DANISH MINISTRY
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Survey and health assessment of chemical substances in hobby products for children

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Danish Technological Institute

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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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Preface

The project ”Survey and health assessment of chemical substances in hobby products for children” was carried out from 15 March 2006 to 30 November 2006 by Danish Technological Institute (DTI), Materials Division, and this report presents the results of the survey.

Responsible project manager was Paul Lyck Hansen, who has also served as the contact person to the Danish Environmental Protection Agency (EPA).

Kathe Tønning held responsibility for the actual survey of the project and responsible for the laboratory analysis was Eva Jacobsen, Chemistry and Water Technology, with Head of Section Paul Lyck Hansen as quality controller.

M.Sc. Bjørn Malmgren-Hansen has been responsible for the health assessment (consumer exposure), risks and environmental impacts with cand.scient. Ole Chr. Hansen as quality controller. Further, Uffe Thomsen has assisted in the quality assurance of the health assessment.

The purpose of the project has been to elucidate the impact of any problematical substances detected in hobby products for children based on worst case scenarios.

The hobby products investigated in this project are marker pens, glitter glue, acrylic paint and shrink plastic

Summary and conclusion

Hobby products such as glue, paint, colours, marker pens and textiles are in the hands of children every day, but the marketing of these products is not specifically targeted at children, because these products are used in many other and different connections.

Therefore the products are not always manufactured with due consideration to the fact that children are more sensitive than adults to the effects of hazardous substances.

This survey focuses on the following hobby products:

- Marker pens
- Glitter glue
- Acrylic paint
- Shrink plastic

In the survey children are defined as persons up to an age of 14.

Survey activities

Our investigation activities are described below:

- ***Retailers***
  In total we went to 21 places of purchase, hereunder 3 hobby stores, 4 toy stores, 2 department stores, 3 supermarkets, 2 discount stores, 1 bookshop, 2 DIY centres, 1 museum shop, 1 post office, 1 paper store, and 1 wholesaler. The product selection was made in consultation with the shop assistants and the selection was based on the requirement that the products should appeal to children and should sell well. Subsequently, questionnaires were submitted to the contact persons.

- ***Web search***
  The shops searched over the internet were toys chain stores or similar, which had also physical shops. Further, more of the webshops had a product range within hobby materials which was primarily directed at professional users.

- ***Child care institutions***
  We have been in phone contact with a number of child care institutions (2 nurseries, 2 recreational clubs and 1 after school centre) to obtain information about what type of hobby products they were buying within the different product groups and how they handled their procurement.

- ***Art schools/art clubs for children***
  Phone contacts were established and subsequently questionnaires were submitted to a number of art schools/clubs.

- ***Catalogue search***
  Advertising matters and shopping catalogues for e.g. child care institutions were reviewed and questionnaires were submitted to relevant distributors and importers.

- ***Manufacturers and suppliers***
  Questionnaires have been submitted to totally 36 distributors and importers of marker pens, glitter glue, acrylic paint and shrink plastic.

- ***The Joint Council for Creative and Hobby Materials (FFFH)***
  The FFFH is an association of manufacturers, suppliers and distributors of hobby materials in Denmark. FFFH[1] reports that an increasing number of municipalities requests their child and juvenile institutions to use products which comply with the labelling guidelines of FFFH.
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Consumption of hobby products

Statistics Denmark was not able to provide consumption figures of the 4 product groups.

According to Statistics Denmark there were 1,015,879 children below 14 years in 2006 and it is presumed that most children were in daily contact with markers pens, whereas not nearly all children are users of the three other product groups (glitter glue, acrylic paints, and shrink plastic).

Chemical analysis

The analysis proved that more critical substances were likely to be volatile, organic components and it was therefore decided to focus on this substance group in the chemical screening and the subsequent quantitative analyses. In addition, X-ray analysis has been carried out for determination of inorganic components and NIR-analysis.

To obtain sufficient sensitivity with the applied analysis method and thus the lowest possible detection limit, it was decided to use gas chromatography combined with mass spectrometry as analysis principle.

Initially, a chemical screening was made in order to determine any volatile, organic substances present in the products. The initial screening detected more than 70-80 different organic substances. Around 50 of these were classified as being hazardous to health. In consultation with the EPA it was decided to quantify approx. 20 substances.

Tabel 0.1 shows the results of the quantitative analyses of the products with the highest content of the substances listed in the table.

Table 0.1 Selected results of the substances with the highest quantified content

Substance	Content in mg/g												
Sample no.	10	15	16	17	25	26	29	33	45	50	53	55	61
Aniline									0.22				
p-chloroaniline												0.37	
N-Methylaniline													
C.I Pigment Red 3													
N,N-Dimethylacetamide				0.4									
Bis(2-ethylhexyl)adipate	0.35												

[1] Telephone conversation on 9th August 2006 with Birger Schjerning; Schjerning Colours

Substance / Sample no.	Content in mg/g												
	10	15	16	17	25	26	29	33	45	50	53	55	61
p-Anisidine													
2-Ethoxyethanol					19								
Citral			0.7										
2-Ehylhexyl acrylate													0.35
Formaldehyde		59				46	13	63		110	9.5		

By a comparison of the quantitative analysis and the results of the chemical screenings it has been observed that the different colour types from the same product may contain different components.

Within the scope of this project it has not been possible to carry out analyses of all the colour variants in the analysed products and it is thus possible that more of the products may contain components with higher content of the identified substances than demonstrated in connection with the quantitative analyses. Likewise, there may be hazardous substances which have not been identified, because the relevant colour variant was not taken out for analysis.

Health assessment

When children work with marker pens, gel pens, glitter glue and acrylic paint skin contact and absorption through the skin is almost unavoidable. The substances may also be absorbed orally if children are sucking their fingers or are mouthing the objects. Exposure scenarios have been made for skin and oral absorption of marker and gel pens, glitter glue and acrylic paint assuming that ink/paint has been applied to the child's palms, corresponding to 50 cm^2 and a weight of the product corresponding to approximately 0.05 g marker pen, 1.25 g acrylic paint or 3 g glitter glue. It is assumed that the same amount can be taken in orally.

Tabel 0.2 lists the substances with long-term effects such as carcinogenic, mutagenic or reprotoxic effects (CMR) and allergenic substances.

The demonstrated health effects can be seen from Tabel 0.2.

Table 0.2 CMR and allergenic substances in marker pens, glitter glue, and acrylic paint

Substance	Allergenic	Reprotoxic	Carcinogenic	Mutagenic
Aniline	X		X (R40)	X
p-chloroaniline	X		X (R45)	
N-methyl aniline			X (possibly from related substances)	
C.I.Pigment Red 3			X (possibly from tests)	
N,N-dimethylacetamide		X (reproduction, child during pregnancy)		
Bis(2-ethylhexyl)adipate		X (teratogenic in rats)		
P-anisidine			X (possibly from related substances)	
2-Ethoxy ethanol		X (reproduction, child during pregnancy)		
Citral	X			
2-ethylhexyl Acrylate	X			
Formaldehyde	X		X (R40)	
0,m el p. chloroisocyanat benzene	X			
Phenol				X
N-methyl-p-anisidine	X		X	X

Substance	Allergenic	Reprotoxic	Carcinogenic	Mutagenic
Triethanolamine	X			
N-phenyl-2-pyridinamine	X			
D-limonene	X			
Benzyl alcohol	X			
2(3H)-furanone, 5butyldihydro-	X			

In total we detected:

- 12 allergenic substances
- 7 substances with possible or proved carcinogenic effect
- 3 substances with mutagenic effect
- 3 substances with reprotoxic effect

P-chloroaniline is for example carcinogenic at concentrations on 2 mg/kg/day in mice and rats, and the substance is classified as carcinogenic in category 2, as can cause cancer. The content of p-chloroaniline in the acrylic paint no. 55 is analysed to be 0.37 mg/g. The exposure via skin is estimated to be 0.031 mg/kg body weight/day when it is assumed that the uptake is 100 % and 1.25 g of paint is in contact with the skin. This gives a margin of safety on 65, and the margin of safety should in this case be 1000. This gives an unacceptable high exposure of p-chloroaniline , which effect both the risk of cancer and an effect on the red blood cells. P-chloroaninline can also cause sensitisation with contact to the skin. Acrylic paint no. 55 is no longer sold.

The pigment C.I, pigment red 3 has been found in acrylic paint no. 54 in the concentration 104 mg/g. Carcinogenic effects has been seen in 2 % of test animals (rats) at concentrations on 830 mg/kg and weight loss has also been seen in 10 % of the animals at this concentration. It has not been shown that these carcinogenic effects can be transferred to humans. The oral exposure can be estimated to be 8.7 mg/kg bodyweight, when it is assumed that 1.25 g of paint is taken in. This gives a margin of safety on 95 and a small risk.

The solvent 2-ethoxy ethanol is found in a pink and a red marker pen with product no. 25 in the concentrations 1.9 % and 0.74% respectively. The substance is classified as harmful to reproduction in category 2. The risk assessment shows that there is no risk when children are exposed to 0.05 g of the substance from a marker pen. The product is not legal, as it is not allowed to sell chemical substances and preparations with concentrations of CMR-substances higher classification limit. Marker pens are preparations since it contains ink, which is a preparation, and the purpose of the ink is to come out of the marker pen. The marker pens are not legal and are no longer sold.

The result is that hazardous substances have been found in 10 products, 5 being glitter glue products, 4 acrylic paint products and one gel pen. It should be noted that only a part quantity of the marker pens in each product has been analysed (one product is e.g. a packet with a number of marker pens in different colours).

The aroma pens contained the allergenic substances d-limonene, benzyl alcohol and citrale in concentrations of between 0.01 and 0.1 percentage weight

An estimate of maximum evaporation of formaldehyde in a small child's room shows that the formaldehyde content in 6 gram (approx. 6 ml) glitter glue will at the max contribute with up to 25 % of the recommended indoor climate

concentration in a child's room of the size 3 * 3 * 2 m. It is assessed that there are no health effects when glitter glue is used in a small room, but it is recommended that activities with larger amounts of glitter glue (several tubes) should not take place in small child's rooms with insufficient air renewal.

A wide range of the products contain substances classified as harmful to health, but only a small part of the products pose a risk, but both children and adult will be exposed to the substances from different sources. It is therefore disturbing that so many substances in the hobby products have these serious effects.

The following products did not contain CMR or allergenic substances.

Acrylic paint: nos. 7, 8, 9, 18, 34, 35, 36, 40, 41, 48, 49, 51, and 56
Marker pens: nos. 1, 11, 12, 22, 30, 31, 32, 39, 42, 43, 47, 62, 63, and 64
Gel pens: no. 4 and 44
Glitter glue: nos. 13, 14, 23, 28, 38, 53 – however, formaldehyde with concentrations < 0.01 mg/g has been detected in products nos. 13, 23, 28, 38, and 53

Legislation

The analysed products are covered by Statutory Order no. 329 on classification, packaging, labelling, sales, and storage of chemical products, 2002.

Hobby products for children are considered toys and are covered by Statutory Order on Toys no. 1116, 2003 if the Danish Safety Technology Authority estimate the products as toys. The Statutory Order refers to the standards DS/EN 71-1 - 71-7 with safety and health requirements to toys. An EU standard for organic substances, DS/EN 71-9, has been completed, but is not yet legally implemented. The products with the carcinogenic effect, primarily amines aniline, p-chloral-aniline and anisidine do not observe the requirements in the standard for organic substances DS/EN 71-9, as the substances may not be identified in coloured liquids from toys. The only risk identified is from p-chloroaniline.

Environmental assessment

The results of the environmental assessment show that liberation of the chemical substances through washed off residues of ink and paint from the children's hands does not represent a threat to the water environment.

Sammenfatning og konklusioner

Danske børn er dagligt i kontakt med en lang række forskellige hobbyprodukter som fx lim, maling, farver, tuscher og tekstiler. Disse produkter er sjældent målrettet specifikt til børn, da de kan anvendes i mange forskellige sammenhænge. Der er derfor heller ikke nødvendigvis taget hensyn til, at børn har andre forudsætninger end voksne med hensyn til eksponering for evt. sundhedsskadelige stoffer.

Der er i nærværende projekt fokuseret på følgende hobbyprodukter til børn:

- Tuschpenne
- Glimmerlim
- Akrylfarver
- Krympeplast

Børn er defineret som personer op til 14 år.

Kortlægning

I kortlægningen indgår følgende aktiviteter:

- ***Kontakt til detailhandel***
  I alt 21 butikker er besøgt; heraf 3 hobbyforretninger, 4 legetøjsforretninger, 2 stormagasiner, 3 supermarkeder, 2 discountbutikker, 1 boghandler, 2 byggemarkeder, 1 museumsshop, 1 posthus, 1 papirhandel og endelig 1 grossist. Valget af indkøbte produkter er foretaget i samråd med personalet i den pågældende butik, idet der er taget udgangspunkt i, at der skal være tale om produkter, der appellerer til børn, og produkter, der "sælger godt". Der er efterfølgende sendt spørgeskema til de besøgte forretninger.

- ***Søgning på internettet***
  De fundne internetbutikker er primært enten legetøjskæder eller lignende, der også har fysiske butikker, som er besøgt, eller internetbutikker, hvis produktsortiment henvender sig til professionelle bruger og ikke appellerer til børn.

- ***Kontakt til børneinstitutioner***
  Der har været rettet telefonisk kontakt til en række børneinstitutioner (2 børnehaver, 2 fritidsklubber og 1 fritidshjem) for at få oplyst, hvilke produkter de anvender inden for de enkelte produktgrupper, og hvorledes institutionerne foretager indkøb.

- ***Kontakt til kunstskoler/kunstklubber for børn***
  Der har været rettet telefonisk kontakt til en række kunstskoler/-klubber for børn, og der er efterfølgende sendt spørgeskema til en række af kunstskolerne/-klubberne.

- ***Søgning i kataloger***
  Reklamekataloger såvel som indkøbskataloger for fx børneinstitutioner er gennemset, og der er rettet henvendelse i form af spørgeskemaer til relevante forhandlere og importører.

- ***Kontakt til producenter og leverandører***
  Der er udsendt spørgeskema til i alt 36 forhandlere, producenter og importører af henholdsvis tuschpenne, glimmerlim, akrylfarver og krympeplast.

- ***Kontakt til Fællesrådet For Formnings- og Hobbymaterialer (FFFH)***
  FFFH er en forening af producenter, leverandører og forhandlere af hobbymaterialer i Danmark. FFFH oplyser, at et stadigt stigende antal kommuner har vedtaget, at der i deres børne- og ungeinstitutioner alene anvendes produkter, der er mærket efter FFFHs mærkningssystem.

Forbrug af hobbyprodukter til børn

Det har ikke været mulig at foretage en mængdemæssig opgørelse af forbruget af de 4 produktgrupper via Danmarks Statistik.

Ifølge Danmarks Statistik udgjorde antallet af børn under 14 år i 2006 1.015.879, og det må antages, at stort set alle disse børn/unge regelmæssigt er i kontakt med tuschpenne, mens det ikke nødvendigvis er alle børn, der anvender de øvrige 3 produktgrupper (glimmerlim, akrylfarver og krympeplast).

Kemiske analyser

Den udførte kortlægning viste, at det var overvejende sandsynligt, at de mest kritiske indholdsstoffer var flygtige, organiske komponenter, hvorfor det blev valgt i forbindelse med den udførte kemiske screening samt de efterfølgende kvantitative målinger at fokusere på denne stofgruppe. Derudover er der udført røntgenmålinger for indhold af uorganiske komponenter samt NIR-analyser.

For at opnå en tilstrækkelig følsomhed med den anvendte analysemetode og derigennem den lavest mulige detektionsgrænse, blev det valgt at anvende gaschromatografi kombineret med massespektrometri som analyseprincip.

Der blev først gennemført en kemisk screening med det formål at konstatere, hvilke flygtige, organiske stoffer der kunne måles i de undersøgte produkter. Ved den indledende screening blev der konstateret indhold af mere end 70-80 forskellige organiske stoffer. Omkring 50 af stofferne blev klassificeret med en mulig sundhedsskadelig effekt. Det blev i samråd med Miljøstyrelsen valgt at kvantificere ca. 20 stoffer.

I Tabel 0.1 ses resultaterne af de kvantitative analyser for de produkter, hvori der er konstateret det højeste indhold af de i tabellen nævnte stoffer.

Tabel 0.1 Udvalgte resultater for stofferne med de højeste kvantificerede indhold

Stof / Prøvenr.	Indhold i mg/g												
	10	15	16	17	25	26	29	33	45	50	53	55	61
Anilin									0,22				
p-Chloranilin												0,37	
N-Methylanilin													
C.I Pigment Red 3													
N,N-Dimethylacetamid				0,4									
Bis(2-ethylhexyl)adipat	0,35												
p-Anisin													
2-Ethoxyethanol					19								
Citral			0,7										
2-Ehylhexyl acrylat													0,35
Formaldehyd		59				46	13	63		110	9,5		

Der er i forbindelse med de udførte kvantitative målinger sammenholdt med målinger udført under den kemiske screening observeret, at de forskellige farvevarianter fra samme produkt kan indeholde forskellige komponenter.

Det har ikke været muligt inden for rammerne af dette projekt at foretage målinger af alle farvevarianter af de undersøgte produkter. Det kan således ikke udelukkes, at et eller flere af produkterne kan indeholde komponenter med større indhold af de identificerede stoffer end dokumenteret i forbindelse med de udførte kvantitative målinger, eller at der er sundhedsmæssigt problematiske stoffer, der ikke er blevet identificeret, idet den pågældende farvevariant ikke er blevet udvalgt til analyse.

Sundhedsvurdering

Tuschpenne, gelpenne, glimmerlim og akrylfarver vil, når børn benytter produkterne, i en vis udstrækning ende på huden, hvorfra stofferne kan blive optaget. Alternativt kan stofferne optages via munden, når børnene sutter på fingre, tuscher eller pensler. Der er opstillet eksponeringsscenarier for optag via hud og oralt via munden af tusch, gelpenne, glimmerlim og akrylmaling for børn og unge med udgangspunkt i, at to barnehåndflader bemales, hvilket svarer til 50 cm^2 og en vægt af produktet svarende til ca. 0,05 g tusch, 1,25 g akrylmaling eller 3 g glimmerlim. Det antages, at den samme mængde kan indtages oralt.

I de undersøgte produkter er der fundet en række sundhedsskadelige stoffer.

I Tabel 0.2 er vist stoffer med langtidseffekter i form af kræftfremkaldende, mutagene eller reproduktionsskadende effekter (CMR) samt allergene stoffer.

Tabel 0.2 CMR-stoffer og allergene stoffer i tuscher, glimmerlim og akrylfarver

Stof	Allergifrem-kaldende	Reprotoksiske effekter	Kræftfremkaldende effekter	Mutagene effekter
Anilin	X		X (R40)	X
p-chloranilin	X		X (R45)	
N-methyl anilin			X (muligvis ud fra beslægtede stoffer)	
C.I.Pigment Red 3			X (muligvis ud fra forsøg)	
N,N-dimethylacetamid		X (forplantning, barn under graviditet)		
Bis(2-ethylhexyl)adipat		X (teratogent i rotter)		
P-anisidin			X (muligvis ud fra beslægtede stoffer)	
2-Ethoxy ethanol		X (forplantning, barn under graviditet)		
Citral	X			
2-ethylhexyl acrylat	X			
Formaldehyd	X		X (R40)	
0,m el p. chloroisocyanat benzen	X			
Phenol				X
N-methyl-p-anisidin	X		X	X
Triethanolamin	X			
N-phenyl-2-pyridinamin	X			
D-limonen	X			
Benzyl alkohol	X			
2(3H)-furanone, 5butyldihydro-	X			

Samlet er der i produkterne fundet:

- 12 allergene stoffer
- 7 stoffer med mulig eller bevist kræftfremkaldende effekt
- 3 stoffer med mutagen effekt
- 3 stoffer med reprotoksisk effekt

P-chloranilin er bl.a. kræftfremkaldende ved en koncentration på 2 mg/kg/dag i mus og rotter, og stoffet er klassificeret som kræftfremkaldende i kategori 2, kan fremkalde kræft. I produkt nr. 55, som er en akrylmaling er indholdet af p-chloranilin målt til 0,37 mg/g. Eksponering via hud er beregnet til 0,031 mg/kg kropsvægt/dag med en antagelse om, at der optages 100 %, og 1,25 g af malingen kommer i kontakt med huden. Det giver en sikkerhedsmargin på 65, og denne bør i dette tilfælde ligge på 1000. Dvs. at der fra dette produkt er en uacceptabel høj udsættelse fra p-chloranilin, som både giver en risiko for kræft og effekt på røde blodlegemer. Herudover kan stoffet give overfølsomhed ved kontakt med huden. Akrylmalingen bliver ikke længere solgt.

