Survey of chemical substances in consumer products

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Survey of fluorescent substances in consumer products

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Preface

The objective of the present project is to survey the chemical substances that are used in fluorescent products and whether consumers are exposed to a health risk when using the products.

The Danish Environmental Protection Agency (Danish EPA) has financed the project as a part of the programme “Survey of chemical substances in consumer products". Danish Technological Institute has prepared the project by during the period May 2003 to November 2003.

Shima Dobel and Frank Jensen from the Danish EPA and Paul Lyck Hansen, Danish Technological Institute have formed the steering group of the project and have followed the project.

Vagn Nielsen, Anders Feilberg, and Anne Dilani Pedersen have made the survey and analyses of the project. Kirsten Pommer has made the qualitative screenings on health issues and Ole Christian Hansen has made the quality assurance of the report.

Summary and conclusions

Fluorescent Products

The objective of the present project is to survey the chemical substances used in fluorescent products that are retailed at the Danish market. Health assessments are made on chosen chemical compounds found in the products.

When surveying the Danish retail for products containing fluorescent the following types of products have been found:

- carnival makeup
- Hairspray
- Spray painting
- Textil colorants, decoration colorants
- Stamp ink
- Toys (hard and soft plastic goods, slime, pearls)
- Signal tape
- Light sticks
- Textiles
- Various types of sport equipment such as compass and watches

After having contacted distributors, importers, different trades and made internet surveys it has been established that the primarily used fluorescent systems are zinc sulphide and strontium-aluminium pigments. Furthermore, a series of CI-colorants, which all are approved in accordance with Statutory Order on Cosmetic Products, no 489) are identified.

When using the following products there is a risk of direct exposure and/or children are the target group. Therefore the products are been selected for qualitative chemical analyses:

- Soft plastic toys
- Slime
- Carnivals makeup
- Hairspray
- Textil colorants
- Decoration colorants
- Stamp ink
- Light sticks

The Association of Danish Cosmetics, Toiletries, Soap and Detergent Industries (SPT) has been contacted and they have stated that no cosmetic products containing fluorescent substances are sold in Danish retail.

The retailing chain Dansk Supermarked has informed that fluorescent products are no longer in their product line.

Chemical Analyses

The chemical analyses consist of x-ray – and GC-MS screenings for inorganic and organic additives.

The x-ray analysis shows that the greater part of the products contains sulphur, calcium, and zinc, thus, metal sulphides such as zinc sulphide and calcium sulphide are present in the products. In one product, pearls, substances such as aluminium, strontium, zirkonium, europium, and dysprosium have been detected, indicating the presence of strontium-aluminium compounds.

At GC-MS analysis organic components such as methyl parabene, 4-hydroxy-benzoic acid, tributyl-acetyl-citrate, dibutyl phthalate, and dimethyl phthalate have been identified. Methyl parabene and 4-hydroxybenzoic acid are used as preservatives in cosmetics and may cause allergic reactions and inflammation of the skin. Phthalates and tributyl-acetyl-citrate are used as plasticizers or may be background pollution from the raw materials, the production equipment or the packaging. The substances detected at the GC-MS analysis do not have any fluorescent effect.

Health Assessment

The substances detected at the chemical analyses have been assessed basically to establish whether health risk such as skin contact, eye contact, ingestion and possible chronic effects may occur caused by using the products. An actual risk assessment cannot be carried out, as the quantity of the detected substances is not known.

As for a part of the substances, the data information available has been rather limited. The results of each specific substance assessment are as follows:

- Zinc sulphide (CAS no: 1314-98-3) will probably not cause any health problems, as zinc sulphide / zinc compounds do not possess properties that cause significant acute or chronic effects.
- Strontium-aluminium-complexes are activated by lanthaniodes (Eu, Dy and Nd). It is estimated that aluminium and strontium, which have been found in the products, do not represent any critical health risks. Lanthanoides, however, are very sparsely described and it is therefore not possible to estimate whether the substances can cause any allergic or chronic effects on the health.
- Methyl parabene (CAS no: 99-76-3) is assumed not to cause any health risk provided that the limit of content in cosmetic products is met.
- A red colorant, (CI 16035) and two blue colorant (CI 42090 and CI 77007) have been assessed. As for the red colorant CI 16035 no information on allergic or other chronic effects has been found. As for the blue colorant CI 42090 allergy occur when ingested by particularly sensitive persons. No chronic effects have been observed. Based on this information it is assessed that the colorant CI 16035 and CI 42090 will probably not cause any health risks. As far as the blue colorant concerns CI 77007 it has only been possible to establish that the fact that the substance does not cause sensitisation, and it is therefore not possible to determine whether it may cause health risks.

- 4-hydroxybenzoic acid (CAS no: 99-96-7) is mildly skin irritating agent and moderate eye irritating. The substance has a low toxicity when ingested. Chronic effects have not been observed.
- Tributylacetyl citrate (CAS no: 77-90-7) has properties that may cause inflammation of the eyes. Other health effects are considered insignificant.
- Dimethyl phthalate (CAS no: 131-11-3) and dibutyl phthalate (CAS no: 84-77-2) have properties that may cause inflammation of the eyes, but presumably no chronic effects. Dibutyl phthalate is unwanted due to the risk of teratogenic and endocrine disrupting effects.

Conclusion

In 2003 fluorescent products such as carnivals makeup, hairspray, spray painting, decoration and textile colorants, stamp ink, slime- and plastic toys, signal tape, light sticks, textiles and various sport equipment such as compasses and watches in the Danish retail.

Analyses and health assessments have been made on selected products due to the fact that when using the following products there is a risk of direct exposure and/or children are the target group. The products in question are carnival makeup, hairspray, decoration and textile colorants, stamp ink, slime- and plastic toys, light sticks.

The conclusion on the health assessment on the detected substances with fluorescent effect is:

- Zinc sulphide, which has been detected in ink, decoration and textile colorants, makeup, and plastic toys, will not cause any health risks, as zinc sulphide/zinc compounds do not possess properties that may cause significant acute or chronic effects.

- Lanthanoides in luminous pigments (strontium-aluminium-complexes), detected in pearls, may cause a health risk, but the data is insufficient to reach to a final conclusion.

The conclusion on the health assessment on the detected substances that do not contain any fluorescent effect is:

- As for the blue colorant, CI 77007, noted in the declaration of content on the makeup and the hairspray, it is not possible to determine if it may cause any health problems due to the lack of information.

- Dimethyl phthalate, detected in the decoration colorant, makeup and hairspray, may cause inflammation of the eyes and it is suspected to have teratogenic effects. Compared to the predicted concentrations in the products the risk for human health effects is very low.

The present knowledge on health risks caused by products containing fluorescent substances is very limited. However, it can be proven that the actual illumination from fluorescent and phosphorescent substances does not cause any health risk. The emitted light beam will always have a longer

wavelength (that is less rich on energy) than the absorbed light, as a part of the absorbed radiation energy will be transformed to heat.

Sammenfatning og konklusioner

Fluorescerende produkter

Formålet med dette projekt er at kortlægge hvilke kemiske stoffer, der anvendes i fluorescerende produkter på det danske marked. På udvalgte kemiske forbindelser foretages sundhedsmæssige vurderinger.

Ved gennemgang af fluorescerende produkter på det danske marked er der fundet følgende produkttyper:

- Karnevals makeup
- Hårspray
- Spraymaling
- Tekstilfarve, dekorationsfarve
- Stempelink
- Legetøj (hårde og bløde plastvarer, slim, perler)
- Signaltape
- Knæklys
- Tekstil
- Div. sportsudstyr som kompas og ure

Ved kontakt til forhandlere, importører, brancher og internetsøgninger er det fastlagt, at de anvendte fluorescerende systemer er fortrinsvis zinksulfid og strontium-aluminium pigmenter. Der er desuden oplyst en række CI-farvestoffer, som alle er godkendte ifølge kosmetikbekendtgørelsen (Bekendtgørelsen om kosmetiske produkter, nr. 489).

Følgende produkter, hvor der er risiko for direkte eksponering og/eller har børn som målgruppe, blev udvalgt til kvalitative kemiske analyser:

- Blødt plast legetøj
- Slim
- Karnevals makeup
- Hårspray
- Tekstilfarve
- Dekorationsfarve
- Stempelink.
- Knæklys

Ved kontakt til brancheforeningen for Sæbe, Parfume og tekniske/kemiske artikler oplyses det, at der ikke sælges fluorescerende kosmetiske produkter.

Detailkæden Dansk Supermarked har oplyst, at der ikke længere er fluorescerende produkter i varesortimentet.

Kemiske analyser

De kemiske analyser består af røntgen – og GC-MS screeninger for henholdsvis uorganiske og organiske tilsætningsstoffer.

