butylpropanate) and aliphatic and aromatic hydrocarbons (e.g. C_8-C_9 alkanes, xylene, and methylstyrene). These compounds are present in most products and it is characteristic that they are also present in the water-based products. The compounds may either be added to the product to optimise the solubility of one or more additives or it may be introduced with the products raw material (e.g. as a solvent).

There are a number of other – and less volatile – compounds in some of the products in moderate/large amounts. E.g. phthalates (e.g. diethyl-phthalate), high-boiling aromatic and aliphatic hydrocarbon (e.g. cyclohexane-derivatives, C_{16}-C_{17} aromates, and pentamethylheptane), alcoholes (e.g. phenoxy-ethanol), and 4-cyano-cyclohexene. The purpose of the presence of these compounds is varying and may be as surface active compounds preservative agents, dispersing agents etc.

3.3 Quantitative determination of metals (ICP)

The results of the specific metal analyses are given in table 4. All results are stated in mg/kg.

Table 4 Results of metal analyses. The results are stated in mg/kg.

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

LOD: Means the limit of detection
-: Means below the LOD
*: Means not analysed

As mentioned at the X-ray analysis the products have been analysed for antimony, cupper, and lead in products 1 and 2 that are both felt-tip pens. The analysis was performed on the dye with the largest amount of cupper and lead at the X-ray analysis. Thus the results in table 4 most likely provide the maximum content in the respective product series colour shades. The analysed dyes were dark blue for sample 1 and reddish brown for sample 2. Random colours have been analysed in the remaining products thus it has not been possible to establish whether the values represent the average values.

3.4 Quantitative determination of azo dyes

The analysis for azo dyes determines aromatic amines that have been segregated from the azo dyes. This analysis includes a total of 20 amines originating from the prohibited azo dyes.

The amines included in the analysis are as follows:

- 2,4-Diaminoanisol
- 2,4-Toluylenediamine
- o-Toluidine
- 4,4-Oxydianiline
- Benzidine
- p-Chloraniline
- p-Cresidine
- 4,4'-Methylendianiline
- 2-Naphthylamine
- 4,4-Thiodianiline
- 3,3-Dimethoxybenzidine
- 4-Chlor-o-toluidine
- 2,4,5-Trimethylaniline
- 3,3-Dimethylbenzidine (= o-Tolidin)
- 3,3-Dimethyl-4,4-diaminodiphenyl methane
- 4-Aminodiphenyl
- 3,3-Dichlorobenzidine
- 4,4-Methylene-bis(2-chlor-anilin)

The products 1, 4, 10, 11, and 12 were analysed for azo dyes. The selected products did not detect azo dyes above the limit of detection. The limit of detection is 30 mg/kg

3.5 Quantitative determination of volatile and semi-volatile compounds (GC/MS screening)

The following eight products were selected in co-operation with the Danish Environment Protection Agency for content analysis of extractable organic compounds (GC/MS screening). The below mentioned table provides the result of this analysis. The compounds marked with # are calculated to external standard (uncertainty 15-20% RSD), all other compounds are calculated to internal standard (uncertainty 50-200% RSD).

Table 5. Results of the GC/MS screening. The results are given in mg/kg.

