

Survey and release of chemical substances in "slimy" toys

Nanna Svendsen
Søren F. Pedersen
Ole Chr. Hansen
Eva Pedersen
Nils Bernth
Danish Technological Institute

Survey of Chemical Substances in Consumer
Products, **No. 67** 2005

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

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

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

Content

CONTENT	3
PREFACE	7
SUMMARY AND CONCLUSIONS	9
1 INTRODUCTION	18
1.1 INTRODUCTION	18
1.2 PURPOSE	18
1.3 PROCEDURE	19
2 MARKET ANALYSIS	22
2.1 INTRODUCTION	22
2.2 STATISTICS	22
2.3 TRADE ORGANISATION	22
2.4 THE PRODUCERS	23
2.5 THE RETAIL TRADE	23
2.6 PHTHALATES	23
3 ANALYSIS RESULTS	25
3.1 FTIR SCREENING	25
3.1.1 <i>Equipment and methods</i>	25
3.1.2 <i>Results from the FTIR screening</i>	25
3.1.3 <i>Summary of the FTIR screening</i>	26
3.2 QUANTITATIVE DETERMINATION OF PHTHALATE BY GC-MS	27
3.2.1 <i>Analysis method</i>	27
3.2.2 <i>Analysis results for phthalates</i>	27
3.2.3 <i>Summary</i>	28
3.3 HEADSPACE ANALYSIS RESULTS FROM SCREENING	28
3.3.1 <i>Analysis method</i>	28
3.3.2 <i>Results from the headspace analysis</i>	28
3.3.3 <i>Summary of the headspace analyses</i>	33
3.4 GC-MS ANALYSIS RESULTS FROM SCREENING	33
3.4.1 <i>Analysis method</i>	33
3.4.2 <i>Results from the GC-MS screening analysis</i>	33
3.4.3 <i>Summary of the GC-MS screening analysis</i>	33
3.5 ICP ANALYSIS RESULTS FROM SCREENING	37
3.5.1 <i>Analysis method</i>	37
3.5.2 <i>Results from the ICP-MS screening</i>	37
3.5.3 <i>Summary of the ICP-MS screening</i>	37
3.6 BORIC ACID DETERMINATION BY ICP-AES	38
3.6.1 <i>Analysis method</i>	38
3.6.2 <i>Results from the boric acid determination by ICP-AES</i>	38
3.6.3 <i>Summary of boric acid determination by ICP-AES</i>	38
4 SCREENING FOR POSSIBLE HARMFUL EFFECTS	39
4.1 SCREENING BY "HEADSPACE"	39
4.1.1 <i>Screening for possible harmful effects on the basis of the headspace analyses</i>	39

4.1.2	<i>Proposal for selected organic substances</i>	43
4.1.3	<i>Proposal for selected inorganic substances</i>	49
4.1.4	<i>Conclusion headspace</i>	49
4.2	SCREENING OF POSSIBLE HARMFUL EFFECTS BASED ON THE MIGRATION ANALYSES	50
4.2.1	<i>Screening by migration</i>	51
4.2.2	<i>Proposal for selected organic substances</i>	52
4.2.3	<i>Conclusion based on the migration analyses</i>	54
4.3	CONCLUSION ON SCREENING OF POSSIBLE HARMFUL EFFECTS	55
4.4	SELECTION OF SUBSTANCES FOR QUANTITATIVE DETERMINATION	56
5	QUANTITATIVE ANALYSES	57
5.1	HEADSPACE ANALYSIS RESULTS FROM QUANTITATIVE DETERMINATION	57
5.1.1	<i>Headspace method description</i>	57
5.1.2	<i>Headspace analysis results</i>	57
5.2	GC-MS ANALYSIS (QUANTITATIVE DETERMINATION) MIGRATION	57
5.2.1	<i>GC-MS Analysis method description</i>	57
5.2.2	<i>GC-MS Analysis results</i>	57
5.3	ICP-MS ANALYSIS (QUANTITATIVE DETERMINATION)	59
5.3.1	<i>ICP-MS Analysis method description</i>	59
5.3.2	<i>ICP-MS Analysis results</i>	59
6	EXPOSURE SCENARIOS	61
6.1	INTRODUCTION	61
6.2	EXPOSURE SCENARIOS	62
6.2.1	<i>Introduction</i>	62
6.2.2	<i>Methodology</i>	63
6.2.3	<i>Exposure via inhalation</i>	65
6.2.4	<i>Dermal exposure</i>	66
6.2.5	<i>Oral exposure</i>	68
6.2.6	<i>Total exposure</i>	69
6.3	EVALUATION OF INDIVIDUAL SUBSTANCES	70
6.3.1	<i>2-Butanone</i>	70
6.3.2	<i>2-Butoxyethanol</i>	74
6.3.3	<i>3-Carene</i>	76
6.3.4	<i>Cyclohexanone</i>	79
6.3.5	<i>Diethylglycol dibenzoate</i>	83
6.3.6	<i>Ethylbenzene</i>	85
6.3.7	<i>2-Hexanone</i>	88
6.3.8	<i>2-Phenoxyethanol</i>	90
6.3.9	<i>2-Phenylmethylenoxtanal (alpha-Hexylcinnamaldehyd)</i>	93
6.3.10	<i>D-Limonene</i>	95
6.3.11	<i>alpha-Pinene</i>	98
6.3.12	<i>1,2-Propanediol</i>	100
6.3.13	<i>2-Propenoic acid 2-methyl-methylester (methyl methacrylate)</i>	103
6.3.14	<i>N-Propylbenzamide</i>	105
6.3.15	<i>N-Acetylbenzamide</i>	106
6.3.16	<i>Styrene</i>	107
6.3.17	<i>Toluene</i>	110
6.3.18	<i>Xylene</i>	115
6.3.19	<i>Boron</i>	119
6.3.20	<i>Nickel</i>	123
6.4	CONCLUSION OF HEALTH ASSESSMENT	124
7	HEALTH ASSESSMENT OF TWO ADDITIONAL PRODUCTS	128

7.1	INTRODUCTION	128
7.2	SCREENING AND QUANTITATIVE ANALYSES	128
7.3	IDENTIFIED SUBSTANCES	128
7.4	CLASSIFICATION OF IDENTIFIED SUBSTANCES	129
7.5	ASSESSMENT OF 2 ADDITIONAL PRODUCTS	131
7.6	CONCLUSION	136
8	REFERENCES	137

Encl. A:	List of purchased slimy toys
Encl. B:	FTIR analysis results from screening
Encl. C:	Headspace analysis results from screening
Encl. D:GC-MS Analysis results from screening
Encl. E:	ICP Analysis results from screening
Encl. F:	Analysis results from boric acid determination by ICP-AES
Encl. G:	Headspace calculations
Encl. H:	GC-MS quantitative analysis results
Encl. I:	ICP quantitative analysis results
Encl. J:	Boric determination by ICP-AES
Encl. K:	Supplementary tests - Analysis results for headspace analyses stated in mg/m ³
Encl. L:	Quantitative determination of phthalate by GC-MS

Preface

The project *Survey and release of chemical substances in "slimy" toys* is a part of the Danish Environmental Protection Agency's (E P A) joint efforts in connection with survey of chemical substances in consumer products. The project is divided into four phases.

Phase 1: Survey of the market for "slimy" toys, incl. a survey of which types are found on the market. Survey based on literature, data sheets and trade contacts showing which chemical substances are used in such products. Phase 1 has been carried out by Danish Technological Institute, Centre for Plastics Technology, by M.Sc. Nanna Svendsen in the period March - May 2004.

Phase 2: Qualitative analysis. For selected slimy toys the following has been carried out:

- a. **screening analysis by FTIR showing which materials the toys have been manufactured from and possible content of phthalates**
- b. qualitative screening analysis for elements by ICP and quantitative analysis for content of boric acid
- c. qualitative analysis showing which substances are being released to the air by headspace analysis combined with GC-MS
- d. qualitative analysis showing which substances are being released to artificial saliva and sweat by GC-MS
- e. quantitative determination of content of phthalates

Phase 2 has been carried out by Danish Technological Institute, Centre for Plastics Technology by B.Sc. (Chem.Eng.) Søren F. Pedersen and Centre for Chemical and Water Technology by Process Technologist Eva Pedersen and Cand. Scient. Nils Bernth in the period May - June 2004.

Phase 3: Screening for harmful effects from the migrated/released substances and - together with the Environmental Protection Agency - selecting which substances are quantitatively to be analysed for, when the release is measured. Phase 3 has been carried out by Danish Technological Institute, Centre for Chemical and Water Technology by Ole Chr. Hansen in the period June - July 2004.

Phase 4: Quantitative analysis of selected substances release to artificial saliva and sweat by GC-MS and ICP. Quantitative analysis of selected constituents in certain products. Quantitative determination of selected constituents through calculation based on qualitative screening by headspace. Preparation of exposure scenarios at the released substances.

Phase 4 has been carried out by Danish Technological Institute, Centre for Chemical and Water Technology by Process Technologist Eva Pedersen and Cand. Scient. Nils Bernth and Cand. Scient. Ole Chr. Hansen in the period September - October 2004.

Written report prepared by:
Nanna Svendsen, survey and final report
Søren F. Pedersen, FT-IR analyses
Nils Bernth, inorganic chemistry

Eva Pedersen, organic chemistry
Ole Christian Hansen, health assessment

Summary and conclusions

As a part of the Danish Environmental Protection Agency's survey of chemical substances in a number of consumer products, knowledge of which substances are contained in "slimy" toys is requested. The aim of the project is to give a survey of the chemical substances that might be contained in rubbery and slimy toys. This knowledge can be used in connection with guidance of manufacturers and importers, and possible recommendations to the consumers to avoid certain substances in this kind of toys. Furthermore, the project will form the basis of evaluating unique batches of similar toys, when they get on the market.

Phase 1 concerns examination of the slimy toys market in Denmark. Furthermore, it has been examined which materials they consist of, or which materials are constituents, and to which degree they appeal to children and which age group.

It has not been possible to get information from the manufacturers regarding substances in their products. However, the detail trade has delivered data sheets. The biggest importer of slimy toys in Denmark is K. E. Mathisen A/S (K. E. Leg).

In phase 2, the following qualitative analyses have been carried out:

- a. **screening analysis by means of FTIR in order to determine which materials the toys are made of and possible content of phthalates**
- b. qualitative screening analysis of elements by means of ICP and quantitative analysis of boric acid content
- c. qualitative analysis of the substances released to the air by means of headspace analysis combined with GC-MS
- d. qualitative analysis of the substances released to artificial saliva and sweat by means of GC-MS
- e. quantitative determination of content of phthalates

The FTIR analyses show two types of "slime", partly an aqueous type, hydrogels, and partly a type based on hydrocarbons with a small content of styrene. The aqueous slime contains glycerol and acrylate and in some cases materials, which we have not been able to identify by FTIR. In a number of cases, parabenes have been added. Generally, in the slime products made of hydrocarbons we cannot detect other components.

The quantitative determination of phthalates showed that one of the products exceeded the threshold limit value of 0.05 weight%.

At the preliminary headspace analyses, we have identified all the substances, which might degas from the slimy toys (except for light aldehydes). At the headspace analyses of the 14 slimy toys (of which a few were analysed on exterior part and interior liquid part, totally 20 analyses), we found 61 identified single substances and various groups of substances consisting of various aliphatic and aromatic hydrocarbons, which are stated in groups characterised by the number of carbon-atoms, and finally 6 compounds, which could not be identified.

At the migration analyses of the 14 slimy toys (of which a few were analysed on exterior part and interior part, totally 17 analyses) we found 22 identified single substances and various groups of substances consisting of various aliphatic and aromatic hydrocarbons, which are stated in groups characterised by the number of carbon-atoms, and finally 6 compounds, which could not be identified, but they were all fatty acids.

The qualitative screening analyses by ICP show a considerable content of boron in 3 of the samples (DK-01, TO-01 and TO-02). Boron might have been added as preservative in the form of boric acid or sodium borate, as - at the same time - a content of sodium has been measured. However, other sodium sources might have been added too, e.g. from sodium benzoate, which is also a preservative. The content of elements such as aluminium, calcium, potassium and zinc, which has been detected in most of the samples, presumably derives from fillers or auxiliary constituents used in the production of the products. Furthermore, the detection of traces from a few heavy metals in some of the samples is supposed to derive from contaminations from fillers and possibly from production equipment and production conditions.

Phase 3 deals with screening for possible harmful effects from substances, which are being released from slimy toys. A screening has been made of the substances, which have been identified by the headspace analyses. The screening is based on a literature survey in order to secure that the substances focused on at the quantitative analyses are the most relevant.

Based on the identified chemical compounds a screening for possible harmful substances has been made. The screening is based on the classifications in the List of Dangerous Substances and available information on effects that potentially may cause concern to the consumer, if the release of the chemical substance is too high.

Some substances were detected, which might be considered to be problematic substances, and some, which may be of concern.

According to agreement with the Danish Environmental Protection Agency, the following substances are suggested for a closer examination:

Organic substances:

alpha-Pinene
2-Butanone
2-Butoxy-ethanol
3-Carene
Cyclohexanone
Diethylglycol dibenzoate
d-Limonene
Ethylbenzene
2-Hexanone
2-Phenoxy ethanol
2-Phenylmethylene octanal
1,2-Propandiol
2-Propenoic acid 2 methyl-methyl ester (methyl-methacrylate)
N-Propyl benzamide + N-acetyl benzamide
Styrene
Toluene

Xylene

Inorganic substances

Boron

Nickel

Phase 4 deals with the quantitative analyses and preparation of exposure scenarios at the released substances. Because most problematic substances were detected by headspace at the screening, and because this screening is not immediately quantitative, it has been necessary to determine the amount and the release of these substances by means of calculations made on the basis of the screening analysis.

The problematic substances, which are migrated to artificial saliva and sweat, are determined quantitatively by GC-MS.

In addition, a quantitative ICP-MS analysis of nickel has been carried out.

For the health assessments, we have used parameters for small children in the scenarios, as the consumer in this case in particular is assumed to be children. It cannot be precluded that the pungent smell, which is observed from some products, may cause acute effects like eye-, nose- and throat irritations. At long term exposure there is a possibility that a few substances may cause contact allergy at particularly sensitive individuals.

The scientific committee for cosmetic products has identified 26 substances as recognized contact allergens (SCCNFP 1999). These substances have later been regulated in Directive 2003/15/EC (EC 2003). 2 out of these 26 substances were detected in the examination: D-Limonene was found in 3 products and hexylcinnam aldehyde in 1 product.

In addition, of other substances, which are potentially allergenic, we have detected 3-carene, *alpha*-pinene and nickel. All 3 are terpenes. D-Limonene, 3-carene (7 products) and *alpha*-pinene (8 products) were only detected in the headspace analyses. It is a little uncertain whether the effect from contact allergens is the same at an exposure via the respiratory tract as at skin contact, but they are or can be rediscovered in aerosols, which may potentially also settle on skin surfaces.

Boron was detected in 3 products, at a maximum of 0.8% of the products. It is assessed that a health risk cannot be excluded at contact with the liquid in one of the products.

Nickel was detected in 2 products, at a maximum of 0.0003% of the toy. Consequently, it is assessed that the nickel content does not immediately constitute a problem, unless one is particularly sensitive (nickel allergy).

For the rest of the substances it applies that none neither occur as volatile substances nor migrated to sweat or saliva in such concentrations that absorptions should cause concern when letting children play with the products.

However, it should be noted that the consumer (child) may handle more than one slimy toy simultaneously or at intervals, thus increasing the exposure to one or more chemical substances correspondingly. Other sources of the same chemicals may also be present in the surroundings of the play activity. This may also contribute to the total exposure.

Sammenfatning og konklusioner

Som et led i Miljøstyrelsens kortlægning af kemiske stoffer i en række forbrugerprodukter ønskes viden om, hvilke stoffer der indgår i "slimet" legetøj. Projektet skal skabe et overblik over, hvilke kemiske stoffer gummiagtigt og slimet legetøj kan indeholde. Denne viden kan bruges i forbindelse med vejledning af producenter og importører og evt. anbefalinger til forbrugerne om at undgå visse stoffer i denne slags legetøj. Desuden vil projektet skabe et grundlag til at vurdere engangspartier af lignende legetøj, når det kommer på markedet

I Fase 1 er der foretaget en undersøgelse af, hvilke typer produkter der er på markedet i Danmark. Endvidere en undersøgelse af, hvilke materialer de er lavet af, eller som indgår i dem, samt i hvor høj grad disse henvender sig til børn og i hvilken aldersgruppe.