Farvestoffet C.I. pigment red 3 er fundet i akrylmaling med produkt nr. 54 i en koncentration på 104 mg/g. Ved en koncentration på 830 mg/kg er der set kræftfremkaldende effekter i 2 % af forsøgsdyr (rotter) og vægttab for 10 %. Det er dog ikke bevist, at de kræftfremkaldende effekter kan overføres til mennesker. Når den orale indtagelse beregnes med udgangspunkt i, at der indtages 1,25 g, er det orale indtag 8,7 mg/kg kropsvægt/dag, hvilket giver en sikkerhedsmargen på 95 og dermed en mindre risiko.

Opløsningsmidlet 2-ethoxy ethanol er fundet i en lyserød og en rød tusch med produkt nr. 25 i koncentrationer på hhv. 1,9 % og 0,74 %. Stoffet er klassificeret som skadeligt for forplantningsevnen i kategori 2. Risikovurderingen viser dog ingen risiko når børn udsættes for 0,05 g fra tuschen. Produktet er dog ulovligt, da man ikke må sælge kemiske stoffer og produkter til private, som indeholder CMR-stoffer over klassificeringsgrænsen. Tuscher anses for at være kemiske produkter, da væsken i tuschen er et kemisk produkt, som er beregnet til at komme ud. Tuscherne er derfor ulovlige at sælge til private, og de bliver ikke længere solgt.

Der er i alt fundet 10 produkter med tuschpenne, 5 produkter med glimmerlim og 4 produkter med akrylmaling og én gelpen med stoffer der har sundhedsskadelige effekter. Det skal bemærkes, at der kun er undersøgt en delmængde af tuschpennene i hvert produkt (et produkt er fx en pakke med en række tuschpenne i forskellige farver).

I de undersøgte dufttuscher er fundet de allergene stoffer d-limonen, benzylalkohol og citral i koncentrationer på mellem 0,01 og 0,1 vægtprocent.

Et estimat af maksimal fordampning af formaldehyd i et lille børneværelse viser, at formaldehydindholdet i 6 gram (ca. 6 ml) glimmerlim maksimalt kan bidrage med op til 25 % af den anbefalede maksimale indeklimakoncentration i et børneværelse på 3 * 3 * 2 m. Der vurderes ikke at være sundhedsmæssige effekter ved, at der arbejdes med glimmerlim i et lille børneværelse, men det anbefales ikke at lade børn arbejde med kreationer, hvor der over kort tid bruges større mængder glimmerlim (flere tuber), i små lukkede børneværelser med dårligt luftskifte, da det bidrager til den samlede eksponering fra hjemmet..

Mange af de undersøgte produkter indeholder stoffer, der er klassificeret som skadelige for sundheden. Det er kun få produkter, som i sig selv udgør en risiko, men man skal tage i betragtning at børn og voksne udsættes for stofferne fra flere forskellige kilder. Det er bekymrende, at der i så stor udstrækning anvendes stoffer der har så alvorlige effekter, som der er fundet her.

I følgende produkter er der ikke fundet CMR- eller allergene stoffer.

Akrylmaling: nr. 7, 8, 9, 18, 34, 35, 36, 40, 41, 48, 49, 51 og 56
Tuschpenne: nr. 1, 11, 12, 22, 30, 31, 32, 39, 42, 43, 47, 62, 63 og 64
Gelpenne: nr. 4 og 44
Glimmerlim: nr. 13, 14, 23, 28, 38, 53 - dog er der identificeret formaldehyd med koncentration < 0,01 mg/g i nr. 13, 23, 28, 38 og 53

Lovgivning

De undersøgte produkter er omfattet af bekendtgørelse nr. 329 om klassificering, emballering, mærkning, salg og opbevaring af kemiske produkter, 2002.

Hobbyprodukter til børn betragtes som legetøj og er omfattet af legetøjsbekendtgørelsen nr. 1116, 2003, hvis Sikkerhedsstyrelsen vurderer produkterne til at være legetøj. I legetøjsbekendtgørelsen refereres til standarderne DS/EN 71-1 til 71-7 med sikkerheds- og sundhedskrav for legetøj. I EU regi er udarbejdet en standard for organiske stoffer DS/EN 71-9 som ikke er implementeret i lovgivningen endnu. Produkterne med de kræftfremkaldende primære aminer anilin, p-chloranilin og anisidin overholder ikke krav i standarden for organiske stoffer DS/EN 71-9, idet stofferne ikke må kunne detekteres i farvede væsker fra legetøjet. Det er dog kun for p-chloranilin der identificeres en risiko.

Miljøvurdering

Resultaterne af miljøvurderingen viser, at udledning af stofferne via afvaskede rester af tusch og maling fra børnenes hænder ikke udgør en risiko for vandmiljøet.

1 Survey

Danish children are in daily contact with a number of different hobby products as for instance glue, paint, colours, marker pens and textiles. As these products are not specifically targeted at children they are not manufactured with due consideration to the fact that children are more inclined to have direct skin contact (and even mucosa contact) to the products and are less conscious of the content of hazardous substances. Further children have a higher breathing rate than adults relative to their body weight, and are thus more exposed than adults at a given concentration of volatiles.

Although labelling directives exist, which enable parents and purchasers in daycare institutions to choose products with the lowest possible content of hazardous substances, there is generally a need for more information on this issue.

The analysed products are covered by Statutory Order No. 329 about classification, packaging, labelling, sale and storage of chemical products, 2002. Thus, products shall be labelled according to the requirements in the Statutory Order.

If the Danish Safety Technology Authority estimates hobby articles to be toys, then the toys shall have a CE-mark and the products are covered by the health and safety requirements to toy (Statutory Order No. 1116, 2003). Hobby articles like glue or paint that have a content of dangerous substances shall be labelled with a risk label that shows the safety and risk.

The below hobby product groups for children are included in the survey:

- Marker pens
- Glitter glue
- Acrylic paint
- Shrink plastic

These product types constitute a representative selection of the product range in the shops. Marker pens and acrylic paint are used by both children and juveniles (and adults) for drawing and painting. Shrink plastic is a relatively new material within hobby articles. Glitter glue is a less defined product, which is presumed to appeal especially to children.

1.1 Purpose

The purpose of the project is to examine which hobby products are available on the Danish market and what is the consumption pattern.

Further, data have been collected from manufacturers and suppliers on content of substances in the various products.

1.2 Limitation

Marker pens, acrylic paint etc. used by children are not necessarily marketed to children, as more of the products are actually used by both children and adults.

For the 4 product groups (marker pens, acrylic paint, glitter glue and shrink plastic) the following delimitations have been made:

- Marker pens: 1) Marker pens, which through the packaging, colour or other appeal directly to children. 2) Marker pens, primarily for use on paper. ***Marker pens intended for window panes, textiles, and china or similar are not covered by the study.***

- Glitter glue: Products containing a mix of glue and glitter and glitter powder which is used in combination with glue. Gel pens are included under glitter glue.

- Acrylic paint: 1) Acrylic colours/paint, primarily for use on canvas. 2) Acrylic paint, primarily applied with tools (brushes or similar). ***Finger paint is thus not covered by our survey.***

- Shrink plastic: Mainly used by children.

Children are defined as persons up to the age of 14.

1.3 Method/procedure

Approaches were made to:

- Retailers
- Web search
- Child care institutions
- Children's art schools/art clubs
- Catalogue search
- Manufacturers and suppliers
- FFFH
- Statistics Denmark
- Other contacts

1.4 Implementation

1.4.1 Retailers

Visits were paid to a number of retailers (total 20) and to one wholesaler and their assortment of the 4 product groups was inspected.

The retailers were:

- Hobby shops, 3
- Toy stores, 4
- Department stores, 2

- Supermarkets, 3
- Discount stores, 2
- Bookshops, 1
- DIY centres, 2
- Museum shop, 1
- Post office, 1
- Paper store, 1
- Wholesaler, 1

Product samples have been bought in all the visited shops and at the wholesaler. The products to be selected, which were all bought in consultation with the shop assistant, should appeal directly to children and should sell well.

Subsequently, questionnaires were submitted to the visited shops or to their headquarters.

1.4.2 Web search

The applied search words and their hits on the web appear from Table 1.1.

Table 1.1 List of search words and number of hit

Search word
Marker pens
Marker pens + children
Glitter glue
Glitter glue + children
Acrylic paint
Acrylic paint + children
Shrink plastic
Shrink plastic + children

We did not buy any products over the internet, as the webshops were toys chain stores or similar, which had also physical shops. Further, more of the webshops had a product range within hobby materials which was primarily directed at professional users.

We found, however, one or two smaller internet shops with a reduced product range for children. These web sites typically focus more on activity proposals and application examples.

1.4.3 Child care institutions

A number of child care institutions have been contacted (2 nurseries, 2 recreational clubs and 1 after school centre) in one municipality to find out which products they were using within the individual product groups and how they were undertaking their shopping activities.

The institutions, we were in contact with, used only suppliers, which observed the requirements for hobby products laid down by the municipality.

Their shopping was effected through sales representative visits, online ordering, or phone ordering. In cases where the institutions faced an acute need for a specific hobby material, such purchase was made in a specified hobby shop.

1.4.4 Art schools/art clubs for children

We made phone contact to a number of art school/clubs for children and questionnaires were sent out concerning estimated consumption, product names, etc.

Questionnaires were submitted to the following art schools and clubs:

- Statens Museum for Kunst, Billedskole (Visual arts school)
- Børneværkstedet, Århus Kunstakademi (Children's workshop)
- Århus Billedskole; Brobjergskolen (Visual arts school)
- Børnekulturhuset Fyrtøjet; Odense (Children's culture house)
- Børnekulturhuset; Brønshøj (Children's culture house)
- Den Kreative Skole; Fredericia (Creative school)

Three of the submitted 6 questionnaires were responded.

1.4.5 Catalogue search

Advertising matter including shopping catalogues for e.g. child care institutions have been reviewed and questionnaires have been sent to relevant distributors and importers.

1.4.6 Manufacturers and suppliers

Questionnaires have been submitted to a total of 36 distributors, manufacturers and importers of markers pens, glitter glue, acrylic paint, and shrink plastic with questions about i.a. product name, sales figures and substances of each product.

At the time of the deadline only 6 companies had responded and a reminder resulted in further 4 responses, i.e. 10 responses were received out of 36 possible! Additionally, more of these were inadequately filled in.

1.4.7 Contact to FFFH

The Joint Council for Creative and Hobby Materials (FFFH) is an association of manufacturers, suppliers and distributors of hobby materials in Denmark. Today, about 25 companies are associated to the FFFH, and manufacturers, importers and distributors are equally represented. FFFH has elaborated labelling guidelines and specific criterion for creative and hobby materials.

The FFFH guidelines classify the hobby products in according to four specified categories, labelled A, B, C and D[2].

Products labelled A may be used by children from the age of 3. The A label implies that these products comply with the safety criterions of the FFFH.

Products labelled B can be used by children from an age of 5 years, but under adult expert guidance. The product does not meet the most restrictive demands of FFFH (A)[2].

[2] www.FFFH.dk

Products labelled C may not be used by children and juveniles under the age of 15. These products do not comply with neither the EU regulations (The Toy Directive) or with the criterions of the FFFH[2].

D-labelled products may only be used by adults. The D label implies that the products are labelled with a danger symbol, e.g. harmful, irritant or inflammable substances[2].

Apart from the classification the FFFH labelling system also include information about substances in the products and an instruction in use and storage. The information about the product substances are based on information from the manufacturer.

FFFH[3] reports that an increasing number of municipalities require from their child and juvenile institutions that they are using products which comply with the labelling guidelines of FFFH.

1.4.8 Statistics Denmark

Contact has been made to Statistics Denmark and information has been retrieved from the database "StatBank Denmark".

The information achieved from Statistics Denmark was partly about the possibility of specifying the extent of consumption of the individual product groups and partly data on the children population under the age of 14.

1.4.9 Other contacts

1.4.9.1 SKI Statens og Kommunernes Indkøbs Service A/S (National Procurement Ltd. – Denmark)

We contacted SKI to find out whether there was any call-off agreement on hobby products for children which was, however, not the case.

1.5 Purchased products

The selection criterion for purchase of primarily marker pens and glitter was that the packaging should appeal to children in the form of illustrations and/or colours. Further the shop assistants were questioned about which products within the specific product group they were selling with children as target group.

Based on the application possibilities of shrink plastic this product is presumed primarily to appeal to children.

Acrylic paints sometimes come in packagings which are very attractive to children; however, the product group as such is not specifically targeted at children but is sold to both children and adults.

Within the 4 product groups we have chosen articles which according to the shop personnel products sell in larger amounts.

[3] Telephone conversation on 9. august 2006 with Birger Schjerning; Schjerning Colours

The products purchased cover both the cheap and the expensive end of the market.

1.5.1 Marker pens

Marker pens are easy-accessible as they can be bought everywhere: at gas stations, convenience stores, kiosks, department stores, bookshops, hobby shops etc. Part of the marker pens sale consists of lots as part of e.g. one of the main attractions in the weekly advertising paper or in a discount shop.
The product group itself is easily defined (pens with felt tip), whereas it is a bit more difficult to distinguish between pens to be used by children and pens to be used by adults. There are two easy identifiable groups: marker pens for professional use and pens which through the packaging or colours or similar are aimed at children. But in-between there is a grey zone in this product group where a systematic and unambiguous definition cannot be made. This fact has impact on not only the purchase of these products but also on the importers' and manufacturers' specification of their product range.

Within the group marker pens we have purchased in total 26 units with each 1-50 items.

The price of the purchased marker pens is in the range of DKK 0.49-15.00 per pen.

Table 1.2 gives a survey of the marker pen types, shop type and the price.
Table 1.2 list of marker pens purchased

Product no.	Type of shop	Quantity per unit	Price per unit in DKK
1	Bookshop	10	3.00
3	Bookshop	5	13.99
5	Bookshop	10	12.00
10	Discount store	50	0.49
11	Department store	10	1.00
12	Department store	10	2.00
16	Hobby shop	8	3.63
17	Hobby shop	12	2.42
22	Discount chop	6	0.83
25	Supermarket	50	0.60
30	Toy stores	12	2.50
31	Supermarket	10	2.50
32	Supermarket	12	2.08
39	Wholesaler	1	11.19
42	Department store	8	6.24
43	Department store	5	9.99
45	Department store	10	15.00
46	Toy stores	12	4.92
47	Toy stores	10	5.90
52	Paper store	12	5.38
57	Supermarket	10	3.00
58	Supermarket	12	1.91
59	Supermarket	20	1.00
62	Toy store	12	4.16
63	Toy store	10	3.50
64	Museum shop	10	9.98

1.5.2 Glitter glue

Glitter glue is a product group which appeals to the aesthetic sense of children, especially girls, but is also used by adults for e.g. invitation cards etc. Like marker pens, glitter glue products are imported in lots, which are sold as special offers and do not become a regular part of product collection.

Within this product group we have bought 11 units with each 1-9 items. The glitter glue has been bought partly as a kind of pen (cartridge in soft squeezable materials), and as loose glitter to be dusted on glue.

The price for the purchased products lies between DKK 1.00 and DKK 9.67 per glitter pen/cartridge with glitter.

Details about the purchase appear from Table 1.3.

Table 1.3 List of purchased glitter glue products

Product no.	Type of shop	Quantity per unit	Price per unit in DKK
13	Department store	6	3.33
14	Hobby shop	3	9.67
15	Hobby shop	5	7.80
23	Post offices	5	1.00
26	Supermarket	6	4.99
28	Toy stores	3 + 6	4.44
29	Toy stores	6	6.66
33	Supermarket	6	3.66
38	Wholesaler	1	7.75
53	Toy stores	6	6.66
50	Paper store	6	7.08

We have chosen to include gel pens in our survey, although they can be classified neither as marker pens nor as glitter product. We have provided only a few products in this category (3 packets with 3, 6, and 30 pens, respectively).

Gel pens appeal to both children and adults. According to the shop assistants gel pens with glitter are mainly sold to children, whereas the adults are buying the pens without glitter.

The price for the products is between DKK 1.67 and DKK 11.65 per glitter pen/glitter cartridge.

Details about the purchase appear from Table 1.4.

Table 1.4 List of purchased gel pen products

Product no.	Type of shop	Quantity per unit	Price per unit in DKK
2	Bookstore	6	2.49
4	Bookstore	30	1.67
44	Department store	3	11.65

1.5.3 Acrylic paint

A very few of the products are aimed directly at children. Some of the products, however, were packed in a way that would primarily appeal to children or they were available in toy stores.

Acrylic paint products, bought in convenience stores, hobby shops, and DIY centres, were selected in consultation with the shop assistant.

In total we bought 18 units of acrylic paint. 15 of the units were single tubes/bottles/jars and 3 of them came in a package with 12 small tubes/jars.

The price was in the range of DKK 7.99 to DKK 66.46 per 100 ml.

Information about the purchased acrylic paint, the shop and the price appears from Table 1.5.

Table 1.5 List of purchased acrylic paint products

Product no.	Shop type	Volume per unit	Price per 100 ml in DKK
6	Discount stores	75 ml	13.28
7	Discount stores	75 ml	13.28
8	Discount stores	75 ml	13.28
9	Discount stores	12 x 1,8 ml	33.94 (0.61 per unit)
18	Hobby shop	500 ml	13.80
34	Supermarket	75 ml	33.27
35	Supermarket	75 ml	33.27
36	Supermarket	75 ml	33.27
40	Wholesaler	200 ml	19.97
41	Wholesaler	500 ml	7.99
48	Toy stores	100 ml	22.00
49	Toy stores	100 ml	22.00
51	Paper store	12 x 10 ml	66.46 (6.65 per unit)
54	DIY centre	250 ml	13.98
55	DIY centre	12 x 12 ml	20.80 (2.50 per unit)
56	Supermarket	250 ml	13.98
60	DIY centre	100 ml	24.00
61	DIY centre	100 ml	24.00

1.5.4 Shrink plastic

Shrink plastic is a relatively new article and is sold in a limited number of shops. In this project we succeeded in finding the product only in a couple of hobby shops. In the other shop types, the shop assistants did not even know that the product existed, and moreover, we have been asked by importers, manufacturers and similar what shrink plastic was. According to FFFH[3] shrink plastic is on its way out again after only 2-3 years on the market.

Within this product group we have bought 5 units with 1 to 5 sheets per unit.

The price of the products was in the range of DKK 7.95 to DKK 17.44 per sheet.

Information about the shrink plastic, the shop and the price appear from Table 1.6.

Table 1.6 List of purchased shrink plastic products

Product no.	Shop type	Sheets per pack	Price per sheet in DKK
19	Hobby shop	4	11.00
20	Hobby shop	4	11.00
21	Hobby shop	5	7.95
24	Hobby shop	3	8.17
37	Wholesaler	1	17.44

1.6 Consumption

It was not possible to get a quantitative specification of the consumption of the 4 product groups from Statistics Denmark.

SKAT (the Danish Tax Authority) states that marker pens have their own KN-code[4] but it is not possible to determine how the consumption is distributed on children and adults.

[4] KN-code is an 8-digit product code number (KN ~ Kombineret Nomenklatur)

According to SKAT, the 3 other product groups (glitter glue, acrylic paint and shrink plastic), have no individual KN-code.

The information provided by manufacturers, importers and distributors is not sufficiently comprehensive and precise to make an estimate of the consumption in Denmark.

According to Statistics Denmark there were 1,015,879 children below 14 years in 2006 and it is presumed that most children were in daily contact with markers pens, whereas not nearly all children are users of the three other product groups (glitter glue, acrylic paints, and shrink plastic).

1.7 Product ingredients

Upon purchase of the hobby products covered by this project, we contacted distributors, manufacturer and importers to get information about i.a. contents of substances in their products.

Only 10 of the 36 distributors, manufacturers and importers returned the questionnaires and of not all of these answered the questions about substances in the products. The questions regarding content of substances were not limited to the products included in this project, but did also include other products within this category.

2 Screening of product ingredients

Based on information achieved about substances collected during the survey phase, chemical screenings have been carried out for organic and inorganic components, respectively.

Dependent on product group (marker pens, glitter glue, gel pens, acrylic paint and shrink plastic) an analysis program has been set up for screening for content of harmful substances, therefore, this substance group has been put in focus in the chemical screening.

Apart from the screening quantitative X-ray analyses have been carried out for identification of inorganic substances in acrylic paint, glitter glue, and shrink plastic. The results are described in chapter 3, Quantitative chemical analyses.

The shrink plastic products have been screened by NIR-spectrometry to determine whether they contain PVC which may contain phthalates.

Table 1.2, Table 1.3, Table 1.4, Table 1.5, and Table 1.6 give an overview of the screenings of all products.

2.1 Applied analysis method for screening

The chemical screening is based on GC/MS-analysis and NIR-spectrometry, respectively. The specific parameters for the applied methods are described below.