Ved røntgen analyse ses, at der i størstedelen af produkterne findes svovl, calcium og zink, således at metalsulfider som zinksulfid og calciumsulfid er tilstede. I ét produkt, perler, findes elementer som aluminium, strontium, zirkonium, europium og dysprosium, hvilket indikerer strontium-aluminium-forbindelser.

Ved GC-MS analyse identificeres organiske komponenter som methylparaben, 4-hydroxy-benzoesyre, tributyl-acetyl-citrate, dibutylphthalat og dimethylphthalat. Methylparaben og 4-hydroxybenzoesyre anvendes som konserveringsmidler i kosmetik og kan give anledning til allergi og hudirritation. Phthalaterne og tributyl acetyl citrate anvendes som blødgører eller kan være baggrundsforurening fra råvarer, produktionsudstyr eller emballage. De fundne stoffer, ved GC-MS analyse, har ingen fluorescerende effekt

Sundhedsmæssige vurderinger

Stoffer der blev fundet ved de kemiske analyser, blev vurderet med hovedvægten på at belyse forhold omkring hudkontakt, øjenkontakt og indtagelse samt eventuelle kroniske virkninger. En egentlig risikovurdering er ikke gennemført, da mængden af de påviste stoffer ikke er kendt.

For en del af stofferne var det meget begrænset hvilke data, det var muligt at fremskaffe. Resultaterne af de enkelte stofvurderinger er:

- Zinksulfid (cas. nr.: 1314-98-3) vil antagelig ikke medføre sundhedsmæssige problemer, da zinksulfid / zinkforbindelser ikke besidder egenskaber, der fører til væsentlige akutte eller kroniske skader.
- Strontium-aluminium-komplekser exiteres af lanthanoider (Eu, Dy og Nd). Det vurderes at aluminium og strontium, som de forekommer i produkterne, ikke besidder nogen betænkelige sundhedsmæssige egenskaber. Lanthanoiderne derimod er meget sparsomt beskrevet, og det kan ikke vurderes, om disse stoffer vil give anledning til irritationer, allergiske effekter eller kroniske skader.
- Methylparaben (cas nr.: 99-76-3) antages ikke at medføre nogen sundhedsmæssig risiko, såfremt grænsen for indhold i kosmetik overholdes.
- Et rødt farvestof, (CI 16035) og to blå farvestoffer (CI 42090 og CI 77007) er vurderet. For det røde farvestof CI 16035 foreligger der ingen oplysninger om irritationer, allergi eller andre kroniske effekter. For det blå farvestof CI 42090 er der set allergi hos særligt følsomme personer ved indtagelse af stoffet. Der er ikke konstateret andre kroniske effekter. På baggrund af ovenstående vurderes, at farvestofferne CI 16035 og CI 42090 antagelig ikke vil give anledning til sundhedsmæssige problemer. For det blå farvestof CI 77007 har det kun været muligt at konstatere, at stoffet ikke medfører sensibilisering, og derved ikke muligt at afgøre, om der kan forekomme sundhedsmæssige problemer.
- 4-hydroxybenzoesyre (cas. nr.: 99-96-7) er mildt hudirriterende og moderat øjenirriterende. Stoffet har en lav giftighed ved indtagelse. Kroniske effekter er ikke observeret for stoffet.
- Tributylacetyl citrat (cas. nr.: 77-90-7) har egenskaber, der kan medføre øjenirritationer. Andre sundhedsmæssige påvirkninger anses for minimale.
- Dimethylphthalat (cas. nr.:131-11-3) og dibutylphthalat (cas.nr.: 84-77-2) har egenskaber, der kan forårsage øjenirritaioner, men antageligt ikke

blivende skader. Dibutylphthalat er problematisk på grund af risikoen for fosterskadende og hormonforstyrrende effekter.

Konklusion

På det danske marked er der i 2003 fundet produkter som karnevals makeup, hårspray, spraymaling, dekoration- tekstilfarve, stempelink, slim- og plastlegetøj, signaltape, knæklys, tekstil og div. sportsudstyr som kompas og ure.

Der er foretaget analyser og sundhedsmæssig vurdering på udvalgte produkter, hvor der er risiko for direkte eksponering og/eller har børn som målgruppe. Det er produkter som karnevals makeup, hårspray, dekoration-tekstilfarve, stempelink, slim til leg, plastlegetøj, knæklys

Konklusion på sundhedsmæssig vurdering af identificerede stoffer med fluorescerende effekt:

- Zinksulfid, der er fundet i ink, dekorations- og tekstil-farve, makeup samt plastlegetøj, vil ikke medføre sundhedsmæssige problemer, da zinksulfid/zinkforbindelser ikke besidder egenskaber, der kan føre til væsentlige akutte eller kroniske skader.

- Lanthanoiderne i de selvlysende farvepigmenter (strontium-aluminium-komplekser), der er fundet i perler, kan udgøre et sundhedsmæssigt problem, men der mangler data for at opnå en endelig afklaring.

Konklusion på sundhedsmæssig vurdering af stoffer der er identificeret, men som ikke har fluorescerende effekt:

- For det blå farvestof, CI 77007, der er deklareret i makeup og hårspray, er det ikke muligt at afgøre om der kan forekomme sundhedsmæssige problemer, på grund af datamangel.

- Dimethylphthalat, der er fundet i dekorationsfarve, makeup og hårspray, kan forårsage irritationer af øjne og er mistænkt for fosterskadende effekter. Sammenlignet med de formodede koncentrationer i produkterne er risikoen for sundhedsmæssige effekter dog minimal.

Den eksisterende viden om skadelige effekter forårsaget af produkter, der udsender lys, er temmelig begrænset. Det kan imidlertid fastslås, at selve lysemissionen fra fluorescerende og phosphorescerende stoffer ikke er skadelig udgør, idet den emitterede stråling altid vil have en længere bølgelængde (dvs. være mindre energirig) end det absorberede lys, da en del af den absorberede strålingsenergi vil omdannes til varme.

1 Introduction

1.1 Objective

The objective of the project is to form a general view of fluorescent substances used in selected consumer products and to assess whether they may cause any health risk for the user of the product.

The project has been carried out in two phases:

- In phase 1 a general view of the fluorescent substances in the Danish retail is formed. Then a data collection has been made, by contacting distributors, importers, and different trades. Information on the selected products has been supported by chemical analyses.
- In phase 2 an assessment of the health properties of the selected substances has been made and it has been assessed whether the fluorescent substances are released when using the products.

1.2 Types of Fluorescence

Numbers of consumer products contain substances that under certain conditions will have illuminating effect. Such substances can be divided into fluorescent and phosphorescent substances and substances, which give a lumnious effect, when exposed to radioactive radiation. Substances, which can have an illuminating effect due to chemical reaction (chemiluminiscense), also occur in certain products (UK Department of Trade and Industry and Danish EPA).

Fluorescent substances are chemical compounds which, spontaneously give an illuminating effect influenced by visible or ultraviolet light, i.e. when substances *absorb* incident light (Gilbert, A. and Baggott, 1991). When the influence of light ceases the radiation of the substance ceases, too. A familiar example is the use of stamps at discotheques etc., which can only be seen under the light of a special UV-lamp. Fluorescense can also be induced by visible light.

Phosphorescent substances differ from fluorescent substances in that the radiation passes over a longer period of time and can continue even after the influence of light has ceased. (Gilbert, A. and Baggott, 1991). An example is stars of plastic etc., which can be placed in the ceiling and appears luminously for a period after the light has been turned off. Besides, there are products that hold radioelements and therefore are able to give an illuminating effect (AccessScience, 2003). An example on these incidents is watches with hands that can be seen in the dark.

Chemiluminiscense occurs when two or more separate substances are constituent parts of an adequate chemical reaction that releases energy in the form of light. An example on chemiluminiscense is the so-called light sticks, which contain an ampoule with one type of liquid, surrounded with another type of liquid. When the stick is stressed the ampoule is broken and the liquids

are mixed and will then make the stick appears luminously (UK Department of Trade and Industry and Danish EPA).

1.3 Fluorescent Substances

Fluorescent substances are typically non-volatile organic compounds. The exact chemical name of a fluorescent substance is often not available from the manufacturer. In some cases it is stated in the literature that the substance in question is hetero cyclic aromatic compounds which contain nitrogen. A part of this type of substances are under suspicion of be carcinogenic to humans (National Research 1981, California Environmental, 1997).

Phosphorescent substances in products are typically metal sulphides, of which zinc sulphide is the most commonly used. Calcium- and strontium sulphide occurs as well. Metal sulphides are activated in the presence of other metals such as copper, manganese etc.