Det har ikke været muligt at få oplysninger fra producenterne angående indholdsstoffer i deres produkter. Detailhandelen har derimod leveret tilgængelige data ark. Den største importør af slimet legetøj i Danmark er K. E. Mathisen A/S (K. E. Leg).

I Fase 2 er der udført følgende kvalitative analyser:

- a. screeningsanalyse ved FTIR for fastlæggelse af, hvilke materialer legetøjet er fremstillet af samt evt. indhold af phthalater
- b. kvalitativ screeningsanalyse for grundstoffer ved ICP samt kvantitativ analyse for indhold af borsyre
- c. kvalitativ analyse af, hvilke stoffer der kan afgives til luften ved headspace analyse kombineret med GC-MS
- d. kvalitativ analyse af, hvilke stoffer der afgives til kunstigt spyt og sved ved GC-MS
- e. kvantitativ bestemmelse af phthalatindhold

Ved FTIR analyserne ses der to typer af "slim", dels en vandig type, hydrogeler og dels en type baseret på hydrocarboner med et lille indhold af styren. Ved de vandige slim er set indhold af glycerol og acrylat samt i nogle tilfælde materiale, vi ikke kunnet identificere med FTIR. Der er i en del tilfælde tilsat parabener. Ved slimprodukterne fremstillet af hydrocarboner kan vi generelt ikke se andre komponenter.

Den kvantitative bestemmelse af phthalater viste, at et af produkterne overskred grænseværdien på 0,05 vægt%.

Ved de indledende headspace analyser er alle de stoffer, der kunne tænkes at afgasse fra slimlegetøjet (på nær lette aldehyder) identificeret. Ved headspace analyserne på de 14 stykker slimlegetøj (hvoraf enkelte er analyseret på ydre del og indre væskedel, i alt 20 analyser) blev der fundet 61 identificerede enkeltstoffer og forskellige grupper af stoffer bestående af forskellige alifatiske og aromatiske kulbrinter, som er anført i grupper karakteriseret ved antal af kulstof-atomer, og endelig 6 forbindelser, der ikke kunne identificeres.

Ved migrationsanalyserne på de 14 stykker slimlegetøj (hvoraf enkelte er analyseret på ydre del og indre del, i alt 17 analyser) blev der fundet 22 identificerede enkeltstoffer og forskellige grupper af stoffer bestående af forskellige alifatiske og aromatiske kulbrinter, som er anført i grupper karakteriseret ved antal af kulstof-atomer, og endelig 6 forbindelser, der ikke kunne identificeres, ud over at de alle var fedtsyrer.

De kvalitative screeningsanalyser vha. ICP viser et væsentligt indhold af bor i 3 af prøverne (DK-01, TO-01 og TO-02). Bor kan være tilsat som konserveringsmiddel i form af borsyre eller som natriumborat, idet der samtidigt er målt indhold af natrium. Der kan dog også være andre natriumkilder, fx fra natriumbenzoat, som også er et konserveringsmiddel. Indhold af grundstoffer som aluminium, calcium, kalium, magnesium og zink, påvist i de fleste af prøverne må antages at komme fra fyld- eller hjælpestoffer anvendt i produktionen af produkterne. Endvidere må påvisning af spor af enkelte tungmetaller i flere af prøverne, antages at hidrøre fra forureninger fra fyldstoffer og evt. fra produktionsudstyr og produktionsforhold.

Fase 3 omhandler screening af eventuelle sundhedsskadelige effekter fra stoffer, som afgives fra slimet legetøj. Der er foretaget screening af de stoffer, der er identificeret ved headspace analyserne. Screeningen er baseret på litteraturoplysninger og har til formål at sikre, at de stoffer, som der fokuseres på ved de kvantitative analyser, er de mest relevante.

Baseret på de identificerede kemiske forbindelser er der foretaget en screening af eventuelle flygtige sundhedsskadelige stoffer. Screeningen har taget udgangspunkt i klassificeringer på Listen over farlige stoffer og umiddelbart tilgængelige oplysninger om effekter, der kunne være potentielt problematiske for forbrugeren, hvis afgivelsen af stofferne fra slimlegetøjet er for stor. Der blev fundet en del stoffer, der kan anses for problematiske stoffer, og en del der umiddelbart synes at kunne være problematiske.

Efter aftale med Miljøstyrelsen blev følgende stoffer udvalgt til nærmere vurdering:

Organiske stoffer:

alfa-Pinen
2-Butanon
2-Butoxyethanol
3-Caren
Cyclohexanon
Diethylglycoldibenzoat
d-Limonen
Etylbenzen
2-Hexanon
2-Phenoxyethanol
2-Phenylmethylenoktanal
1,2-Propandiol
2-Propenoic acid 2 methyl-methylester (methylmethacrylat)
N-Propylbenzamid + N-acetylbenzamid
Styren
Toluen
Xylen

Uorganiske stoffer

Bor
Nikkel

Fase 4 omhandler de kvantitative analyser og udarbejdelse af eksponerings-scenarier ved de afgivne stoffer. Da der ved screeningen blev fundet flest problematiske stoffer ved headspace, og da denne screening ikke umiddelbart er kvantitativ, har det været nødvendigt at bestemme mængden og afgivelsen af disse stoffer vha. beregninger foretaget på baggrund af screeningsanalysen. De problematiske stoffer, der er migreret til kunstigt spyt og sved, blev bestemt kvantitativt ved GC-MS. Derudover er der foretaget en kvantitativ ICP-MS analyse af nikkel.

Til sundhedsvurderingerne er der, da forbrugerne i dette tilfælde især er antaget at være børn, i de anvendte scenarier benyttet parametre for små børn. Den kraftige duft, der er observeret fra enkelte produkter, kan ikke udelukkes at kunne give akutte effekter som irritation af øjne, næse og hals. For enkelte stoffer kan der ved længere tids eksponering være tale om, at muligheden for kontaktallergi ikke kan udelukkes for særligt følsomme individer.

Den videnskabelige komite for kosmetiske produkter har identificeret 26 stoffer som erkendte kontaktallergener (SCCNFP 1999). Disse stoffer er senere blevet reguleret ved Direktiv 2003/15/EC (EC 2003). Af dem er der i undersøgelsen fundet 2 af de 26 stoffer: D-Limonen blev fundet i 3 produkter og hexylcinnamaldehyd i 1 produkt.

Af andre stoffer, der er potentielt allergene, er der derudover fundet 3-careen, *alfa*-pinen og nikkel. Alle 3 terpenener, D-limonen, 3-careen (7 produkter) og *alfa*-pinen (8 produkter), blev kun fundet i headspace analyserne. Om effekten fra kontaktallergener er den samme ved en eksponering via luftveje som ved hudkontakt, er lidt usikkert, men de er eller kan også genfindes i aerosoler, som potentielt også kan lægge sig på hudflader.

Bor blev fundet i 3 produkter, højst med 0,8% af produktet. Det er vurderet, at ved kontakt med væsken i et af produkterne, kunne en sundhedsmæssig risiko ikke udelukkes.

Nikkel blev fundet i 2 produkter, højst med 0,0003% af legetøjet. Det er derfor vurderet, at nikkelindholdet ikke umiddelbart udgør et problem, medmindre man er særlig følsom (nikkelallergi).

For de øvrige stoffer er det gældende, at ingen forekommer hverken som flygtige stoffer eller migreret til sved eller spyt i sådanne koncentrationer, at optagelser skulle give betæneligheder ved at lade børn lege med produkterne.

Det bør dog bemærkes, at forbrugeren (barnet) kan lege med mere end ét stykke slimet legetøj samtidig eller med mellemrum og derved øge sin eksponering for et eller flere kemiske stoffer tilsvarende. Der kan desuden være andre kilder til de samme kemiske stoffer i de omgivelser legen foregår. Det vil også bidrage til den totale eksponering.

Abbreviations

ADI	Acceptable Daily Intake. Estimated intake, which is assumed not to have any adverse effects. Can be acute or chronic. Is usually based on additives in food
bw	body weight
B value	The contribution value: Defined in Miljøstyrelsen 2002 as a company's total maximum permissible contribution to the air pollution outside the area of the company. If the B value is used, it is used directly, as it is calculated from NOAEL levels and with safety factor
CAS	Chemical Abstract Service
DL	Detection level
DVN	The Danish Institute for Informative Labeling
EC	Effect concentration
EC ₅₀	Median effect concentration, i.e. the concentration where effects are observed in 50% of the test animals
h	Hour(s)
LC ₅₀	Median lethal concentration, i.e. the concentration where 50% of the test animals are dead
LD ₅₀	Median lethal dose, i.e. the dose where 50% of the test animals are dead
LOAEL	Lowest Observed Adverse Effect Level
MAK	Maksimaler Arbeitsplatz Konzentration. Limit value for working environment defined by German working environment authorities
MOS	Margin of Safety, which is the distance between the estimated exposure and the concentration which is considered not to constitute a health risk (e.g. NOAEL)
Ni	Nickel
NOAEL	No Observed Adverse Effect Level
Repr.	Repro-toxic
RfC	Inhalation reference concentration. A concentration in air (e.g. µg/m ³) which is an estimate of a daily exposure by inhalation that is assumed to be without adverse effects by inhalation during a human lifetime. It is presumed that a threshold limit value exists for the toxic effect used to derive the value
RFD	Oral reference Dose, which is an estimate of a daily exposure by intake (e.g. µg/kg bw/day) that is assumed to be without adverse effects by intake during a human lifetime. It is presumed that a threshold limit value exists for the toxic effect used to derive the value
TCA	Tolerable Concentration in Air (inhalation exposure). Dutch value, which in principle is comparable with RfC
TDI	Tolerable daily intake. Estimated as intake that is assumed not to have any adverse effects. Can be acute or chronic. Is usually based on pollutants
TGD	Technical Guidance Document: EU guidance in risk assessment of chemicals
TLV	Threshold Limit Value relevant for the working environment. Typically a time weighted average value over 8 hours is used
TWA	Time Weighted Average

1 Introduction

1.1 Introduction

In the shops, there are many toys, which are rubbery and slimy, e.g. “slimy balls” and “sticking animals”. The chemical composition of these products is mostly unknown, and a lot of these types of toys are sold as unique batches, which are only on the market for a short period. The toys are very popular, not very expensive and are consequently bought by the children themselves. The CE marking of the toys does not necessarily take into account the content and amount of possible harmful substances.

Today, it is prohibited to produce, import or sell toys and some infants' articles to children at the age of 0-3 years, if the products contain more than 0.05 weight% phthalates. A great deal of slimy toys is produced of or containing plasticised PVC. A frequently used plasticiser for especially PVC is phthalates. Consequently, in phase 2 of the examination screening for phthalates, among other things, has been carried out.

In certain cases, slimy toys may be designed as a cosmetic product, and in these cases, they are included in the EU Cosmetics Directive (Directive 76/767/EØF). Cosmetic products must not be of harm to the consumers; however, it is the responsibility of the industry to make sure that these products do not constitute any health risk to the consumers.

In the Danish Environmental Protection Agency's Statutory Order, it says: *“Everyone who sells cosmetics is responsible that both container and outer packing, if any, is provided with the following information”:*

- *Company name and address*
- *Weight or volume*
- *Durability date*
- *Safety directions*
- *The number of the fabrication series*
- *What is the use of the product*
- *The declaration of contents must inform of all ingredients, named by weight, at the time they are added to the product*

Two cosmetic products have been included in this examination. The products fulfil the demands for declaration of contents in the Cosmetics Directive.

1.2 Purpose

The purpose of the project is to give a survey of the chemical substances that might be contained in rubbery and slimy toys and evaluate the exposure of chemical substances from the toys. It has been examined which chemical substances are used in the toys, and - in case the substances give cause to concern - whether these are released during use.

1.3 Procedure

Phase 1 concerns a market analysis of slimy toys, including a survey of which types are on the market. Survey has been carried out through literature, data sheets and trade contacts of the chemical substances used in such products.

This information has been procured from four sources:

- Search via the Internet
- Purchase of slimy toys
- Through contact to suppliers and producers, whose identity appeared from the packaging
- Through contact to a range of relevant shops and organisations

Phase 2 concerns qualitative analyses of selected slimy toys.

These analyses comprise screening by means of FTIR for identification of polymer types, phthalates and - to some extent - inorganic dyes. This analysis has been carried out partly on the product and partly on an extract in order to get a standard for which substances the toys may contain.

Furthermore, a qualitative screening for content of heavy metals has been carried out on the toys by means of ICP-MS.

Previous examination of "real" slime products showed the presence of boric acid; consequently, a quantitative determination of boron through inductive-coupled-plasma atomic emission spectrometry (ICP-AES) has been included in the project.

A preliminary screening analysis of more types of slimy toys showed the presence of volatile solvents. Therefore, the project has included an analysis showing which volatile compounds might be released to the air when handling the toys. The analysis was carried out by headspace technique combined with GC-MS.

In order to determine which substances are released by contact to skin or saliva, migration analyses have been carried out in artificial sweat solution produced according to ISO 105-E04 and to artificial saliva produced according to Amtliche Sammlung von Untersuchungsverfahren nach § 35 LMBG No. 82.10 1, the saliva recipe has been copied from DIN std, no. 53 160. The extraction was carried out for 24 hours at 40°C according to DS-EN 1186-3. The substances, which are being released to saliva and/or sweat, have been analysed and identified by means of GC-MS.

The following qualitative analyses have been carried out:

- Screening for polymer types, inorganic dyes and phthalates by FTIR
- Identification of inorganic dyes and heavy metals by ICP-screening
- Quantitative analysis of boric acid by ICP-AES
- Quantitative determination of phthalates
- Screening of degassing of volatile substances by means of headspace and GC-MS
- Screening of release of organic compounds at migration to artificial sweat and saliva by GC-MS
- Identification of up to twenty organic compounds by comparison with NIST library spectra

- Determination of the proportional composition of the identified substances

Phase 3 deals with screening for possible harmful effects from substances, which are being released from slimy toys.

A screening has been made of the substances, which have been identified by the qualitative analyses. The screening is based on a literature survey in order to secure that the substances focused on at the quantitative analyses are the most relevant.

After the qualitative analyses have been carried out, the results are evaluated. Data regarding the individual substances in the form of NOAEL, LOAEL or other relevant data are used, as far as they are available. As an alternative to the substances, whose data are not available, QSAR-data have been used. A comparison has been made with EU's classification criteria.

Phase 4 deals with quantitative analyses and exposure scenarios. The following quantitative analyses have been carried out:

- Quantification of selected organic compounds in artificial saliva and sweat by GC-MS
- Determination of the amount and release to the air of selected organic substances by means of calculations made on the basis of the headspace screening analysis
- Quantification of selected inorganic dyes and metals by ICP-analysis

Exposure scenarios have been made based on the expected exposures of the consumers of "slimy" toys. The exposure pathway was via the skin (hands and body) or by oral intake in the cases where depositions or residues from "slimy" toys on hands/fingers are subsequently put into the mouth. A *worst-case* situation would e.g. be, if the toy is put into the mouth and perhaps comes to pieces, and "slime" and content in liquid state are taken in orally. The third exposure pathway is possible via inhalation, since experience shows that some slimy toys release smell/scent.

The principles of the evaluations are based on EU's revised Technical Guidance Document (TGD) for risk assessments. In consideration for realistic *worst case*, the exposed consumers will be children with a body weight of 10 kg.

2 Market analysis

2.1 Introduction

It has been examined which types of products are on the market in Denmark. Furthermore, it has been examined which materials they are made of and which substances they contain, and to what extent they appeal to children and at which age group.

Going through the market for slimy toys has made it clear that they can advantageously be split up into two types of toys, *direct and indirect* slimy toys. The direct slimy toys are toys, which only consist of one component, while the indirect toys are toys, which consist of more components, of which the slimy toys are often found inside the toys. Usually, the indirect toys do not constitute the direct exposure. However, if the toy breaks, the consumer will be exposed to the slimy substance.

2.2 Statistics

According to Danmarks Statistik, the yearly consumption of articles from the category "Games, toys and hobby articles" constitute approx. 4 billions DKr. If one looks isolated at families with two adults and two children the yearly consumption constitutes approx. 1.7 billions DKr. corresponding to 3,567 DKr. per family. These figures have been slightly falling compared to year 2000. However, compared to year 1980 it is a doubling. The importers estimate that the category "slimy" toys constitute less than 1% of the total consumption.