2.1.1 Qualitative GC/MS-screening

From the qualitative GC/MS-screening of the products a number of partial samples were taken, with the objective of obtaining a wide choice of the different colour variations in the various products.
Depending on product type 3 different extractions have been made.

Marker pens and gel pens
Half of one marker pen has been analysed corresponding to 0.1–1 g sample (excl. felt cartridge and depending on type), which was extracted with 10 ml dichloromethane with bromobenzene and o-terphenyl as internal standards.

Glitter glue
Approx. 2 g glitter glue has been weighed out and subsequently suspended in water and extracted with 3 ml pentane with toluene-d_8 og naphthalene-d_8 additives as internal standards.

Acrylic paints
Approx. 0.1 g was weighed off and subsequently extracted in a mix of 10 ml methanol and 15 ml dichloromethane added bromobenzene and o-terphenyl as internal standards.

The extracts were then analysed by GC/MS chromatography. The analysis parameters used for GC/MS-analysis are shown in Table 2.1.

Table 2.1 GC/MS analysis parameters

GC/MS-instrument	Agilent HP 5973 ALS
GC-parameters	Carrier gas: Helium, constant flow at 1.5 ml/min. Oven program.: 35 ºC for 1 min., 10 ºC/min. to 325 ºC, 325 ºC for 2 min. Column: CP-sil 5CB, 25 m x 0,25 mm id., 0.25 µm film thickness
MS-parameters	Autotune Scan mode: 35-550 m/z Solvent delay: 3 min

In connection with the screening the detected components were alone identified through a comparison with the NIST MS-library. AMDIS was used as deconvolution software.

2.1.2 NIR-spectrometry screening of shrink plastic

One sheet of the shrink plastic with a radius of 40 mm was analysed directly in the NIR- instrument. The spectra were compared visually with spectra of the reference substances.

Table 2.2 NIR analysis parameter

NIR-instrument	Technicon 500
Analysis area	1000-2500 nm
Interval	5 nm

2.2 Results – chemical screening

The substances identified by the screening are summarised in the following tables.

The results have been classified in product types and the detected substances are marked by an ”X”. All identified substances are provided with CAS-no.

In connection with the screening there has not been made an assessment of the amount of the identified substances.

Within the scope of this project it was not possible to analyse all the colour variations in the analysed products. In order to investigate the variations of substances in one product, all the colour variations in product no. 16 was included in the chemical screening.

2.1.3 GC/MS-screening results - marker pens

Table 2.3 GC/MS screening results of markers pens

Identification	CAS-no.	Sample no.												
		1	22	3	5	10	11	12	16	17	30	31	32	39
Propylene glycol	57-55-6							X	X	X	X			
N,N-Dimethylacetamide	127-19-5									X				
3-Hexen-1-ol	544-12-7								X					
Ethylbenzene and xylenes	100-41-4						X							
1,3-Butanediol	107-88-0				X									
1-Hydroxy-2-propanone	116-09-6	X							X					
Cyclohexanone	108-94-1					X								
1,2-Propanediol-2-acetate	6214-01-3	X							X					
2-Butoxy-ethanol	111-76-2			X										
Hexylene glycol	107-41-5	X												
1,3-Dioxan	505-22-6								X					
Diethylene glycol	111-46-6		X	X	X							X	X	X
Glycerine	56-81-5						X							X
o-Methylstyrene	611-15-4					X								
2-Pyrrolidinone	616-45-5													X
N-Methyl-aniline	100-61-8					X								
1,4-Dioxaspiro(4,5)decane	177-10-6					X								
2-(2-(2-Methoxyethoxy)ethoxy)-ethanol acetate	3610-27-3		X									X	X	
2-(2-Butoxyethoxy)-ethanol	112-34-5		X		X									
Methenamine	100-97-0			X										
1,2,3-Propantriol diacetate	102-62-5	X							X				X	
Triethylene glycol	112-27-6				X									
4,4-Dimethyl-2,5-dioxo-1-imidazolindinemethanol	16228-00-5			X	X									
Tetramethylindoline	13034-76-9											X		
1,2,3-Propantriol triacetate	102-76-1	X	X						X				X	X
5,5-Dimethyl-2,4-imidazolidinedione and similar compounds	77-71-4			X	X									
1,3,3-Trimethyl-2-methylen indoline	118-12-7											X		
3-Phenyl-2-propenoic acid methyl ester	103-36-6								X					
3-Methoxy-4,7-dimethyl-1H-isoindole	100813-60-3					X						X		
2,4,7,9-Tetramethyl-5-decyn-4,7-diol	126-86-3			X										
1-Hexyl-3-butenyl acetate	2833-33-2	X	X											
5-Hexyldihydro-2(3H)-Furanone	706-14-9								X					
Tetraethylen glycol	112-60-7									X				
3-Isopropyl-2,3-dimethyl-Indolin	18781-62-9											X		
Carbamic acid, butyl-,3-iodo-2-propynyl ester	55406-53-6				X									
4-(Diethylamino)-Benzaldehyde	120-21-8											X		
2,2'-(Phenylimino)bis-ethanol	120-07-0									X				
Pentaethylene glycol	4792-15-8									X				
Trogers base	72151-03-2					X								
Hexagol	2615-15-8									X				
1,4-Benzen dicarboxyl acid bis(2-hydroxyethyl) ester	959-26-2			X	X					X				
2-Butenedioic acid bis(2-ethylhexyl) ester	141-02-6									X				
Cyclopentanecarboxylic acid octyl ester	100912-19-4					X								
Heptaethylen glycol	5617-32-3									X				
Oleic acid	112-80-1											X		
bis-2(Ethylhexyl) hexanedioic acid ester	103-23-1					X								
Diisooctyl phthalate	117-84-0					X								
Octaethylen glycol	5117-19-1									X				

Table 2.3 Results of GC/MS screening of marker pens

Identification	CAS-no.	Sample no.												
		42	43	45	46	52	57	58	59	62	63	64	25	47
Propylene glycol	57-55-6		X	X										X
2-Ethoxy ethanol	110-80-5												X	
2-Butoxy-ethanol	111-76-2		X	X							X	X	X	
Benzaldehyde	100-52-7	X								X				
Diethylene glycol	111-46-6	X					X	X	X	X	X	X	X	
Glycerine	56-81-5	X									X	X		
1,1'-Oxydi-2-propanol	110-98-5					X				X			X	
2-Ethyl-1-hexanol	104-76-7												X	
Ditert.butoxy methane	2568-93-6		X											
Acetophenone	98-86-2	X												
1-Propanol, 3,3'-oxybis-	2396-61-4												X	
Pyrrolidinone	616-45-5												X	
1,2,3-Propantriol monoacetate	106-61-6											X		
Chlorobenzaldehyde	89-98-5								X					
2-Ethyl hexane acid	149-57-5		X											
2-(2-Butoxyethoxy)-ethanol	112-34-5	X									X			
p-Meth-1-en-8-ol	98-55-5										X			
p-Anisidine	104-94-9						X							
1,2,3-Propantriol diacetate	102-62-5											X		
N-Methyl-p-anisidine	5961-59-1						X	X						
Isobornyl acetate	125-12-2										X	X		
Tetramethylindoline	13034-76-9						X							
1,2,3-Propantriol triacetate	102-76-1	X	X									X		
1,3,3-Trimethyl-2-methylene indoline	118-12-7						X	X	X					
Triethanolamine	102-71-6			X	X									
3-Methoxy-4,7-dimethyl-1H-isoindol	100813-60-3						X	X						
Methylparabene	99-76-3					X				X				
Tetraethylen glycol	112-60-7		X										X	
N-Phenyl-2-pyridinamine	6631-37-4						X	X	X					
4-(Diethylamino)-benzaldehyde	120-21-8						X							
4-(2-Cyanoethyl)methylamino-benzaldehyde	94-21-3						X	X						
Sorbitol	50-70-4	X												
1,4-Benzenedicarboxylic acid bis(2-hydroxyethyl) ester	959-26-2				X									

Table 2.4 Results of GC/MS-screening of sample no. 16

Identification	CAS-no.	Red	Green	Brown	Orange	Yellow	Light blue	Pink	Black
Propylene glycol (1,2-proanediol)	57-55-6	X		X	X	X	X	X	X
1-Butanol, 3-methyl-, acetate or isomer	123-92-2						X		
3-Hexen-1-ol	544-12-7	X						X	
Hexanal	66-25-1							X	
1-Hexanol	111-27-3							X	
1-Butanol, 3-methyl-, acetate or isomer	123-92-2						X		
1,2-Propanediol, diacetate	623-84-7			X					
D-Limonene	5989-27-5				X				
Benzyl alcohol	100-51-6								X
Eucalyptol	470-82-6		X						
2-Furanmethanol, 5-ethyenyltetrahydro-.alpha.,alpha.,5-trimethyl-,cis-(or isomer!)	5989-33-3					X			
Benzene, methyl (1-methylethenyl)-	26444-18-8					X			
1,3,7-Octatriene, 3,7-dimethyl or 3-carene	502-99-8				X				

Identification	CAS-no.	Red	Green	Brown	Orange	Yellow	Light blue	Pink	Black
3-Caren	13466-78-9					X	X		
Nonanal	124-19-6				X				
Isopulegol	7786-67-6		X						
Cyclohexanone, 5-methyl-2-(1-methylethyl)-	529-00-0		X						
Acetic acid, phenylmethyl ester	140-11-4								X
L-menthol	2216-51-5		X						
Menthol	89-78-1		X						
Benzene, 1-methyl-4-(1-methylethenyl)	1195-32-0					X			
Cyclohexanol, 5-methyl-2-(1-methylethyl)-, [1R-(1-alpha-,2.beta.,5.alpha.)]- or menthol or corresponding terpene	2216-51-5		X						
Decanal	112-31-2				X				
Pulegon	89-82-7		X						
Beta-myrcene	123-35-3					X			
2(3H)-Furanone, 5-butyldihydro-	104-50-7			X					
2,6-Octadienal, 3,7-dimethyl-	5392-40-5				X	X			
Isopulegolacetate	57576-09-7		X						
Triacetin	102-76-1	X						X	
Piperonal	120-57-0			X					
cis-2,6-Dimethyl-2,6-octadien	2492-22-0					X			
2-Propenoic acid, 3-phenyl-, methyl ester	103-26-4	X							
Benzaldehyde, 3-hydroxy-4-methoxy-	621-59-0						X		
Dodecanal	112-54-9				X				
Caryophyllene	87-44-5		X						
2(3H)-Furanone, 5-hexyldihydro-	706-14-9	X		X					

2.1.4 GC/MS screening results – glitter glue

Table 2.5 GC/MS- screening results - glitter glue

Identification	CAS-no.	Sample No.										
		53	33	28	13	14	15	23	26	29	38	50
Phenol	108-95-2								X			
2-Ethyl-1-hexanol	104-76-7									X		
2-Phenoxy ethanol	122-99-6	X	X	X						X		
n-Alkanes (C21+)						X						

2.1.5 GC/MS screening results - gel pens

Table 2.6 Results of GC/MS screening - gel pens

Identification	CAS-no.	Sample no.		
		2	4	44
Diethylene glycol	111-46-6		X	
Glycerine	56-81-5		X	X
Methylparabene	99-76-3		X	
1H-Benzotriazole	95-14-7		X	
BHT	128-37-0	X		
3,3'-Dimethylbenzedine	119-93-7	X		

2.1.6 GC/MS screening results - acrylic paints

Table 2.7 Results of GC/MS screening of acrylic paints

Identification	CAS-no.	Sample No.								
		6	7	8	9	18	34	35	36	40
Propylene glycol	57-55-6						X			
2-Butoxy-ethanol	111-76-2				X					
Dipropylene glycol monomethyl ether	34590-94-8					X				
Glycerine	56-81-5									
1-(2-Methoxypropoxy)-2-propanol	13429-07-7					X				
Benzoic acid, methyl ester	93-58-3				X					
Chloroaniline	106-47-8	X								
2,2,4-Trimethyl-1,3-pentandiol	144-19-4	X								
2-(2-Butoxyethoxy)-ethanol	112-34-5	X	X	X						
Propanoic acid, 2-methyl-, 2,2-dimethyl-1-(2-hydroxy-1-methylethyl)propyl ester	74367-33-2	X	X	X	X	X		X	X	
Propanoic acid, 2-methyl-, 3-hydroxy-2,4,4-trimethylpentyl ester	74367-34-3	X	X	X	X	X	X	X	X	
1-Dodecanol	112-53-8	X		X					X	
Diethylene glycol dibenzoate	120-55-8				X					
Bis(2-butoxyethyl) phthalate	117-83-9									X

Table 2.7 Results of GC/MS-screening of acrylic paints

Identification	CAS-no.	Sample no.								
		41	48	49	54	55	51	61	60	56
Dipropylene glycol monomethyl ether	34590-94-8							X	X	
Glycerine	56-81-5			X						
1-(2-Methoxypropoxy)-2-propanol	13429-07-7							X	X	
Chloroaniline	106-47-8					X				
Chloroisocyanato benzene	104-12-1					X				
2-Phenoxy ethanol	122-99-6	X								
2-Propenoic acid, 2-ethylhexyl ester	103-11-7							X	X	
1-Propanol, 2,2'-oxybis-	108-61-2						X			
1-Propanol, 3,3'-oxybis-	2396-61-4						X			
Propanoic acid, 2-methyl-, 2,2-dimethyl-1-(2-hydroxy-1-methylethyl)propyl ester	74367-33-2							X	X	
Propanoic acid, 2-methyl-, 3-hydroxy-2,4,4-trimethylpentyl ester	74367-34-3							X	X	
Butanedioic acid, bis(2-methylpropyl) ester	925-06-4						X			
Butanedioic acid, methyl-, bis(1-methylpropyl) ester	57983-31-0						X			
Hexanedioic acid, bis(2-methylpropyl) ester	141-04-8						X			
2-Naphthalenol, 1-[(4-methyl-2-nitrophenyl)azo]- (Toluidine Red)	2425-85-6				X					

2.1.7 NIR-spectrometry analysis of shrink plastic

Table 2.8 Results of NIR-screening of shrink plastic

Identification	CAS-no.	Sample no.				
		19	20	21	24	37
Polystyrene	9003-53-6	x	x	x	x	X

2.2 Selection of substances for quantification

A number of different substances were identified by the initial chemical screening. In consultation with the Danish EPA a selection was made of the product substances to be quantified.

The selection was made on basis of the information stated in Table 2.9 and on a prioritization model which is described below.

Table 2.9 Substances detected by GC/MS by screening of selected products

Name	CAS-no.	Classification	Presence No. of products	Selected [1]
2-Ethoxy ethanol	110-80-5	REP2;R60-61 R10 Xn;R20/21/22	1	X
N,N-Dimethylacetamide	127-19-5	REP2;R61 Xn;R20/21	1	X
1-Hydroxy-2-propanone	116-09-6	** Not in list maybe as propanone XI;R36 R66	1	
Cyclohexanone	108-94-1	R10 Xn;R20	1	X
2-Butoxy-ethanol	111-76-2	Xn;R20/21/22 Xi;R36/38	7	
Hexylene glycol	107-41-5	Xi;R36/38	1	
1,3-Dioxane	505-22-6	* Xn;R22	1	
Benzaldehyde	100-52-7	Xn;R22	14	
Diethylene glycol	111-46-6	Xn;R22	1	X
Phenol	108-95-2	T;R23/24/25 C;R34 Xn;R48/20/21/22 MUT3 ;R68	1	X
O-Methylstyrene	611-15-4	Xn;R20 N;R51/53	1	
Pyrrolidone	616-45-5	* Xn;R22	2	
Acetophenone	98-86-2	Xn;R22 Xi;R36	1	
N-Methyl-aniline	100-61-8	T;R23/24/25—R;33- - N;50/53	1	X
1,4-Dioxaspiro(4,5)decane	177-10-6	* N;R50/53	1	X
Chloroaniline	106-47-8	CARC2;R45 T;R23/24/25 R43 N;R50/53	2	X
Chloroisocyanato benzene	104-12-1	* Xn;R22 R43	1	X
2-(2-(2-Methoxyethoxy)ethoxy)-ethanol acetate	3610-27-3	* R52/53	3	
Chlorobenzaldehyde	89-98-5	C;R34	1	
2-Ethyl hexan acid	149-57-5	REP3;R63	1	
2-(2-Butoxyethoxy)-ethanol	112-34-5	Xi;R36	5	
2-Phenoxy ethanol	122-99-6	Xn;R22 Xi;R36	5	X
2-Propenoic acid, 2-ethylhexyl ester	103-11-7	Xi;R37/38 R43	2	X
p-Anisidine	104-94-9	Tx;R26/27/28 R33 N;R50	1	
Methenamine	100-97-0	F;R11 R42/43	1	
2-Phenoxy ethanol	122-99-6	Xn;R22 Xi;R36	5	
4,4-Dimethyl-2,5-dioxo-1-imidazolindinemethanol	16228-00-5	* Xn;R22	2	
N-Methyl-p-anisidine	5961-59-1	* Mut3;R40 Carc3;R40 R43	2	
1,2,3-Propantriol triacetate	102-76-1	** Not in list (eye irritation hsdb)	5	
3-Phenyl-2-propenoic acid methyl ester	103-36-6	** Not in list, ethyl cinnamate pheromone	1	
Triethanolamine	102-71-6	* R43	2	
3-Methoxy-4,7-dimethyl-1H-isoindol	100813-60-3	**Not in list maybe as 3131-52-0 R41	2	X
1-Dodecanol	112-53-8	*N;R51/53	3	
Methylparabene	99-76-3	Not in list, parabene (least hazardous)	3	
5-Hexyldihydro-2(3H)-Furanon	706-14-9	** Not in list (chemid:LD50 rat intravenous=56 mg/kg)	1	
1H-Benzotriazol	95-14-7	*Xn;R22	1	
Butylized hydroxytoluene (BHT)	128-37-0	*Xn;R22;R50/53	1	
N-Phenyl-2-pyridinamin	6631-37-4	*R43	3	
Hexanedioic acid, bis(2-methylpropyl) ester = Diisobutyladipate)	141-04-8	*N;R51/53	1	
4-(Diethylamino)-benzaldehyde	120-21-8	*Xn;R22	1	
4-(2-Cyanoethyl)methylamino-benzaldehyde	94-21-3	** Not in list benzaldehyde is marked R22	2	

Name	CAS-no.	Classification	Presence No. of products	Selected [1]
3,3'-Dimethylbenzedine	119-93-7	Carc2;R45 Xn;R22 N;R51/53	1	
1,4-Benzenedicarboxylic acid bis(2-hydroxyethyl) ester = Bis(hydroxyethyl)terephthalate	959-26-2	** Phthalate	4	X
2-Butenedioic acid bis(2-ethylhexyl) ester	141-02-6	*R43	1	
Bis(2-butoxyethyl) phthalate	117-83-9	* N;R50/53, ** phthalate	1	
Bis-2(ethylhexyl) hexanedioic acid ester (Bis(2-ethylhexyl)adipat)	103-23-1	** Phthalate	1	
Diisooctyl phthalate	117-84-0	** Phthalate	1	
2-Naphthalenol, 1-[(4-methyl-2-nitrophenyl)azo]- (Toluidine Red)	2425-85-6	** Azo dye	1	X

1: Substances for quantification have been chosen based on their hazardous effect, expected concentration and presence in products as described below

*: Self-classification, see text
**: Additional information, see text

Table 2.9 shows only substances classified according to the List of Dangerous Substances ***(Miljøministeriet, 2005)***, the Advisory List for Self-classification.

The substances are shown according to their retention time on a volatile scale. Thus substances at the top of the list are easily emitted to air and therefore also present a higher risk of absorption via the respiratory system.

The classification of the substances marked "*" is taken from the advisory list for self-classification (***Vejledende liste, Miljøstyrelsen 2001***).

Substances marked "**" have been found relevant for analysis as they belong to a substance group which contains undesirable hazardous components (.e.g. phthalates).

Apart from the substances selected for quantification, there is probably formaldehyde content in the glitter glue and pheromones in the aroma pens in product No.16, these substances will be subjected to a quantitative analysis.

Prioritization has been based on an assessment of health hazard * concentration, where the substance concentration level is estimated from the peaks in the gas chromatography in the qualitative analysis.

By assessing the relative health hazard, the substances marked T, Tx and CMR or allergens are weighted more than substances marked Xn, Xi.

In the selection we have tried to have the substances represented relative to how often they appear in the products.

Based upon the selection of substances hazardous to the environment and health we have picked 12 products which represent the most important of the substances and most likely have the highest concentrations.

Products selected for substance quantification
Marker pens
No. 10 in orange and purple
No. 16 in red, brown, orange, yellow and black

No. 17 in red and pink
No. 25 in red and pink
No. 45 in green and white
No. 57 in orange and pink
The price ranges between 0.49-3.63 DKK apart from product No. 45, which is more expensive.