	1	4	5	6	7	9	10	12
Acetone	-	45	-	-	-	-	-	25
Alcohol	-	-	150	-	-	-	-	-
Azacyclotridecan-2-on	-	-	-	-	51	-	-	-
Benzaldehyde	-	3.6	-	-	-	-	-	-
Benzene, 1,3-dimethyl	-	12	-	-	-	-	-	-
Benzene, 1,4-dichloro	9.9	-	-	-	-	-	-	-
Benzene, 2,4-diisocyanato-1-methyl	-	3.2	-	-	-	-	-	-
Benzenamine, 5-chloro-2,4-dimethoxy	-	20	-	-	-	.	-	-
Benzophenon	-	-	-	-	-	8,6	-	-
1-Butanol#	150	650	690	-	77	190	-	620
2-Butylamine	-	-	-	-	53	-	-	-
Butylated hydroxytoluene (BHT)	-	-	-	-	16	-	-	-
n-Butylether#	-	110	11	-	-	-	-	19
Caprolactame#	-	-	-	-	1100	-	-	-
2-Chloro-4-dimethylamino-6-t-butylpyrimidin	-	23	-	-	-	-	-	-
Cyanocyclohexene	-	-	-	-	-	-	110	-
1,3,5-Cycloheptatrien	-	6.5	-	-	-	-	-	-
Cyclohexane, 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethyl	-	-	-	-	270	-	-	-
Cyclohexanol, 4-(1,1-dimethylethyl)- (isomer compounds)	-	48	-	-	-	-	-	-
1,3-Cyclopentanedione, 2-ethyl	-	-	-	-	-	-	98	-
Cyclopropane, nonyl*	-	-	10	-	-	-	-	-
Diethylene glycol# (isomer compounds)	53000	-	6200	-	-	-	-	-
Diisopropylene glycol#	2300	-	5000	3100	5100	390	-	4900
4,4-Dimethyl oxazolidine*	-	-	-	-	-	200	150	-
1,4-Dioxane	11	-	-	-	-	4.7	-	-
Ethanol, 2-(2-butoxyethoxy)#	-	-	-	-	460	-	-	-
Ethanol, 2-(2-ethoxyethoxy)#	590	-	-	-	-	-	-	-
Ethanol, 2-phenoxy#	-	460	-	-	-	-	4900	-
Ethene, 1,2-dichloro	-	-	14	-	-	-	-	-
Ethylbenzene	-	19	-	-	-	-	-	-
Glycerine **	-	-	11000	27000	-	-	-	-
Hexa(methoxymethyl) melamine	-	-	-	-	-	-	73	67
Hexamethylene tetramine#	-	49	800	-	11	22	570	860
Hexanol, 2-ethyl	-	20	-	-	-	-	-	-
Hexanoic acid	-	4.1	-	-	-	-	-	-
Isobutane	-	3500	2000	-	-	-	-	-
Isopropyl alcohol	1300	-	-	-	-	-	-	-
Methylene chloride	-	-	62	-	130	-	-	-
7-Nitro-1,3,5-triazadamantan	-	-	53	-	-	-	-	-
Nonoic acid	-	-	14	-	-	-	-	-
Octanol, butyl	-	-	-	-	11	-	-	-

	1	4	5	6	7	9	10	12
Octane acid*	-	-	-	-	-	-	7.1	-
2-Oxepanon	-	6.4	-	-	-	-	-	-
Parabenes (sum)	-	-	-	-	-	-	600	-
Phthalate	9.8	-	5.2	-	-	7.8	-	-
2-Propanol, 1-(2-methoxy-1-methylethoxy) (isomer compounds)	-	220	-	-	-	-	190	180
2-Propanol, 1-(2-methoxypropoxy)	-	210	-	-	-	-	-	100
2-Propene acid, 2-methyl-, methyl ester	-	8.9	-	-	-	-	-	-
2-Pyrrolidione, 1-methyl#	-	-	-	-	740	-	-	-
Propane acid, butyl ester#	-	44	-	-	-	-	-	15
1-Propene-1.2.3-tricarboxylsyre, tributyl ester (isomer compounds)*	-	-	-	-	1500	-	-	-
Propylene glycol#	370	2300	36	-	3300	-	7100	-
Styrene	-	6.6	-	-	-	-	3.8	-
Sulfo succinic acid -bis-2-ethylhexyl ester	-	150	-	-	-	-	-	-
1,1,3,3 Tetramethylbutyl phenol	-	-	-	-	-	-	-	24
Tetrasiloxane, decamethyl	-	-	-	-	6.8	-	-	-
Tributyl acetyl citrate	-	29	-	-	-	-	-	-
Tributyl citrate (isomer compounds)	-	-	-	-	13000	-	-	-
Tributyl phosphate	-	-	-	-	-	-	-	63
Triethylamine#	-	-	-	-	2100	-	-	-
2,4,4-Trimethyloxazolidine*	-	-	-	-	-	28	24	-
Urea*	-	200	-	-	-	-	-	-
Sum of other grouped compounds:								
Alkanes	-	22	-	-	1600	7.3	8000	3900
Alkenes	-	-	14	-	-	-	18	150
Chloralkanes	-	-	34	-	4.2	-	190	-
Cykliske ether	-	26	-	-	-	-	-	-
Esters	-	8.9	-	-	-	-	-	-
Ether	11	-	-	-	-	8.5	-	-
Unidentified	75	-	-	3900	33	23	1100	1600

- Means not determined
* Indicates the best possible identification
** Overestimated due to interference from other peaks
\# Calculated to external standard

Several types of glycols were determined in the products as diisopropylene glycol, diethylene glycol, propylene glycol, 2-propanol, 2-(2-butoxyethoxy) ethanol, and 2-(2-ethoxyethoxy) ethanol. These glycols are typically used as solvents. Caprolactam is applicable as solvent for polymers.

Tributyl citrate can be used as softener in e.g. toner/pigments. Glycerine is used as solvent; however, it is also applicable as a surface-active agent, i.e. as a component able to retain water and thus prolonging the drying time. Hexamethylene tetramine is used as hardener in certain products.

Isobutane was determined in the two pop-up products.