2.3 Trade organisation

Contact has been made to the trade organisation Legetøjsbranchens Fællesråd (LF)

in order to gather information regarding the market for slimy toys. LF act as consultants to their members and make sure that they are upgraded with regard to new rules, laws, directives, news letters and warnings. In cases of doubt LF only interfere on product level. The trade organisation does not have their own code of practice, but they see to that the members comply with the legislation. Laws and rules are typically communicated to the trade organisation through the Danish Environmental Protection Agency and EuroCommerce.

Another trade organisation is the Joint Council for Creative and Hobby Materials (FFFH). The joint council is a confederation of producers, importers and dealers of hobby articles in Denmark. Today, the "joint council" consists of 25 companies evenly divided among producers, importers and dealers. They do, however, inform that the category slimy toys, as far as they know, are not included in their set of requirements for chemical toys.

2.4 The producers

The most part of slimy toys is produced in the East, either China or Taiwan. It has not been possible to procure information from these producers regarding the chemical composition of their products, usually referring to their fear for copying of these products.

2.5 The retail trade

The biggest importer of slimy toys in Denmark is K. E. Mathisen A/S (K. E. Leg), who informs that at present they have approx. 10 different products belonging to the category "slimy toys", and two new are on the way. K.E. Mathiesen has a quality policy in this field, and the chemical composition of the products is being tested on a regular basis.

Another big importer is Top-Toy, which owns the BR-shops and the Toy's"R"US centres. Top-Toy also has a quality policy, and their products are being examined by a toxicological consultant, if the producer would not inform of the constituents of the product.

Slimy toys are considered a fashion phenomenon, and this type of sale is most often only large for a very limited period.

Slimy toys are most frequently sold as unique batches, which are not at the market for a long time, and consequently they should appeal to the so-called 10 DKr.'s markets. On application to this type of shops, they all informed that they do not sell slimy toys. They often see it on fairs, but they do not think it appeals to their customers.

Today, there are two big chains of groceries at the Danish market: Coop Danmark (among others the chains of shops Kvickly, Irma, Fakta, SuperBrugsen, Dagli'Brugsen and LokalBrugsen) and Dansk Supermarkeds Gruppe (SG) (among others the chains of shops Bilka, Føtex, Netto and A-Z).

Both chains of groceries check that the toys are delivered with CE-mark. In cases of perfumery or make-up, the product complies with the Cosmetics- as well as the Toys Directive.

Occasionally, the net shops sell slimy toys, too. The products are most often imported by K.E. Leg and delivered with certification and marked "Not suitable for children under 3 years of age".

2.6 Phthalates

Many slimy toys are manufactured from or containing plasticised plastic. A frequently used plasticiser for particularly PVC is phthalates.

As phthalates are suspected to be an endocrine disruptor, and some are classified as rep 2+3, The Danish Ministry of Environment and Energy have issued Statutory Order no. 151 of 15 March 1999 banning phthalates in toys for children at the age of 0-3 years and in some articles for small children etc. Everyone who produces, imports or sells one or more of the above-mentioned products, are responsible that the rule is obeyed according to the regulation.

According to a report of 2003 from the Danish Environmental Protection Agency *Status on phthalates*, Danish Trade & Service have prepared a plan for voluntary phasing out of phthalates in toys for older children.

Consequently, the examination has included screening for phthalates, among other things.

Description of products:

Identification No.	Description
DK-01	Approx. 10 cm multicoloured rubbery saurian
DK-02	Approx. 4 cm blue and soft octopus
DK-03	Approx. 4 cm lilac and soft fish
BO-01	Pink rubber hose. Approx. 20 cm long
K-01	Yellow, transparent ball with insect inside
K-02	Lilac spiked pig space hopper with light-emitting diode, approx. 10 cm in diameter
K-03	Pink rubbery hand
BR-01	Pink transparent liquid-filled softball with insect inside. Approx. 5 cm in diameter. Made in China
F-01	Transparent liquid-filled egg with "yolk". Approx. 5 cm long
TO-01	Green slime with insects inside
TO-02	Hard plastic container with green slime inside
TO-03	Blue gel for hair, skin and lips
G-01	Multicoloured octopus approx. 20 cm long with tiny balls inside
TI-01	Green 10 cm liquid-filled stick. Made in China
B-01	Red tomato. Approx. 5 cm in diameter
B-02	Green slime with figure inside
R-01	Green liquid-filled ball with spikes
A-01	Transparent liquid-filled disc with stars inside
EX-01	Green slime
EX-02	Slime with cola scent

3 Analysis results

3.1 FTIR screening

3.1.1 Equipment and methods

For the FTIR analyses, a Nicolet Magna 550 FTIR equipment with installed optical bench has been used. The bench gathers the IR pencil of rays to approx. 2 mm in diameter, supplied with FTIR microscope with diamant cell.

The specimens have been cut out from the examined samples by means of a scalpel. In the case of jelly materials, the diamond cell has been used, as it presses all the materials to a thin film of approx. 10 μm . At the measurements, the pencil of rays is approx. 100 μm . In the case of thermoplastic materials, the sample preparation has consisted of hot-pressing of approx. 2 to 5 mg of material for film with a thickness of 10 to 20 μm . This film has been analysed by screening.

In the case of extraction, methylene chloride has been used. After drying, the evaporation residue has been ground with potassium bromide and finally pressing of a tablet, on which the analysis has been done. A sample amount of approx. 1 mg is used.

Interpretation of the FTIR spectra has been done partly based on experience and partly according to our reference library, among others "Hummel Polymer and Additives" and through external search on "FTIRsearch.com".

In addition to the actual material analyses, we have looked for various additives.

In connection with additives, which might be added in relatively small amounts, only in the cases where over approx. 0.1 weight% is added and that the additive has strong absorption bands outside the absorptions from the polymer, it will be detectable.

3.1.2 Results from the FTIR screening

The FTIR screening was carried out as follows: on all purchased "slimy toys" FTIR analysis has been carried out on all types of material detected on each product. Results are stated in Table 3.1 and in Enclosure B.

Table 3.1 Results from the FTIR screening

No.	Description	Exterior product	Content (most frequently liquid)	Accessories
DK-01	Multicoloured rubbery saurian	Hydrocarbon with an aromatic content	Hydro gel, primarily water and glycerol	
DK-02	Blue and soft octopus	Hydrocarbon with a small aromatic content		
DK-03	Lilac and soft fish	Hydrocarbon with a small aromatic content		
BO-01	Pink rubber hose	Hydrocarbon with a small aromatic content		
K-01	Yellow, transparent ball with insect inside	Hydrocarbon with a small aromatic content	Yellow liquid cannot be unambiguously identified by FTIR	Fish is made of SBS (styrene-butadiene-styrene) elastomer
K-02	Lilac spiked pig space hopper with light-emitting diode	Hydrocarbon with a small aromatic content		Transparent ball is made of PS (polystyrene)
BR-01	Pink transparent liquid-filled softball with insect inside	Hydrocarbon with a small aromatic content	Liquid cannot be unambiguously identified by FTIR	Spiders are made of an SBS (styrene-butadiene-styrene) elastomer
F-01	Transparent liquid-filled egg with "yolk"	Hydrocarbon with a small aromatic content	The liquid might be water with preservative agent (Na benzoic acid salt)	Yellow ball is made of hydrocarbon with a small aromatic content
TO-01	Green slime with insects inside	Hydro gel with a content of "parabene"		Animals are made of LDPE, low density polyethylene
TO-02	Green slime	Hydro gel with a content of "parabene"		
TO-03	Blue gel for hair, skin and lips	Water-glycerol gel		
G-01	Multicoloured octopus with tiny balls inside	Hydrocarbon with a small aromatic content		Small balls are made of PS (polystyrene)
K-03	Pink rubbery hand	Hydrocarbon with a small aromatic content		
B-01	Red tomato	Hydrocarbon with a small aromatic content	The liquid is aqueous and seems to be thickened with an acrylic polymer	
B-02	Green slime with figure inside	Hydro gel with a content of "parabene"		Animals are made of phthalate plasticised PVC with chalk
TI-01	Green liquid-filled stick	Hydrocarbon with a small aromatic content	The liquid is aqueous with a small content of a component, which cannot be unambiguously identified by FTIR	
R-01	Green liquid-filled ball with spikes	Hydrocarbon with a small aromatic content	The liquid is aqueous with a small content of a component, which cannot be unambiguously identified by FTIR	
A-01	Transparent liquid-filled disc with stars inside	Hydrocarbon with a small aromatic content	The liquid contains water, but also a considerable amount of a component, which might be a modified glycerol	

3.1.3 Summary of the FTIR screening

At the analyses two types of "slime" are detected, partly an aqueous type, hydro gels, and partly a type based on hydrocarbons with a small content of styrene.

At the aqueous slime, content of glycerol and acrylate has been detected, and - in some cases - material which we have not been able to identify by FTIR. In a number of cases, parabenes have been added. Generally, in case of the slime products made of hydrocarbons, we cannot detect other components.

3.2 Quantitative determination of phthalate by GC-MS

3.2.1 Analysis method

Analyses programme for phthalates

Determination of content of selected phthalates

Component	CAS no.
Dimethyl phthalate (DMP)	131-11-3
Diethyl phthalate (DEP)	84-66-2
Dibutyl phthalate (DBP)	84-74-2
Butyl benzyl phthalate (BBP)	85-68-7
Di-(2-ethylhexyl)-phthalate (DEHP)	117-81-7
Di-n-octyl phthalate (DNOP)	117-84-0
Di-iso-nonyl phthalate (DINP)	28553-12-0
Di-isodecyl phthalate (DIDP)	26761-40-0

A weighed out sample amount was extracted with dichloromethane added deuterium-marked internal standards in the form of DEHPd₄ and BBP-d₄ by ultrasound for 2 hours. The extract was analysed by gas chromatography combined with mass spectrometer detector (GC-MS) in scan mode.

The components were identified on the basis of the actual retention times and mass spectra.

Calibration curves were made for each of the selected phthalates.

Recommended limits of detection (LOD):

Single components: 20 µg/g (0.002% m/m)

DINP and DIDP: 50 µg/g (0.005 % m/m)

3.2.2 Analysis results for phthalates

Sample no.	Lab. no.	Component	µg/g	% (m/m)
DK-01	30396-1	Di-iso-nonyl phthalate (DINP)	1800	0.18
F-01 (white)	30396-8	Diethyl hexyl phthalate (DEHP)	20	0.0020
F-01 (yellow)	30396-8	Diethyl hexyl phthalate (DEHP)	21	0.0021
R-01	30396-17	Diethyl hexyl phthalate (DEHP)	17	0.0017
A-01	30396-18	Diethyl hexyl phthalate (DEHP)	27	0.0027
EX-02	30396-20	Diethyl hexyl phthalate (DEHP)	81	0.0081

Sample no.	Lab. no.	Comments
DK-02	30396-2	No content of phthalates above the mentioned limits of detection was detected
DK-03	30396-3	
K-01	30396-5	
BR-01	30396-7	
TO-03, gel	30396-11	
G-01	30396-12	
K-03	30396-13	
EX-01	30396-19	

3.2.3 Summary

The quantitative determination of phthalates shows that one of the products exceeded the threshold limit value of 0.05 weight%.

3.3 Headspace analysis results from screening

3.3.1 Analysis method

Qualitative analysis of the degassing components by headspace analysis, for the purpose of identification.

After the receipt, the samples were put in an airproof rilsan bag. Glass tubes with a fixed adsorbent (Tenax tube) were placed next to them in the rilsan bag. The Tenax tubes were subsequently analysed by thermal desorption combined with gas chromatography with mass spectrometer detector (ATD/GC-MS).

A Perkin-Elmer TurboMass Spectrometer with Perkin-Elmer ATD 400 was used.

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

3.3.2 Results from the headspace analysis

Results are stated in Table 3.2 and Enclosure C.

For each piece of slimy toy the identified components in the degassing have been listed, and the relative amount of each component is stated as a percentage part of the total degassing from the sample (total VOC content).

The stated percentage share of total VOC-content has been calculated on the assumption that all detected components have the same response for the same amount.

Table 3.2 Detected substances at headspace analysis (% m/m)

Component	CAS no	DK-01, exterior	DK-02, exterior	DK-03, exterior	K-01, exterior	K-01, liquid	BR-01, exterior	BR-01, liquid	F-01, exterior	TO-01, exterior	TO-02, exterior	TO-03, liquid	TO-03, gel	G-01, exterior	K-03, exterior	TI-01, exterior	TI-01, liquid	R-01, exterior	R-01, liquid	A-01, exterior	A-01, exterior	
		1	2	3	5	5B	7	7 B	8	9	10	11	11	12	13	16	16 B	17	17 B	18	18	
Benzaldehyde	100-52-7													1,3								
Butanal	123-72-8								0,2	0,6	0,7			2,8								
Butanol	71-36-3								0,2				2,6	1		3						
Butandiol + alcohol, e.g. ethanol, 2-propanol	110-63-4+													35	55	4,3						
Dimethyl-1,4-dioxan (C6 H12 O2) etc.	e.g. 10138-17-7																	0,9			1,7	
2-Butanon	78-93-3															2,3	9					
2-Butoxy-ethanol	111-76-2		0,6	0,1					1,8				0,7	0,6				0,8	66			
n-Butyl ether	142-96-1										1,5					2,2	2					
3-Carene	13466-78-9		1,4	0,4					0,1					0,3		0,6						
3-Carene	80-56-8						0,2															
Cyclohexanol	108-93-0								0,3													
Cyclohexanone	108-94-1	0,2	2,8	0,4	2,9	24			0,4	63	30	2,3	3,3							6		
2-Cyclohexen-1-one	930-68-7									0,1												
d-Limonene	5989-27-5		0,9	0,2										0,4	0,4							
Decanal	112-31-2															0,4	1					
2-Decanon	693-54-9															0,4						
Dichloromethane	75-09-2																					3
1,1-Dimethoxypropan	4744-10-9																					5
N,N-Dimethyl formamide	68-12-2										0,4											
Dodecanal	112-54-9																	0,8				
Ethanol	64-17-5																		0,2	27		
Ethyl acetate	141-78-6														1,9							
Ethylbenzene	100-41-4	1,3	11	2,2	13	6	79	4,2		10	16	0,7	39	16	14	9	0,8			45	100	
2-Ethyl butanal	97-96-1							0,2	2,4													
2-Ethyl-1-hexanol	104-76-7		0,6	0,2					3,6	7,7												
Eucalyptol (C10H18O)	470-82-6				0,2																	
Heptanal	111-71-7															1,3	3					
Heptanol	53535-33-4																3					
2-Heptanon	110-43-0															3,3	10					
3-Heptanon	106-35-4																1					
2-Heptenal	18829-55-5								0,5													
Hexanal	66-25-1	<0,1	0,6	0,1			0,3		2,6	1,5				0,4	1,8	0,7						
2-Hexanon	591-78-6															2,7	8					
1-Methoxy-2-propanol	107-98-2								1				0,4									
3-Methylbutanal	590-86-3								0,3													
2-Methyl-1-propanol	78-83-1										6,9	1,3										
Nonanal	124-19-6																					
Nonanol	143-08-8															1,1	1					
Octane	111-65-9										1,1											
Octanal	124-13-0									1,2	0,7											
2-Octanon	111-13-7															2,1	5					
2-Octen-1-ol	18409-17-1									0,6						2,4	6					
2-Pentanon	107-87-9															1,1	9					
2-Phenoxy ethanol	122-99-6												3,9									
alpha-Pinene	80-56-8	0,1	3,4	0,7	3,8			0,3			1,1	0,4	0,7			1,2						
Beta-Pinene	127-91-3		0,6	0,1																		
1-Propanol	71-23-8									1,1			0,7									
2-Propanol	67-63-0										20											
1,2-Propanediol	4254-15-3						7						66									
2-Propenoic acid 2 methyl-methyl ester (Methyl methacrylate)	80-62-6												7,2									
1-Propenyl benzene	873-66-5																					x (2)
Styrene	100-42-5									5,1			2									
Tetrahydrofuran	109-99-9													3,4	0,4	1						
Toluene	108-88-3	4,2	18	5,9	66	70	7,1	8	6	2,3	17	30	6,9	10	7,2	10	10	1			2,1	
3,3,5-Trimethyl cyclohexene-1-ol	78-59-1											5,7	2,3			1,2	3					
Undecanal	112-44-7															0,9						
m-, p-Xylene	108-38-3/106-42-3	incl. in (1,3)	incl. in (11)	incl. in (2,2)	incl. in 13	incl. in 6	incl. in 74	incl. in 79	incl. in 4,2	0,5	incl. in 10	incl. in 1,4	1	incl. in 39	incl. in 16	incl. in 14	incl. in 9	incl. in 0,8		incl. in 45	incl. in 100	
o-Xylene	95-47-6	incl. in (1,3)	incl. in (11)	incl. in (2,2)	incl. in 13	incl. in 6	incl. in 74	incl. in 79	incl. in 4,2	0,5	incl. in 10	incl. in 1,4	1	incl. in 39	incl. in 16	incl. in 14	incl. in 9	incl. in 0,8		incl. in 45	incl. in 100	
Aliphatic hydrocarbons etc.			60																			
C7H14 and C7H16 aliphatic hydrocarbons					1,8																	
C7 - C9 aliphatic hydrocarbons					8,1											29						
C8H16 aliphatic hydrocarbons							1,3		0,4													
C9H12 aromatic hydrocarbons							5,9	3	0,6		7,7					4,5					3,2	
C9H12 + C10H14 aromatic hydrocarbons					3,3																	
C9H20 aliphatic hydrocarbons										5,3												
C10 - C16 aliphatic hydrocarbons			60																		46	
C10-C14 aliphatic hydrocarbons							10,8	3	85	16		16			15			96				
C10H14-aromatic hydrocarbons		0,5							0,6		15			3,8								
C10H16					1																	
C10H16O	e.g. 5948-04-9								0,2													