Gel pens
No. 4 in metallic yellow and pastel pink
The cheapest product.

Acrylic paint
No. 54 in red-302
No. 55 in green and ultramarine blue
No. 61 in metallic cubber
The selected colours cover the price spread.

Glitter glue
No. 26 in gold, purple, green and silver
No. 29 in orange/yellow, pink, light blue and gold
The products are at medium price level.

Shrink plastic
No products have been selected as they did not contain PVC, which may contain phthalates.

3 Quantitative chemical analyses

In consultation with the Danish EPA we selected a number of the identified substances for quantification.

3.1 Applied method for the quantitative analyses

The quantitative analyses are based on GC/MS and X-ray analysis. The specific parameters for the applied method are described in the following:

3.1.1 Quantitative GC/MS analysis

3 different extractions have been made dependent on product type:

Marker pens and gel pens
Half of a marker pen equivalent to 0.1-1 g sample (excl. felt cartridge and depending on type), was extracted with 10 ml dichloromethane with bromobenzene and o-terphenyl as internal standards.

Glitter glue
1 g was weighed out, suspended in water and subsequently and extracted in 3 ml pentane with brombenzene and o-terphenyl as internal standards.

Acrylic paints
0.1 g weighed out and extracted in a mix of 10 ml methanol and 15 ml dichloromethane with brombenzene and o-terphenyl as internal standards.

The extracts were subsequently analysed by GC/MS.

Table 3.1 GC/MS analysis parameters

GC/MS-instrument	Agilent HP 5973 ALS
GC-parameters	Carrier gas: Helium, constant flow at 0.8 ml/min Oven program.: 40 ºC in 0 min., 10 ºC/min. at 300 ºC, 300 ºC in 0 min. Column: Zebron ZB-5ms w/Guardian, 30 m x 0,25 mm id., 0,25 µm film thickness
MS-parameters	Autotune Scan mode: 40-550 m/z Solvent delay: 3.10 min

Calibration of the applied method is made from the detection limit to approx. 2-20 mg/g sample dependent on the individual parameter and the weighed-out sample. The detection limit appears from the following tables.

The uncertainty factor is calculated based on double determination and will appear from the following tables.

For the selected samples the extracts from the qualitative screening have been re-analysed. No weight and double determination have been recorded in connection with the qualitative determination, thus the uncertainty for these analyses cannot be determined.

3.1.2 X-ray measurement

The samples were cut in sizes to fit into the X-ray equipment.

The samples were analysed directly and the content of elements with atomic number higher than 10 were analysed against standards of pure elements or simple salts.

The degree of accuracy of the analysis method is ± 20 %.

Table 3.2 Parameters for X-ray analysis

X-ray equipment	Wavelength dispersive X-ray equipment model Philips PW 2400 with UNIQUANT calculation program
Counting time	6-20 sec. per element
Power, tube	2400 W

3.1.3 Formaldehyde measurement

0.01-0.5 g sample was suspended in 5 ml water. The content of formaldehyde is derivated with PFBOA and analysed by SPME-GC/MS.

Table 3.3 GC/MS analysis parameters

GC/MS-instrument	Thermo Electron DSQ
GC-parameters	Carrier gas: Helium, constant pressure at 20 psi Oven program.: 35 ºC for 5 min., 25º C/min. to 260 ºC held for 2 min. Column: ZB-1MS, 20 m x 0,18 mm id., 0,18 µm film thickness
MS-parameters	Autotune Scan mode: 40-300 m/z Solvent delay: 0,1 min
SPME-parameters	SPME-fibre: 85µm Carboxen/PDMS

Calibration of the applied method has been made in the range of 0.05 -1500 mg/kg.

The detection limit for the applied analysis method is determined to 0.05 mg/kg and the uncertainty factors appear from Table 3.8.

3.1.4 Ingredients in marker pens

Table 3.4 Analysis results - marker pens mg/g (± standard deviation in mg/g)

Identification	CAS-no.	Product no.				Detection limit
		10 Purple	10 Orange	17 Red	17 Light green	
2-Ethoxy ethanol	110-80-5	-	-	-	-	0,05-0,5
N,N-Dimethylacetamide	127-19-5	-	-	0,22 (±0,01)	0,40	0,01-0,1
Cyclohexanone	108-94-1	1,1 (±0,1)	0,54	-	-	0,01-0,1
2-Butoxy-ethanol	111-76-2	-	-	-	-	0,01-0,1
Diethylene glycol	111-46-6	-	-	-	-	0,1-1
Aniline*	62-53-3	-	-	-	-	0,01-0,1
N-Methyl-aniline	100-61-8	-	0,44	-	-	0,01-0,1
1,4-Dioxaspiro(4,5)decane	177-10-6	0,32 (±0,03)	-	-	-	0,01-0,1
Pyrrolidinone	616-45-5	-	-	-	-	0,01-0,1
p-Anisidine	104-94-9	-	-	-	-	0,01-0,1
N-Methyl-p-anisidine	5961-59-1	-	-	-	-	0,01-0,1
Triethanolamine	102-71-6	-	-	-	-	3-30
3-Methoxy-4,7-dimethyl-1H-isoindol**	100813-60-3	0,16 (±0,01)	0,27	-	-	0,01-0,1
N-Phenyl-2-pyridinamine	6631-37-4	-	-	-	-	0,01-0,1
4-(Diethylamino)-benzaldehyde	120-21-8	-	-	-	-	0,01-0,1
4-(2-Cyanoethyl)methylamino-benzaldehyde***	94-21-3	-	-	-	-	0,3-3
bis(2-Ethylhexyl)-hexanedioic acid ester	103-23-1	0,32 (±0,02)	0,35	-	-	0,01-0,1

"-" Below the detection limit.

Table 3.4 Analysis results - marker pens mg/g (± standard deviation in mg/g)

Identification	CAS-no.	45 Green	45 White	57 Orange	57 Pink	25 Pink	25 Red	Detection limit
2-Ethoxy ethanol	110-80-5	-	-	-	-	19 (±3)	7,4	0,05-0,5
N,N-Dimethylacetamide	127-19-5	-	-	-	-	-	-	0,01-0,1
Cyclohexanone	108-94-1	-	-	-	-	-	-	0,01-0,1
2-Butoxy-ethanol	111-76-2	-	-	-	-	-	0,11	0,01-0,1
Diethylene glycol	111-46-6	-	-	16 (±2)	>100	10 (±1)	>100	0,1-1
Aniline*	62-53-3	0,22 (±0,05)	-	-	-	0,11 (±0,02)	-	0,01-0,1
N-Methyl-aniline	100-61-8	0,99 (±0,18)	-	0,10 (±0,01)	-	-	-	0,01-0,1
1,4-Dioxaspiro(4,5)decane	177-10-6	-	-	-	-	-	-	0,01-0,1
Pyrrolidinone	616-45-5	-	-	-	-	0,61 (±0,15)	7,44	0,01-0,1
p-Anisidine	104-94-9	-	-	-	0,12	-	-	0,01-0,1
N-Methyl-p-anisidine	5961-59-1	-	-	-	0,36	-	-	0,01-0,1
Triethanolamine	102-71-6	-	13	-	-	-	-	3-30
3-Methoxy-4,7-dimethyl-1H-isoindol**	100813-60-3	0,40 (±0,06)	-	-	0,24	-	-	0,01-0,1
N-Phenyl-2-pyridinamine	6631-37-4	-	-	-	0,05	-	-	0,01-0,1
4-(Diethylamino)-benzaldehyde	120-21-8	-	-	-	0,04	-	-	0,01-0,1
4-(2-Cyanoethyl)methylamino-benzaldehyde***	94-21-3	-	-	-	4,3	-	-	0,3-3
bis(2-Ethylhexyl) hexanedioic acid ester	103-23-1	-	-	-	-	-	-	0,01-0,1

"-" Below the detection limit

* The content of aniline is estimated against N-methyl-aniline.
** Content of 3-methoxy-4,7-dimethyl-1H-isoindol.
*** The compound is estimated against 4-(diethylamino)-benzaldehyde as the relevant standard could not be provided.

Table 3.5 Analysis results for sample no. 16, mg/g (± standard deviation in mg/g)

Identification	CAS-no.	16 Red**	16 Brown	16 Orange	16 Yellow	16 Black	Detection limit
D-Limonene	5989-27-5	-	-	0,21 (±0,04)	-	-	0,01
Benzyl alcohol	100-51-6	-	-	-	-	0,96 (±0,05)	0,01
5-Butyldihydro-2(3H)-Furanone*	104-50-7	-	0,43 (±0,13)	-	-	-	0,01
Citral (3,7-dimethyl-2,6-octadienal)	5392-40-5 (trans: 106-26-3, cis: 141-27-5)	-	-	0,30 (±0,06)	0,70 (±0,05)	-	0,01
5-Hexyldihydro-2(3H)-furanone	706-14-9	0,07	0,28 (±0,13)	-	-	-	0,01

"-" Below the detection limit

* The compound is estimated against 5-hexyldihydro-2(3H)-Furanone, as the relevant standard could not be provided.

** The precise weight and the uncertainty factor is not known as it is extracted in connection with the qualitative screening. The result is calculated against an average weight of no. 16, brow.

3.1.5 Ingredients in acrylic paint

Table 3.6 Analysis results for acrylic paint, mg/g (± standard deviation in mg/g)

Identification	CAS-no.	Product no.			Detection limit
		54 Red	55 Ligth green	61 Cubber	
Chloroaniline	106-47-8	-	0.37 (±0.08)	-	0.1
2-Propenoic acid, 2-ethylhexyl ester	103-11-7	-	-	0.35 (±0.08)	0.1
Propanoic acid, 2-methyl-, 2,2-dimethyl-1-(2-hydroxy-1-methylethyl)propyl ester*	74367-33-2	-	-	1.44 (±0.97)	0.1
Propanoic acid, 2-methyl-, 3-hydroxy-2,4,4-trimethylpentyl ester*	74367-34-3	-	-	1.79 (±0.03)	0.1
2-Naphthalenol, 1-[(4-methyl-2-nitrophenyl)azo]- (Toluidine Red)	2425-85-6	104 (±11)	-	-	20

"-" Below the detection limit.

* The compound is estimated against 2-ethyhexyl-2-propenoic acid ester, as the relevant standard could not be provided.

Table 3.7 Elements in acrylic paint, mg/g

Identification	CAS-no.	8 Black	18 Pink	34 Yellow	35 Ultramarin	36 Rose madder	41	Detection limit
Chrome		-	-	-	-	-	0,034	0,01
Nickel		-	-	-	-	-	-	0,01
Copper		-	-	-	-	-	-	0,01
Zinc		-	-	0,039	0,021	-	-	0,01
Silver		-	-	-	-	-	-	0,01
Tin		-	0,015	-	-	-	0,035	0,01
Barium		-	-	-	-	0,10	-	0,01
Lead		0,021	-	-	-	-	-	0,01

"-" Below the detection limit.

Table 3.7 Elements in acrylic paint, mg/g

Identification	CAS-no.	49 Silver	51 Dark brown	54 Red-302	55 Ultra marin blue	60 Silver	61 Metallic cubber	Detection limit
Chrome		-	0,047	-	-	-	-	0,01
Nickel		-	-	-	-	-	0,043	0,01
Copper		-	0,059	-	-	-	-	0,01

Zinc		-	-	-	0,017	-	-	0,01
Silver		-	-	-	-	0,025	-	0,01
Tin		0,075	0,013	-	-	0,022	-	0,01
Barium		-	-	160	0,61	5,0	5,1	0,01
Lead		-	-	0,024	-	-	-	0,01

”-” Below the detection limit.

3.1.6 Content in glitter glue

Table 3.8 Formaldehyde in glitter glue

Product no.	Formaldehyde [mg/kg]	Uncertainty factor [%-RDS]
13 pink	0,43	2,1
15 red	59	9,6
23 green	0,06	18
26 purple	46	0,21
28 green	0,94	36
29 light blue	13	7,1
33 gold	63	0,80
38	0,59	17
50 purple	110	13
53 gold	9,5	11

Table 3.9 Analysis results - glitter glue, mg/g (± standard deviation in mg/g)

Identification	CAS-no.	Sample no.		Detection limit
		26 Silver	29 Pink	
Phenol	108-95-2	0.054 (±0,003)	-	0.02
2-Phenoxy ethanol	122-99-6	-	0.24 (±0.01)	0.02

”-” Below the detection limit

Table 3.10 Elements in glitter glue, mg/g

Identification	CAS-no.	Sample no.						Detection limit
		14 Red	26 Gold	28 Dark purple	33 Green	38	50 Orange	
Chrome		0.17	0.066	-	-	-	-	0.01
Copper		-	-	0.12	0.015	-	-	0.01
Zinc		-	-	-	-	0.017	0.22	0.01
Tin		1.1	0.017	-	-	-	-	0.01
Antimony		-	-	0.22	-	-	-	0.01

”-” Below the detection limit

3.1.7 Elements in shrink plastic

Table 3.11 Elements in shrink plastic, mg/g

Identification	CAS-no.	Sample no.					Detection limit
		19	20	21	24	37	
Aluminium		0.16	-	-	-	0.62	0.02
Silicium		0.096	-	-	-	0.21	0.02
Calcium		1.7	-	-	-	0.19	0.01
Titanium		11	-	-	-	17	0.01
Zinc		0.13	0.084	0.079	0.079	0.20	0.01

”-” Below the detection limit

The X-ray analysis revealed no other elements.

3.2 Comments on the results of the quantitative analyses

By a comparison of the findings of the quantitative analysis and the findings of the chemical screening it has been observed that the different colour variations in the same product often contain different components.

Within the scope of this project it has not been possible to analyse all colour variations of the selected products. Therefore, it is possible that one or more of the products may contain components with a larger content of the identified substances than recorded in the quantitative analyses, or may contain not identified hazardous substances, because the colour variation was not taken out for analysis.

These variations are also assumed to be the reason why more of the components, revealed by the qualitative screenings, were not detected in the same product in connection with the quantitative analyses, as these were carried out on different colours variations. In addition, deconvolution software was used in the qualitative analysis, making it possible to detect contents in small amounts, which could not subsequently be quantified.

Sample no. 4 was selected for the quantitative analysis. In the colour variation selected for the analysis it was not possible to detect any of the substances, which were identified in connection with the screening.

3.3 Legislation and standards

Liquids in marker pens, glue, and acrylic paint are thus covered by the requirements in Statutory Order No. 329 on classification, packaging, labelling, sale, and storage of chemical substances and products, 2002 cf. § 1 and § 2.

The Danish Safety Technology Authority has classified the hobby products to be covered by the regulations stipulated in the Statutory Order No. 1116 on toys.

The order stipulates that toys may not be marketed if they constitute a hazard to the safety or the health of the consumers. Appendix 2 of the order includes the limit values for heavy metals and states that toys may not contain dangerous substances or preparations as defined in directive 67/548/EØF and directive 88/379/EØF in amounts which may be hazardous to children.

As mentioned in the Statutory Order, Appendix 3, there are a number of standards regarding safety regulations for toys (DS/EN 71-1 to DS/EN 71-7). Three new standards have been completed for organic chemical substances (***DS/EN 71-9, EN 71-10 and EN 71-11***), but these standards are not harmonised.

This standard lay down requirements to accessible liquids in toys under item 4.2, saying that the liquids may not be classified as toxic, harmful, corrosive, irritant or sensitizing according to directive 1999/45/EC. Beyond this, there may not be any substances classified as carcinogenic, mutagenic or reprotoxic classified as category 1 and 2.

Table 1 standard EN 71-9 specifies limits for coloured liquids, as the requirements to colorants (table 2b) and primary aromatic amines (table 2C)

shall be observed. Table 2c specifically mentions 4-chloraniline, o-anisidine and aniline, which were all found in the products. Under A11 it is stated that these substances may not be detected in toys according to (***DS/EN 71-11***).

It should be mentioned that the detected concentration of substances is in the range of 100-400 ppm, which is far beyond the detection limits stipulated in the standard.

The conclusion is that primary aromatic amines have been detected in marker pens and acrylic paint in concentrations beyond the requirements to the detection limits in (***DS/EN 71-9 and DS/EN 71-11).*** Marker pens and acrylic paint with primary amines do not comply with the standards for content organic substances.

3.4 Prioritization of substances in hobby products

Based on the health screening described in chapter 2.2 and the quantitative analysis we have in consultation with the Danish EPA selected a number of substances for extended health assessment.

The substances are:

- Aniline
- P-chloroaniline
- N-methylaniline
- C.I. Pigment Red 3
- N,N-Dimethylacetamide
- Bis (2-ethylhexyl)adipate
- p-anisidine
- 2-ethoxy ethanol
- Citral
- 2-ethylhexyl acrylate

The health effects of formaldehyde have also been assessed.

Substances used for assessment of environmental effect:

- Aniline
- Chloraniline

These substances are extremely toxic for aquatic organisms and –chloraniline alone is difficultly degradable, and the substances are therefore suitable for assessment of a worst case effect.

4 Health Assessment

4.1 Introduction

This chapter assesses the potential health effects of the identified substances. The assessment focuses on children of nursery and school age.

Information is available for each of the quantified substances on their identity and their chemical and physical properties. The data comprises structure, melting point, boiling point, density, vapour pressure and solubility.

The available literature in the field has been reviewed and focus has been put on ability to absorption via the skin and effects of oral intake. The most important test results and effects are presented. The object has been to find data on NOAEL/LOAEL (No or Low Observed Adverse Effect Levels) for the selected substances or other relevant available data.

Based on the NOAEL or similar data and the amount of substance the child is exposed to, the safety margin can be calculated (MOS), enabling us to assess whether the substance has a potential adverse health effect when using the tested products.

4.2 Method

4.2.1 Exposure paths

At the preliminary health screening hazardous substances were found in marker pens, gel pens, glitter glue, and acrylic paint, but not in shrink plastic.

It is assumed that the substances are absorbed in the body by oral intake via the mucous membranes in the mouth, when children are mouthing the objects or by penetration of the skin. Substances with a high vapour pressure may be absorbed through inhalation and via the lungs by e.g. evaporation from drawings etc.

4.2.2 Exposure scenarios

The absorbed amount will depend on the children’s use of the products.

The following is based on interviews with parents and known practice in nurseries/schools.

Regarding marker pens and gel pens it is well-known that children like to paint on their skin, to suck on the pens and even use the pens as lipstick. The paint may also be rubbed off from the drawings to the skin.

When using marker pens and gel pens a relatively limited amount of substances are slowly transferred to the paper.

Glitter glue may be applied to the skin, when the children squeeze out the glue or they touch their creations before the glue is dry (the glue dries up slowly). Children also tend to suck on objects, using them as lipsticks, etc. Larger areas of paper may rapidly be covered by glue and evaporation of the glue will occur.

Acrylic paint can be transferred directly to the skin partly during the creation process partly during the drying and indirectly orally, when children are sucking their fingers or the paint brushes. Relatively large areas will be covered by the paints and evaporation will occur.

There is no information in TGD (***2003***) regarding the transferred amount, therefore, we have set up some realistic exposure scenarios based on interviews with parents.

Exposure scenarios

Marker pens and gel pens

Skin contact

It is assumed that an area corresponding to two child palms of 5*5 cm (50 cm^2) is painted, and in worst case this happens once a day. Substances are assumed to be absorbed according to log K_{OW}. The amount being transferred to paper is determined by painting a square on paper, weighing the applied amount and calculating weight per exposure area (see Table 4.1). The amount is determined to 0.05 g for 50 cm^2.

Oral intake

It is assumed that the amount of oral intake corresponds to the amount absorbed via the skin (0.05 g/day).

Respiratory passages

The amount is assumed to be limited. For diffusible substances an estimate is made of the instant evaporation of all transferred substances to the local zone (1,5 m^3) and to a typical children's room with a volume of 18 m^3. The values are compared to the occupational exposure limit; OEL.

Glitter glue

Skin contact

Larger amounts may be applied to the skin. As worst case it is assumed that children transfer 3 ml = 3 g to the skin, equivalent to the weight of a densely painted area of 50 cm^2 (see Table 4.1).

Oral intake

The worst case is assumed similar to the amount transferred by skin contact (3 g).

Inhalation
For diffusible substances an estimate was made of instant evaporation of all transferred substance to the local zone (1,5 m^3) and to a typical children's room with a volume of 18 m^3. The values are compared to the threshold limit value (TLV).

Acrylic paint
Skin contact
The amount of acrylic paint applied to the skin is larger than for marker pens. As worst case is assumed an amount corresponding to a densely painted area of 50 cm^2 (see Table 4.1). The amount is determined to 1.25 g.

Oral intake
Worst case corresponding to the amount for skin contact. (1.25 g).