Plastic pipes etc. (eg. necklaces), which may result in chemiluminiscense, contain inter alia phthalates (UK Department, Danish EPA2001) and poly cyclic aromatic compounds (UK Department), which are under suspicion of being hazardous. It has been prohibited to sell this type of necklaces in the Danish retail since 1997 (Danish EPA, 2001).

Luminous watches, compasses etc. which illuminate without any influence of light and without any prior chemical reaction, may contain traces of the radio active element Radium (AccessScience, 2003). Radium forms radio active particles that sends out radioactive radiation (alpha particles), that can be absorbed by a suitable solid material, usually zinc sulphide (AccessScience, 2003). It implies that the zinc sulphide gets energetically excited and then gives an illuminating effect.

In the following chapters all the mentioned systems are described as ”fluorescent”.

2 Product Descriptions

A number of fluorescent products have been purchased. The products are described in Table 2.1.

Table 2.1: Product Descriptions

Product name	Product Descriptions
1. Pink ink	Ink for stamps, which are used the back of a hand at the entrance of discotheques. Is luminous when exposed to UV light
2. Green ink	
3. Yellow ink	
4. Frisbee	Luminous when exposed to ordinary light
5. Comforter	The ring is luminous when exposed to ordinary light
6. Glow slime	Green slime, luminous when exposed to ordinary light
7.Winnie the Pooh silhouettes	Plastic hanging, luminous when exposed to ordinary light
8. Finger monsters	Figures to put on our fingers, luminous when exposed to ordinary light
10. Decoration colorant	Can be used at masks etc. Luminous when exposed to ordinary light
11. Textile colorant	Luminous when exposed to ordinary light
12. Pearls	Luminous when exposed to ordinary light
13. Orange makeup	Luminous when exposed to ordinary light
14. Green makeup	Luminous when exposed to ordinary light
15. Snowflakes	Plastic hanging, luminous when exposed to ordinary light
16. Yellow hairspray	Luminous when exposed to ordinary light
17. Green hairspray	Luminous when exposed to ordinary light
19. Large light stick	Used as a light source. Illuminates when bent
20. Small light stick	Stick that illuminates when bent. Used by fishermen and sportsmen
21. Compass	Luminous when exposed to ordinary light
23. Spray painting	Luminous when exposed to ordinary light
24. Signal tape	Luminous when exposed to ordinary light. Used for marking at factories etc.

3 Result of the Collection of Data

3.1 Collection of Data

The collection of data by contacting distributors, importer, manufacturers, and trades and by searching on the Internet is shown in Table 3.1. It has been of great importance to get a thorough knowledge on the fluorescent system. In several cases it has not been possible to get hold of detailed information. Products, which may get in contact with skin when using it, have been selected for further chemical analyses. The products in question are either fluid, made of soft rubber or consist of gasses (spray). In Table 3.1 these products are emphasised with a *.

Table 3.1: Content

Product	Declaration of content/Contact with manufacturers and others	Fluorescent System
1. Pink ink *	Glycerol, propan-1-2-diol	?
2. Green ink *	Glycerol, propan-1-2-diol	?
3. Yellow Ink *	Glycerol, propan-1-2-diol	?
4. Frisbee	Crude oil, ethylacetate	?
5. Conformer	Rubber latex, polypropylene, ZnS	ZnS
6. Glow slime *	ZnS	ZnS
7. Winnie the Pooh Silhouettes	ZnS	ZnS
8. Finger Monsters *	ZnS	ZnS
10. Decoration colorant *	Water-based	?
11. Textile colorant *	ZnS	ZnS
12. Pears *	-	?
13. Orange makeup *	Appendix C	ZnS
14. Green makeup *	Appendix C	ZnS
15. Snowflakes	ZnS	ZnS
16. Yellow hairspray *	Appendix C	?
17. Green hairspray *	Appendix C	?
19. Light stick *	-	?
20. Trendy light stick	Non-toxic/non-flammable	?
21. Compass	ZnS, Sr oxide aluminate	ZnS, Sr oxide aluminate
23. Spray painting	Crude oil, ethylacetate	?
24. Signal tape	ZnS, Sr-Al pigments	ZnS, Sr-Al pigments

? = The collection of data gave no information on the fluorescent system

3.2 Luminous Components

As a result of contacting distributors, manufacturers/importers and by searching on the Internet the following luminous components have been found:

Zinc sulphide (ZnS, CAS-no 1314-98-3)

- also ZnS:Cu possibly also Si

Zinc sulfide is activated by Cu and Si, by substitution in the crystal lattice.

Strontium-aluminium pigments (www.jlkindustries.com). The complexes are activated by e.g. europium- and dysprosium ions. I.e. the complexes need energy to become fluorescent.

- $SrAl_2O_4$: Strontium-aluminium-oxide is activated by Eu^{+2}, Dy^{+3} (green)
- $Sr_4Al_{14}O_{25}$: Strontium-aluminium-oxide is activated by Eu^{+2}, Dy^{+3} (blue)

4 Methods of Analysis

For the qualitative analysis of the selected the following techniques have been used.

1) Identification of inorganic additives in x-ray fluorescence spectrometry (EDXRF).

2) Qualitative identification of fluids and organic additives in gaschromatography with mass spectrometric detection (GC-MS).

4.1 Identification of Inorganic Additives

Screening analyses have been made of the elements by using the EDXRF-analysis with EDAX-equipment branded EAGLE III on the products in question. Using the technique the products can be analysed for elements with Z > 11, i.e. sodium and then in the periodic system. The detection limits are typically 0,05 w/w% for the light elements and < 0,01w/w% for heavy elements. The analyses are made in vacuum to obtain signals for the light elements.

4.2 Qualitative Identification of Fluids and Organic Additives

Fluids/solid materials are decomposed/extracted with a suitable solvent. Dilutions and extracts are analysed gaschromatographic with a mass spectrometric detection. For identification of single components the MS NIST98 information retrieval is used. For analysing the products with GC-MS, column and temperature programme is used as described below.

GC-MS	Thermoquest Finnigan Trace GC 2000
Column	RTX-S w/Intergra-Guard: 15 meter; 0,25 mm ID; 0,25 µm dF
Temperature programme	40ºC(1min) - 15º C/min - 270ºC(3min)
Injection temperature	40ºC
Detection limit	0,1 µg/mL

5 Results

In the present chapter the results of the screening of elements and organic additives by x-ray analysis and gaschromatographic analysis with mass spectrometric detection, respectively, are presented.

5.1 Identification of Inorganic Additives

The result of the EDXRF x-ray analysis is shown in Table 5.1.

Table 5.1: Inorganic Substances Detected when screening for Elements

Product	X-ray Results																		
	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Mn	Fe	Cu	Zn	Br	Sr	Zr	Eu	Dy
1. Pink ink				X		X	X	X	X	X		X							
2. Green ink				X		X	X	X	X	X		X	X	X	X				
3. Yellow Ink				X		X	X	X	X	X		X		X					
6. Glow slime					X	X		X	X					X					
8. Finger Monsters				X		X	X							X					
10. DecorationColorant				X	X	X		X	X					X					
11. Textile colorant				X		X			X					X					
12. Pearls		X	X						X					X		X	X	X	X
13. Orange makeup	X					X								X					
14. Green makeup	X			X		X		X						X					
16. Yellow hairspray						X				X									
17. Green hairspray					X	X				X									
19. Light stick							X												

Table 5.1 shows that sulphur, calcium, and zinc have been detected in the majority of the products, which indicates that metal sulphides, zinc sulphide, and calcium sulphide are present. In one product, no. 12 (pearls), elements such as aluminium, strontium, zirconium, europium, and dysprosium have been detected. It indicates the presence of strontium-aluminium compounds as mentioned in section 3.2. A bromine compound has been detected in product no. 2, Green ink.

In hairspray no 16 and 17 titanium has been detected. According to the declaration of content it is derived from titanium dioxide that is used a white pigment without fluorescent effect. Sulphur is derived from many of the colorants: Acid Yellow 3 (CAS no 8004-92-0), Tartrazine (CAS no 1934-21-0) and Acid Blue (CAS no 2650-18-2), cf. Table 5.3. The x-ray results show no content of fluorescent substances in these products. In no 19 (Light stick) only the presence of chlorine has been detected, thus, no information on the fluorescent system can be obtained. In no 1 (Pink ink) the presence of zinc

sulphide cannot be established as in no 2 and 3 (Green ink and Yellow ink). Thus, no information on the fluorescent system can be obtained.

Substances such as zinc sulphide, bromine, and strontium-aluminium compounds have been chosen for a health assessment in chapter 6.

5.2 Identification of Organic Additives

The results from the qualitative gaschromatographic analysis are shown in Table 5.2.