Component	CAS no.	DK-01, exterior	DK-02, exterior	DK-03, exterior	K-01, exterior	K-01, liquid	BR-01, exterior	BR-01, liquid	F-01, exterior	TO-01, exterior	TO-02, exterior	TO-03, lip-gloss	TO-03, gel	G-01, exterior	K-03, exterior	TI-01, exterior	TI-01, liquid	R-01, exterior	R-01, liquid	A-01, exterior	A-01, exterior	
		1	2	3	5	5B	7	7 B	8	9	10	11	11	12	13	16	16 B	17	17 B	18	18	
C11-C14 aliphatic hydrocarbons + decahydro-naphthalenes+ methyl decahydro-naphthalenes + cimethyl decahydro-naphthalenes	94			90																		
C11 H22																5	7					

3.3.3 Summary of the headspace analyses

At the headspace analyses of 14 slimy toys (of which a few were analysed on exterior part and interior liquid part, totally 20 analyses), we found 61 identified single substances and various groups of substances consisting of various aliphatic and aromatic hydrocarbons, which are stated in groups characterised by the number of carbon-atoms, and finally 6 compounds, which could not be identified.

The majority (80%) of the examined products are main components in the degassing aliphatic hydrocarbons, primarily C10-C14 and aromatic hydrocarbons such as toluene, xylenes and trimethyl benzenes. Two of these products furthermore contain more volatile aliphatic hydrocarbons such as C7-C8. In two of the products (TO-01 and TO-02) cyclohexanone constitutes 63% and 30% respectively of the total degassing. Other samples are characterised by the content of alcohols. It should be noticed that a few of the products contain traces of D-limonene (allergenic odorant).

3.4 GC-MS Analysis results from screening

3.4.1 Analysis method

Screening of extracts from artificial saliva and sweat by GC-MS.

Sample preparation

1-2 g sample - accurately weighed out - was in a Red Cap bottle added 20 ml artificial saliva solution or artificial sweat solution and extracted in an end-over-end shaker for 4 hours in heating chamber at 40°C. The extract was moved to a 20 ml calibrated flask, filled until 20 ml with saliva- or sweat solution and added deuterium-marked internal standards in the form of benzene, toluene, p-xylene and naphthalene, together with 1 ml pentane. The calibrated flasks were shaken for 10 min, after which the pentane phase was isolated.

Analysis

The pentane extracts were analysed by GC-MS in scan mode.

Apparatus

An HP gas chromatograph 5890 with an HP mass spectrometer 5972 was used.

3.4.2 Results from the GC-MS screening analysis

Results are stated in Table 3.3 and in Enclosure D.

3.4.3 Summary of the GC-MS screening analysis

At the migration analyses of the 14 slimy toys (of which a few were analysed on exterior part and interior part, totally 17 analyses) we found 22 identified single substances and various groups of substances consisting of various aliphatic and aromatic hydrocarbons, which are stated in groups characterised by the number of carbon-atoms, and finally a group of 6 compounds, which could not be identified, but they were all fatty acids.

Table 3.3 Detected substances at sweat extraction analysis ($\mu\text{g/g} = \text{mg/kg}$)

Component	CAS no.	DK-01, exte-rior	DK-02, exte-rior	DK-03, exte-rior	K-01, exte-rior	K-01, gel	BR-01, exte-rior	F-01, exte-rior	F-01, inte-rior	TO-01, exte-rior	TO-02, exte-rior	TO-03, lip-gloss	TO-03, gel	G-01, exte-rior	K-03, exte-rior	TI-01, exte-rior	R-01, exte-rior	A-01, exte-rior
		1	2	3	5	5 B	7	8	8 C	9	10	11	11	12	13	16	17	18
Benzoic acid-butylester	136-60-7									10	0.7							
Benzoic acid-phenylester	93-99-2									0.3	1.1							
Benzoic acid-propylester	2315-68-6									12	0.8		1.5					
Butyl parabene	94-26-8												0.9					
Cyclohexanone	108-94-1			0.2						57	0.6				0.1			
Diethylglycol dibenzoate etc.	e.g. 120-55-8									127+99	25+4.1							
Ethanol-2-(butoxy ethoxy)-acetate	112-15-2	0.2																
Ethyl parabene	120-47-8												2.2					
Methyl dihydrojasmonat	24851-98-7												0.2					
5-Methyl-2-(1-methylethyl-cyclohexanol)	23283-97-8																0.1	
Methyl parabene	99-76-3									3.9	2.2		1.6					
Naphthalene	91-20-3	0.02																
2-Phenoxy ethanol	122-99-6							0.4	0.5				145				1.8	
2-Phenylmethylen octanal (=hexylcinnam aldehyde)	101-86-0												0.3					
1,2-Propandion-1-phenyl-2-oxim	119-51-7									5.8	0.2							
N-Propyl benzamide + N-acetyl benzamide	10546-70-0, 1575-95-7									2.4	0.7							
Propyl parabene	94-13-3									5.3	1.9		0.6					
Toluene	108-88-3	0.25	0.10	0.15	1.8			0.16	0.23					0.05	<0.02	<0.05		<0.05
o-, m-, p-Xylene	95-47-5, 108-38-3, 106-42-3						2.3							0.1				0.90
Ethylbenzene	100-41-4						incl. in 2.3							incl. in 0.1				incl. in 0.90
3,3,5-Trimethyl cyclohexen-1-one	78-59-1							0.06	0.05				0.3					
Aliphatic hydro carbon >C14H30						0.1										2.0		

Table 3.3 Detected substances at the saliva extraction analysis ($\mu\text{g/g} = \text{mg/kg}$)

Component	CAS no.	DK-01, exterior 1	DK-02, exterior 2	DK-03, exterior 3	K-01, exterior 5	K-01, gel 5 B	BR-01, exterior 7	F-01, exterior 8	F-01, interior 8 C	TO-01, exterior 9	TO-02, exterior 10	TO-03, lip-gloss 11	TO-03, gel 11	G-01, exterior 12	K-03, exterior 13	TI-01, exterior 16	R-01, exterior 17	A-01, exterior 18
Benzoic acid-butylester	136-60-7									5.1	0.4							
Benzoic acid-phenylester	93-99-2									0.2	0.2							
Benzoic acid-propylester	2315-68-6									6.9	0.5							
Butyl parabene	94-26-8																	
Cyclohexanone	108-94-1			0.2						14	0.2			<0.05				
Diethylglycol dibenzoate etc.	e.g. 120-55-8									115+114	16+ 3.7							
Ethanol-2-(butoxy ethoxy)-acetate	112-15-2	0.2																
Ethyl parabene	120-47-8																	
Methyl dihydrojasmonat	24851-98-7																	
5-Methyl-2-(1-methylethyl-cyclohexanol)	23283-97-8																0.2	
Methyl parabene	99-76-3									1.8	0.6							
Naphthalene	91-20-3	0.02																
2-Phenoxy ethanol	122-99-6							0.5	0.3								1.6	
2-Phenylmethylen octanal (=hexylcinnamaldehyd)	101-86-0																	
1,2-Propandion-1-phenyl-2-oxim	119-51-7									3.0	0.8							
N-Propyl benzamide + N-acetyl benzamide	10546-70-0, 1575-95-7									36	1.6							
Propyl parabene	94-13-3									3.3	1.2	23						
Toluene	108-88-3	0.31	0.09	0.26	1.9		0.17	0.21	0.29					<0.05	<0.02	<0.05		<0.05
o-, m-, p-Xylene	95-47-5, 108-38-3, 106-42-3						2.4							0.08				0.86
Ethylbenzene	100-41-4						incl. in 2.4							incl. in 0.08				incl. in 0.86
3,3,5-Trimethyl cyclohexen-1-one	78-59-1							0.05	0.03			1.4				0.7		
Aliphatic hydro carbon >C14						0.1									3.0			
Fatty acids												31.4						

3.5 ICP analysis results from screening

3.5.1 Analysis method

Sample preparation

Approx. 500 mg sample - accurately weighed out - was prepared by means of microwave induced heating in a PFA autoclave with 20 ml 7 M HNO₃ (sub boiling quality). The resulting solution was filtered and consequently diluted to 50 ml with demineralised water (Milli-Q Plus).

Repeat preparation was carried out.

Blank tests were correspondingly prepared.

Standard

Standards and control tests were made based on a Merck multi-element standard solution VI by diluting with 2.8 M HNO₃.

The internal standard mixture was made based on Perkin-Elmer single-element standards of Ge, Rh and Re by diluting with 0.14 M HNO₃.

Apparatus

A Perkin-Elmer Sciex Elan 6100 DRC Plus ICP mass spectrometer with FIAS 400 flow injection system and autosampler AS 93 Plus was used.

Screening analysis

The prepared samples, added "on-line" germanium, rhodium and rhenium as internal standards, were screened for the content of trace elements through inductive-coupled-plasma mass spectrometry (ICP-MS) using the expert programme TotalQuantII, which - on the basis of an instrument response curve for the elemental substances from mass 6 (Li) to mass 238 (U) - quantifies the content. The instrument response curve was updated by means of a multi-element standard containing Li, Be, B, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Mo, Ag, Cd, Te, Ba, Tl, Pb, Bi and U, which covers all of the mass area. Elemental substances like Br, C, Cl, F, N, O, P, S and Si are not quantified because of interferences.

3.5.2 Results from the ICP-MS screening

Results are stated in Enclosure E.

3.5.3 Summary of the ICP-MS screening

The screening analyses show a considerable content of boron in 3 of the samples (DK-01, TO-01 and TO-02). Boron might be added as a preservative in the form of boric acid or sodium borate, as a sodium content has also been measured. However, there might be other sodium sources, e.g. sodium benzoate, which is also a preservative. Content of elements such as aluminium, calcium, potassium, magnesium and zinc, detected in most of the samples, presumably derives from fillers or auxiliary constituents used in the production of the products. Furthermore, the detection of traces from a few heavy metals in some of the samples is supposed to derive from contaminations from fillers and possibly from production equipment and production conditions.

Nickel is classified: Carc3;R40 R43. Most nickel compounds are classified because of the allergenic property with R43, May cause sensitization by skin contact.

A number of nickel compounds are either known to have a cancer-causing effect or suspected to have a cancer-causing effect, like e.g. nickel carbonate or nickel sulphate.

Furthermore, most nickel compounds are classified as harmful to the environment with R50/53, very toxic to aquatic organisms and not degradable. Nickel was detected in the screening in 2 products (TO-01 and A-01), but only in small amounts.

3.6 Determination of Boron by ICP-AES

3.6.1 Analysis method

Analysis

The solutions prepared under point 3.5.1 were analysed quantitatively for the content of boron through inductive-coupled-plasma atomic emission spectrometry (ICP-AES).

Standards

Boron standards were made from a Perkin-Elmer stock solution through dilution with 2.8 M HNO₃.

Apparatus

A Perkin-Elmer Optima 3300 DV inductive-coupled-plasma atomic emission spectrometry with autosampler AS-90 plus was used.

3.6.2 Results from the determination of boron by ICP-AES

Results are stated in Enclosure F and Table 3.4 below.

Table 3.4 Result of quantitative analysis of boron

Lab mark	Sample mark	Part sample	B µg/g	Total content % (m/m)	% RSD	DL µg/g
30396-1	DK-01	Exterior	-	-		1
30396-1	DK-01	Liquid	8400	0.84	1.2	1
30396-9	TO-01	Exterior	653	0.07	0.94	1
30396-10	TO-02	Exterior	1170	0.12	4.7	1

%RSD indicates the percentage relative standard deviation based on repeat determination

"-" indicates less than the limit of detection listed in the rightmost column

DL indicates the limit of detection

3.6.3 Summary of the determination of boron by ICP-AES

The quantitative determination of boron by ICP-AES confirms results achieved by the ICP-MS screening of all samples. The higher content (25-45%) in the samples DK-01, TO-01 and TO-02 determined by ICP-AES compared with the ICP-MS screening must be seen based on the fact that the concentrations in the measuring solutions by ICP-MS screening of these samples are far above the calibration area.

4 Screening for possible harmful effects

4.1 Screening by "headspace"

For the screening of possible harmful substances the purchased products were analysed by headspace, i.e. evaporation from slimy toys (cf. section of methods). This means that the detected amounts of released substances (μg per g slimy toys) calculated from total VOC must be handled with some caution. The numerical values, however, give a certain impression of relative amounts (cf. analysis method description and total result in Enclosure C).

The preliminary qualitative screening was performed as a headspace analysis. The toys were placed in a plastic bag together with adsorbent at room temperature (approx. 20°C) for 24 hours to collect all potential volatile compounds. The gas samples were analysed by capillary column gas-chromatography combined with mass spectrometer detection (GC-MS). The results show which organic compounds that evaporate from the slimy toys and their mutual relative proportion. A summary is shown in Table 3.2.

At the preliminary headspace analyses, all the substances, which might evaporate from the slimy toys (except for light aldehydes) are identified. At the headspace analyses of the 14 slimy toys (of which a few were analysed on exterior part and interior liquid part, totally 20 analyses), were found 61 identified single substances and various groups of substances consisting of various aliphatic and aromatic hydrocarbons, which are stated in groups characterised by the number of carbon-atoms, and finally 6 compounds, which could not be identified.

4.1.1 Screening for possible harmful effects on the basis of the headspace analyses

Based on the identified chemical compounds a screening for possible volatile harmful substances has been made. The screening is based on the classifications in the List of Dangerous Substances and available information on effects that potentially may cause concern to the consumer, if the migration of the chemical substance is too high.

A number of volatile substances were detected, which might be considered to be problematic substances, and some, which may be of concern. These substances are shortly reviewed below as well as other classified substances. The substances are presented in alphabetical order (Table 4.1).