Inhalation
For volatile substances an estimate is made of instant evaporation of all transferred substance to the local zone (1,5 m^3) and to a typical children's room with a volume of 18 m^3. The values are compared to occupational exposure limit; OEL.

Table 4.1 Results of tests with densely colouring/painting of 100 cm^2 paper

No.	Type	Weight (g/100 cm^2)
17	Marker pen	0.108
45	Market pen	0.134
4	Gel pen	0.195
54	Acrylic paint	2.760
55	Acrylic paint	3.059
61	Acrylic paint	1.785
26	Glitter glue	5.550
29	Glitter glue	6.186

	g	Set value
Marker pen	0.121	0.1
Gel pen	0.195	0.2
Acrylic paint	2.535	2.5
Glitter glue	5.868	6

Weight
The weight of the exposed children is for worst case scenario determined to 15 kg, corresponding to a 3-year old child.

It is estimated that all children will get in contact with the products.

Exposure scenarios are defined according to EU's Technical Guidance Document (***TGD, 2003***).

Intake of a substance through skin or orally is calculated as:

$I = Q * M * F/BW$

Where:
I Intake per day per kg body weight

Q Concentration of substance (mg substance/gram sample)
M Intake amount (gram per day)
F Fraction of substance absorbed
BW Body weight (kg)

If no data are available for skin absorption, 100% absorption is assumed (F = 1), if the substance log K_{OW} is < 4, and 10 % absorption (F = 0,1), if log K_{OW} is < -1 and log K_{OW} > 4.

If no data are available for absorption through the mucous membranes in the mouth (orally), absorption is assumed to be 100 % i.e. F = 1.

Risk assessment
In the health risk assessment the calculated exposure, i.e. absorption shall be compared to NOAEL or similar values. As NOAEL is typically based on animal tests, the margin of safety (MOS) is calculated by dividing NOAEL in mg/kg b.w by the intake.

If the data for animal are based on a high quality chronic long-term study the safety margin in the risk assessment will typically be 10. The safety factors used for derivation of a NOAEL for humans are often based on animal tests with e.g. mice or rats. For instance a factor 10 is used for extrapolation between species (different species) and a factor 10 is used for protecting sensitive individuals within the species such as children. If the data are based on LOAEL or a subchronic study an additional safety factor is being added (typically 10). The total safety factor is the combined product of the individual safety factors.

In the assessment of health effects MOS is not used for sensitizing effects as they have no lower concentration limit.

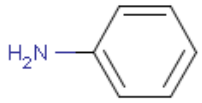
4.3 Selected substances

The substances described in the following have been identified as being the most important in terms of health risk by use.

4.3.1 Aniline

4.3.1.1 Identity

Name	Aniline
CAS-no.	62-53-3
EINECS-no.	200-539-3
Molecular formula	C_6H_7N
Substance composition	



Molecular weight (g/mol)	93.13
Synonyms	Benzenamine, phenylamine
Description	The substance is an oil liquid, colourless in its pure state.
Boiling point	184.1 ºC (***Lide, D.R., 1998-1999***)
Melting point	-6 ºC (***Lide, D.R., 1998-1999***)
Solubility	36,000 mg/l, 25 ºC, water (***Yalkowski SH, 1992***) Miscible with ethanol, ethyl ether, acetone (***Lide, D.R, 1998-1999***)
Distribution coefficient Log K_{ow}	0.9 (***Hansch, 1995***)
Vapour pressure	0.49 mm Hg at 25 ºC (***Daubert, T.E., 1989***)
Odour	Aromatic amine-like odour (***NIOSH, 1997***)

4.3.1.2 Detected amounts

The substance was detected in product no. 45 (green colour) in a concentration of 0.22 mg/gram (0.022 %) and in product no. 25 (pink) with 0.11 mg/kg.

4.3.1.3 Function

Aniline is used for synthesis of a number of chemicals, i.a. rubber accelerators, colorants, herbicides, pesticides, pharmaceutical substances (HDSB) and (***EC 2004).***

4.3.1.4 Classification and limit values

The substance is included in the List of Dangerous Substances (***Miljøministeriet, 2005)*** and is classified as:

T;R23/24/25	Toxic by inhalation, skin contact and if swallowed
R48/23/24/25	Serious health effects by long-term exposure through inhalation, skin contact and if swallowed
Carc 3;R40	Potential carcinogenic effect
Xi;R41	Risk of serious eye injury
R43	Allergic contact dermatitis
Mut3;R68	Risk of permanent health damage
N;R50	Very toxic for aquatic organisms.

The threshold limit value for occupational health and safety is 1 ppm, corresponding to 4 mg/m^3 with an HK note, which means that the substance can be absorbed through the skin and is included in the list of carcinogenic substances (***AT 2005***).

The B-value, indicating the maximum concentration acceptable in the environment, is perhaps a better measure in this connection. The B-value is 0.08 mg/m^3 (see B-value Guideline, ***EPA 2002***).

4.3.1.5 Health effects

We have retrieved data regarding health effects in TOXNET and related databases. The substance has its own fact sheet in IUCLID and an EU risk assessment is worked out (EC 2004).

Acute toxicity

The substance is toxic.

Acute toxicity if swallowed based on animal tests indicate that the substance is on the verge of being toxic (LD_{50} rat close to 200 mg/kg):

- LD_{50} rat, oral 250 mg/kg (***Lewis, R.J.,1996***)
- LD_{50} dog 195 mg/kg (***Lewis, R.J., 1996***)
- LD_{50} rat skin 1,400 mg/kg (***Lewis, R.J.,1996***)
- LC_{50} mouse inhalation 175 ppm, 7 hours (***Lewis, R.J., 1996***)

The substance oxidizes iron II to iron III in haemoglobin, thus forming methaemoglobin, whereby the oxygen transport in the blood is reduced.

More accidents have been reported about human exposure to aniline. Thus, an oral intake of 60 ml or 876 mg/kg is fatal ***(Janik-Kurylcio et al., 1973).***

In the EU risk assessment(***EU risk assessment, 2004***) aniline is from an overall assessment of a number of data for animals and humans classified toxic with risk phrases R23,R24,R25 (see also comments about the methemoglobin forming effects of the substance group under p-anisidine).

Aniline is strongly irritating to eyes (***Lewis, R.J., 1996).***Aniline is easily absorbed orally, by skin contact and by inhalation. Data in the EU risk assessment (***EU risk assessment, 2004***) indicate a skin absorption of more than 38 %.

Subchronic toxicity
Aniline has a sensitizing effect demonstrated on hamsters (***Goodwin et al., 1981***) and in patch tests, where about 5-9 % reacted positively on aniline (***Meneghini et al., 1963***) and (***Angelini et al., 1975***).

Repeated exposure to aniline will have a hemotoxic effect.
In a 14-day inhalation test with rats a LOAEC of 17 ppm was demonstrated (***EPA, 1981***).

Chronic toxicity
A 103-week test with repeated addition of aniline in the rat feed showed hemotoxic effects at levels as low as LOAEL = 7 mg/kg/day (***CIIT, 1982***). The test also established tumours in 39 % of the rats at a dosage of 72 mg/kg/day, 1.1 % tumours at 22 mg/kg/day and 0 % at 7 mg/kg/day. In the tests a NOAEL of 21 mg/kg/day was calculated for development toxicity.

The values for the hemotoxic effect at repeated exposure is in (***EU risk assessment, aniline, 2004)*** used for calculating a safety factor of 107 at dermal absorption of 7 mg/kg/day.
For an adult a critical exposure level is calculated to 7/107 = 0.065 mg/kg/day or 5 mg/person/day (70 kg/person).

Assuming 100 % absorption via the skin, orally and by inhalation a critical level has been calculated for inhalation of 0.5 mg/m^3 for 8 hours light work with an air consumption of 10 m^3 and a body weight of 70 kg.

The values for the detected tumours have been used for calculating a safety factor for carcinogenic effects in humans (***EU risk assessment, 2004)***. A multistage model is used which indicates a risk level of $9.1 \cdot 10^{-4}$ at 1 mg aniline/kg/day for rats. The model is linear at low concentrations.

Based on the model above, the risk level, where an acceptable low effect exists, (the critical level) has been preset to $1 \cdot 10^{-4}$, equivalent to 0.11 mg/kg/day for rats. A factor of 10 is assumed for interpolation between species and further a correction for exposure time has been made. Thus an adult, who is exposed to the substance during working hours, will have a correction factor of (75 years * 52 weeks * 7 days)/(40 years * 48 weeks * 5 days) = 2.84. The critical exposure level for skin absorption is then 0.11/10 * 2.84 = 0.03 mg/kg/day or 2 mg/person/day.

Regarding development toxicity the (***EU risk assessment, 2004)*** uses a safety factor of 10 for interpolation between species, by which a critical exposure level is calculated to 2.1 mg/kg/day.

Summary
A hemotoxic effect has been established in rats with a LOAEL = 7 mg/kg/day for aniline.

The substance may be carcinogenic (R40) and sensitizing.

At a risk level of 10^{-4} for carcinogenic effect the critical exposure level by skin absorption is 0.03 mg/kg/day.

4.3.1.6 Exposure scenarios
The maximum content in a marker pen is 0.22 mg per gram.

The exposed area is assumed to be 50 cm^2 and it is further assumed that the aniline is absorbed before it is washed off after e.g. 1 hour which is realistic with log K_{OW} = 0.9. Tests have proven that the amount of ink transferred to 50 cm^2 is 0.05 gram. Afterwards the maximum intake is calculated on assumption of 100 % skin absorption.

Intake, skin = 0.22 mg/g * 0.05 g/15 kg = 0.00073 mg/kg b.w./day.

Oral intake is assumed to be the same whether the child is sucking his fingers or sucking on a pen.

4.3.1.7 Assessment
Based on the LOAEL for hemotoxic effect on rats a safety margin of MOS = 7/0.00073 = 9500 is found, which is almost 100 times above the safety factor of 107, which is stipulated in (***EU risk assessment, 2004)*** for skin contact.

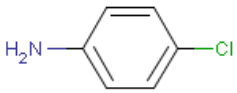
As to the carcinogenic effect the intake amount = 0.03/0.00073 = 40 times below the critical exposure level for carcinogenic effects with a risk factor of 10^{-4}.

The concentration of aniline in a marker pen is 0.022 %. The ink from the marker pen will be applied to the skin in the same way as creams and other cosmetics. Compared to the Statutory Order (***Statutory Order On Cosmetics Products, 2006***), the substance should be declared on a product label (required for > 0.01 % for substances to be washed off and >0,001 % for substances which cannot be washed off). Aniline shall be labelled with R43, “Allergic contact dermatitis”, it is therefore assessed that if the marker pen comes in contact with skin it can cause risk of senbilisation.

4.3.2 p-chloroaniline

4.3.2.1 Identity

Name	p-chloroaniline
CAS-no.	106-47-8
EINECS-no.	203-401-0
Molecular formula	C_6H_6ClN
Substance composition	



Molecular weight	127,57 g/mol
Synonyms	4-chloraniline 1-amino-4-chlorobenzen p-chlorphenylamine
Description	Consists of colourless crystals
Boiling point	232 ºC (***O'Neil, M.J. (ed.), 2001***)
Melting point	72,5 ºC (***O'Neil, M.J. (ed.), 2001***)
Solubility	3.900 mg/l, 25 ºC (***Kilzer L et al; 1979***). The substance is soluble in alcohol, ether, acetone, carbon disulphide (***O'Neil, M.J. (ed.), 2001***)
Distribution coefficient Log K_{ow}	1,83 (***Hansch, C., Leo, A., D. Hoekman, 1995***)
Vapour pressure	0,071 mm Hg at 25 ºC (***Daubert, T.E., R.P. Danner, 1989***)
Odour	Vague, sweet characteristic amine odour (***U.S. Coast Guard, Department of Transportation, 1984-5***)

4.3.2.2 Detected amounts

The substance was detected in 2 acrylic paint products (nos. 6 and 55). The amount is quantified in one product (no. 55) to 0.37 mg/g.

4.3.2.3 Function

The substances are used in the production of colorants, agrochemical (pesticides) and in medicine. The content is assumed to be remains from colorant production.

4.3.2.4 Classification and limit values

The substance is included in the List of Dangerous Substances (EPA***, 2005)*** and is classified as:

T;R23/24/25	Toxic by inhalation, skin contact and if swallowed
Carc.cat.2;R45	Carcinogenic
R43	Allergic contact dermatitis
N;R50-53	Very toxic for aquatic organisms May cause undesired long term effects to the water environment

There is no limit value for occupational health and safety.

4.3.2.5 Health effects

Data regarding health effects have been retrieved in TOXNET and related databases.

Acute toxicity

The substance is toxic:

- LD_{50} rat, oral 200-480 mg/kg (IARC, 1972-present)
- LD_{50} mouse, oral 100 mg/kg (***Lewis, R.J. 1996***)
- LD_{50} cat, dermal 239 mg/kg (***Lewis, R.J. 1996***)

According to (***CICAD, 2003***) studies of rats, mice and cats have established that the substance is a stronger methaemoglobin former than aniline. The haemoglobin binding index is thus 569 at a concentration of 0.6 mmol/kg in rats against a factor 22 at 0.47 mmol aniline/kg.

Cyanosis and methemoglobinaemia have been reported for premature babies poisoned by p-chloroaniline in connection with an incubator. The incubator was equipped with a humidifier with chlorhexidine solution, which may decompose to p-chloroaniline when heated. A concentration of methaemoglobin between 6.5 and 45.5 % was found against a normal value below 2.3 % and a fatal concentration over 70 % (***CICAD, 2003)***.

(See also comments on methemoglobin forming effect of the substance group under p-anisidine).

The substance is classified as an eye irritant (***International Labour Office, ILO 1983***).

Subchronic toxicity

Tests on guinea pigs show that p-chloroaniline can be classified as a skin sensitizing substance (***CICAD, 2003).***

Chronic toxicity

A 103-week test with repeated addition of aniline in the rat feed showed hemotoxic effects (increased methaemoglobin level, impact on number of reticulytes etc.) by all dosage levels including the lowest value of 2 mg/kg/day (***CICAD, 2003***).

The substance appeared to be carcinogenic in a number of tests. A large number of tumours were detected by a dosage of 18 mg/kg in 103 weeks (36 out of 50 male rats), by 6 mg/kg it is 3 out of 50, by 2 mg/kg 1 tumour and no one in controls (***CICAD, 2003***). Females are less responsive than males.

For mice a significant increase was observed in the number of hemangiosacoma at 0 (2 out of 20), 2.5 mg/kg (9 out of 50), and 5 mg/kg (14 out of 50) for male mice in 78-week test with 13 following weeks for observation. Same for hepatocellular carcinomas at 0 (3 out of 50), 3 mg/kg (7 out of 49), 10 mg/kg (11 out of 50) and 30 mg/kg (17 out of 50) in a 103-week feeding test (***IARC, 1972- present***).

A comparison of the two chronic 103-week rat tests indicates that the carcinogenic effect of p-chloroaniline is higher than aniline.

In (***CICAD, 2003***) it is stated that the available screening tests indicate a possible mutagenicity of p-chloroaniline.

A reference dose exists for chronic oral exposure of p-chloroaniline based on a 78-week feeding test with rats and a LOAEL of 12.5 mg/kg. A safety factor of 3000 gives an RfD of 0.004 mg/kg/day (***IRIS, 1995***).

Summary
Chronic data for hemotoxic effect of p-chloroaniline in rats gives LOAEL = 2 mg/kg/day.

RfD for chronic oral exposure is 0.004 mg/kg/day.

The substance has sensitizing effect.

The substance is carcinogenic (R45) in rats and mice. Carcinogenic effect in % level is observed already by 2 mg/kg/day.

4.3.2.6 Exposure scenarios
The maximum content in acrylic paint no. 55 is 0.37 mg per gram.

The exposed area is assumed to be 50 cm^2 and it is further assumed that all p-chloroaniline is absorbed before washing off after e.g. 1 hour which is realistic with log K_{OW} = 1.8. Tests have proven that the amount of ink transferred to 50 cm^2 is 1.25 gram.

Intake, skin = 0.37 mg/g * 1.25 g/15 kg = 0.031 mg/kg b.w./day.

It is assumed that the max. oral intake by e.g. finger sucking or sucking a paintbrush is 1 ml or approx. 1 gram, corresponding to max. skin absorption.

4.3.2.7 Assessment
Based on the LOAEL for hemotoxic effect on rats the safety margin will be 2/0.031= 65.

The margin is rather low as it is based on LOAEL, therefore, apart from a factor 100, a factor 10 for extrapolation from LOAEL to NOAEL should be added.

This is confirmed by the RfD = 0.004 mg, which is by 8 times below the calculated intake.

Additionally, there may be carcinogenic effects, which are observed in rats and mice already by a dose of 2 mg/kg/day. These effects have no lower limit but decrease with degree of concentration. The critical exposure level for carcinogenic effects is expected to be the same - or even below the level for aniline, where the critical exposure level is 0.03 mg/kg at a risk level of 10^{-4}. The level is exceeded in acrylic paint no. 55 as the absorbed amount is 0.031 mg/kg/day and there is thus a significant risk of a carcinogenic effect af the absorbed quantity of acrylic paint. Product no. 55 is no longer sold.

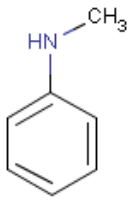
The paint will be applied to the skin in the same way as creams and other cosmetics. When compared to the Statutory Order (***Statutory Order on Cosmetics Products, 2006***), the substance should be labelled with declaration of contents (required for > 0.01 % for substances to be washed off and >0,001

% for substances which cannot be washed off). P-chloroaniline shall be labelled with R43, "Allergic contact dermatitis", it is therefore assessed that if the marker pen comes in contact with skin it can cause risk of senbilisation.

4.3.3 N-methylaniline

4.3.3.1 Identity

Name	N-methylaniline
CAS-no.	100-61-8
EINECS-no.	202-870-9
Molecular formula	C_7H_9N
Substance composition	



Molecular weight	107.15 g/mol
Synonyms	Methylphenylamine Aniline, N-methyl
Description	Colourless or faint yellow liquid
Boiling point	196,25 ºC (***Riddick, J.A. et al., 1985***)
Melting point	-57 ºC (***Riddick, J.A. et.al., 1985***)
Solubility	5.624 mg/l water at 25 ºC (***Yalkowsky SH, Dannenfelser RM, 1992***). Soluble in ethanol, ether and carbon tetrachloride (***Lide, D.R. (ed.), 1994-1995***)
Distribution coefficient Log K_{ow}	1.66 (***Hansch, C. and A. Leo, 1987***)
Vapour pressure	0.453 mm Hg at 25 ºC (***Daubert, T.E., R.P. Danner, 1989***)
Odour	Vague ammonia-like odour (***NIOSH, 1994***)

4.3.3.2 Detected amounts

The substance was detected in 4 marker pens in products nos. 10 and 45. 0.44 mg/g is quantified in no. 10, orange, and 0.99 mg/g in no. 45, green.

4.3.3.3 Function

The substance is used as chemical intermediate and solvent (HDSB).

4.3.3.4 Classification and limit values

The substance is included in the List of Dangerous Substances (EPA***, 2005)*** and classified as:

T;R23/24/25	Toxic by inhalation, skin contact and if swallowed
R33	May be accumulated in the body by repeated use
N;R50-53	Very toxic for aquatic organisms; May cause long-term damage to the water environment.

The threshold limit value for occupational health and safety is 0.5 ppm, equivalent to 2.25 mg/m^3 with a note H, which means it can be absorbed through the skin.

4.3.3.5 Health effects

Data on health effects have been retrieved in TOXNET and related databases.

Acute toxicity

- LD_{50} rat, oral 951 mg/kg (***National technical, 1982***)
- LD_{50} rabbit, skin 1,77 mL/kg (***American Industrial, 1962***)
- LD_{lo}, cat, intravenously 24 mg/kg (***American conference, 1991***)

The data for rats indicate that the substance is hazardous to health, but it is classified as toxic. Its tendency to form haemoglobin may, however, justify this classification. (Please also see comment under p-anisidine).

Human poisoning has not been reported, but the clinical toxilogical effect is expected to comparable with aniline poisoning, hereunder methaeglobinaemi with signs of cyanosis. Like aniline the substance oxidizes iron II to iron III in haemoglobin, thus forming methaemoglobin, whereby the oxygen transport in the blood is reduced (***American conference, 1991***).

Subchronic toxicity

Data covering this substance are sparse. Based on its chemical structure the effects may be expected to be in-between those of N,N-dimethylaniline and aniline.

Data for N,N-dimethylaniline (CAS-no.121-69-5) from a 13-week feeding test with rats (10 males, 10 females) indicate a LOAEL of 31 mg/kg. Similar tests have been made on mice, indicating NOAEL=32 mg/kg (***IUCLID dataset N,N-dimetylaniline, 2000***).