Table 5.2: Identified Organic Components

Product	Extractor/solvent	Organic component	CAS. no
1. Pink ink	Dichlormethane	-	-
2. Green ink	Dichlormethane	-	-
3. Yellow Ink	Dichlormethane	-	-
6. Glow slime	Ethyl acetate	Methyl parabene	99-76-3
		4-hydroxy-benzoic acid	99-96-7
8. Finger Monsters	Dichlormethane	Tributyl acetyl citrate	77-90-7
10. Decoration colorant	Dichlormethane	Dimethyl phthalate	131-11-3
11. Textile colorant	Acetonitrile	-	-
13. Orange makeup	Dichlormethane	Dimethyl phthalate	131-11-3
14. Green makeup	Dichlormethane	Dimethyl phthalate	131-11-3
16. Yellow hairspray	Dichlormethane	Unsaturated hydrocarbon	Not identified
17. Green hairspray	Dichlormethane	Unsaturated hydrocarbon	Not identified
19. Light stick	Dichlormethane	Dimethyl phthalate	131-11-3
		Dibutyl phthalate	84-74-2
		Trichloro compound	Not identified

'-' No results a qualitative GC-MS Screening

Table 5.2 shows that the substances identified in the products:

Organic component	CAS no
Methyl parabene	99-76-3
4-hydroxy-benzoic acid	99-96-7
Tributyl acetyl citrate	77-90-7
Dibutyl phthalate	84-74-2
Dimethyl phthalate	131-11-3

Methyl parabene and 4-hydroxybenzoic acid are used as preservatives in cosmetics and cause allergic reactions and skin inflammation. Phthalates and tributyl acetyl citrate are used as plasticizers, however, it can also come from background pollution from raw materials, production equipment or packaging. The detected substances have no fluorescent effect. As no other substances have been identified, a health assessment will be made on all five substances in chapter 6.

5.3 Declared Colorants

In Table 5.3 shows the colorant mentioned on the declarations of content of four products (13. Orange makeup, 14. Green makeup, 16. Yellow hairspray, 17. Green hairspray). The colorants mentioned on the declaration of content are noted with CI-number. Table 5.3 also includes the chemical name, CAS no and other well-known synonyms of the colorant.

It should be noted that it does not appear on the declarations of content what the quantity of the colorants present in the product is.

Table 5.3 shows that the three colorants first mentioned (CI 11710 (no 13 + 14), CI 15880 (no 13+14), CI 16035 (no 16+17)) are azo colorants. In accordance with the Statutory Order on Cosmetic Products CI 11710 must only be used in products which do not get in contact with the mocous membranes.

As far as the other colorants concerns the Statutory Order on Cosmetic Products states that CI 74260 (no 16) must not be used in products that are to be used around the eyes.

As for the two chromium-based colorants CI 77288 (no 16) and 77289 (no 13+14+16) it is stated that they must not contain chromate ions.

All the other colorants can be used in all cosmetic products in accordance with the Statutory Order on Cosmetic Products. No documentation has been retrieved stated that the declared colorants have a fluorescent effect. A visual assessment of the hairspray no 16 and no 17 showed that the colour can be characterised as 'neon'-colour and not as luminous.

Table 5.3 Declared Colorants in Product 13, 14, 16, and 17

CI-number	Products	Chemical name	CAS-no	Note
11710	13+14	2-((4-Chloro-2-nitrophenyl) azo)-N-(2-chlorophenyl)-3-oxobutanamid- e	6486-23-3	C.I. Pigment Yellow 3
15880	13+14	-Naphthalenecarboxylic acid, 3-hydroxy-4-((1-sulfo-2-naphthalenyl)azo)-, calcium salt (1:1)	6417-83-0	D&C Red No. 34
16035	16 + 17	2-Naphthalenesulfonic acid, 6-hydroxy-5-((2-methoxy-5-methyl-4-sulfophenyl)azo)-, disodium salt	25956-17-6	FD & C Red no. 40
19140	16 + 17	1H-Pyrazole-3-carboxylic acid, 4,5-dihydro-5-oxo-1-(4-sulfophenyl)-4-((4-sulfophenyl)azo)-, trisodium salt	1934-21-0	FD & C Yellow no. 5 Tartrazine
42090	16 + 17	Ammonium, ethyl(4-(p-(ethyl(m-sulfobenzyl)amino)-alpha-(o-sulfophenyl) benzylidene)-2,5-cyclohexadien-1-ylidene)(m-sulfobenzyl)-, hydroxide, inner salt, diammonium salt	2650-18-2	C.I. Acid Blue 9
45430	17	3',6'-Dihydroxy-2',4',5',7'-tetraiodospiro(isobenzofuran-1(3H),9'- -(9H)xanthen)-3-one, disodium salt	16423-68-0	Erythrosine sodium FD and C Red 3
47005	16 + 17	2-(2-Quinolyl)-1,3-indandione disulfonic acid disodium salt	8004-92-0	Acid yellow 3 C.I. D & C Yellow no. 10
74260	16	C.I. Pigment Green 7	1328-53-6	Phthalocyanine Green
77000	16 + 17	C.I. Pigment Green 7	1328-53-6	Phthalocyanine Green
77007	13+14 + 16	C.I. Pigment Blue 29	57455-37-5	Ultramarine blue
77266	16 + 17	Carbon black	1333-86-4	Pigment black 6 Pigment black 7
77288	16	Chrome oxide (Cr2O3)	1308-38-9	
77289	13+14 + 16	Chromic oxide hydrated	12001-99-9	Pigment green 18
77480	16 + 17	Gold powder	7440-57-5	Pigment metal 3
77891	16 + 17	Titanium dioxide	13463-67-7	Pigment white 6

5.4 Selected Substances

As agreed with Danish EPA fluorescent substances such as zinc sulphide and strontium-aluminium-complexes, and the below mentioned list of substances have en selected for a health assessment as described in chapter 6. It should be noted that the quantity of the detected substances in the products is not known, as they have been detected using qualitative analyses.

- Methyl parabene
- CI 16035, 42090, and 77007
- 4-hydroxybenzoic acid
- tributylacetyl citrate
- dibutyl phthalate and dimethyl phthalate.

As agreed with Danish EPA fluorescent substances such as zinc sulphide and a-s- compounds have been selected for a health assessment as well as the above-mentioned list. The assessment is described in chapter 6.

6 Assessment of the Substances

As mentioned in the introduction fluorescent substances can have an illuminating effect either by being affected by visible or ultraviolet light or by a chemical reaction. It requires supplying of energy before a substance can illuminate the atoms have to be excited by something. Zinc sulphide can be excited by radium. However, radium has not been detected in the analyses. Strontium-aluminium-complexes can be excited by lanthanoides. Strontium and aluminium have been detected in the analyses.

The following assessment is based on a characterisation of the substances and the retrieval of possible data on health issues that describes effects on skin, eyes, ingestion as well as possible chronic effects. The health assessment has been made based on the qualitative analyses and an assumption of the content in the analysed products.

6.1 Zinc sulphide

6.1.1 Identity and Physical/Chemical Properties

Zinc sulphide has CAS-no 1314-98-3. The substance is often described as C.I.Pigment White 5. The molecular formula of the substance is ZnS and its molecule weight is 97.46 g/mole.

Zinc sulphide is crystalline. There are two forms of crystals. Alpha crystals, described as Wurtzit, are hexagonal crystals. Beta crystals, described as Speralit, are cubic crystals. Both types of crystals are colourless.

The boiling point of the substance is 1185°C and the melting point is 1700°C. The density of alpha crystals is 3.99 and of beta crystals 4.10 (Lewis, R.J., 1993).

Zinc sulphide is insoluble in alkaline liquids and soluble in diluted mineral acids. The alpha form has a density of 6.9 mg/litre water and the beta form has a density of 6.5 mg/litre water at 18°C. (Weast, R.C. 1987-1988.)

6.1.2 Health Properties

It has only been possible to retrieve rather little information on the substance. Zinc sulphide is described in HSDB with few pieces of information. Furthermore, the substance is shortly described in Safe Handling of Color Pigments (1993).

6.1.2.1 Acute Effects

It is stated that zinc sulphide has a very low toxicity. At ingestion LD_{50} is larger than 5000 mg/kg (however, the experiment is not described in details). At inhalation of dust from the pigment mechanic irritation may occur. At skin and eyes contact inflammations may occur (Safe Handling of Color Pigments, 1993).

HSDB refers to an article that only mentions that zinc sulphide in golf balls can be harzardous to the health if they go to pieces. It is indicated that large quantities of (without any indication of a specific quantity) may cause inflammation of and damage to the eyes (Grant, 1986). It is, however, assumed to be irrelevant in the present assessment of the substance.

Other information on inflammation of skin and eyes has not been retrieved.

Zinc compounds have a rather low toxicity when ingested, however, large quantity of soluble salts may cause vomiting and diarrhoea (Browning, E., 1969).