Table 4.1 Classification of substances detected in headspace analysis

Component	CAS no.	Classification	
Benzaldehyde	100-52-7	Xn;R22	Harmful. Harmful if swallowed
Butanal	123-72-8	F;R11	Highly flammable
Butanol	71-36-3	R10 Xn;R22 Xi;R37/38-41 R67	Flammable. Harmful. Harmful if swallowed. Irritant. Irritating to respiratory system and skin. Risk of serious damage to eyes. Vapours may cause drowsiness and dizziness
Butandiol + alcohol, e.g. ethanol, 2-propanol	110-63-4+		
Dimethyl-1,4-dioxane (C ₆ H ₁₂ O ₂) or similar	e.g. 10138-17-7		
2-Butanone	78-93-3	F;R11 Xi;R36 R66 R67	Highly flammable. Irritant. Irritating to eyes. Repeated exposure may cause skin dryness or cracking. Vapours may cause drowsiness and dizziness
2-Butoxyethanol	111-76-2	Xn;R20/21/22 Xi;R36/38	Harmful. Harmful by inhalation, in contact with skin and if swallowed. Irritant. Irritating to eyes and skin
n-Butylether	142-96-1	R10 Xi;R36/37/38	Flammable. Irritant. Irritating to eyes, respiratory system and skin
3-Carene	13466-78-9		
3-Carene	80-56-8		
Cyclohexanol	108-93-0	Xn;R20/22 Xi;R37/38 (conc.)	Harmful. Harmful by inhalation and if swallowed. Irritant. Irritating to respiratory system and skin
Cyclohexanone	108-94-1	R10 Xn;R20 (conc.)	Flammable. Harmful. Harmful by inhalation
2-Cyclohexen-1-one	930-68-7		
d-Limonene	5989-27-5	R10 Xi;R38 R43 N;R50/53	Flammable. Irritant. Irritating to skin. May cause sensitization by skin contact. Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
Decanal	112-31-2		
2-Decanone	693-54-9		
Dichlormethan	75-09-2	Carc3;R40	Limited evidence of carcinogenic effects
1,1-Dimethoxypropane	4744-10-9		
N,N-Dimethylformamide	68-12-2	Rep2;R61 Xn;R20/21 Xi;R36	Reprotox. cat 2. May impair fertility. Harmful. Harmful by inhalation and in contact with skin. Irritant. Irritating to eyes
Dodecanal	112-54-9		
Ethanol	64-17-5	F;R11	Highly flammable
Ethylacetate	141-78-6	F;R11 Xi;R36 R66 R67	Highly flammable. Irritant. Irritating to eyes. Repeated exposure may cause skin dryness or cracking. Vapours may cause drowsiness and dizziness
Ethylbenzene	100-41-4	F;R11 Xn;R20	Highly flammable. Harmful. Harmful by inhalation

Component	CAS no.	Classification	
2-Ethylbutanal	97-96-1		
2-Ethyl-1-hexanol	104-76-7		
Eucalyptol (C ₁₀ H ₁₈ O)	470-82-6		
Heptanal	111-71-7		
Heptanol	53535-33-4		
2-Heptanone	110-43-0	R10 Xn;R20/22	Flammable. Harmful by inhalation and if swallowed
3-Heptanone	106-35-4	R10 Xn;R20 Xi;R36	Flammable. Harmful by inhalation. Irritant. Irritating to eyes
2-Heptenal	18829-55-5		
Hexanal	66-25-1		
2-Hexanone	591-78-6	R10 T;R48/23 Rep3;R62 R67	Flammable. Toxic: danger of serious damage to health by prolonged exposure through inhalation Possible risk of impaired fertility. Vapours may cause drowsiness and dizziness
1-Methoxy-2-propanol	107-98-2	R10	Flammable
3-Methylbutanal	590-86-3		
2-Methyl-1-propanol	78-83-1	R10 Xi;R37/38-41 R67	Flammable. Irritant Irritating to respiratory system and skin. Risk of serious damage to eyes. Vapours may cause drowsiness and dizziness
Nonanal	124-19-6		
Nonanol	143-08-8		
Octane	111-65-9	F;R11 Xi;R38 Xn;R65 R67 N;R50/53	Highly flammable. Irritant. Irritating to skin. Harmful. Harmful: may cause lung damage if swallowed. Vapours may cause drowsiness and dizziness. Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
Octanal	124-13-0		
2-Octanone	111-13-7		
2-Octen-1-ol	18409-17-1		
2-Pentanone	107-87-9		
2-Phenoxyethanol	122-99-6	Xn;R22 Xi;R36	Harmful. Harmful if swallowed. Irritant. Irritating to eyes
alpha-Pinene	80-56-8		
beta-Pinene	127-91-3		
1-Propanol	71-23-8	F;R11 Xi;R41 R67	Highly flammable. Irritant. Risk of serious damage to eyes. Vapours may cause drowsiness and dizziness
2-Propanol	67-63-0	F;R11 Xi;R36 R67	Highly flammable. Irritant. Irritating to eyes. Vapours may cause drowsiness and dizziness
1,2-Propanediol	4254-15-3		

Component	CAS no.	Classification	
2-Propenoic acid 2 methyl-methylester (methylmethacrylat)	80-62-6	F;R11 Xi;R37/38 R43	Highly flammable. Irritant. Irritating to respiratory system and skin. May cause sensitization by skin contact
1-Propenylbenzene	873-66-5		
Styrene	100-42-5	R10 Xn;R20 Xi;R36/38	Flammable. Harmful. Harmful by inhalation. Irritant. Irritating to eyes and skin
Tetrahydrofuran	109-99-9	F;R11 R19 Xi;R36/37	Highly flammable. May form explosive peroxides. Irritant. Irritating to eyes and respiratory system
Toluene	108-88-3	F;R11 Xn;R20 <i>(NB changed at ATP29): F; R11 Repr. Cat.3; R63 Xn; R48/20-65 Xi; R38 R67</i>	Highly flammable. Harmful. Harmful by inhalation <i>Added classification; Possible risk of harm to the unborn child Toxic: danger of serious damage to health by prolonged exposure through inhalation – Harmful: may cause lung damage if swallowed. Irritant. Irritating to skin. Vapours may cause drowsiness and dizziness</i>
3,3,5-Trimethylcyclohexen-1-one	78-59-1	Xn;R21/22 Xi;R36/37 Carc3;R40	Harmful. Harmful in contact with skin and if swallowed. Irritant. Irritating to eyes and respiratory system. Limited evidence of carcinogenic effects
Undecanal	112-44-7		
m-, p-Xylene	108-38-3/106-42-3	R10 Xn;R20/21 Xi;R38	Flammable. Harmful. Harmful by inhalation and in contact with skin. Irritant. Irritating to skin
o-Xylene	95-47-6	R10 Xn;R20/21 Xi;R38	Flammable. Harmful. Harmful by inhalation and in contact with skin. Irritant. Irritating to skin
Aliphatic hydrocarbons etc.			
C7H14 and C7H16 aliphatic hydrocarbons			
C8 + C9 aliphatic hydrocarbons			
C8H16	e.g. 1678-91-7		
C9H12 + C10H14 aromatic hydrocarbons			
C9H12 aromatic hydrocarbons			
C9H20 aliphatic hydrocarbons			
C10-C14 aliphatic hydrocarbons			
C10H16			
C10H16O	e.g. 5948-04-9		
C11-C14 aliphatic hydrocarbons			

Component	CAS no.	Classification	
C11-C14 aliphatic hydrocarbons + decahydro-naphthalenes+ methyl decahydro-naphthalenes + dimethyl decahydro-naphthalenes			
C11-C14 aliphatic hydrocarbons			

4.1.2 Proposal for selected organic substances

Benzaldehyde

Benzaldehyde, CAS no. 100-52-7, is classified Xn;R22, (Harmful. Harmful if swallowed). The substance is detected in 1 product (G-01).

Butanal

Butanal, CAS no. 123-72-8 is classified F;R11, i.e. highly flammable. The substance is detected in 4 products (F-01, TO-01, TO-02 and G-01).

Butanol

Butanol, CAS no. 71-36-3 is classified R10 Xn;R22 Xi;R37/38-41 R67, i.e. flammable. Harmful if swallowed. Irritant. Irritating to respiratory system and skin - Risk of serious damage to eyes. Vapours may cause drowsiness and dizziness.

The substance is detected in 4 products (F-01, TO-03, G-01 and TI-01).

The classification is rather serious, but the headspace analysis implies that the exposure may be expected to be rather low.

2-Butanone

2-Butanone, CAS no. 78-93-3, is classified F;R11 Xi;R36 R66 R67 (Highly flammable. Irritant. Irritating to eyes. Repeated exposure may cause skin dryness or cracking. Vapours may cause drowsiness and dizziness. The substance is detected in 1 product (TI-01), in the exterior "slime" as well as in the containing liquid. As the consumer is expected to be exposed to the liquid at some time, a closer assessment is recommended.

2-Butoxyethanol

2-Butoxyethanol, CAS no. 111-76-2 is classified Xn;R20/21/22 Xi;R36/38, i.e. harmful. Harmful by inhalation, in contact with skin and if swallowed. Irritant. Irritating to eyes and skin.

2-Butoxyethanol is readily absorbed after inhalation or through oral or dermal contact (IPCS 1998, CICAD 10). 2-Butoxy-ethanol is a glycol ether commonly used as a solvent in coatings such as varnish and paint.

The substance is detected in several of the slimy toys (6 out of 14 (DK-02, DK-03, F-01, TO-03, G-01 and R-01)). Although the relative amounts are low in the screening, except for the liquid part of R-01, the detection should be assessed.

n-Butylether

n-Butylether, CAS no. 142-96-1 is classified R10 Xi;R36/37/38, i.e. flammable. Irritant. Irritating to eyes, respiratory system and skin. The classification is concentration-dependent. The analyses from the screening indicate low

exposures in the 2 products (TO-02 and TI-01), in which the substance was detected

3-Carene

3-Carene is identified by CAS no. 13466-78-9 (3,7,7-trimethyl-bicyclo 4,1,0-hept-3-ene) and CAS no. 80-56-8 (2,6,6-trimethyl-bicyclo 3,1,1 hept-2-ene). The substance is not classified, but 3-carene is a terpene. The terpenes are generally irritants to the mucous membranes. Turpentine from coniferous trees is skin sensitising. However, the sensitisation has not been confirmed for the individual terpenes with the exception of 3-carene, CAS no. 13466-78-9 (ASS 2000).

The substance is not classified in itself but can be evaluated on the basis of the group of vegetable terpenes, which are classified under vegetable turpentine with the classification Harmful; Xn, and R20/21/22 Harmful by inhalation, in contact with skin and if swallowed. The substance is also classified R65 Harmful: **may cause lung damage** if swallowed. The substance is an Irritant, Xi, with R 36/38, Irritating to eyes and skin and with R43, May cause sensitization by skin contact. The substance is Dangerous to the environment, N, with R51/53, Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. In addition, the substance is flammable. The substance was detected in 7 products (DK-02, DK-03, F-01, TO-03, G-01, TI-01 and BR-01) at low concentrations.

Cyclohexanol

Cyclohexanol, CAS no. 108-93-0, is classified Xn;R20/22 Xi;R37/38, i.e. Harmful. Harmful by inhalation and if swallowed. Irritant: irritating to respiratory system and skin. The classification is concentration-dependent. The substance was detected in 1 product (F-01) at a low concentration.

Cyclohexanone

Cyclohexanone, CAS no. 108-94-1, is classified R10 Xn;R20, i.e. Harmful. Harmful by inhalation. The classification is concentration-dependent. Inhalation may be an actual route of exposure for users of slimy toys. The substance was detected at the screening in 9 out of 14 slimy toys, and with considerably higher concentrations in the analysed liquids (cf. e.g. product K-01).

d-Limonene

d-Limonene, CAS no. 5989-27-5, is classified R10 Xi;R38 R43 N;R50/53, i.e. Irritant: Irritating to skin. May cause sensitization by skin contact. Limonene has been included in the List of Undesirable Substances, due to a reasoned suspicion that it may cause allergy (Miljøstyrelsen 2004). The substance was detected in 4 products (DK-02, DK-03, TO-03 and G-01), but all at low concentrations.

Dichlormethane

Dichloromethane, CAS no. 75-09-2, is classified Carc3;R40, i.e. Limited evidence of carcinogenic effects. The classification is rather serious for a substance in toys. The substance was detected in the liquid in 1 product (TI-01). An assessment would be appropriate.

N,N-Dimethylformamide

N,N-Dimethyl formamide, CAS no. 68-12-2, is classified Rep2;R61 Xn;R20/21 Xi;R36, i.e. toxic to reproduction in category 2. May impair fertility. Harmful by inhalation and in contact with skin. Irritant: irritating to eyes.

The classification is serious, and even though the substance was only detected in one product (TO-02), a further evaluation seems to be necessary.

Ethyl acetate

Ethyl acetate, CAS no. 141-78-6, is classified F;R11 Xi;R36 R66 R67, i.e. Highly flammable. Irritant: irritating to eyes. Repeated exposure may cause skin dryness or cracking. Vapours may cause drowsiness and dizziness. The substance was detected in one product (K-03) at low concentrations.

Ethylbenzene

Ethylbenzene, CAS no. 100-41-4, is classified F;R11 Xn;R20, i.e. Harmful. Harmful by inhalation. (The classification is concentration-dependent).

According to other sources ethylbenzene is irritating to skin, eyes and mucous membranes and may influence the central nervous system (Budavari 1996, IPCS 1996).

The substance was detected in all products from low to very high concentrations. It is recommended to make a further evaluation of the exposure.

Eucalyptol

Eucalyptol ($C_{10}H_{18}O$) with CAS no. 470-82-6 (1,3,3-Trimethyl-2-oxabicyclo 2.2.2 octane), is not classified.

However, the substance reminds of other terpenes or terpenoid substances and may consequently be irritating to skin or mucous membranes. The substance was only detected in one product (K-01) at low concentration.

2-Heptanone

2-Heptanone, CAS no. 110-43-0, is classified R10 Xn;R20/22, i.e. Highly flammable. Harmful by inhalation and if swallowed. The substance was detected in one product (TI-01) at low concentrations from the exterior "slime", but at somewhat higher concentrations in the interior liquid.

3-Heptanone

3-Heptanone, CAS no. 106-35-4, is classified R10 Xn;R20 Xi;R36, i.e. Flammable. Harmful by inhalation. Irritant: irritating to eyes. The substance was detected in one product (TI-01) at low concentration.

Hexanal

Hexanal, CAS no. 66-25-1, is not classified. However, in literature it is mentioned that hexanal is irritating to respiratory systems, eyes (Grant 1986) and skin. The irritation has been observed on skin and in eyes of laboratory animals (Larsen *et al.* 1999). The substance was detected in 9 products (DK-01, DK-02, DK-03, BR-01, TO-01, TO-02, G-01, K-03 and TI-01) at low concentrations.

2-Hexanone

2-Hexanone, CAS no. 591-78-6, is classified R10 T;R48/23 Rep3;R62 R67, i.e. Flammable. Toxic: danger of serious damage to health by prolonged exposure through inhalation. Possible risk of impaired fertility. Vapours may cause drowsiness and dizziness.

The substance was detected in one product (TI-01), in exterior layer as well as in interior liquid. The classification is so serious that a further evaluation seems necessary.

1-Methoxy-2-propanol

1-Methoxy-2-propanol, CAS no. 107-98-2 is classified R10. Flammable. The substance was detected in 2 products (TO-01 and TO-03) at low concentrations.

2-Methyl-1-propanol

2-Methyl-1-propanol, CAS no. 78-83-1, is classified R10 Xi;R37/38-41 R67, i.e. Flammable. Irritant: irritating to respiratory system and skin. Risk of serious damage to eyes. Vapours may cause drowsiness and dizziness. The substance was detected in 2 products (TO-03 gel and lip-gloss) at low concentrations.

Octane

Octane, CAS no. 111-65-9, is classified F;R11 Xi;R38 Xn;R65 R67 N;R50/53, i.e. Highly flammable. Irritant: irritating to skin. Harmful. Harmful: may cause lung damage if swallowed. Vapours may cause drowsiness and dizziness. The substance was detected in one product (TO-02) at a low concentration.

2-Phenoxyethanol

2-Phenoxy ethanol, CAS no. 122-99-6, is classified Xn;R22 Xi;R36, i.e. Harmful. Harmful if swallowed. Irritant: irritating to eyes. The substance was detected in one product (TO-03) in a small amount.

***alfa*-Pinene**

alpha-Pinene, CAS no. 80-56-8, is not classified under its own name, but if it is included under vegetable turpentine (Miljøministeriet 2002), the classification is R10 Xn;R20/21/22-65 Xi;R36/38 R43 N;R51/53, i.e. Flammable. Harmful. Harmful by inhalation, in contact with skin and if swallowed. Harmful: **may cause lung damage** if swallowed. Irritant. Irritating to eyes and skin. May cause sensitization by skin contact. Finally vegetable turpentine is toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

The substance is moderately toxic by intake, but very toxic by inhalation (Lewis 1992) and a strong irritant to eyes, mucous membranes and skin (Budavari 1996, Lewis 1992). *alpha*-Pinene is known to be a contact-allergen (Thomsen 1990). The substance was detected in 9 products (DK-01, DK-02, DK-03, K-01, F-01, TO-03 (gel and lip-gloss), G-01 and TI-01) at low concentrations.

1-Propanol

1-Propanol, CAS no. 71-23-8, is classified F;R11 Xi;R41 R67, i.e. Highly flammable. Irritant. Risk of serious damage to eyes. Vapours may cause drowsiness and dizziness. The substance was detected in 2 products (TO-02 and TO-03) at low concentrations.