Chronic toxicity

Data are sparse. Based on its chemical structure the effects may be expected to be in-between those of N,N-dimethylaniline and aniline.

A 2-year study has been carried out for N,N-dimethylaniline in rats with doses up to 30 mg/kg. A positive trend was observed for cancer cells in male rat spleens and it was noted that both rats and mice would be able to resist much higher doses.

As the toxilogical properties of N-methylaniline are estimated to be in-between aniline and N,N-dimethylaniline, it may have a potential carcinogenic effect.

Summary

The substance has hemotoxic effects. No data are available on the substance but we know that the LOAEL for rats is 31 mg/kg/day for N,N-dimethylanilind and 7 mg/kg/day for aniline.

LOAEL for N-methyl-aniline is estimated to be between these values and is thus preset to 15 mg/kg/day.

From the data for aniline (potential carcinogenic effect in humans (R40)), and N,N-dimethylaniline (carcinogenic effect in spleens in male rats), it is estimated that N-methylaniline may also have a carcinogenic effect.

4.3.3.6 Exposure scenarios

The maximum content in marker pen was 0.99 mg per gram.
The exposed area is assumed to be 50 cm^2 and it is further assumed that the aniline is absorbed before being washed off after e.g. 1 hour which is realistic with log K_{OW} = 1.66. Tests have proven that the amount of ink transferred to 50 cm^2 is determined to 0.05 g.

Intake, skin = 0.99 mg/g * 0.05 g/15 kg = 0.0033 mg/kg b.w./day.

It is assumed that the max. oral intake by e.g. finger sucking or sucking a marker will be the same.

4.3.3.7 Assessment

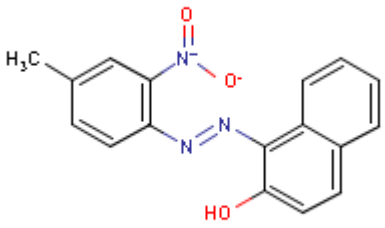
With an estimated LOAEL for hemotoxic effect of 15 mg/kg/day the MOS is calculated to 15/0.0033 = 4545, thus there will be no risk of hemotoxic effects.

The substance may be carcinogenic when comparing to the data from the related substances aniline and N,N-dimethylaniline.

4.3.4 C.I. Pigment Red 3

4.3.4.1 Identity

Name	C.I. Pigment Red 3
CAS-no.	2425-85-6
EINECS-no.	219-372-2
Molecular formula	$C_{17}H_{13}N_3O_3$
Substance composition	



Molecular weight	307,33 g/mol
Synonyms	Toluidine red CI 12120 1-((4-Methyl-2-nitrophenyl)azo)-2-naphthalenol 2-Naphthalenol, 1-((4-methyl-2-nitrophenyl)azo)-
Description	Solid substance
Boiling point	Unknown
Melting point	270-272 ºC (MSDS, 1996)
Solubility	Insoluble (Gosselin, R.E., H.C. Hodge, R.P. Smith, and M.N. Gleason, 1976), estimated to 0.05 mg/l of (***US-EPA 2003***)

Distribution coefficient	6.45 estimated (***US EPA, 2003***)
Log K_{ow}	
Vapour pressure	Very small (solid substance)
Odour	Not known

4.3.4.2 Detected amounts

The substance has been detected in product no. 54 in a concentration of 104 mg/g.

4.3.4.3 Function

The substance is a colorant.

4.3.4.4 Classification and limit values

This substance is not classified according to Directive 67/548/EEC, Annex I, and is thus not included in the List of Dangerous Substances (EPA ***2005***).

4.3.4.5 Health effects

Data on health effects have been found in TOXNET and related databases.

Acute toxicity

Results from feedings tests indicate a very low acute toxicity on rats and mice. LD_{50} for rats is thus expected to be significantly over the 6,500 mg/kg based on the subchronic data below.

Subchronic toxicity

A 2-week feeding test on rats and mice showed no deaths even with up to 100,000 ppm in the feed.

At a 13-week feeding test with 10 mice and 10 rats with up to 50,000 ppm of the substance no deaths were reported. On the assumption that a rat of 200 g eats 15 g feed, 100.000 ppm correspond to a LD_{lo} of over 6,500 mg/kg.

Chronic toxicity

IARC has classified the substance under group 3, covering substances with inconclusive evidence of carcinogenic effect in humans and reduced effect in experimental animals (***IARC, 1972-present***).

In a 2-year feeding test on mice and rats some evidence of carcinogenic effects was seen (***Toxicology, 1992***). Thus there was a positive trend in the number of hepatocellular tumours in female rats (0 ppm: 0/50, 6.000 ppm: 0/50, 12,500 ppm: 1/50 og 25,000 ppm: 10/50).

Tubular tumours in the renal cortex showed positive trends (0 ppm: 0/50, 12500 ppm: 0/50, 25000 ppm: 0/50 og 50000 ppm: 6/50) for male mice just like follicular tumours in the thyroid glad with (0 ppm: 0/50, 12500 ppm: 0/49, 25000 ppm: 1/50 og 50000 ppm: 5/50).

The tests showed no indication of toxic effects.

The test also showed a weight loss of more than 10 % in rates with doses of 12500 and 25000 ppm and in mice with doses of 50000 ppm.

With a conversion factor of 15, the 12.500 ppm for rats correspond to a LOAEL of approx. 830 mg/kg, based on the assumption that a rat of 200 g eats 15 g per day.

Summary
Subchronic feeding tests with rats show that the substance with an LD_{lo} of approx. 3,200 mg/kg is not very toxic.

There is some evidence of carcinogenic effect in rats and mice but not sufficient evidence to prove carcinogenic effect in humans. Carcinogenic effects in the range of 2 % of the experimental animals have been observed at approx. 830 mg/kg for rats, and further the weight loss was over 10 %.

4.3.4.6 Exposure scenarios
The maximum content in a sample is 104 mg per gram.

The exposed area is assumed to be 50 cm^2 and it is further assumed that 10% pigment Red 3 is absorbed before washing off after e.g. 1 hour which is realistic with log K_{OW} = 6.5. Tests have proven that the amount of acrylic paint transferred to 50 cm^2 is determined to 1.25 g. Subsequently, the maximum intake is calculated assuming 100 % oral absorption.

Intake, skin = 104 mg/g * 1.25 g/15 kg/10 = 0.87 mg/kg b.w./day.

It is assumed that the max. oral intake by e.g. finger sucking or sucking a paint brush is 1 ml or approx. 1 gram, corresponding to 10 times the maximum skin absorption.

Intake, oral = 104 mg/g * 1.25 g/15 kg = 8.7 mg/kg b.w./day.

4.3.4.7 Assessment
At a 2-year feeding tests with rats a weight loss of more than 10% was observed at a dose of 830 mg/kg. At the same concentration carcinogenic effects were observed in approx. 2% of the rats.

In the absence of NOAEL for effects, the lowest concentrations where such effects were observed were used.

Based on this, a MOS = 958 by skin absorption is calculated and MOS = 95 by oral intake.

It is estimated that there will be no risk of toxic effects by skin absorption, however, a minor risk by oral intake, as MOS = 100.

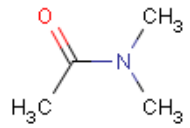
Potential carcinogenic risk would exist, if data from rats could be transferred to humans.

4.3.5 N,N-Dimethylacetamide

4.3.5.1 Identity

Name	N,N-Dimethylacetamide
CAS-no.	127-19-5
EINECS-no.	204-826-4
Molecular formula	C_4H_9NO

Substance composition



Molecular weight	87.12 g/mol
Synonyms	Acetamide, N,N-dimethyl- dimethylacetamide Acetic acid, dimethylamide
Description	Colourless liquid (***NIOSH, 1997***)
Boiling point	163-165 ºC (***Budavari, S. (ed.), 1996***)
Melting point	-18.59 ºC (***Lide, DR (ed.), 2000***)
Solubility	Soluble in benzene, alcohol, acetone, ether (***Lide, DR (ed.), 2000***)
Distribution coefficient Log K_{ow}	-0.77 (***Hansch, C., Leo, A., D. Hoekman, 1995***)
Vapour pressure	2 mm Hg at 25 ºC (***Daubert, T.E., R.P. Danner, 1989***)
Odour	Weak ammonia-like or fishlike odour (***NIOSH, 1997***)

4.3.5.2 Detected amounts

The substance was detected in 2 marker pens in the colours red and light green in product no. 17 in concentrations 0.22 and 0.4 mg/g.

4.3.5.3 Function

The substance is used as solvent in industrial applications (BASF 2006).

4.3.5.4 Classification and limit values

The substance is included in the List of Dangerous Substances (EPA 2005) and is classified as:

Rep2;R61	May harm the unborn child during pregnancy
Xn;R20/21	Harmful by inhalation and skin contact

The threshold limit value for occupational health and safety is 10 ppm, equivalent to 35 mg/m^3 with a note H, which means that the substance can be absorbed through the skin.

B-value is 0.1 mg/m^3 (***EPA 2002***).

4.3.5.5 Health effects

Data on health effects were retrieved in TOXNET and in related databases. The substance is found in IUCLID and is further described in (***Survey no. 42, 2004***).

Acute toxicity

Low acute toxicity:

- LD_{50} rat, oral 4.390 mg/kg (***Prager, J.C., 1995***)
- LD_{50} rabbit, dermal 2.240 mg/kg (***Lewis, R.J, 1996***)
- LC_{50} rat, inhalation, 1 time 2.475 ppm (***Snyder R., 1990***)

Subchronic toxicity
Data for oral dosing of the substance in pregnant rats show a NOEL for maternal toxicity of 65 mg/kg/day and shows also 65 mg/kg/day for teratogenic effect.

Chronic toxicity
At a 90-day feeding test a NOEL of 200 ppm (***Kennedy, 1986***) was determined based on liver effects.
In a 2-year inhalation study with rats exposed to the substance 5 days/week, 6 hours a day, changes occurred in absolute and relative liver weight, at 100 ppm various liver defects followed, but not by a dose of 25 ppm (0.09 mg/l), which is the NOAEL value for inhalation (***IUCLID N,N-dimethylacetamide, 2000***).

Summary
Liver effects were demonstrated at 2000 ppm.
By an assumed rat weight of 200 g and a feed consumption of 20 gram per day this corresponds to NOEL = 20 mg/kg/day.

From an inhalation study with NOAEL = 0.09 mg/l it is possible similarly to calculate a NOAEL = 0.8 * (6 * 60) * 0.09 = 26 mg/kg/day, by a respiration of 0.8 l/min/kg and 6 hours exposure/day.

4.3.5.6 Exposure scenarios
The maximum content in a marker pen was 0.4 mg per gram.

The exposed area is assumed to be 50 cm^2 and it is further assumed that N,N-dimetylacetamide is absorbed before the ink is washed off after e.g. 1 hour which is realistic with log K_{OW} = 0.77. Based on tests, the amount of acrylic paint transferred to 50 cm^2 is determined to 0.05 g.

Intake, skin = 0.4 mg/g * 0.05 g/15 kg = 0.00133 mg/kg k.v./day.

It is assumed that the max. oral intake by e.g. finger sucking or sucking a marker pen is the same.

4.3.5.7 Assessment
A NOEL of 20 mg/kg/day is set for liver effects in rats.

Based on this value the MOS is 20/0.00133 = 15000.

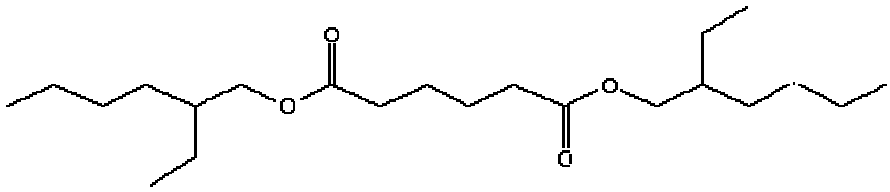
We have therefore assessed that there are no health effects in connection with exposure to N,N-dimethylacetamide in the stated amounts.

4.3.6 BIS(2-Ethylhexyl) Adipate

4.3.6.1 Identity

Name	BIS(2-Ethylhexyl) Adipate
CAS-no.	103-23-1
EINECS-no.	203-090-1
Molecular formula	$C_{22}H_{42}O_4$

Substance composition



Molecular weight	370,57 (***Lide, D.R. (ed.), 1998-1999***)
Synonyms	
Description	Faintly coloured oily liquid (***Lewis, R.J., Sr (Ed.), 1997***)
Boiling point	214 ºC (***Lide, D.R. (ed.), 1998-1999***)
Melting point	-67.8 ºC (***Lide, D.R. (ed.), 1998-1999***)
Solubility	Soluble in ethanol, ethyl ether, acetone and acetic acid (***Lide, D.R. (ed.), 1998-1999***) In water 0.78 mg/l at 22 ºC (***Felder JD et al, 1986***)
Distribution coefficient Log K_{ow}	8.1 ***(Verschueren, K, 1996)***
Vapour pressure	8.5 x 10-7 mm Hg at 20 ºC (***Felder JD et al, 1986***)
Odour	Vague aromatic odour (***Lefaux, R, 1968***)

4.3.6.2 Detected amounts

The substance has been detected in product no. 10 in the colours purple and orange in concentrations of 0.32 and 0.35 mg/g.

4.3.6.3 Function

The substance is a plasticizer. The concentrations are rather low and therefore the plasticizer is not considered to have any technical function, its presence is probably due to a contamination either in connection with the production of the ink liquid or due to migration of the plastic in the marker pen.

4.3.6.4 Classification and limit values

The chemical substance is not in the List of Dangerous Substances (***EPA, 2005***), which means that it is not classified according to directive 67/548/EEC, Annex I.

4.3.6.5 Health effects

Data on health effects were retrieved in TOXNET and related databases. The substance is specified in IUCLID.

Acute toxicity

Very low level of acute toxicity:

- LD_{50} rat, oral 5.610-20.000 mg/kg (***IUCLID dataset bis (2-ethylhexyl)adipate, 2000***)
- LD_{50} mice, oral 15.000 mg/kg (***IUCLID dataset bis (2-ethylhexyl)adipate, 2000***)
- LD_{50} guinea pig, oral 12.900 mg/kg (***IUCLID dataset bis (2-ethylhexyl)adipate, 2000***)

The substance is classified as an eye irritant (***U.S. Coast Guard, 1984-5***).

Subchronic toxicity

In a 19-week one generation study with doses of 0, 28, 170 and 1080 mg/kg/day in 15 male and 30 female rats a reduction in body weight of progeny and increased liver weight of males and females were found with a calculated LOAEL of 1080 mg/kg/day and NOAEL = 170 mg/kg/day.

A 91-day study of rats and mice established reduced body weight when dosing 700 and 1500 mg/kg/day, but not at 400 mg/kg/day.

The tests have been used for estimating the RfD = 0.6 mg/kg/day with a factor 10 for both species uncertainty and for species variations, and a factor 3 for lack of reliable data from a multigeneration study (***IRIS, Bis-2-ethyl hexyl) adipate, 1989***).

A study with development toxicity demonstrated minor effects on skeletons at 170 mg/kg and 1080 mg/kg, but not at 28 mg/kg/day, where NOAEL for teratogenic effect is set to 28 mg/kg/day (IUCLID dataset bis (2-ethylhexyl) adipate 2000).

The mentioned data for development toxicity have been used for calculation of TDI (tolerable daily intake) of 0.3 mg/kg/day (***OECD SIDS, 2000***).

Chronic toxicity
A 2-year study with 50 male and 50 female rats and a similar number of mice with resp. 12.500 ppm and 25.000 ppm demonstrated statistically significant hepatocellular carcinoma and adenoma in female mice, these cannot however be related to effects in humans (***DHHS/NTP, 1982***).

IARC has classified the substance in group 3 (Cannot be classified with regard to carcinogenic effect in humans) (***IARC, 1972-present***).

Summary
The substance causes increased liver weight with an estimated NOAEL of 170 mg/kg in a subchronic study with rats.

A teratogenic effect has been established for rats with a LOAEL = 170 mg/kg/day and NOAEL = 28 mg/kg/day.

The substance cannot be classified with regard to carcinogenic effect in humans.

4.3.6.6 Exposure scenarios
The maximum content in a marker pen was 0.35 g per gram.

The area is assumed to be 50 cm^2 and it is further assumed that 10 % of bis (2-ethylhexyl) adipate absorbed before the ink is washed off, e.g. after 1 hour, based on the high value of log K_{ow}= 8.1. Based on tests the amount of ink transferred to 50 cm^2 determined to be 0.05 gram. Based on this the maximum intake is calculated assuming 100 % oral absorption.

Intake, skin = 0,35 mg/g * 0.05 g/15 kg/10 = 0.00012 mg/kg b.w./day.

The oral intake is assumed to be by 10 times higher due to 100 % absorption e.g. when sucking fingers or on the marker pen.

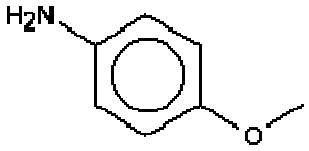
4.3.6.7 Assessment

From the effect on liver weight of rats, the MOS is = 170/0.00012 = 1.45 millions by skin absorption and 145,000 by oral intake. It can thus be concluded that there are no health effects connected with intake of the substance, it should however be noted that possible carcinogenic effects in humans have not been investigated in detail.

4.3.7 P-Anisidine

4.3.7.1 Identity

Name	P-Anisidine
CAS-no.	104-94-9
EINECS-no.	203-254-2
Molecular formula	C_7H_9NO
Substance composition	



Molecular weight	123,15 g/mol
Synonyms	4-anisidine Aniline, 4-methoxy- benzenamine, 4-methoxy-
Description	White crystals (***Gerhartz, W. (exec ed.), 1985***)
Boiling point	243 ºC (***Lide, DR (ed.), 2000***)
Melting point	57.2 ºC (***Lide, DR (ed.), 2000***)
Solubility	Soluble in benzene, solubility very good in ether and ethanol (***Lide, DR (ed.), 2000***) In water 21,000 mg/l 20 ºC (***Verschueren, K., 2001***)
Distribution coefficient Log K_{ow}	0.95 (***Hansch, C., Leo, A., D. Hoekman, 1995***)
Vapour pressure	3.0×10^{-2} mm Hg at 20 ºC (***Verschueren, K., 2001***)
Odour	Amine-like odour (***NIOSH, 1997***)

4.3.7.2 Detected amounts

The substance is detected in marker pen no. 57 in pink in a concentration of 0.12 mg/g. Further, the related substance N-methyl para-anisidine was present in a concentration of 0.36 mg/g.

4.3.7.3 Function

p-Anisidine is an intermediate used for production of colorants.

4.3.7.4 Classification and limit values

p-Anisidine is specified in the List of Dangerous Substances and is classified as:

Tx;R26/27/28	Very toxic by inhalation, skin contact and if swallowed
R33	Accumulated in the body by repeated use
N;R50	Very toxic for aquatic organisms

For comparison the isomer o-anisidine (CAS-no. 90-04-0) is classified as:

T;R23/24/25	Toxic by inhalation, skin contact and if swallowed
Carc.Cat.2;R45	May be carcinogenic
Mut.Cat.3;R68	Risk of permanent damage to health

and N-methyl p-anisidine (CAS-no. 5961-59-1):

Mut3;R40 Carc.3;R40	May be carcinogenic
R43	Allergenic by skin contact

The threshold limit value for occupational health and safety for p-anisidine is 0.1 ppm, equivalent to 0.5 mg/m^3 with a note H, which means that the substance can be absorbed through the skin (***AT 2005***).

4.3.7.5 Health effects

Data on health effects were retrieved from TOXNET and other relevant databases. The substance is not listed in IUCLID, but EUCLID data exist for the related substance o-anisidine CAS-no. 90-04-0.

Acute toxicity

Data for p-anisidine specify:

- LD_{50} rat, oral 1400 mg/kg (***Lewis, R.J. 1996***)
- LD_{50} rat skin 3200 mg/kg (***Lewis, R.J. 1996***)
- LD_{50} mouse, oral 1300 mg/kg (***Prosolenko, 1976***)

Just like aniline the substances oxidizes iron II to iron III in haemoglobin, thus forming methaemoglobin, whereby the oxygen transport in the blood is reduced.

Workers which were exposed to 0.4 ppm for 3.5 hours per day for 6 months thus developed anaemia and were chronically poisoned. (***American conference, 1991***).

The acute toxicity for rats classifies p-anisidine as hazardous to health. Studies with cats establish that it develops anaemia by intravenous dosing. Thus the methaemoglobin went up from 1.1 to 11.5 % by an intravenous dosing of only 7.7 mg/kg for cats, whereas the level in mice rose from 0.66 to 4.8 % by one single dose. Therefore the substance is classified toxic with R23/R24/R25 in ***(EU risk evaluation o-anisidine 2002).***

We have found no reason to classify p-anisidine as Tx (very toxic). A classification would be expected to be the same as for o-anisidine, but data on the substance are sparse.