At homepage of the National Consumer Agency of Denmark (updated September 8, 2003) a comment is made saying that: "Our children were given some luminous figures that illuminates when the light in the nursery is off. What make the figures illuminate and are the harzardous? We asked Danish EPA who informed us that it is zinc sulphide that makes the figures luminous. Zinc sulphide is quite harmless. No matter whether the figures are luminous or not."

6.1.2.2 Chronic Effects

In general, zinc compounds is not considered carcinogenic (U.S. Environmental Protection Agency's Integrated Risk Information System, 2000).

If zinc is ingested in an abnormal quantity it may be absorbed in and liberated from the body for a number of years without causing any types of symptoms or damaging to the stomach and intestinal canal, kidneys etc (Hamilton, A. and H. L. Hardy, 1974).

It has not been possible to retrieved information that clarifies whether zinc sulphide may cause sensitisation or allergy. As no reports have been retrieved in either HSDB or IRIS it is assumed that the substance does not cause any of these effects.

6.1.2.3 Total Aassessment

It is assumed that persons mainly get in contact with the substance when applying lotion that contains the substance.

The quantity of zinc sulphide in the analysed samples is not known. However it is assessed, that the substance will presumably not cause health problems as zinc sulphide and zinc compounds do not possess properties that cause considerably acute or chronic injuires.

6.2 Strontium-aluminium Complexes

Strontium-aluminium complexes appear in many forms. They are compounds of strontium, aluminium and oxygen. In order to be fluorescent they are activated by lanthanoides such as e.g. Europium, Dysprosium, and Neodymium. Complexes, found at an Internet search, are as follows (www.jlkindustries.com):

Strontium-aluminium oxide:
$SrAl_2O_4$, activated by Eu^{+2} and Dy^{+3}
$Sr_4Al_{14}O_{25}$, activated by Eu^{+2} and Dy^{+3}

It has not been possible to identify the mentioned complexes with e.g. a CI-number or CAS-no.

The following screening implies health issues of the individual ions that the complexes consist of.

6.2.1 Strontium

Strontium is an alkali metal that mainly appears as the ion Sr^{2+}. It is assumed that it is the non-radioactive strontium (molecule weight 87) unlike the radioactive strontiom-90. Therefore the focus of the screening is on strontium-87.

The average daily intake (ADI) of Sr-87 is assessed to be 2 mg (Beliles RP; 1994).

Strontiumoxides and -hydroxides are moderate alkali compounds (Lewis, 1996).

Acute poisoning of test animals resulted in increased salivation, vomiting, colic, and diarrhoea. Rats died after having ingested the substance due to dyspnoea and cats died due to cardiac arrest. The test does not indicate the given doses (National Research Council, 1981).

In an older study, NOAEL and LOAEL are determined for rats. NOAEL is determined to be 525 mg/kg per day and LOAEL to be 633 mg/kg per day (Storey E, 1961).

No information has been retrieved on possible chronic effects due to exposure for strontium.

6.2.2 Aluminium

Aluminium normally appears as aluminiumoxide with CAS-no 1344-28-1 and molecular formula Al_2O_3. The following observations are based on data retrieved for aluminiumoxide.

When searching for information aluminium and aluminiumoxide, retrieved data on health issues are mainly focusing on inhalation of dust and other particles containing aluminiumoxide and other substances. Referring to the use of the substance it is not relevant for the present assessment of the substance.

Dissolved aluminiumoxide do rarely have an irritating effect but dry powder of the substance may cause inflammations or cauterization of the skin and mucous membranes. When ingesting concentrated solutions or a quantity of the solid substance the mouth, throat, and stomach and intestinal canal can be severely irritated and cause indisposition, vomiting, stomach pains, and diarrhoea (Thienes, C. and T.J. Haley, 1972).

If pots and pans of aluminium are used the intake of aluminium will be increased. The same will happen if taking certain types of non-prescription drugs. An increased intake from 25 mg per day till over 1 gram is not unusual (Friberg, L. *et al.*, 1986).

Another survey estimates the daily intake of aluminium to be between 30 and 50 mg (Bjorksten JA, 1982).

There are no statements in the above-mentioned surveys that the quantities of consumed aluminium cause health problems at increased ingestion.

No data have been retrieved that implies that aluminiumoxide may cause long-term effects at skin or eye contact.

Based on the scanty information it is assessed that aluminiumoxide present in colorant complexes in products do not cause any significant health risk as the substance is mixed in a liquid or paste and can therefore not be inhaled.

6.2.3 Europium, Dysprosium and Neodymium

6.2.3.1 Properties

The rare earth metals or lanthanoides includes e.i. europium, dysprosium, and neodymium. Hirano and Suzuki (1996) have tested the toxicity of these three substances and certain other substances.

It is i.e. stated that the lethal dose for oral or interperitonal ingestion is between 10 and 700 mg/kg depending of the substance and the species of animals.

There are no indications of carcinogenic properties based on tests on animals or mutagenicity in in-vitro tests. Lanthanoides have certain repro-toxic effects such as low birth weight, but there are no teratogenic effects.

Ogawa *et al.*, 1995, have carried out experiments with europiumchloride. In a 28 days rat test it was shown that oral intake at 200 mg mg/kg/day or above caused weight loss. By ingestion of 1000 mg/kg/day injuries and irritations of the stomach and intestinal canal were observed.

When retrieving information on health effects, no data were found whether lanthanoides may have any irritating effects on skin or eyes. Neither has it been clarified whether the substances can absorbed through skin or may cause any allergic reactions.

It seems that lanthanoides have an acute toxicity above 10 mg/kg, which implies that they can be classified as toxic.

6.2.3.2 Assessment

It has not been possible to find information on NOAEL or e.g. TDI on the three substances. Based on a LD_{50} for rats, oral at 10 mg/kg and a safety factor of 1000 NOAEL will be on a level less than 10 µg/kg. Assumed that a child weights 10-20 kg the ingestion should be less than 0,1 mg per day.

Assuming that 10 gram of a lotion or the like is used and it contains 1% colouring pigment, the content of colouring pigment will be 100 mg.

In pigment: $SrAl_2O$, activated by Eu^{+2} and Dy^{+3} the total molecule weight will be 521 gram, and lanthanoides will make up for 60%. The lanthanoides will, thus, make up for 60 mg of the 100 mg of colouring pigment. If a child ingests this quantity it may cause a health risk to the child.

In pigment: $Sr_4Al_{14}O_{25}$, activated by Eu^{+2} and Dy^{+3} the total molecule weight will be 1443 gram, and lanthanoides will make up for 22%. The lanthanoides will, thus, make up for 22 mg of the 100 mg of colouring pigment. If a child ingests this quantity it may cause a health risk to the child.

If NOAEL is assumed to be 0.01 mg/kg body weight per day, as mentioned earlier, and if the weight of a child is about 15 kg an acceptable intake will be 0.15 mg per day. Assuming that the colouring pigment contains 50% lanthanoides, an acceptable intake of the colouring pigment will be 0.3 mg per day. If a lotion contains 1% coloring pigment the acceptable intake of the lotion will be 30 mg per day. If the lotion contains 0.1% colouring pigment the level of an acceptable intake will be about 300 mg/day.

As described above an intake of quantities considerably below 1 gram creme per day may have an effect on the health.

6.2.4 Total Assessment

It is most difficult to assess the impact that colouring pigment complexes have on the health when the quantities are unknown. Furthermore, the data on the detected substances are few.

It is assessed that the substances strontium and aluminium do not have much influence on the health. It is assessed that lanthanoides, europium, dysprosium, and neodymiun may cause a health risk, if the substances are ingested even in very small quantities.

It has not been possible to evaluate the risk of irritations and allergy caused by lanthanoides due to the insufficient data.

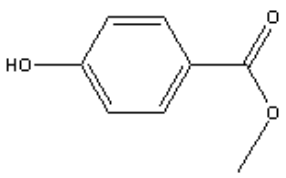
6.3 Other Substances

6.3.1 Methyl parabene

Methyl parabene is described in the report ”Survey of chemical substances in carnival and theatre make up”, no 5/2002 (Petersen *et al.*, 2002). The health issues described in the report are used in the present report.

6.3.1.1 Identity

Methyl parabene has CAS-no 99-76-3 and the molecular formula $C_8H_8O_3$. The molecule weight is 152.15 g/mole and the structure of the substance is a methyl ester of 4-hydroxybenzoic acid as shown below:



The melting point of the substance is 131ºC and the boiling point 270-280ºC (O'Niel, MJ *et al.*, 2001).

6.3.1.2 Health Issues

Methyl parabene is not on the list of dangerous substances. The substance is mentioned in the Statutory Order on Cosmetic Products. Cosmetic products may contain 0.4% of the substance and with other parabenes 0.8% in total.