2-Propanol

2-Propanol, CAS no. 67-63-0, is classified F;R11 Xi;R36 R67, i.e. Highly flammable. Irritant: irritating to eyes. Vapours may cause drowsiness and dizziness. The substance was detected in one product (TO-03) at low concentration.

1,2-Propanediol

1,2-Propanediol, CAS no. 4254-15-3, is not classified, but it was detected in 2 products (TO-03 and BR-01), and in one of them (TO-03 gel) at high concentrations. It is therefore suggested to make a further evaluation of the substance.

2-Propenoic acid 2 methyl-methylester (methylnmethacrylat)

2-Propenoic acid 2 methyl-methyl ester, (methylnmethacrylate), CAS no. 80-62-6 is classified F;R11 Xi;R37/38 R43, i.e. Highly flammable. Irritant. Irritating to respiratory system and skin. May cause sensitization by skin contact. The substance was detected in one product (TO-03 gel). Based on the classification it is suggested to examine the exposure more closely.

Styrene

Styrene, CAS no. 100-42-5, is classified R10 Xn;R20 Xi;R36/38, i.e. Flammable. Harmful. Harmful by inhalation. Irritant Irritating to eyes and skin. The classification is concentration-dependent. The health effects of concern are that styrene is considered to be neuro-toxic. Influence on the neurological development seems to be the most sensitive effect, which has been found. The substance was detected in 2 products (TO-02 and TO-03) at low concentrations.

Tetrahydrofuran

Tetrahydrofuran, CAS no. 109-99-9, is classified F;R11 R19 Xi;R36/37, i.e. Highly flammable. **May form explosive peroxides.** Irritant. Irritating to eyes and respiratory organs.

The substance was detected in 2 products (K-03 and TI-01) at low concentrations.

Toluene

Toluene, CAS no. 108-88-3, is classified F;R11 Xn;R20, i.e. Highly flammable. Harmful. Harmful by inhalation. However, it should be noted that the classification has been made more rigorous (ATP 29) as follows:

F; R11 Repr.Cat.3;R63 Xn; R48/20-65 Xi; R38 R67, i.e. Possible risk of harm to the unborn child. Toxic: danger of serious damage to health by prolonged exposure through inhalation. - Harmful: may cause lung damage if swallowed. Irritant. Irritating to skin. Vapours may cause drowsiness and dizziness.

The substance was detected in all products. In one product (K-01) toluene was found in quite large amounts, in the exterior part of the toy as well as in the liquid inside. Based on the widespread occurrence and the classification the exposure should be examined more closely.

3,3,5-Trimethylcyclohexen-1-one

3,5,5-Trimethyl-2-cyclohexen-1-one, CAS no. 78-59-1, is classified Xn;R21/22 Xi;R36/37 Carc3;R40, i.e. Harmful. Harmful in contact with skin and if swallowed. Irritant. Irritating to eyes and respiratory system. Carc3: Limited evidence of carcinogenic effects.

The substance was detected in 3 products (TO-03 (gel and lip-gloss) and TI-01) at low concentrations. Nevertheless, a further evaluation is recommended based on the classification.

Xylene

m-, p- and o-Xylene, with CAS no. 108-38-3 / 106-42-3 / 95-47-6, is classified R10 Xn;R20/21 Xi;R38, i.e. Flammable. Harmful. Harmful by inhalation

and in contact with skin. Irritant. Irritating to skin. The classification is concentration-dependent.

The substances were detected in most of the products. In the screening analyses xylenes are hardly separable from ethylbenzene. Xylene was detected in a very high concentration (BR-01), and in another product ethylbenzene and xylene occur as the total mixture (100%). The exposure should be further evaluated.

Aliphatic hydrocarbons

The aliphatic hydrocarbons are presented one by one or in groups like e.g.:

C₇H₁₄ and C₇H₁₆ aliphatic hydrocarbons

C₈ + C₉ aliphatic hydrocarbons

C₉H₂₀ aliphatic hydrocarbons

C₁₀-C₁₄ aliphatic hydrocarbons

C₁₁-C₁₄ aliphatic hydrocarbons

C₁₁-C₁₄ aliphatic hydrocarbons + decahydronaphthalenes+ methyldecahydronaphthalenes + dimethyldecahydronaphthalenes

C₁₁-C₁₄ aliphatic hydrocarbons

The aliphatic hydrocarbons may be chained or branched.

The alkanes C₉₋₁₉ (nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane, octadecane, nonadecane) have been grouped in the measurements. Dermatitis, irritation, influences on the central nervous system and anaesthetic effects have been observed for many of the aliphatic hydrocarbons. The effects are increased by increased molecular weight.

The alkanes, C₁₂₋₂₆-branched and chained, are adopted on the List of Dangerous Substances under CAS no.: 90622-53-0, EINECS no.: 292-454-3 (Miljøministeriet 2002) with the classification: Carc2;R45, i.e. May cause cancer.

Aromatic hydrocarbons

The aromatic hydrocarbons are presented one by one or in groups, like e.g.:

C₈H₁₆ E.g. 1678-91-7 (ethyl cyclohexane)

C₉H₁₂ + C₁₀H₁₄ aromatic hydrocarbons

C₉H₁₂ aromatic hydrocarbons

C₁₀H₁₆O e.g. 5948-04-9 (2-methyl-5-(1-methylethenyl)-cyclohexanone)

C₁₁-C₁₄ aromatic hydrocarbons + decahydronaphthalenes + methyldecahydronaphthalenes + dimethyldecahydronaphthalenes

A further evaluation will be complicated by the fact that they are grouped in the analysis.

Aldehydes – in general

Aldehydes are typically volatile organic compounds characterised by their irritating properties. Aldehydes irritate skin, eyes and the upper respiratory tract. The low molecular weight aldehydes, the halogenated aliphatic aldehydes, and the unsaturated aldehydes are particularly irritating. The mucous membranes of the nasal and oral passages and the upper respiratory tract are affected, producing a burning sensation, an increased ventilation rate, bronchial constriction, choking, and coughing. The eyes tear, and a burning sensation is noted on the skin of the face. During low exposures, the initial discomfort may abate after 5 to 10 minutes, if the exposure is ceased but the sensation will recur if exposure is resumed after the interruption (Clayton and Clayton 1981).

4.1.3 Proposal for selected inorganic substances

ICP screening showed trace occurrence of a number of substances. They are evaluated to be present in the form of inorganic compounds, which are included in the manufacturing of the product, fillers and pollutants in fillers or residues from dyes.

The majority of the substances are close to the limits of detection. The few that occur in larger amounts, are most frequently substances, which are less essential in this context, such as sodium, calcium and other salts. One single exception is boron, which has been quantitatively determined.

Boron

The assessment could be based on studies on boric acid, CAS no. 10043-35-3, which is proposed classified Repr.Cat.2;R60 - 61, i.e. May impair fertility and may cause harm to the unborn child.

Boron was detected in large amounts in 2 products (DK-01, TO-01), and a further evaluation is recommended.

Nickel

Nickel is classified: Carc3;R40 R43. Most nickel compounds are classified allergenic - R43, i.e. May cause sensitization by skin contact.

A number of nickel compounds are either known carcinogenic or are suspected carcinogenic such as e.g. nickel carbonate and nickel sulphate.

Skin contact with nickel is very essential, as most nickel compounds may cause allergenic reactions at sensitised persons.

Nickel was detected in the screening in 2 products (TO-01 and A-01), however in small amounts. Based on the allergenic properties of nickel a further evaluation is recommended.

4.1.4 Conclusion headspace

Based on the above arguments the following substances are suggested for a further evaluation:

Organic substances:

2-Butanone
2-Butoxyethanol
Cyclohexanone
Dichlormethan
N,N-Dimethylformamide
Ethylbenzene
2-Hexanone
1,2-Propanediol
2-Propenoic acid 2 methyl-methylester (methylmethacrylat)
Toluene
3,3,5-Trimethylcyclohexen-1-one
Xylene

Inorganic substances

Boron
Nickel

Based on the detected substances the following slimy toys are suggested for quantitative analyses and further evaluation of the selected substances:

TI-01, green liquid-filled stick

Based on the detection of 2-butanone, dichloromethane, 2-hexanone and 3,3,5-trimethylcyclohexen-1-one.

R-01, green liquid-filled ball with spikes

Based on the detection of 2-butoxy-ethanol.

K-01, yellow, transparent ball with insect inside

Based on the detection of cyclohexanone and toluene.

TO-02, hard plastic container with green slime inside

Based on the detection of N,N-dimethyl formamide.

BR-01, pink transparent liquid-filled softball with insect inside

Based on the detection of ethylbenzene and xylene.

A-01, transparent liquid-filled disc with stars inside

Based on the detection of ethylbenzene and nickel.

TO-03, blue gel for hair, skin and lips

Based on the detection of 1,2-propanediol, 2-propenoic acid 2 methyl-methyl ester (methyl-methacrylate) and 3,3,5-trimethylcyclohexen-1-ol.

DK-01, multicoloured rubbery saurian

Based on the detection of boron.

TO-01, green slime with insects inside

Based on the detection of boron and nickel.

4.2 Screening of possible harmful effects based on the migration analyses

Migration analyses have been carried out in order to screen for possible harmful substances, which may be released from slimy toys when getting in contact with the consumer. The analyses have been made with artificial sweat in order to assess the release at skin contact (dermal contact) and with artificial saliva in order to assess the release when putting the toys in the mouth (oral contact). At the analysis 1-2 g weighed sample has been used, added 20 ml artificial saliva solution or artificial sweat solution and extracted for 4 hours in an incubator at 40°C, cf. section of methods.

This means the detected amounts of released substances (μg per g slimy toys) are quantitative measurements over 4 hours, during which all potentially migrating compounds are collected (cf. analysis method description and total result in Enclosure D). A summary is presented in Table 4.2.

At the migration analyses of the 14 slimy toys (of which a few were analysed on exterior part and interior part, totally 17 analyses) were found 22 identified single substances and 3 groups of substances, e.g. aliphatic hydrocarbons or hydrocarbons with carbon chain lengths above C14, and finally a group of 6 compounds, which could not be identified, but they were all fatty acids.

4.2.1 Screening by migration

Based on the identified chemical compounds a screening for possible harmful substances among the migrated substances has been made. The screening is based on the classifications in the List of Dangerous Substances and available information on effects that potentially may cause concern to the consumer, if the release of the substances from the slimy toys is too high.

Ten substances were detected, which might be considered problematic substances, and some, which may be of concern. These substances are shortly summarised below in Table 4.2 as well as the detected classified substances. The substances are presented in alphabetical order.

Table 4.2 Classification of substances detected in artificial sweat- and saliva extract analysis

Component	CAS no.	Classification	
Benzoic acid butylester	136-60-7	Xn;R22 N;R51/53 (Advisory list)	Harmful. Harmful if swallowed
Benzoic acid phenylester	93-99-2	R43 N;R51/53 (Advisory list)	May cause sensitization by skin contact
Benzoic acid propylester	2315-68-6		
Butylparabene	94-26-8		
Cyclohexanone	108-94-1	R10 Xn;R20	Flammable. Harmful. Harmful by inhalation
Diethylglycol dibenzoate or similar	120-55-8		
Ethanol-2-(butoxyethoxy)-acetate	112-15-2		
Ethylparabene	120-47-8		
Methyldihydrojasmonate	24851-98-7		
5-Methyl-2-(1-methylethyl-cyclohexanol)	23283-97-8		
Methylparabene	99-76-3		
Naphthalene	91-20-3	Xn;R22 N;R50/53 <i>(changed in ATP29): Carc. Cat.3; R40 Xn; R22 N; R50-53</i>	Harmful. Harmful if swallowed <i>Limited evidence of carcinogenic effects</i>
2-Phenoxyethanol	122-99-6	Xn;R22 Xi;R36	Harmful. Harmful if swallowed. Irritant. Irritating to eyes
2-Phenylmethylenoctanal (=hexylcinnamaldehyde)	101-86-0		Reasoned suspicion of allergenic fragrance (List of undesirable substances)
1,2-Propandion-1-phenyl-2-oxime	119-51-7	R43 (Advisory list)	May cause sensitization by skin contact
N-Propylbenzamide + N-acetylbenzamide	10546-70-0, 1575-95-7		
Propylparabene	94-13-3		

Component	CAS no.	Classification	
Toluene	108-88-3	F;R11 Xn;R20 <i>(NB changed in ATP29):</i> F; R11 Repr. Cat.3: R63 Xn; R48/20-65 Xi; R38 R67	Highly flammable. Harmful. Harmful by inhalation. <i>Added:</i> <i>Possible risk of harm to the unborn child.</i> <i>Toxic: danger of serious damage to health by prolonged exposure through inhalation – Harmful: may cause lung damage if swallowed.</i> <i>Irritant. Irritating to skin.</i> <i>Vapours may cause drowsiness and dizziness</i>
o-, m-, p-Xylene	95-47-5, 108-38-3, 106-42-3	R10 Xn;R20/21 Xi;R38	Flammable. Harmful. Harmful by inhalation and in contact with skin. Irritant. Irritating to skin
Ethylbenzene	100-41-4	F;R11 Xn;R20	Highly flammable. Harmful. Harmful by inhalation
3,3,5-Trimethylcyclohexen-1-one	78-59-1	Xn;R21/22 Xi;R36/37 Carc3;R40	Harmful. Harmful in contact with skin and if swallowed. Irritant. Irritating to eyes and respiratory system. Limited evidence of carcinogenic effects
Aliphatic hydrocarbon >C14			
Hydrocarbons >C14			
Fatty acids			

4.2.2 Proposal for selected organic substances

At the migration analysis, using artificial saliva and sweat, the same substances - more or less - were detected, and frequently in approximately the same concentrations.

Benzoic acid butylester

Benzoic acid butylester, CAS no. 136-60-7, is not classified in the List of Dangerous Substances, however it is self classified Xn;R22 N;R51/53 (Advisory list, Miljøstyrelsen 2001), i.e. Harmful. Harmful if swallowed. The substance was detected in 2 products; one of them, however, only in small amounts.

Benzoic acid phenylester

Benzoic acid phenylester, CAS no. 93-99-2, is not classified in the List of Dangerous Substances, however it is self classified R43 N;R51/53 (Advisory list), i.e. May cause sensitization by skin contact. Like the above-mentioned, the substance was detected in 2 products.

Benzoic acid propylester

Benzoic acid propylester, CAS no. 2315-68-6, is not classified but follows the two above-mentioned benzoic acid esters. The substance was detected in 3 products.

Parabenes

Four parabenes were detected:

Methylparabene, CAS no. 99-76-3
Ethylparabene, CAS no. 120-47-8
Propylparabene, CAS no. 94-13-3
Butylparabene, CAS no. 94-26-8

Parabenes is the name of a group of chemical substances, which are frequently used as preservatives in cosmetics, food and medicaments to prevent bacterial- and fungal growth in the products. It is often noted that the substances are endocrine disrupters. Parabenes are very slightly allergenic, and they rarely cause allergy. Parabene allergy is particularly observed at persons, which have had severely chronic eczema and/or venous leg ulcer, where the skin is frail making it easier for the allergenic substances to penetrate the skin. The substances were detected in 3 products at low concentrations. Apparently the concentrations are below levels, which might cause problems.

Cyclohexanone

Cyclohexanone, CAS no. 108-94-1, is classified R10 Xn;R20, i.e. Flammable. Harmful. Harmful by inhalation. The substance was detected in 4 products, but only one of them (TO-01) in large amounts.

Diethylglycol dibenzoate

Diethylglycol dibenzoate or the like, CAS no. e.g. 120-55-8, is not classified. However, the substance occurs in considerable amounts, for which reason an evaluation would be appropriate.

Naphthalene

Naphthalene, CAS no. 91-20-3, is classified Xn;R22 N;R50/53, and the classification is further updated in ATP29 with *Carc. Cat.3;R40, i.e. Limited evidence of carcinogenic effects*. However, the substance was only detected in one product in trace concentrations.

2-Phenoxy ethanol

2-Phenoxy ethanol, CAS no. 122-99-6 is classified Xn;R22 Xi;R36, i.e. Harmful. Harmful if swallowed. Irritant. Irritating to eyes. The substance was detected in 4 products and in large amounts in one of them (TO-03, gel). A further evaluation is suggested.

2-Phenyl-methyleneoctanal

2-Phenyl-methyleneoctanal (=Hexylcinnamaldehyde), CAS no. 101-86-0, is not classified in the List of Dangerous Substances. However, there is a reasoned suspicion that the substance is an allergenic fragrant according to the List of Undesirable Substances. The substance was detected in one product (TO-03, gel) at a low concentration.