Subchronic toxicity

The substance is mild sensitizing and may cause contact allergy (***Lewis, R.J, 1996***).

The substance was not mutagenic in S.typhimurium and there were no morphological changes in young guinea pig cells (***IARC, 1972-present***).

No relevant data found.

Data exist on the related substance o-anisidine, where a 28-day experiment with rats with daily doses of 0, 16, 80 and 400 mg/kg showed a NOAEL of 16 mg/kg/day, as the dosage of 80 mg/kg developed yellow urine and faint haemolytic anaemia.

A comparison with anilines shows a hemotoxic effect of 7 mg/kg against 2 mg/kg for p-chloro aniline. It is assumed that NOAEL for p-anisidine for hemotoxic effects is at the same level as o-anisidine, being 16 mg/kg/day.

Chronic toxicity
A 103-week test with rats and mice with 55 of each gender could not demonstrate a certain carcinogenic effect of the substance in concentrations of up to 0.6 % for rats and 1 % for mice. (***DHEW/NCI, 1978***).

It should be noted that the related substance CAS-no. 90-04-4 has been found carcinogenic in a 2-year study with rat and mice, with doses of 0, 5000 and 10,000 ppm (1 %) o-anisidine in the rat feed and 0, 2500, 5000 ppm in the mice feed. There was a strong statistical significance by doses higher than or equivalent to 5,000 ppm with finds in the bladder. Also in rats there was a significant increase of cancer cells in the liver at the highest concentration of LOAEL for rats of 256 mg/kg/day ***(EU risk evaluation o-anisidine, 2002).***

Summary
The substance is hemotoxic with a NOAEL of 16 mg/kg/day based on the o-anisidine values.

No carcinogenic effect of p-anisidine was found, but the isomer o-anisidine is carcinogenic in rats at doses of 256 mg/kg/day and is classified with an R45. Another related substance N-methyl-p-anisidine is potential carcinogenic (R40).

4.3.7.6 Exposure scenarios
The maximum content in ink was 0.12 mg per gram.

The exposed area is assumed to be 50 cm^2 and it is further assumed that all anisidine is absorbed before washing off, e.g. after 1 hour, which is realistic with log K_{OW} = 0.95. Based on tests, the amount of ink transferred to 50 cm^2 was determined to 0.05 gram.

Intake, skin = 0.12 mg/g * 0.05 g/15 kg = 0.0004 mg/kg b.w./day.

The oral intake is assumed to be same for finger sucking as for sucking on the pen.

4.3.7.7 Assessment
With a NOAEL for hemotoxic effect of 16 mg/kg/day for o-anisidine, MOS can be calculated to = 16/0.0004 = 40,000 thus it is assessed to have no hemotoxic effects.

The substance is estimated potential carcinogenic compared to data on the isomer o-anisidine and the related substance N-methyl-p-anisidine.

4.3.8 2-Ethoxy Ethanol

4.3.8.1 Identity

Name	2-Ethoxy ethanol
CAS-no.	110-80-5
EINECS-no.	203-804-1
Molecular formula	$C_4H_{10}O_2$
Substance composition	

Molecular weight	90.12 g/mol
Synonyms	Glycol monoethyl ether Ethylene glycol monoethyl ether Ethanol, 2-ethoxy-
Description	Colourless liquid (***NIOSH, 2001***)
Boiling point	135.6 ºC (***Lewis, R.J., Sr (Ed.), 1997***)
Melting point	-70 ºC (***O'Neil, M.J. (ed.), 2001***)
Solubility	Miscible in all ratios with acetone, benzene, tetrachloride, ethyl ether, methanol, and water (***Flick, E.W. (ed.), 1991***)
Distribution coefficient Log K_{ow}	-0.32 (***Hansch, C., Leo, A., D. Hoekman, 1995***)
Vapour pressure	5.31 mm Hg at 25 ºC (***Daubert, T.E., R.P. Danner, 1989***)
Odour	Faint, pleasant ether-like odour (***NIOSH, 2001***)

4.3.8.2 Detected amounts

The substance is detected in marker pen no. 25 in a pink and red colour in concentrations of 19 and 7.4 mg/gram.

4.3.8.3 Function

The substance is used as solvent in paint, ink and lacquer and also for increasing the stability of emulsions with colorants.

4.3.8.4 Classification and limit values

The substance is included in List of Dangerous Substances and (***Miljøministeriet, 2005***) classified as:

R10	Flammable
Rep. cat.2;R60	May be harmful to reproduction
R61	May harm the unborn child during pregnancy
Xn;R20/21/22	Dangerous by inhalation, skin contact, and if swallowed

The threshold limit value for occupational health and safety is 5 ppm, equivalent to 18.5 mg/m^3 with a note H, which means that the substance can be absorbed through the skin (***AT 2005***).

B-value is 0.2 mg/m^3 (***Miljøstyrelsen 2002***).

4.3.8.5 Health effects

Data on health effects have been retrieved in TOXNET and related databases. The substance is found in IUCLID. Description is additionally based on ***(Kortlægning no. 60, 2005).***

Acute toxicity

The substance is hazardous to health according to the below values:

- LD_{50} rat, oral 1.746 mg/kg (***IUCLID dataset 2-ethoxyethanol, 2000***)
- LD_{50} mouse, oral 1.519 mg/kg (***IUCLID dataset 2-ethoxyethanol, 2000***)
- LD_{50} rabbit, dermal 3.300 mg/kg (***IUCLID dataset 2-ethoxyethanol, 2000***)
- LC_{50}, 3 hours, rat, inhalation 19.700 mg/m^3 (***IUCLID dataset 2-ethoxyethanol, 2000***)

Subchronic toxicity

In a 13-week study the substance was fed orally to dogs in concentrations of 0, 46, 93 and 186 mg/kg/day. Based on testicle oedema, reduction in haemoglobin concentration hematocrit values NOAEL was determined to 93 mg/kg/day (***IUCLID dataset 2-ethoxyethanol, 2000***).

In a 13-week inhalation study the rats were exposed to 0, 92, 380, 1485 mg/m^3 for 6 hours/week, 5 hours a day. At the highest concentration we established reduction in the hypophysis weight of males and drop of the number of leucocytes in females; thus a NOAEL was determined to 103 ppm (380 mg/m^3) (Barbee et al. 1984).

Additionally, there was a drop in fertility by 300 mg/kg/day for male rats (***IUCLID dataset 2-ethoxyethanol, 2000***) and drop in fertility in mice of both genders were observed at LOAEL = 1500 mg/kg/day and NOAEL = 750 mg/kg/day.

Chronic toxicity

No data found.
A reference value for chronic inhalation for humans was calculated on the 13-week inhalation test to be RfC = 0.2 mg/m^3 (***IRIS, 1991***).

Summary

Data relevant for children are NOAEL = 93 mg/kg based on effect by oral dosing of dogs.

For rats a NOAEL= 380 mg/m^3 was determined based on effects by inhalation.

On the assumption of 100 % absorption, a respiration of 0.8 l/min/kg, 6 hours daily exposure, the inhalation test corresponds to a NOAEL of 109 mg/kg/day, which is the same level as NOAEL for dogs.

4.3.8.6 Exposure scenarios

Max. Content in marker pen was 19 mg per gram.

The exposed area is assumed to be 50 cm^2, and it is further assumed that all 2-ethoxyethanol is absorbed before the ink is washed off, e.g. after 1 hour, which is realistic with a log K_{ow} = -0.32. Based on tests the amount of ink transferred to 50 cm^2 is determined to 0.05 gram.

Intake, skin = 19 mg/g * 0.05 g/15 kg = 0.063 mg/kg b.w./day.

The oral intake is assumed to be the same whether the child is finger sucking or sucking on a marker pen.

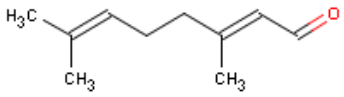
4.3.8.7 Assessment

Based on NOAEL = 93 mg/kg/day for effects by oral dosing of dogs the safety margin is MOS = 1468. Being a subchronic study a safety factor of 1000 is appropriate. It is assessed that there are no health effects of 2-ethoxyethanol by the absorbed amounts.

4.3.9 Citral

4.3.9.1 Identity

Name	Citral
CAS-no.	5392-40-5
EINECS-no.	226-394-6
Molecular formula	$C_{10}H_{16}O$
Substance composition	



Molecular weight	152,23 g/mol
Synonyms	2,6-Octadienal, 3,7-dimethyl- 3,7-Dimethyl-trans-2,6-octadienal
Description	The substance is liquid at room temperature
Boiling point	226-228 ºC (***Chemicals Inspection and Testing Institute; 1992***)
Melting point	< -10 ºC (***Chemicals Inspection and Testing Institute; 1992***)
Solubility	In 5 volume parts 60 % alcohol in all ratio benzyl benzoate, diethyl phthalate, glycerol, propylene glucol, mineral oil, 95 % alcohol. (***Lewis, R.J., Sr (Ed.), 1993***) In water 1.34X10^3 mg/l at 37 ºC (***Yalkowsky SH, Dannenfelser RM, 1992***)
Distribution coefficient Log K_{ow}	2,76 (***IUCLID citral, 2000***)
Vapour pressure	< 1hPa at 50 ºC (***IUCLID citral, 2000***)
Odour	Strong lemon like odour (***Fenaroli's Handbook of Flavor Ingredients, 1975***)

4.3.9.2 Detected amount

The substance is detected in marker pen no. 16 in orange and yellow colours at concentrations of 0.3 and 0.7 mg/gram.

4.3.9.3 Function

The substance is a basic material for production of pheromones and is used directly as pheromone at a level of 50 ppm (***IUCLID citral, 2000***).

4.3.9.4 Classification and limit values

The substance is specified in the List of Danish Substances (***Miljøministeriet, 2005***) and classified as:

Xi;R38 Irritating to skin
R43 May be allergenic by skin contact.

4.3.9.5 Health effects

Data on health effects were retrieved in TOXNET and related databases. The substance is included in IUCLID.

Acute toxicity

The substance is not toxic as it appears from below:

- LD_{50} rat, oral 4960 mg/kg (***IUCLID Citral, 2000***)
- LD_{50} mouse, oral 6000 mg/kg (***IUCLID Citral, 2000***)
- LD_{50} rabbit, skin 2250 mg/kg (***IUCLID Citral, 2000***)
- LD_{50} mouse, intravenous 460 mg/kg (***IUCLID Citral, 2000***)

Citral is a skin irritant (***IUCLID Citral, 2000***). In a test of 19 oily perfumes and 20 synthetic perfumes on 50 male volunteers it appeared to be the most skin irritant substance (***Motoyoshi K et al, 1979***).

Subchronic toxicity

The substance is sensitizing. In a patch test on 680 persons, 16 persons reacted positive equivalent to 2.3 % (***IUCLID Citral, 2000)***.

In tests with repeated feeding of 5 male and 5 female rats five days per day during a fortnights with concentrations of 570, 1140, 2280 mg/kg only a minimal influence of epithelium cells was observed at the highest concentration. Based on this the NOAEL was determined to 1140 mg/kg/day (***IUCLID Citral, 2000)***.

In another 13-week feeding test with rats no effects were observed even at the highest concentration of 833 mg/kg/day, of which NOAEL> = 833 mg/kg/day (***IUCLID Citral, 2000)***.

A 46-week feeding test with rats demonstrated effects in the stomach at 1000 mg/kg/day, but not at 200 mg/kg/day. The NOAEL was thus determined to 200 mg/kg/day (***OECD SIDS, 2001***).

Test for mutagenicity (AMES test on salmonella and test on cells from guinea pigs) showed no sign hereof (***IUCLID citral, 2000).***

The developmental toxic effects of citral were analysed in tests with rats fed with citral and maize oil for a period of 6-15 days during pregnancy. The concentration varied between 60 mg/kg/day and 1000 mg/kg/day. NOAEL for toxic effect on the mother animal was 125 mg/kg/day. Developmental toxic effects were observed in all concentrations hereunder reduced weight increase and a higher level of minor abnormalities in the skeleton of foetus than observed in the control group. Based on the LOAEL for development toxicity is determined to 60 mg/kg/day. Teratogenic effects were not observed even at 1000 mg/kg/day. (***IUCLID citral, 2000)***.

Chronic toxicity
No relevant data found.

Summary
Citral is irritant and sensitizing to skin.

Repeated feeding of rats shows effects at 1000 mg/kg/day with a NOAEL of 200 mg/kg/day.

For development toxicity the LOAEL = 60 mg/kg/day for rats, whereas the toxic effect for the mother animal is observed at 125 mg/kg/day, which has not been assessed relevant for children and juveniles.

4.3.9.6 Exposure scenarios
The maximum content in a marker pen was 0.7 mg per gram.

The exposed area is assumed to be 50 cm^2, and it is further assumed that citral is absorbed before the ink is washed off, e.g. after one hour, which is realistic with Log K_{ow} = 2.76 and the low vapour pressure. The Amount of ink transferred to 50 cm^2 is determined to 0.05 gram.

Intake, skin = 0.7 mg/g * 0.05 g/15 kg = 0.00233 mg/kg b.w./day.

The oral intake is assumed to be same whether the child is finger sucking or sucking on a marker pen.

4.3.9.7 Assessment
With a NOAEL of 200 mg/kg and a MOS of 86,000 is calculated. It is assessed that there are no toxic effects for children and juveniles by the ingested concentration.

If expecting mothers (who are not the target of the assessment) were exposed in the same way, the MOS is 26000 for development toxicity in the foetus. This safety margin is sufficient to avoid developmental toxic effects.

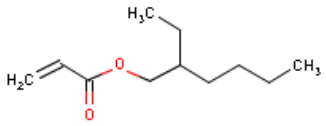
The substance is highly allergenic with a concentration in a marker pen of 0.07 %. The ink will be in skin contact in the same ways as creams and other cosmetics. When comparing with (***Statutory Order No. on Cosmetic Products, 2005***), the product should be labelled with substance name (required for > 0.01 % for substances, to be washed off, and > 0.001 % for substances, which are not washed off). Citral shall be labelled with R43, “Allergic contact dermatitis”, it is therefore assessed that if the marker pen comes in contact with skin it can cause risk of senbilisation.

4.3.10 2-Ethylhexyl acrylate

4.3.10.1 Identity

Name	2-Ethylhexyl acrylate
CAS-no.	103-11-7
EINECS-no.	203-080-7
Molecular formula	$C_{11}H_{20}O_2$

Substance composition



Molecular weight	184,28
Synonyms	2-Propenoic acid, 2-ethylhexyl ester Acrylic acid, 2-ethylhexyl ester
Description	Colourless liquid (***Lide, DR (ed.), 2000***)
Boiling point	214-218 ºC (***Lewis, R.J, 1997***)
Melting point	-90 ºC (***Lide DR, 2000***)
Solubility	100 mg/l, 25 ºC (***Chemicals inspection, 1992***)
Distribution coefficient Log K_{ow}	4.09 (***US EPA,2003***)
Vapour pressure	0.178 mm Hg at 25 ºC (***Daubert,1989***)
Odour	Pleasant (***Clayton,1993-94***)

4.3.10.2 Detected amounts

The substances were found in acrylic paint nos. 60 and 61. In product no. 61 a content of 0.35 mg/gram was quantified.

4.3.10.3 Function

The substance is used for production of plastics, coatings and waterbased paints (***Lewis R.J, 1997***). The detected concentrations are small and are presumed to be residues from the production.

4.3.10.4 Classification and limit values

The substance is specified in the List of Dangerous Substances (***Miljøministeriet, 2005)*** and is classified as:

Xi;R37/38	Respiratory and skin irritation
R43	May be allergenic by skin contact

No Danish limit value for occupational health and safety exists for this substance.

B-value is 0.01 mg/m^3 (***Miljøstyrelsen 2002***).

4.3.10.5 Health effects

Data on health effects were retrieved in TOXNET and related databases. The substance is specified in IUCLID. An EU Health Risk Assessment exist (***EU:2005).***

Acute toxicity

The substance is not acutely toxic:

- LD_{50} rat, oral 5600 mg/kg (***IUCLID dataset, 2-ethylhexylacrylate, 2000***)
- LD_{50} mouse, oral 4400 mg/kg (***IUCLID dataset, 2-ethylhexylacrylate, 2000***)
- LD_{50} rat, dermal 12000 mg/kg (***IUCLID dataset, 2-ethylhexylacrylate, 2000***)

- LD_{50} rabbit, dermal 7540 mg/kg (***IUCLID dataset, 2-ethylhexylacrylate, 2000***)

The substance is strongly irritant to skin (***IUCLID dataset, 2-ethylhexylacrylate, 2000***) and (***Lewis, R.J., 1996***).

Subchronic toxicity
The substance is strongly sensitizing in tests on guinea pigs. ***(EU Risk assessment 2-ethylhexyl acrylate, 2005***). Further there are results of positive patch tests in humans – however in at limited number, e.g. 5 volunteers, who all reacted positive on 5 % substance in olive oil. A number of acrylates are generally known as allergenic.

From data of repeated inhalation of the substance in rats for 90 days a NOAEC was found of 10 ppm (0.075 mg/l) for local effects in the air pipe and a NOAEC of 30 ppm for systemic effects (lethargy, ptosis and reduced body weight).

A number of tests verified that the substance is not in vivo mutagenic.

In an inhalation test where pregnant rats from the 6th to 20th day of the pregnancy inhaled up to 100 ppm of the substance, a NOAEC for toxicity in the mother animal of 75 ppm (0,56 mg/l) was found. Development toxicity was not observed even at the highest concentration of 100 ppm.

In ***(EU Risk assessment 2-ethylhexyl acrylate, 2005***) data from the inhalation study is used for calculation of NOAEL for systemic effects by skin exposure using the following data: weight rat = 250 g, inhalation 0.8 l/min/kg, daily exposure 6 hours. The result is a NOAEL of 66 mg/kg/day for oral intake or skin absorption. In (***EU Risk assessment 2-ethylhexyl acrylate, 2005***) the following safety factors are valid for humans: Subchronic to chronic: 2, species variation: 4 and a factor 3 for variation within the species, giving a safety factor of 24.

No long-term studies exist on carcinogenity by oral dosing. Test with application on the skin of mice resulted in tumours, which is ascribed to a non genotoxic mechanism originating from skin irritation with skin lesions.

Tests with the hydrolysis product acrylic acid, which has no oral carcinogenic effect, and the negative mutagenic test, the substance has been assed carcinogenic in guinea pigs ***(EU Risk assessment 2-ethylhexyl acrylate, 2005***).

Chronic toxicity
No data found.

Summary
NOAEL for systemic effect is estimated to 66 mg/kg/day.

The substance is an irritant.

4.3.10.6 Exposure scenarios
Maximum content in a sample of acrylic paint is 0.35 mg per gram.

The exposed area is set to 50 cm^2 and it is assumed that 10 % of the 2-ethylhexyl acrylate is absorbed before the paint is washed off, e.g. after 1 hour,

based on Log K_{ow}= 4,09. The amount of acrylic paint transferred to 50 cm^2 is determined to 1.25 gram.

Intake, skin = 0.35 mg/g * 1.25 g/15 kg/10 = 0.00292 mg/kg b.w./day.

It is assumed that a maximum oral intake by finger sucking or sucking on brushes is 1 ml or approx. 1 gram, equivalent to approx. 10 * the maximum skin absorption or 0.0292 mg/kg/day.

4.3.10.7 Assessment

Based on NOAEL = 66 mg/kg/day for systemic effects in rats is calculated MOS = 66/0.00292 = 22628 by skin absorption and MOS = 66/0.0292 = 2263 by oral intake.

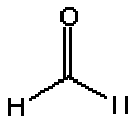
These values are more than 180 times higher than the safety factor of 24 from ***(EU Risk assessment 2-ethylhexyl acrylate, 2005***). From this it is assessed that there are no health effects at the assumed doses.

2-Ethylhexyl acrylate shall be labelled with R43, "Allergic contact dermatitis", it is therefore assessed that if the paint comes in contact with skin it can cause risk of senbilisation.

4.3.11 Other substances: Formaldehyde

Below data retrieved from (***Kortlægning, babyprodukter***)

Name	Formaldehyde
CAS-no.	50-00-0
EINECS-no.	200-001-8
Molecular formula	CH_2O
Substance composition	



Molecular weight	30,03
Synonyms	Formalin Methanal
Description	The substance is a gas
Boiling point	-19 ºC
Melting point	-92 ºC
Solubility	40,000 mg/l, 25 ºC
Distribution coefficient Log K_{ow}	0.35
Vapour pressure	3890 mm Hg at 25 ºC

4.3.11.1 Detected amounts

The substance is detected in 10 glitter glue products. Concentrations above 0.01 mg/gram were detected in products no. 15: 0.059, no. 26: 0.043, no. 29: 0.013, no.33: 0,063 and no.50: 0.111 mg/gram.