Methyl parabene can be used as an antioxidant and as a preservative in food. It is allowed to add up till 300 mg/kg of methyl-, ethyl- and propyl parabene.

Methyl parabene has a very low toxicity (LD_{50} over 5000 mg/kg). The EU Commission has laid down an ADI of 10 mg/kg body weight. A NOAEL for all parabenes of 1000 mg/kg body weight has been laid down as well.

No mutagenic or carcinogenic effects have been detected. Teratogenic effects have been detected at very height concentrations (LOAEL approx. 9000 kg/kg body weight).

It is established that methyl parabene does not cause skin inflammation when in contact with intact skin. In contact with the eyes no persistent irritation has been noted. The same goes for ingestion. Parabenes does practically not have any sensitising effect at normal skin. LOAEL for contact with normal skin is above the allowed concentration in cosmetic products.

6.3.1.3 Assessment

Based on the above, it is assessed that if the limit value for the content of methyl parabene is respected the substance will not cause any health risk.

6.3.2 CI 16035, 42090 and 77007

The three colorants are described in the report ”Survey of chemical substances in carnival and theatre make up”, no 5/2002 (Petersen *et al.*, 2002). The health issues described in the report are used in the present report.

6.3.2.1 CI 16035

The colorant CI 16035 has CAS-no 25956-17-6 and the chemical name is 2-Naphthalene sulfonic acid, 6-hydroxy-5-((2-methoxy-5-methyl-4-sulfophenyl)azo)-, disodium salt. The colorant is e.i. also known under the name FD & C Red no. 40.

The molecular formula of the substance is $C_{18}H_{14}N_2Na_2O_8S$ and the molecule weight is 469.4 g/mole.

The estimated values for the melting point is 350°C, and the boiling point is estimated to be 872°C.

The substance is allowed as a colorant in foods. Maximum value is 500 mg/kg for a number of colorants in total. The colorant is allowed in cosmetic products.

There are very few data on the colorant. There is no information on acute toxicity and no incidences of allergy have been reported.

It is assumed that the substance is not mutagenic as the substance has been tested negative in an Ames test. No side effects occurred in a test on pregnant rats at an oral dose of up till 1000 mg/kg.

It has not been possible to find any information on cancer or injuries to the organs.

It is assumed that NOAEL for the colorant is more than 1,000 mg/kg body weight.

6.3.2.2 CI 42090

The colorant CI 42090 has CAS-no 2650-18-2 and the chemical name is ammonium, ethyl(4-(p-(ethyl(m-sulfobenzyl)amino)-alpha-(o-sulfophenyl) benzylidene)-2,5-cyclohexadien-1-ylidene)(m-sulfobenzyl)-, hydroxide, inner salt, diammonium salt. The colorant is also known as C.I. Acid Blue 9.

The molecular formula of the substance is $C_{37}H_{34}N_2Na_2O_9S_3$ and the molecule weight is 792.8 g/mole.

The melting point of the substance is 283°C and the boiling point is estimated to be 1184°C.

The substance is allowed as a colorant in foods. Maximum value is 500 mg/kg for a number of colorants in total. The colorant is allowed in cosmetic products. An ADI of 12,5 mg/kg body weight is determined.

The substance inflames human skin and tests at rabbits show inflammation of the eyes. From the report about carnival and theatre make up (5/2002) no information is given regarding amounts or concentrations, that might cause an effect.

Allergy has been seen on very sensitive persons if the substance has been ingested. No other chronic effects have been found.

It is estimated that NOAEL for the colorant is 2,000 mg/kg body weight.

6.3.2.3 CI 77007

The colorant CI 77007 has CAS-no 57455-37-5. The substance has the chemical names C.I. Pigment Blue 29 or Ultramarine Blue.

The molecular formula of the substance is $Na_7Al_6Si_6O_{24}S_3$ and the molecule weight is 971.5 g/mole. No furthermore information on the identity of the substances has been found.

The substance is not allowed as a colorant in food but is allowed in cosmetic products.

Information on the substance is very limited. However, data show that CI 77007 does not provoke allergic reactions at contact.

6.3.2.4 Total Assessment

All three colorants are allowed in cosmetic products. The colorants CI 16035 and CI 42090 are also allowed as colorants in food.

As for the red colorant CI 16035 a NOAEL of 1,000 mg/kg body weight has been determined. There is no information on inflammation, allergy or other chronic effects.

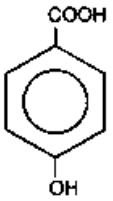
As for the blue CI 42090 a NOAEL on 2,000 mg/kg body weight has been determined. Allergy has been observed on very sensitive persons when the substance has been ingested. No other chronic effects have been seen.

As for the blue colorant CI 77007 it has only been possible to establish that the substance does probably not provoke allergic reactions.

Based on the above-mentioned, the assessment of the colorants CI 16035 and CI 42090 is that they may not cause any health risk. As for CI 77007 it is not possible to determine whether health risks may occur.

6.3.3 4-hydroxybenzoic acid

The 4-hydroxybenzoic acid has CAS-no 99-96-7. The substance is also known as salicylic acid. The molecular formula of the substance is $C_7H_6O_3$ and the molecule weight is 138,12 g/mole. The structure of the substance is:



The substance is allowed in cosmetic products. It is stated that 4-hydroxy-benzoic acid and salts and esters of benzoic which may be added max. 0.4% for acid esters except benzyl esters and 0.8 % for ester compounds.

The substance is used as a flavour agent (FAO/WHO, 2003). It is stated that there is no risk of using the substance at the ordinary used level when the substance is used as a flavour agent.

Two tests using the Ames test have been reported. They show that there are no signed of mutagenic effects at doses of 100-5000 µg/ml (Mikulasova and Bohovicova, 2000).

4-hydroxy-benzoic acid is described in an OECD report from 2000 on substances (UNEP, 2000). In the report it is stated that the substance has an LD_{50}, oral, rat of more than 2,000 mg/kg. The substance causes mild inflammation on the skin, causes moderate inflammation on the eyes and is sensitising in a small degree.

The substance has been tested in experiments with rats with the purpose of disclosing the toxicological and teratogenic effects of the substance. Rats were administered 40, 200 and 1,000 mg/kg/day. It caused irritations of the respiratory passage and small alterations in the blood without causing any permanent effects or modifications of the organs. No signs of effect on the health appeared after repeated exposure at the highest dose of 1,000 mg/kg.

Teratogenic effects were not observed at doses of 1,000 mg/kg/day. The substance is not geno-toxic, in accordance with negative results from bacteria tests. Tests on mice showed estrogenic effects.

Based on the above-mentioned tests NOEAL of 1,000 mg/kg/day can be established regarding the repeated exposure and the teratogenic effects.

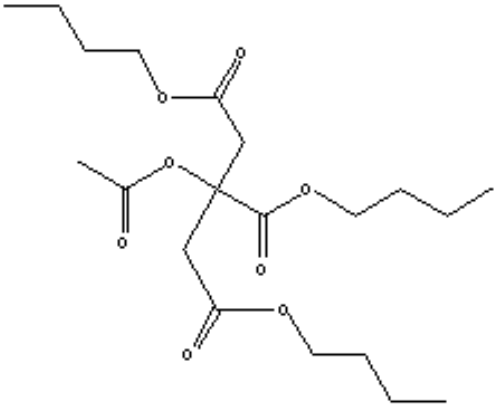
If the applied dose is below the limit in the Statutory Order on Cosmetic Products the content of the substance in lotion will be max. 0.4% equivalent to 4 mg/gram lotion. If a child ingests 10 gram of the lotion the ingestion will be 40 mg 4-hy-droxybenzoic acid corresponding to approx. 3 mg/kg body weight. This is far below the mentioned NOAEL of 1.000 mg/kg/day.

6.3.4 Tributyl acetyl citrate

6.3.4.1 Identity
The substance tributyl acetyl citrate has CAS-no 77-90-7. The substance has the molecular formula $C_{20}H_{34}O_8$ and a molecule weight of 402.88 g/mole.

The melting point of the substance is –80°C. The boiling point is at 1 mmHg determined to be 172-174°C (Clayton and Clayton, 1993-94).

The structure of the substance is as follows:



The substance is generally used as a plasticizer, but can also be used as a flavour agent.

6.3.4.2 Health risk
The health risks of using the substance tributyl acetyl citrate is described in Miljøprojekt No. 590, Environmental and Health Assessment of Alternatives to Phthalates and to flexible PVC (Stuer-Lauridsen *et al.*, 2001). The following description is a summary of the report.

Tributyl acetyl citrate has a very low acute toxicity. LD_{50} in rats has been determined to be 31.4 gram pr. kg body weight.