1,2-Propandione-1-phenyl-2-oxime

1,2-Propandione-1-phenyl-2-oxime, CAS no. 119-51-7 is not classified in the List of Dangerous Substances, but it is self-classified R43 (Advisory list), i.e. May cause sensitization by skin contact. The substance was detected in 2 products at low concentrations.

Benzamide

N-Propyl benzamide + N-acetyl benzamide, CAS no. 10546-70-0 and 1575-95-7, are not classified in the List of Dangerous Substances. The substance

was detected in 2 products and in an average amount in one of them (TO-01). A further evaluation is suggested.

Toluene

Toluene, CAS no. 108-88-3, is classified F;R11 Xn;R20, i.e. Highly flammable. Harmful. Harmful by inhalation. As mentioned under "headspace" the classification is more rigorous in ATP 29 with:

Repr. Cat. 3;R63 Xn;R48/20-65 Xi;R38 R67, i.e. Possible risk of harm to the unborn child. Toxic: danger of serious damage to health by prolonged exposure through inhalation – Harmful: may cause lung damage if swallowed. Irritant. Irritating to skin. Vapours may cause drowsiness and dizziness.

The substance was detected in 11 products. Although the concentrations are very low, an evaluation is suggested.

Xylene

o-, m-, p-Xylene, CAS no. 95-47-5, 108-38-3, 106-42-3, is classified R10 Xn;R20/21 Xi;R38 (concentration- dependent), i.e. Flammable. Harmful. Harmful by inhalation and in contact with skin. Irritant. Irritating to skin. The substance was detected together with ethylbenzene in 3 products at low concentrations. An evaluation is suggested.

Ethylbenzene

Ethylbenzene, CAS no. 100-41-4, is classified F;R11 Xn;R20, i.e. Highly flammable. Harmful. Harmful by inhalation. The substance was detected together with xylene in 3 products at low concentrations. An evaluation is suggested.

3,3,5-Trimethylcyclohexen-1-one

3,3,5-Trimethylcyclohexen-1-one, CAS no. 78-59-1, is classified Xn;R21/22 Xi;R36/37 Carc3;R40, i.e. Harmful. Harmful in contact with skin and if swallowed. Irritant. Irritating to eyes and respiratory system. Limited evidence of carcinogenic effects. The substance was detected in 4 products at low concentrations. Due to the severe classification an evaluation is suggested.

4.2.3 Conclusion based on the migration analyses

On the basis of the above arguments the following substances are suggested for a further evaluation (previously mentioned substances under "headspace" are written in italics).

Cyclohexanone

Diethylglycol dibenzoate

2-Phenoxyethanol

N-Propylbenzamide + N-acetylbenzamide

Ethylbenzene

Toluene

3,3,5-Trimethylcyclohexen-1-one

Xylene

Based on the detected substances the following slimy toys are suggested for quantitative analyses and a further evaluation of the selected substances:

TO-01, green slime with insects inside

Based on the detection of cyclohexanone, diethylglycol dibenzoate, N-propylbenzamide + N-acetylbenzamide.

TO-02, hard plastic container with green slime inside

Based on the detection of cyclohexanone, diethylglycol dibenzoate, N-propylbenzamide + N-acetylbenzamide.

TO-03, gel

Based on the detection of 2-phenoxyethanol.

TO-03, lip-gloss

Based on the detection of 3,3,5-trimethylcyclohexen-1-one.

K-01, yellow, transparent ball with insect inside

Based on the detection of toluene.

DK-01, multicoloured rubbery saurian

Based on the detection of toluene.

BR-01, pink transparent liquid-filled softball with insect inside

Based on the detection of ethylbenzene and xylene.

4.3 Conclusion on screening of possible harmful effects

On the basis of the above arguments the following substances are suggested for a further evaluation:

Organic substances

2-Butanone

2-Butoxyethanol

Cyclohexanone

Dichloromethane

Diethylglycol dibenzoate

N,N-Dimethyl formamide

Ethylbenzene

2-Hexanone

2-Phenoxyethanol

1,2-Propanediol

2-Propenoic acid 2-methyl-methyl ester (methylmethacrylate)

N-Propyl benzamide + N-acetyl benzamide

Toluene

3,3,5-Trimethylcyclohexen-1-one

Xylene

Inorganic substances

Boron

Nickel

On the basis of the detected substances the following slimy toys are suggested for a further evaluation:

TI-01, green liquid-filled stick

Based on the detection of 2-butanone, dichloromethane, 2-hexanone and 3,3,5-trimethylcyclohexen-1-one.

R-01, green liquid-filled ball with spikes

Based on the detection of 2-butoxyethanol.

K-01, yellow, transparent ball with insect inside

Based on the detection of cyclohexanone and toluene.

TO-02, hard plastic container with green slime inside

Based on the detection of N,N-dimethyl formamide, cyclohexanone, diethylglycol dibenzoate and N-propyl benzamide + N-acetyl benzamide.

BR-01, pink transparent liquid-filled softball with insect inside

Based on the detection of ethylbenzene and xylene.

A-01, transparent liquid-filled disc with stars inside

Based on the detection of ethylbenzene, xylene and nickel.

TO-03, blue gel for hair, skin and lips

Based on the detection of 1,2-propanediol, 2-propenoic acid 2-methyl-methyl ester (methylmethacrylate), 3,3,5-trimethylcyclohexen-1-one and 2-phenoxyethanol.

DK-01, multicoloured rubbery saurian

Based on the detection of toluene and boron.

TO-01, green slime with insects inside

Based on the detection of cyclohexanone, diethylglycol dibenzoate and N-propyl benzamide + N-acetyl benzamide, boron and nickel.

4.4 Selection of substances for quantitative determination

Based on above arguments and according to agreement with the Danish Environmental Protection Agency the following substances are selected for quantitative determination and preparation of exposure scenarios.

alpha-Pinene

2-Butanone

2-Butoxyethanol

3-Carene

Cyclohexanone

Diethylglycol dibenzoate

d-Limonene

Ethylbenzene

2-Hexanone

2-Phenoxyethanol

2-Phenylmethylene octanal

1,2-Propanediol

2-Propenoic acid 2-methyl-methyl ester (methyl-methacrylate)

N-Propyl benzamide + N-acetyl benzamide

Styrene

Toluene

Xylene

Boron (has been determined quantitatively and results are stated in section 3.5)

Nickel

5 Quantitative analyses

5.1 Headspace analysis results from quantitative determination

5.1.1 Headspace method description

For selected components, a quantitative determination of the degassing from the slimy toys was carried out. It was carried out based on samples exposed at the screening analysis. The amount of detected organic components was determined according to external standards of toluene. These standards were prepared on Tenax filters in concentrations of 5 ng to 200 ng and subsequently analysed by thermal desorption combined with gas chromatography-mass spectrometry (ATD/GC-MS).

The stated concentration in mg component/m³ air is a mean value valid for the time of exposure of the Tenax filters and is calculated according to ISO/DIS 16017-2 for passive (diffusive) sampling on solid adsorbents. A sampling rate valid for toluene was used.

5.1.2 Headspace analysis results

The result of the headspace analysis is stated in Enclosure G.

5.2 GC-MS Analysis (quantitative determination) migration

5.2.1 GC-MS Analysis method description

For selected organic components, a quantitative determination of the migration from the slimy toys to artificial saliva and sweat respectively was carried out.

The amount of the selected components was determined according to external standards of the respective analytes. These standards were prepared in 20 ml artificial saliva-solution/artificial sweat-solution and subsequently extracted and analysed as the extracts of the slimy toy.

5.2.2 GC-MS Analysis results

A detailed survey is shown below in Table 5.2 and in Enclosure H. The amounts are stated in µg per g slimy toy.

Table 5.2 Quantitative analysis of selected components in sweat- and saliva-extracts ($\mu\text{g/g} = \text{mg/kg}$)

Component	CAS no.	DK-01, exterior	DK-02, exterior	DK-03, exterior	K-01, exterior	BR-01, exterior	F-01, exterior	F-01, interior	TO-01, exterior	TO-02, exterior	TO-03, gel	G-01, exterior	K-03, exterior	TI-01, exterior	R-01, exterior	A-01, exterior
		1	2	3	5	7	8	8 C	9	10	11	12	13	16	17	18
Cyclohexanone	108-94-1			1.0					430	6.9		0.5				
Diethylglycol dibenzoate	120-55-8								118	26						
Component corresponding to diethylglycol dibenzoate									103	4						
2-Phenoxy ethanol	122-99-6						53	60			16000				120	
2-Phenylmethylene octanal (=Hexylcinnamaldehyde)	101-86-0										8.6					
N-Propyl benzamide + N-acetyl benzamide	10546-70-0, 1575-95-7								*	*						
Toluene	108-88-3	0.20	0.13	0.17	1.4	0.16	0.14	0.19				0.06	<0.05	<0.05		0.05
o-, m-, p-Xylene	95-47-5, 108-38-3, 106-42-3				0.30	1.1	0.26	0.20				0.27				0.81
Ethylbenzene	100-41-4				<0.05	0.56	<0.05	<0.05				<0.05				0.06

Table 5.2 Quantitative analysis of selected components in saliva-extracts ($\mu\text{g/g} = \text{mg/kg}$)

Component	CAS no.	DK-01, exterior	DK-02, exterior	DK-03, exterior	K-01, exterior	BR-01, exterior	F-01, exterior	F-01, interior	TO-01, exterior	TO-02, exterior	G-01, exterior	K-03, exterior	TI-01, exterior	R-01, exterior	A-01, exterior
		1	2	3	5	7	8	8 C	9	10	12	13	16	17	18
Cyclohexanone	108-94-1			0.6					160	7.6	<0.5				
Diethylglycol dibenzoate	120-55-8								65	38					
Component corresponding to diethylglycol dibenzoate									69	7					
2-Phenoxy ethanol	122-99-6						44	17						80	
N-Propyl benzamide + N-acetyl benzamide	10546-70-0, 1575-95-7								*	*					
Toluene	108-88-3	0.27	0.09	0.22	1.5	0.15	0.16	0.24			0.05	<0.05	<0.05		<0.05
o-, m-, p-Xylene	95-47-5, 108-38-3, 106-42-3				<0.05	1.2	0.31	<0.05			0.25				0.79
Ethylbenzene	100-41-4				<0.05	0.64	<0.05	<0.05			<0.05				0.06

*These organic compounds have not been determined quantitatively, as the standards were not commercially available.

For the aromatic hydrocarbons there is a good correspondence between the qualitative screening analysis and the quantitative determination, because internal standards of deuterium-marked aromatic hydrocarbons were used, which have the same recovery as the analyts.

For the rest of the components, where recovery for the analyts is expected to be different from recovery for the internal standards because of considerable chemical differences, there are great deviations between the qualitative and the quantitative determinations.

5.3 ICP-MS Analysis (quantitative determination)

5.3.1 ICP-MS Analysis method description

Quantitative determination of nickel has been carried out in the 2 selected slimy toys. The migration was carried out in artificial saliva-solution/artificial sweat-solution. Subsequently, nickel was determined directly in the extract, which was made sour by means of nitric acid (sub boiling) prior to analysis by FI-ICP-MS with internal standardization.

5.3.2 ICP-MS Analysis results

The result of the analysis is stated below in Table 5.3 and Enclosure I. The amounts are stated in μg per g slimy toy.

Table 5.3 The result of quantitative analysis of nickel

Sample mark	ID no.	Ni $\mu\text{g/g}$	% RSD
30396-9	TO-01 - Slime	0.83	4.0
30396-18	A-01 - Gel	2.96	2.5

These results agree with the results from the screening analysis - within approx. 15%.

As a starting point, these products are not expected to contain nickel; consequently, the detected content is assumed to be contaminations from the manufacture of the products, e.g. from use of nickel-containing catalysts.

6 Exposure scenarios

6.1 Introduction

To evaluate the health risk from using slime toys, effects from selected chemical substances are assessed in relation to the relevant exposure period and exposure route for consumers of the toys.

Exposure period

The exposure period for playing with slimy toys may vary considerably but most commonly is assumed several short-term uses that may vary from a few to several minutes. Assuming a varying exposure period at each use and that the number of use times may also vary, a starting point has been to assume a daily exposure of 60 minutes (1 hour).

This assumption is supported, for instance, by an American study on the playing activity of children. In the study was observed average play activity times of 46-70 minutes and 90 percentiles for children 1 to 17 years of age of 120 to 255 minutes (US-EPA 1997).

Exposure route

During the screening it became clear that many of the substances detected were volatile substances, and a substantial exposure route was via inhalation.

Exposure via inhalation takes place from the air borne concentration of the chemical substance in the breathing zone. The substance may then be taken up by the lungs or after ciliary transport across the mucous membranes to the oesophagus taken up by the stomach-intestine canal.

Dermal exposure is considered relevant as the slimy toys are specifically intended for "handling". The primary exposure is exposure to the skin on hands, but contact to other areas of the body during play can hardly be excluded.

Oral exposure is included since contamination of hands or even mouthing the toys cannot be excluded.

Due to realistic "worst case" the calculations of dermal and oral uptake are assuming a body weight of 10 kg for children. Slimy toys may be intended for little older children, but that younger siblings may or will get hold of them cannot be excluded.

Uptake

Uptake via inhalation, oral or dermal exposure is substance specific and, therefore, dependent of which substances that are found released from the slimy toys. If no information could be found on the specific uptake of the individual substances via inhalation, dermal contact or via mouth or mucous membranes, an uptake of 100% is assumed.

In the study 20 specific substances were selected in co-operation with the Danish Environmental Protection Agency. The selection is based on the classification of the substances, measured amounts, etc. (cf. chapter 4).

The selected substances have been reviewed individually after presentation of the assessment method, cf. below.

Each of the selected substances has been identified by its common name and CAS no. for unambiguously identification. The most common synonyms are stated, and furthermore is mentioned:

- The physical-chemical data of the substances, which may be relevant to the assessment
- The use of the substance in order to evaluate where the potential source of the substance might be
- The classification of the substance
- The effects of the substances on human health have been summarised, partly acute effect levels but also effect levels from long-term studies, if available
- The threshold limit values (TLV) of the substance, valid for the working environment. The available values for tolerable daily intake (TDI), acceptable daily intake (ADI) or reference dose (RfD) are mentioned (for explanation cf. the abbreviation list). It should be noted that TLV values cover the concentration in air in the working environment and not in consumers' homes

Finally, an assessment of the amount of detected released substances has been carried out. This has been performed by calculating / estimating the uptake based on the time of exposure and the body weight of the person (amount/kg body weight/day). If possible, one of the established values for tolerable daily intake (TDI, ADI or RfD) is used for evaluation of the exposure by comparing the values with the obtained analysis results used to estimate the exposure.

The basis is the maximum found value, if they appear in several products. The used uncertainty factors are mentioned in the text. In case more TDI, ADI or RfD values exist, the lowest value is preferred. If no TDI, ADI, RfD values are available, a comparison to a concentration where no adverse effects are observed (NOAEL: No Observed Adverse Effect Level) from a relevant long-term study is used. The procedure is mentioned at the individual substances.

6.2 Exposure scenarios

6.2.1 Introduction

The exposure to the consumer from slimy toys will vary considerably according to use duration, which rooms (size, etc.) the toys are used in, ventilation and handling or area of contact and duration of direct contact. To evaluate the exposure in a standardised way, theoretical exposure scenarios have been derived to illustrate the worst possible but realistic exposures.

To evaluate the exposure of consumers, the following scenarios have been derived:

Exposure via inhalation of volatile substances (exposure via inhalation)
Exposure via skin (dermal exposure)
Exposure via the mouth (oral exposure)

The direct exposure from unwrapping and the first use is assumed to be analogous to the direct exposure measured in the headspace analysis (cf. section on methods). For the evaluation of exposure via inhalation is used a scenario with inhalation of the measured concentration in the breathing zone of 1 m³ and in a room of 20 m³.

Dermal exposure is based on measurements of the substance in extractions to artificial sweat. It is assumed that the amount of substance released (migrated) from the toys during an average time of 1 hour extraction (extraction duration 4 hours) corresponds to the potential dermal exposure.

Oral exposure is based on measurements of the substance in extractions of artificial saliva. It is assumed that the amount of substance released (migrated) from the toys during an average time of 1 hour extraction (extraction duration 4 hours) corresponds to the potential oral exposure.