4.3.11.2 Classification and limit value

Formaldehyde is included in the List of Dangerous Substances and is classified as:

Carc.3;R40	Potential carcinogenic effect
T;R23/24/25	Toxic by inhalation, skin contact and by if swallowed
C;R34	May cause burns
R43	May be allergenic by skin contact

In concentrations of 1-5 % formaldehyde is classified Carc.3;R40 og R43, and in concentrations 0.2-1 % it is classified by an R43.

The Danish limit value for occupational health and safety for this substance is 0.4 mg/m^3 with a note H for skin permeability and K for carcinogenic effect. The rated value for indoor climate is determined to 0.15 mg/m^3 (***Arbejdstilsynet, 2005*** (***Danish Working Environment Authority)***), which is close to the threshold limit value recommended by WHO.

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

4.3.11.3 Health effects

Reference dose for chronic oral exposure, RfD, is 0.2 mg/kg/day. The value is based on a 2-year study with Wistar rats, which were given formaldehyde daily in the water. LOAEL for weight increase and histopathology was 82 mg/kg/day, where the NOAEL was 15 mg/kg/day. By an uncertainty factor of 100 for inter- and intraspecies difference, the RfD value would be 0.2 mg/kg/day.

4.3.11.4 Exposure scenarios

The maximum content in glitter glue is 0.11 mg per gram.

The exposed area is assumed to be 50 cm^2, and it is further assumed that 100 % formaldehyde is absorbed before the glue is washed off, e.g. after 1 hour based on Log K_{ow} = 0,35. It should be mentioned that some formaldehyde will evaporate due to the high vapour pressure. Based on tests the amount of glitter glue transferred to 50 cm^2 is determined to 3 gram.

Intake, skin = 0.11 mg/g * 3 g/15 kg = 0.022 mg/kg b.w./day.

It is assumed that the maximum oral intake will be the same whether the child is sucking fingers or sucking on objects like glitter glue.

4.3.11.5 Assessment

Based on NOAEL = 15 mg/kg/day the safety margin can be calculated to MOS = 15/0,022 = 676 by skin absorption or by oral intake. This corresponds to 9 times below the critical reference dose. There is thus no health effect by intake of the assumed dose.

The substance will give an increased risk of carcinogenic and allergenic effect. Further it contributes to other known sources for formaldehyde in Danish homes, e.g. chipboards, electronic products etc.

4.3.12 Inhalation

To assess the evaporations into the indoor climate it is necessary to carry tests out in climate chambers, which has not been effected in this project.

To be able to assess the risk of inhalation of hazardous substances a number of worst case scenarios have been estimated, where it is assumed that all

substances are evaporated instantaneously to a local area of 1.5 m^3, which is assumed to be the child's inhalation zone. Alternatively, the maximum substance concentration is estimated in a closed child's room with recirculation of 3 * 3 * 2 m = 18 m^3.

4.3.12.1 Formaldehyde

Formaldehyde is found in glitter glue, which is used in amounts of approx. 6 g/100 cm^2 in concentrations of up to 0.11 mg/g.

The substance has a very low occupational threshold limit value (TLV) of 0.4 mg/m^3 and a recommended value for indoor climate of 0.15 mg/m^3.

To obtain the TLV in a local area of 1.5 m^3 the formaldehyde from 5.4 g glue must evaporate instantaneously, which is not realistic, as glitter glue dries up slowly.

In a closed child's room of 18 m^3, the formaldehyde concentration of 6 g glitter glue will be maximum reach 0.04 mg/m^3, which is 10 times below the TLV and 4 times below the recommended indoor climate value.

Our assessment is that there are no health problems connected with inhalation of glue, but in very small closed rooms, the use of one or more tubes of glitter glue may lead to formaldehyde concentrations which contribute considerably to other formaldehyde sources. It is therefore recommended that the room is ventilated properly when working with large volumes of glitter glue.

4.3.12.2 2-ethoxyethanol

2-ethoxyethanol is found in marker pens, which is used in amounts up to 0.1 g/100 cm^2 in concentrations up to 19 mg/g.

The TLV of the substance is 18.5 mg/m^3

To reach the limit value required for a local area of 1.5 m^3 all the ethoxyethanol in 1.5 g ink shall evaporate instantaneously, which is not realistic at a vapour pressure of approx. 5 mm Hg.

In a closed child's room of 18 m^3 without air circulation the ethoxyethanol concentration on 4 densely painted A4 papers correspond to 2.4 gram ethoxyethanol. The concentration of the spread ethoxyethanol will maximum be 2.5 mg/m^3 in the room which is 7 times below the TLV.

The result of the assessment is that there are no health problems connected with inhalation when using marker pens.

4.3.13 Overall conclusion on the health risk assessment

In the analysed products we have found a number of harmful substances. For 11 of these substances we have prepared exposure scenarios and health risk assessments based on scenario with two painted child palms.

The established health effects of the analysed substances appear from Table 4.2 and **Fejl! Henvisningskilde ikke fundet.**.

Table 4.2 Effects of assessed substances

Substance	Irritant and sensitizing effects	Reprotoxic effects	Carcinogenic effects	Mutagenic effects
Aniline	R41 risk of serious eye damage R43 sensitizing		Carc3;R40 Possible carcinogenic effect	Mut3;R68 Risk of permanent damage to health
P-chloroaniline	R43 sensitizing		Carc.cat.2;R45 Carcinogenic	
N-methyl aniline			Potential carcinogenic based on data for N,N-dimethylaniline and aniline	
C.I.Pigment red 3			Potential carcinogenic based on animal tests	
N,N-dimethylacetamide		Rep.2;R61 harmful to unborn child		
Bis(2-ethylhexyl)adipate		Teratogenic in rats		
P-anisidine			Potential carcinogenic based on data for o-anisidine and N-methyl-p-anisidine	
2-Ethoxy ethanol		Rep.cat.2:R60 May be harmful to reproduction with R61 harmful to unborn child		
Citral	R38 skin irritation R43 sensitizing			
2-Ethylhexyl acrylate	R37/38 respiratory and skin irritation R43 sensitizing			
Formaldehyde	R34 Causes burns R43 sensitizing		Carc 3;R40 Potential carcinogenic effect	

There are also other substances in the products that have health effects, but a health assessment is not made. In the products investigated in the report there has been found:

- 12 allergenic substances
- 7 substances with potential or proven carcinogenic effect
- 3 substances with mutagenic effect
- 3 substances with reprotoxic effect

Table 4.3 shows the results of the assessment of their toxic effect.

Table 4.3 Toxic effects of selected substances

Substance	Max.Intake mg per kg b.w.	NOAEL mg/kg b.w. per day	MOS (worst case)	RfD/max. Absorption	Comments
Aniline	0,00073	7	9500		No hemotoxic risk – risk of sensitizing and carcinogenic effects
p-chloroaniline	0,031	2 (LOAEL)	65	0,004	Risk of hemotoxic effect, RfD exceeded by 8 times. Carcinogenic and allergenic risk.
N-methyl aniline	0,0033	15	4545		No hemotoxic risk, but risk of

Substance	Max.Intake mg per kg b.w.	NOAEL mg/kg b.w. per day	MOS (worst case)	RfD/max. Absorption	Comments
		(LOAEL)			carcinogenic effects
C.I. pigment red 3	8,7	830 (LOAEL)	95		No risk of toxic effects by skin absorption, minor risk by oral intake, potential risk of carcinogenic effects
N,N-dimethylacetamide	0,00133	20	15000		No risk
Bis(2-ethylhexyl)adipate	0,0012	170	145000		No risk, but carcinogenic effects not thoroughly investigated
p-anisidine	0,0004	16	40000		No hemotoxic risk, but possible risk of carcinogenic effects
2-ethoxy ethanol	19	93	1468		No risk
Citral	0,0023	200	86000		No risk of toxic effects but may be allergenic
2-ethylhexyl acrylate	0,029	66	2263		No risk of toxic effects but may be allergenic
Formaldehyde	0,022	15	676	0,2	No risk of toxic effects but carcinogenic and allergenic risk

Table 4.4 lists products with toxic effects and CMR or allergenic effects detected in the qualitative or the quantitative analyses.

Table 4.4 Toxilogical effects

Product no.	Type	Toxic effect based on health assessment	Allergenes	Possible carcinogenic substances
2	Gel pen			Yes
3	Marker pen		Yes	
5	Marker pen [3]			
6	Acrylic paint	Possible hemotoxic effect see no.55	Yes	Yes
10	Marker pen			Maybe [3]
15	Glitter glue		Yes [1]	Yes [1]
16	Aroma pen		Yes (3 pheromones in the EU list [4], Plus another allergenic substance)	
17	Marker pen [5]			
25	Marker pen [5]			Yes
26	Glitter glue		Yes [1]	Yes [1, 2]
29	Glitter glue		Yes [1]	Yes [1]
33	Glitter glue		Yes [1]	Yes [1]
45	Marker pen		Yes	Yes
46	Marker pen		Yes	
50	Glitter glue		Yes [1]	Yes [1]
54	Acrylic paint	Minor risk by oral intake		Yes (contains azocolorant)
55	Acrylic paint	Hemotoxic worst case-scenario exceeds limit value (RfD) by 8 times	Yes (2 substances)	Yes
57	Marker pen		Yes (2 substances)	Yes
58	Marker pen		Yes (2 substances)	Yes
59	Marker pen		Yes	
60	Acrylic paint		Yes (1	

Product no.	Type	Toxic effect based on health assessment	Allergenes	Possible carcinogenic substances
			substance)	
61	Acrylic paint		Yes (1 substance)	

1 More than 0.01mg/gram formaldehyde
2 Contains also the mutagenic substance phenol
3 Contains phthalate plasticizer
4 More than 0.1 mg/gram allergenic pheromone
5 Contains reprotoxic substance

Hazardous substances were found in 10 marker pen products, 5 glitter glue products, 4 acrylic paint products and in one gel pen.

The analysed aroma pen contained the allergenic substances d-limonene, benzylalcohol and citral in concentration of between 0.01 and 0.1 weight percentage.

An estimate of maximum evaporation of formaldehyde in a small child's room shows that the formaldehyde content in 6 gram (ca. 6 ml) glitter glue can maximum contribute with up to 25 % of the recommended indoor climate concentration in a room of 3 * 3 * 2 m. It is therefore not recommended to work with large amounts of glitter (several tubes) in small rooms with inferior air circulation.

Generally, the content of heavy metals in the analysed products is low. Thus no contents of lead over 21 ppm and no cadmium was found. The remaining heavy metals probably come from colorants, glitter particles or trace amounts of the substances in the colourants.

The following products contained neither CMR nor allergenic substances:

Acrylic paint: nos. 7, 8, 9, 18, 34, 35, 36, 40, 41, 48, 49, 51, and 56
Marker pen: nos. 1, 11, 12, 22, 30, 31, 32, 39, 42, 43, 47, 62, 63, and 64
Gel pen: nos. 4 and 44
Glitter glue: nos. 13, 14, 23, 28, 38 and 53 – however, formaldehyde was quantified with concentrations < 0.01 mg/g in nos. 13, 23, 28, 38, and 53

5 Environmental assessment

In the assessment of substances a number of environmentally hazardous substances were identified. Totally 12 hazardous substances were detected with R-phrases R50, R51, or R52 and in combination with R53 as well.

An assessment has been made of the effect of two selected substances presented in this project with an assessment of the consequences of discharging the environmentally harmful substances to the water environment in Denmark.

5.1 Aniline

Aniline, CAS-no. 62-53-3 has environmental classification N;R50.

Table 5.1 shows ecotoxilogical data for aniline in fish, daphnia and algae.

Table 5.1 Ecotoxilogical data for aniline

Organism	Value	References
Fisk (*Oncorhynchus mykiss*)	LC_{50}, 96 hours = 10,6 mg/l	(*EU risk assessment, 2004)*
Daphnia (*Daphnia pulex*)	EC_{50}, 48 hours = 0,1 mg/l	(*EU risk assessment, 2004)*
Daphnia (*Daphnia cucullata*)	EC_{50}, 48 hours = 0,68 mg/l	(*EU risk assessment, 2004)*
Daphnia (*Daphnia magna*)	EC_{50}, 48 hours = 0,17 mg/l	(*EU risk assessment, 2004)*
Algae (*Selenastrum capricornutum*)	EC_{50}, 96 hours = 19 mg/l	(*EU risk assessment, 2004)*

Aniline has an octanol-water distribution coefficient of log K_{ow} = 0,9.

Henry's law constant for aniline is 2.02 *10^{-6} atm m^3 /mol at 25 ˚C (*Jayasinghe, 1992*).

Bioaccumulation is determined to BCF=2.6 (***EU risk assessment, 2004)***. Biodegradability tests establish easy degradability of the substance under aerobic conditions. Thus a "closed bottle test" according to OECD 301 D shows a mineralization of 90 % after 30 days. According to OECD 301E the test shows a mineralization of 100 % after 5 days and a modified Sturm test according to OECD 301B shows a mineralization of 90 % after 30 days. The substance is not biodegradable under aerobic conditions.

A SIMPLETREAT calculation gives more than 87 % removal in a waste water plant. (***EU risk assessment, 2004).*** The results can be seen from Appendix II, part 2 in (***TGD, 2003***).

Table 5.1 indicates that the substance is most toxic for daphnia with a toxicity factor of 10 over the requirements for marking with the R-phrase R50.

An EU risk assessment for aniline includes test data where NOEC has been determined for daphnia. The mean value of 3 tests with effect determination over 21 days was used for calculating NOEC =15µg/l.

The estimated zero effect concentration for aquatic organisms $PNEC_{vand}$ is calculated to 1.5 µg/l using an evaluation factor of 10 (***EU risk assessment, 2004).***

5.2 p-chloroaniline

p-chloroaniline, CAS-no.106-47-8 is classified with N;R50-53.

Table 5.2 shows the ecotoxilogical data for fish, daphnia and algae.

Table 5.2 Ecotoxilogical data for p-chloroaniline

Organism	Value	References
Fish (Bluegill *Lepomis macrochirus*)	LC_{50}, 96 hours = 2,4 mg/l	(*CICADe, 2003*
Dafphnia (*Daphnia magna*)	EC_{50}, 48 hours = 0,31 mg/l	(*CICAD, 2003*
Algae (*Scenedesmus subspicatus*)	EC_{50}, 96 hours = 1,14 mg/l	(*CICAD, 2003*

p-chloroaniline has an octanol-water partition coefficient of log K_{ow} =1.83. Henry's law constant is $3.1 * 10^{-6}$ atm m^3/mol at 25 ˚C (*US EPA, 2004*).

Bioaccumulation of fish has a factor in the area of 4-20, whereas the concentration in algae may be considerably higher. This may be due to the absorption to surfaces (***CICAD, 2003).***

Data for biodegradability indicate that the substance is not easy degradable under aerobic conditions. 3 different aerobic biodegradability tests over 28 days of the "closed bottle" type demonstrated a degradation from 0-7 %.

The substance indicates a low degree of biodegradability under anaerobic conditions.
Tests for inherent biodegradability show that the substance can be biodegraded by microorganisms which have sufficient time to adapt to the conditions. Most tests indicated over 60% degradation ***CICAD, 2003)***.

The TGDs SIMPLETREAT model under "inherent biodegradability", appendix II, part 2 of (***TGD, 2003***) states that approx. 41 % is expected to be removed in the sewage plant.

p-chloroaniline is degraded by light with wave lengths over 290 nm with a half-life period of 7 hours and is thus quickly degraded by photolysis in surface water. In the atmosphere the substance is degraded by hydroxyl radicals with an estimated half-life period in the troposphere of approx. 4 hours (***CICAD, 2003)***.

The table indicates that the substance is most toxic for daphnia with a toxicity of up to a factor 3 over the requirements for R50 classification.

In (***CICAD, 2003***) data was found where NOEC in a 21-day test with daphnia is determined to NOEC=0.01 mg/l. This is approximately, the same as for aniline.

From the NOEC the zero effect concentration for aquatic organisms $PNEC_{water}$ be estimated to 1.0 µg/l by using an evaluation factor of 10.

5.3 Assessment of environmentally hazardous substances

The amount of hazardous substances discharged into the water environment through water from the analysed products is estimated below.

Of the substances quantified we found 5 which were harmful to the environment. Three of these were neither easy degradable nor bio-accumulative (R53).

Table 5.3 Environmentally harmful substances in the products

Substance	Classification	Concentration mg/g
Aniline	R50	0,22
p-anisidine	R50	0,11
p-chloroaniline	R50/53	0,37
N-methylaniline	R50/53	1
1,4-dioxaspiro(4,5)decane	R50/53	0,7

The amounts of substances with an R53 classification fed to the sewage plant are listed in Table 5.4.

It is expected that the substances are used by all Danish children of 3-13 years with the exposure scenarios described in the health assessment.

It is assumed that the substances are washed off the skin before absorption and that they are subsequently flushed with the waste water to the sewage plant.

According to Statistics Denmark the population of children at the age of 3-13 years numbered 734.000 persons in 2006.

Table 5.4 Estimate of environmentally harmful substances supplied to the Danish sewage plant from the products analysed

Substance	Type	Total liquid amount (g/day)	Washed off substance (mg/child/day)	Substance led to sewage plant, DK (g/day)
p-chloroaniline	Acrylic paint	1,25 [1]	0,46	348
N-methylaniline	Ink	0,05	0,05	38
1,4-dioxaspiro(4,5)decane	Ink	0,05	0,035	26

1 apart from amounts washed off the skin a certain amount will be flushed by washing clothes. This amounts has not been included in our assessment.

Totally a maximum of 412 gram of the substances are led to sewage plants in Denmark. The most dominant substance is p-chloroaniline with 348 g and it is also the most toxic of the substances. Therefore it is used as "worst case" in order to evaluate the possible environmental impact.

Orientering no. 1, 2005 contains a calculation of the concentrations of the discharged waste water based on an annual volume of 611 millions m^3 (***Punktkilder, 2005***).

From data on biodegradability it is assumed that p-chloroaniline is not degraded significantly in the sewage plant.

Based on the SIMPLETREAT method a limited degradation in sewage treatment plants of 41 % has been estimated for p-chloroaniline.

Table 5.5 calculates the ratio between the maximum discharged concentration in the water environment $PEC_{local,water}$ and the zero-effect value PNEC.

The following calculation formula has been used:

The concentration in the discharged waste water $C_{eff:}$:

$C_{eff} = C_{ind} *(1-f)$, where f is the degradation degree in sewage plants and C_{ind} is concentration in the supplied waste water.

$C_{local, water} = C_{eff}$ /Dilution factor. The dilution factor has been set at 10 as specified in TGD (***Technical Guidance document, 2003***). Any absorption of p-chloroaniline in dissolved form in water has not been taken into account.

The concentration of p-chloroaniline from other sources $PEC_{reg,vand}$ has been fixed to 0 thus

$PEC_{lokal,vand} = PEC_{reg,vand} + C_{lokal,vand} = C_{lokal,vand}$

Table 5.5 Calculated effect on water environment

Parameter	Value
Amount supplied to sewage plant g	348
Concentration in supplied waste water (ug/l)	0.00057
PNEC (µg/l)	1
Assumed degradation in waste water plant %	41
C_{eff} (µg/l)	0.00034
$C_{local, water}$ (µg/l)	0.000034
$PEC_{reg, water}$ (µg/l)	0
$PEC_{local, water}$ (µg/l)	0.000034
$PEC_{local,water}$/PNEC	0.000034

As can be seen the concentration of $PEC_{local,water}$/PNEC << 1 and therefore p-chloroaniline is not expected to have any impact on the water environment. In this connection it shall be noted that p-chloroaniline is found only in a small number of the acrylic paint products, so the average effect is expected to be even lower.

As p-chloroaniline is a representative for the analysed products regarding concentration of substance and toxicity, it is assessed that the amount of environmental harmful substances in the analysed products being flushed into the waters will have no influence on the environment.

6 Abbreviations

BMD	Benchmark dosage level
Carc	Carcinogenic
HDSB	Hazardous Substance Data Bank
IRIS	Integrated Risk Information System
IUCLID	International Uniform Chemical Information Database
LC_{50}	Lethal concentration 50 percent
LD_{50}	Lethal dose 50 percent
LOAEL	Lowest observed adverse effect level
LOEL	Low-observed-effect-level
MOS	Margin of safety LOAEL
Mut	Negative mutagenic effect
NOEC	0- effect level
NOAEL	No adverse effect level, lowest level of permanent damages
NOEL	0-effect level
PNEC	Estimated 0-effect concentration
Rep	Reproductive, harmful to foetus and or reproduction
RfD	Reference dose
TLV	Threshold limit value

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