The substance neither inflames the skin nor cause allergic reactions. It inflames the eyes moderately.

The retrieved information on tributyl acetyl citrate does not describe any mutagenic effects of the substance. A possible risk of cancer cannot be assessed based on the available materials.

A NOAEL value of 100 mg/kg body weight per day has been determined in tests on rats. The tests showed haematological and biochemical alterations and an enlarged liver weight at high doses.

6.3.4.3 Assessment
The quantities in which the substance is used in the relevant products cannot be determined.

If a product contains 1-5 % of the substance and about 10 gram of the product is used, tributyl acetyl citrate is represented by 100 to 500 mg.

If the substance is added as a plasticizer in a product, it will be added in the level 25%. If about 10 gram of the product is used tributyl acetyl citrate will represent 2.5 gram.

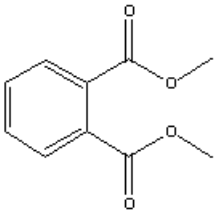
An acceptable intake for a child of 15 kg will be 1,500 mg per day. It will be an unrealistic assumption that the entire product is ingested. It is therefore assumed that the quantities ingested will not be over NOAEL.

It is essential that the substance does not cause skin inflammation and allergic reactions. The substance may cause inflammation of the eyes but it will depend on the other substances present in the product as well.

Summarising, there is a risk of inflammation of the eyes. Other effects on the health are considered insignificant.

6.3.5 Dimethyl phthalate

6.3.5.1 Identity
Dimethyl phthalate (DMP) has CAS-no 131-11-3. The molecular formula of the substance is $C_{10}H_{10}O_4$, and its molecule weight is 194.2 g/mole. The substance is also known as 1,2- benzenedicarboxylic acid dimethyl ester.



DMP has a melting point of 5.5ºC and a boiling point of 283.7ºC. The vapour pressure is 0.003 mmHg and the solubility in water is 4.000 mg/litre.

The substance can be used as a plasticizer or as a solvent for certain colorants.

DMP is described in an IUCLID-Dataset (European Chemicals Bureau, 2000). It shows that DMP is not acute toxic as the mentioned data on LD_{50} is a little above 2000 mg/kg. For dermal exposure the mentioned $LD(D)_{50}$ is above 2000 mg/kg. DMP may cause injuries to the central nervous system when ingested (Budavari, 1996). Prager (1996) states likewise that DMP may

cause burning irritation of the mouth and gullet resulting in vomiting and diarrhea.

According to Budavari, 1996, DMP does not cause inflammation to the skin or can be absorb through the skin. It is mentioned in IUCLID as well that the substance does not inflame the skin but it can inflame the eyes. Grant (1986) states that eye contact with DMP causes considerable pain but does not cause any injuries and at least only limited injuries to the eye (Grant 1986).

IUCLID states that the substance is not sensitising.

In a 21 days test where the lipid-metabolism was surveyed the LOAEL was determined to be 500 mg/kg at oral exposure for rats. In a 90 days test with rabbits, in which skin exposure and injuries to the liver were tested, NOAEL was determined to be 1,200 mg/kg and LOAEL to be 2,400 mg/kg.

Due to insufficient data on the DMP it has not been possible to assess whether the substance may have any carcinogenic effects (U.S. Environmental Protection Agency's Integrated Risk Information System (IRIS).

IUCLID refers to several tests to disclose teratogenic effects of the substance. The lowest NOAEL mentioned is above 400 mg/kg body weight.

6.3.5.2 Assessment

According to the above-mentioned data, DMP may presumably not cause inflammation of the skin. In contact with the eyes irritations may occur, but will probably not cause any permanent effects.

If a product contains 1-5 % of DMP and about 10 gram of the product is used, the substance is represented by 100 to 500 mg.

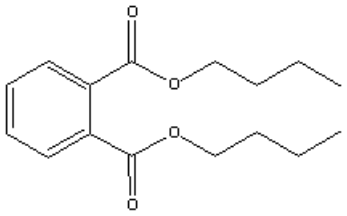
If the substance is added as a plasticizer in a product, the normal level will be around 25%. If about 10 gram of the product is used DMP will represent 2.500 mg.

An acceptable intake for a child of 15 kg will be 6,000 mg per day. It will be an unrealistic assumption that the entire product is ingested. It is therefore assumed that the quantities ingested will not exceed NOAEL.

The use of phthalates in cosmetics and different types of lotions and colorants that are used by children is problematic due to the risk of teratogenic effects. Phthalates in toys for children under 3 years is prohibited.

6.3.6 Dibutyl phthalate

Dibutyl phthalate (DBP) has CAS-no 84-74-2. The molecular formula of the substance is $C_{16}H_{22}O_4$ and the molecule weight 278.3 gram per mole. The substance is also known as 1,2- benzenedicarboxylic acid dibutyl ester.



The melting point of DBP is -35ºC and the boiling point is 340ºC. The substance has a very low vapour pressure of 2×10^{-5} mmHg and a water solubility of 13 mg/litre.

DBP is classified as toxic and harmful to the environment. The classification of the substance is:

Rep2; R61:	May cause harm to the unborn child.
Rep3; R62:	Possible risk of impaired fertility.
N; R50:	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

DBP can be used as a plasticizer for plastic products and as a solvent in colorants and certain types of rubber.

DBP is described in Environmental Health Criteria, no 189 and in EU's Risk assessment Report, no 29.

The acute toxicity of DBP is low. Tests with rats vary from 8 to 20 g/kg and the dermal acute toxicity for rabbits is above 4 g/kg. It is mentioned that acute effects on mice are low activity, respiration distress and inability of co-ordination. DBP is not considered causing allergy (Environmental Health Criteria no. 189).

Laboratory tests on rats indicate that DBP is quickly absorbed in the gastrointestinal system and is mainly distributed to the liver and kidneys in rats. The substance is eliminated by urine as metabolite after ingestion (Environmental Health Criteria no. 189).

Various values for NOAEL and LOAEL are mentioned in the EU's risk assessments. Based on all available studies it is concluede that the LOAEL is 52 mg/kg body weight due to the teratogenic effects in a two-generation-test.

The effects observed after exposure to DBP, are similar to those seen in tests with other phthalates including harm to the unborn child and effects on the testicles (Environmental Health Criteria, no.189). It is i.e. mentioned that if PBP is ingested at high doses it is harmful to the unborn child, but there are no indications of the quantities of the doses in question. Furthermore, the substances are under the suspicion having endocrine disrupting effects.

Due to insufficient data on the DBP it has not been possible to assess whether the substance may have any carcinogenic effects (U.S. Environmental Protection Agency's Integrated Risk Information System (IRIS)).

6.3.6.1 Assessment

According to the above-mentioned data, DBP does not cause inflammation of the skin. In contact with the eyes irritations may occur.

If a product contains 1-5 % of DMP and about 10 gram of the product is used, DBP is represented by 100 to 500 mg.

If used as a plasticizer, 25% of the product can be DBP in a product. The risk will depend on the release from the product.

For the critical effect developmental toxicity is LOAEL for DBP determined to be 52 mg/kg body weight.

Ingestion of 1 gram of a chemical product (e.g. liquid) containing 5 % DBP corresponds to an exposure of 50 mg DPB. If a child weighs 25 kg this will give an exposure of 2 mg/kg body weight. Compared to the LOAL this gives a safety margin of 26, which is below the commonly used value on 100.

Using products with DBP may therefore involve health risks if children play with them even if they only ingest small quantities of DBP from the products.

It is not allowed to sell chemical products to the consumers if the products contain more than 0,2% of DPB.

The use of phthalates in cosmetics and different types of lotions and colorants that are used by children is problematic due to the risk of teratogenic effects. New legislation has been introduced, so it is prohibited to use these substances in cosmetics in the future. Phthalates in toys and certain articles for children under 3 years is prohibited.

6.4 Total assessment

In Table 6.1 the most essential assessments of the tested substances are brought together. The Table shows that

- Lanthanoides in luminous colouring pigments may cause health risks, but the available data is insufficient to reach a final conclusion.
- The blue colorant, CI 77007, may probably cause health risks, but it has not been possible to clarify due to insufficient data.
- Dibutyl phthalate causes inflammation of the eyes and is under the suspicion of being harmful to the unborn child. When the substance is ingested in even very small quantities health risks may occur.

Table 6.1 Overview of Health assessments of The Selected Substances

Substance	CAS-no	Fluorescent	Assessment
Zinc sulphide CI Pigment White 5	1314-98-3	Yes	The substance will probably not cause any health risks, as zinc sulphide/zinc compounds do not have the properties that cause significantly acute or chronic injuries.
Strontium-aluminium complexes	No number available	Yes	It is assessed that strontium and aluminium do not contribute to any health risk of importance. It is assessed that lanthanoides, europium, dysprosium, and neodymiun may cause a health risk if the substances are ingested. It has not been possible to assess whether lanthanoides may cause any risk of inflammation and allergy.
Methyl parabene	99-76-3	No	It is assessed that if the limit of content in cosmetics is observed methyl parabene will not cause any health risk.
Colorants: CI 16035 42090 77007	 25956-17-6 2650-18-2 57455-37-5	No	It is assessed that the colorants CI 16035 and CI 42090 will probably not cause any health problems. As for CI 77007 it has not been possible to decide whether health risks may occur.
4-hydroxy-benzoic acid	99-96-7	No	The substance inflames the skin mildly, the eyes moderately. Beside this, the substance has a low oral toxicity. Chronic effects have not been observed.
Tributyl acetyl citrate	77-90-7	No	Risks of inflammation of the eyes may occur. Other health effects are considered to be minimal.
Dimethyl phthalate	131-11-3	No	DMP may inflame the eyes. The substance is under the suspicion of being harmful to the unborn child. Compared with the quantities in which the substance may be present in the products with the NOAEL value the health risk will, however, be minimal.
Dibutyl phthalate	84-74-2	No	DBP may inflame the eyes. DBP in cosmetics and other types of lotions and colorants is problematic due to risk of teratogenic effects. Ingestion of even small quantities the substance may cause effects on the health.

References

AccessScience http://www.accessscience.com McGraw-Hill 2003.

Bekendtgørelse om kosmetiske produkter, nr. 594 af 6. juni 2000.

Beliles RP; p. 1880 in Patty's Industrial Hygiene and Toxicology. 4th Ed, Vol II, Part C. Clayton GD and Clayton FE, eds. NY,NY: John-Wiley and Sons, Inc (1994).

Bjorksten JA; Comp Therapy 8: 73-6 (1982).

Browning, E. Toxicity of Industrial Metals. 2nd ed. New York: Appleton-Century-Crofts, 1969.

Budavari, S. (ed.). The Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals. Whitehouse Station, NJ: Merck and Co., Inc., 1996. 550.

Budavari, S. (ed.). The Merck Index - Encyclopedia of Chemicals, Drugs and Biologicals. Rahway, NJ: Merck and Co., Inc., 1989. 1324.

California Environmental Protection Agency, *Evidence on the Carcinogenicity of Quinoline and Its Strong Acid Salts*, 1997, http://www.oehha.ca.gov/prop65/hazard_ident/pdf_zip/quinolin.pdf

Clayton, G.D., F.E. Clayton (eds.) Patty's Industrial Hygiene and Toxicology. Volumes 2A, 2B, 2C, 2D, 2E, 2F: Toxicology. 4th ed. New York, NY: John Wiley & Sons Inc., 1993-1994. 3058.

Danish EPA. *Kemi i børns hverdag. Miljøtema nr. 23*, Miljøstyrelsen, 2001. In Danish only.

Environmental Health Criteria 189: Di-n-butyl phthalate. pp. 17-23 (1997) by the International Programme on Chemical Safety (IPCS) under the joint sponsorship of the United Nations Environment Programme, the International Labour Organisation and the World Health Organization.

European Chemicals Bureau, 2000 : IUCLID Dataset for dimenthyl phthalate

EU's Risk Assessment Report no. 29: Dibutylphthalat, final report 2003

FAO/WHO Expert Committee on Food Additives: Summary of Evaluations Performed : 4-HYDROXYBENZOIC ACID: 11 Mar 03.

Friberg, L., Nordberg, G.F., Kessler, E. and Vouk, V.B. (eds). Handbook of the Toxicology of Metals. 2nd ed. Vols I, II.: Amsterdam: Elsevier Science Publishers B.V., 1986.

Gilbert, A. og Baggott, J. *Essentials of Molecular Photochemistry* , Blackwell Science Ltd, Oxford UK, 1991.

Gilman, A.G., T.W. Rall, A.S. Nies and P. Taylor (eds.). Goodman and Gilman's The Pharmacological Basis of Therapeutics. 8th ed. New York, NY. Pergamon Press, 1990.
Grant, W.M. Toxicology of the eye, 3ed ed. Springfield Il, 1986.

Grant, W.M. Toxicology of the Eye. 3rd ed. Springfield, IL: Charles C. Thomas Publisher, 1986. 349.

Hamilton, A., and H. L. Hardy. Industrial Toxicology. 3rd ed.

Hirqano S, Suzuki KT: Exposure, Metabolism, and Toxicity of Rare Earths and Related; Environmental Health Perspectives, Vol. 104, Supplement 1, pages 85-95, 139 references, 1996 .

Lewis, R.J. Sax's Dangerous Properties of Industrial Materials. 9th ed. Volumes 1-3. New York, NY: Van Nostrand Reinhold, 1996.

Lewis, R.J., Sr (Ed.). Hawley's Condensed Chemical Dictionary. 12th ed. New York, NY: Van Nostrand Rheinhold Co., 1993 .

Mikulusova, M. and Bohovicova I., Genotoxic Effect og Vanillin Derivates; BIOLOGIA (BRATISLAVA) 55(3):229-234, 2000.

Miljøministeriets bekendtgørelse nr. 151 af 15. marts 1999 om forbud mod phthalater i legetøj til børn i alderen 0-3 år samt i visse småbørnsartikler m.v.

National Research Council, *Aromatic Amines: An Assessment of the Biological and Environemtal Effects*, National Academy Press, Washington DC, 1981.

National Research Council. Drinking Water & Health, Volume 4. Washington, DC: National Academy Press, 1981. 189.

Ogawa Y, Suzuki S, Naito K., Saito M., Kamata E., Hirose A., Ono A., Kaneko T., Chiba M.,Inaba Y., Kurokawa Y.; Toxicity study of europium chloride in rats. Jour. Of Environmental Pathology Toxocology and Oncology; 14 (1). 1995. 1-9.

O'Niel, MJ et al, editors. The Merck Index: an encyclopedia of chemicals, drugs and biologicals. 123 ed. Whitehouse Station(NJ): Merck & Co; 2001.

Petersen IG, Andersen TT, Larsen JR, Cohr K-H, Borling P, Nielsen AK: Kortlægning af kemiske stoffer i fastelavns- og teatersminke. Miljøstyrelsen. Kortlægning nr. 5, 2002.

Prager, J.C. Environmental Contaminant Reference Databook Volume 2. New York, NY: Van Nostrand Reinhold, 1996. 785.

Safe Handling of Color Pigments (1993) Color Pigment Manufactures Association Inc (CPMA).

Storey, E. 1961. Strontium "rickets" bone calcium and strontium changes. Austral. Ann. Med. 10: 213-222.

Stuer-Lauridsen F, Mikkelsen S, Havelund S, Birkved M, Hansen LP (2001) Enrironmental and Health Assessment of Alternatives to Phthalates and to

flexible PVC. Environmenatl Project No. 590, 2001. Miljøstyrelsen.

Thienes, C., and T.J. Haley. Clinical Toxicology. 5th ed. Philadelphia: Lea and Febiger, 1972. 169.

U.S. Environmental Protection Agency's Integrated Risk Information System (IRIS) on Zinc and compounds (7440-66-6) March 15, 2000.

UK Department of Trade and Industry, *Fluorescent Lightsticks* http://www.dti.gov.uk/homesafetynetwork/cp_rfluo.htm

UNEP (2000): 4-hydroxybenzoic acid, CAS No. 99-96-7. Screening Information Data Sets for High Volume Chemicals (SIDS) Vol 6/12: 175-218. United Nations Environment Programme on Chemicals. Geneva.

Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.

List of Ingredients for 4 products

13. Orange makeup and 14. Green makeup

Aqua
Pvp/va copolymer
Carboner
Aminomethyl propanol
Peg-40 hydrogenated castor oil
Tetrasodium EDTA
Methylparaben
Benzyl alcohol
Methylchloroisothiazolinone
Methylisothiazolinone
Parfum
Disodium distyrylbiphenyl disulfonate
Mica
Zinksulfide
Ci 11710, 15880, 77007, 77289
Do not use in the area of eyes and mouth

16. Yellow hairspray

Butane
Isopropyl alcohol
Propane
Polyvinylcaprolactam
Polyesterpolyamidecocondensate
Hydrogenated castor oil
Propylen glycol
CI 42090, 77891, 77266, 47005, 16035, 77480, 19140, 74260, 77000, 45430:1, 77007, 77289, 77288

17. Green hairspray

Butane
Isopropyl alcohol
Propane
Acrylates copolymer
Rosin acrylate
Pvp/va/vinyl propionate copolymer
Silica
Parfum
CI 77891, 16035, 77266, 77000, 77480, 19140, 45430, 42090, 47005
epoxy rosin