6.2.2 Methodology

For the chemical substances detected as evaporated or migrated to sweat or saliva from the slimy toys, an evaluation of which substances appeared to be the most interesting (cf. section 4). Then a selection was made in agreement with the Danish Environmental Protection Agency. Data on the individual substances are retrieved to perform a health hazard evaluation based on known information from previously prepared Danish or foreign monographs, etc. The found data for threshold limit values or toxicity are then compared to the concentrations estimated in the used scenarios.

The methodology used is approximately the same as recommended in connection to risk assessment in the European Union (EU) i.e. Technical Guidance Document (TGD 2003). In the TGD the potential risk to the consumer is estimated as the ratio between the predicted no-effect concentration (no-adverse-effect level, NOAEL) and the predicted exposure concentration in the surrounding environment (Predicted Environmental Concentration, PEC), i.e. NOAEL / PEC or the estimated uptake in the exposed humans.

NOAEL is based on mammalian data that is often not humans but typically rats, mice and rabbits. Therefore, safety factors are introduced to cover differences extrapolating from other animals to humans. This is expressed either by attaching a fixed safety factor (SF) or by expressing the margin of safety (MOS) which represents the distance between the estimated concentration to the NOAEL. Typically MOS is preferred to be above 100.

The safety factor is interpreted as a margin of safety applied to a NOAEL to produce a value below which exposures are presumed to be without health risk. The safety factor is traditionally composed of a factor 10 for extrapolation between species (animal to human, interspecies variation), a factor 10 to protect the most sensitive individuals of the population (intraspecies variation) such as e.g. children. A third factor is applied depending on the data and may vary. For instance 10 is used if LOAEL (lowest observed adverse effect level)

is used instead of NOAEL or using subchronic data instead of chronic data. The total safety factor is a result from multiplication of the three factors.

The effect level divided with the safety factor is used to evaluate whether there is reason of concern (concern level) or a further refinement of methodology or data is necessary. Thus the assessment may be expressed on basis of concentration divided with the safety factor (such as e.g. ADI, TDI, RfD, RfC) or MOS.

In modern society is used many chemical products. It can be difficult for the single consumer to keep track of them all. The handling of the chemical substances is therefore regulated on basis of an extended chemical legislation. In connection with this project no values have been derived for chemical substances already evaluated by national or international experts in the field.

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

For the evaluation of the individual substances is used the threshold limit values mentioned above and explained below.

The threshold limit value (TLV) valid for the working environment (AT 2002) is generally not used as it is only valid for the working environment and does not cover the consumer at home. The TLV value is presented for information and comparison, if available.

Other limit values included in the health evaluation were:

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

C-value: Contribution value: The C-value is defined in Miljøstyrelsen (2002) as the total maximal allowed contribution to the air pollution from an enterprise to the environment outside the production site. If the C-value is used, it is used directly as the value is calculated from NOAEL levels using a safety factor.

RfC: Reference concentration. RfC is an inhalation reference concentration based on the assumption that a threshold limit value for certain toxic effects exists. The value is based on NOAEC from inhalation studies of subchronic or chronic character and includes safety factors. The value is given in mg/m³.

RfD: Reference dosis. RfD is an oral reference dosis based on the assumption that a threshold limit for certain toxic effects exists. The value is based on NOAEL from subchronic or chronic studies using oral administration and includes safety factors. The value is given in mg/kg body weight/day.

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

on chemical pollutants.

TCA: Tolerable Concentration in Air (inhalation exposure). Dutch value that in principle is comparable to RfC.

The effect level for each piece of slimy toy is based on evaluations of individual substances. The established Danish threshold limit values are used when they exist. When no Danish threshold limit values exist, foreign threshold limit values are used including their background, if available.

The indoor air quality depends on several factors (ventilation, temperature, etc.) and many sources. In this report, only the contribution from slimy toys is considered but it should be noted that other sources to the same chemical compound may exist in the consumer's resident (e.g. by smoking, cooking, volatiles from paint, lacquers, carpets, etc.).

The exposure of the consumer in the home is besides the concentration in the indoor air also dependent on the exposure duration. Because the exposure duration may vary considerably, a maximal exposure of 1 hours is assumed.

6.2.3 Exposure via inhalation

The exposure via inhalation may theoretically extend from the acquisition or purchase of the slimy toys, until it is no longer used (discarded). The substances that the consumer are exposed to during unwrapping and during the initial use period may approximately be assumed to be the substances observed in the "head-space" analyses.

The exposure via inhalation is expressed as the concentration of the chemical substance in the air in the breathing zone and expressed as an average concentration over a reference period, e.g. 1 hour or 1 day. For the consumer of slimy toys the exposure period may be extended from the time the slimy toy is unwrapped and used to considerably longer time, where the toy degasses or if more pieces of slimy toys are used and the duration for all emission products to be ventilated out of the room/home.

For estimation of the exposure via inhalation, the concentration in the air must be known, the inhalation rate and air volume (the breathing zone or the size of the room).

The inhalation rate for an average adult person is set to 20 m³/day corresponding to 0.83 m³/hour (standard in TGD 2003). However, because slimy toys appeal more to children than adults, it is decided to use scenarios for children. For a child several choices are available depending on age and level of activity. For the assessment is chosen a short term scenario with a child at moderate activity and the respiration rate 1.2 m³/time.

For the short-term inhalation scenario is used exposure in the breathing zone that in this context is set to 1 m³.

Even small children can be assumed to get into contact with the toy or be in the same room where the toy is used. Therefore, based on a reasonable "worst case" consideration, a long-term exposure scenario is selected using a respiration rate of 8.3 m³/day (child of 3 to 5 years of age, TGD 2003).

The concentration in closed rooms is assumed to be higher than in ventilated rooms. For the calculation of the concentration in the room it is assumed that the substance is emitted instantly to the entire room and is homogeneously dispersed. The size of the standard room is set to 8 m² and the height 2.5 meter, i.e. the volume of the room is 20 m³.

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

$$C_{inh} = \frac{Q_{prod} \times FC_{prod}}{V_{room}}$$

C_{inh}	Concentration in inhaled air	$\mu\text{g}/\text{m}^3$
Q_{prod}	Quantity of product used in the room	g
FC_{prod}	Weight fraction of the substance in the product	$\mu\text{g}/\text{g}$
V_{room}	Volume of the room	m^3

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

$$I_{inh} = \frac{F_{resp} \times C_{inh} \times IH_{air} \times T_{contact}}{BW} \times N_{event}$$

I_{inh}	Amount inhaled substance	$\mu\text{g}/\text{kg bw}/\text{d}$
F_{resp}	Inhalable or respirable fraction of the substance	set to 1 (i.e. 100%)
C_{inh}	Concentration in the air	$\mu\text{g}/\text{m}^3$
IH_{air}	Inhalation rate	m^3/time cf. above
$T_{contact}$	Duration of exposure	timer
N_{event}	Number of events	(per day)
BW	Body weight	kg Child: 10 kg

6.2.4 Dermal exposure

In a scenario for dermal exposure is assumed that the product is used by hand, which thereby is primarily exposed. However, slimy toys may also get in contact to other parts of the body and, thus, an actual exposure area may be difficult to establish. Therefore, it is chosen to use the release from the toy per time unit in the migration test as the average amount to which the consumer is exposed.

Before percutaneous exposure the chemical compound has to migrate from the toy to the skin. When the compound has reached the skin, the compound may be absorbed percutaneous to the blood stream and then distributed throughout the body. The uptake after contact may be from "free" chemical compounds released from the toy or from degradation products. The degradation of the compounds may take place in the toy, via bacteria or enzymes on the skin or in the gastrointestinal-tract after absorption.

As the chemical compounds are located on the exterior of the toy, or potentially can be released or migrate from the toy, an extraction solution simulating sweat has been used. The substances detected by the extraction are the substances that potentially may be absorbed via the skin by contact to the toy.

The exposure can be expressed in the equation (TGD 2003) which is modified to the used exposure scenario:

$$U_{derm} = \frac{Q_{prod} \times Fc_{migr} \times T_{contact} \times N_{event}}{BW}$$

where:

U_{derm}	Potential uptake of the compound	µg/kg bw/day
Q_{prod}	Amount of product	g
Fc_{migr}	Fraction of product used in the measurement of the concentration of chemical substance in the extract (amount migrated substance per unit weight of product)	µg/g
$T_{contact}$	Duration of contact at each exposure event	hours
N_{event}	Number of exposure events	per day
BW	Body weight	kg

As basis is assumed that a child plays with the slimy toy one or several times each day. The total dermal exposure duration is assumed to be maximum 1 hour/day. The child's body weight is set to 10 kg.

This means that the calculations are performed as released (migrated) substance during an average of 1 hour (based on an analysis extraction period of 4 hours) × exposure duration/day × fraction absorbed/kg body weight:

Thus dermal absorption = Weight of toy × µg substance released/hour × 1/4 (hours) × (% absorption/100%) × exposure duration (hour/day) / 10 (kg) = µg/kg body weight per day.

The contact time of 1 hour/day through a prolonged period is assumed to be exaggerated. However, if this results in no problems, then no concern is relevant at shorter exposure periods.

Absorption

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

Depending on the exposure and/or the compound's lipophilicity the dermal penetration is assumed to be insignificant for very lipophilic compounds with a log Kow more than 5 (OECD 1993). Also dermal penetration is considered very small for compounds with a log Kow less than -1 (i.e. very hydrophilic) and for compounds with a molecular weight above 700 (Vermeire *et al.* 1993). According to a Dutch model, the dermal absorption is estimated to 10% for compounds with a molecular weight above 500 g/mol and a log Kow <-1 or >4 (De Heer 1999). The latter values are also included in the TGD (2003).

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

$$A_{\text{derm}} = U_{\text{derm}} \times F_{\text{abs}}$$

where:

A_{derm}	Potential uptake of the chemical substance	mg/kg bw/day
U_{derm}	Potential dermal exposure	mg/kg bw/day
F_{abs}	Fraction of the substance absorbed via the skin	default: 1 (=100%)

The dermal absorption of metals is presumed very small. For zinc, the dermal absorption is 2% in liquid zinc compounds and in solids assumed 0.2% in the EU risk assessment (ECB 2004). For chromium low penetration rates of ^{51}Cr have been observed: 0.07% in 3 hours and 0.18% in 50 hours (Fairhurst and Minty 1989). Approximately the same relation is assumed in the scenarios for dermal absorption of metals but modified to 0.2% for all metals.

In the latest draft to the risk assessment of nickel, for nickel salts is used 2% as absorbed fraction by dermal contact (nickel sulphate, nickel chloride, nickel nitrate and nickel carbonate). For nickel metal is found a dermal absorption of 0.2% based on an *in vivo* study on humans (MST 2003).

6.2.5 Oral exposure

By oral exposure the absorption takes place after release (migration) of the compounds from the slimy toy and mixing with the saliva. Uptake is assumed to take place over the epithelium in the mouth cavity or in the gastrointestinal-tract.

As basis for the assessment of the oral intake is used the general equations described in relevant references (TGD 2003, OECD 1993, Bremmer and van Veen 2002).

The equations are then adjusted to an equation fit for the actual scenario with measurements of chemical substances migrated to artificial saliva. Surface area of the toys was not used as most were so small that the child with a little dexterity may get in contact with (by licking, sucking or chewing on) the total surface.

$$I_{\text{oral}} = \frac{Q_{\text{oral}} \times F_{\text{C}_{\text{migr}}} \times F_{\text{orl}} \times T_{\text{contact}} \times N_{\text{event}}}{BW}$$

where

I_{oral}	Intake of the compound	µg/kg bw/day
Q_{oral}	Amount of product	g
$F_{\text{C}_{\text{migr}}}$	Fraction of product used in the measurement of the concentration of chemical substance in the extract (amount migrated substance per unit weight of product)	µg/g
F_{orl}	Fraction absorbed (bioavailable part)	
T_{contact}	Time for contact each time	min.
N_{event}	Number of events per day	min/day
BW	Body weight	kg

As basis is assumed that a child plays with the slimy toy one or several times each day. The total oral exposure duration is assumed to be maximum 60 minutes or 1 hour/day. The child's body weight is set to 10 kg.

The analysis results represent the amount migrated to the saliva extracts after 4 hours of extraction. The amount is recalculated to release per hour. This means that the calculations are performed as released (migrated) substance (based on an analysis extraction period of 4 hours) × exposure duration/day × fraction absorbed/kg body weight:

Thus oral absorption = Weight of toy × µg substance released/hour × 1/4 (hours) × (% absorption/100%) × exposure duration (1 hour/day) / 10 (kg) = µg/kg body weight per day.

Oral intake is especially relevant for the product which as lipstick is directly aimed to put on the lips (TO-03, lip gloss). As a worst case all of the product may be taken up orally.

It is noted that oral intake also may take place by hand-to-mouth, i.e. hands or fingers, which have touched the product, and then are placed in the mouth. This may result in transference of substance from the fingers to the mouth. Especially for a sticky product like slimy toys such a contribution must be considered likely and not insignificant. As information in the reference literature (Bremmer and van Veen 2002, Green 2002, Kiss 2001) indicate that hand-to-mouth averages 3 to 10 minutes that part is considered included in the selected exposure period of 1 hour.

Absorption

After exposure to the mouth cavity the chemical substance has to pass the epithelium before actual absorption may take place. Only few data for oral absorption of the selected substances have been found. The oral uptake across the epithelium (oral absorption) is therefore estimated for many of the substances.

The same methodology as given for dermal absorption (cf. above) is used.

By standard evaluation or where no information is available, a typical oral absorption of 100% (TGD 2003) is used.

6.2.6 Total exposure

If the consumer is exposed to the same substance from the same product via different exposure routes, the total uptake can be added.

No assessment of the single slimy toy versus another has been performed. Partly because it was not the purpose to evaluate single slimy toys, and partly because the number was too small. The purpose of the survey was to evaluate which substances and the amount of substances slimy toys released. Finally, the detected concentrations are so low that by the short exposure duration such an exercise would be of limited value by normal consumer patterns.

However, it should be noted that the consumer (child) may handle more than one slimy toy simultaneously or at intervals, thus increasing the exposure to one or more chemical substances correspondingly. Other sources of the same chemicals may also be present in the surroundings of the play activity. This may also contribute to the total exposure.

6.3 Evaluation of individual substances

For the evaluation of individual substances the below mentioned substances have been selected in co-operation with the Danish Environmental Protection Agency.

Organic substances

2-Butanone
2-Butoxyethanol
3-Carene
Cyclohexanone
Diethylglycol dibenzoate
Ethylbenzene
2-Hexanone
D-Limonene
2-Phenoxyethanol
2-Phenylmethylenoethanol (hexylcinnamaldehyde)
alfa-Pinene
1,2-Propanediol
2-Propenoic acid 2-methyl-methylester (methyl methacrylate)
N-Propylbenzamide + N-acetylbenzamide
Styrene
Toluene
Xylene

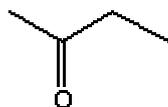
Inorganic substances

Boron
Nickel

6.3.1 2-Butanone

Identification

Name	2-Butanone
CAS no.	78-93-3
EINECS no.	201-159-0
Molecular formula	C ₄ H ₈ O
Molecular structure	



Molecular weight	72.12 g/mol
Synonyms	Butanone (EINECS name) Ethylmethylketone Methylethylketone MEK

The melting point is -86.6°C. The boiling point is 79.5°C (Budavari 1996). The vapour pressure is 12077 Pa at 25°C (90.6 mmHg). The water solubility is 223 g/l at 25°C (EPI). The partition coefficient log K_{ow} is experimentally determined to 0.29 (Hansch *et al.* 1995).

Use

2-Butanone is used in a number of industrial applications. The primary use of 2-butanone, accounting for approximately 63 percent of all known

consumption, is as a solvent in protective coatings. 2-Butanone is also used as a solvent in adhesives; printing inks; paint removers; in the production of magnetic tapes; and in dewaxing lubricating oil.

Classification

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

F;R11	Highly flammable
Xi;R36	Irritating to eyes
R66	Repeated exposure may cause skin dryness or cracking
R67	Vapours may cause drowsiness and dizziness.

Effects on health

Of data on acute effects are found:

Acute oral, rat	LD ₅₀	3400 mg/kg bw	IUCLID 2000
Acute oral, mouse	LD ₅₀	3140 mg/kg bw	IPCS 1993
Acute dermal, rat	LD ₅₀	6400-8000 mg/kg bw	IUCLID 2000
Acute dermal, rabbit	LD ₅₀	6480 mg/kg bw	IUCLID 2000
Acute inhalation, rat	LC ₅₀ (4 h)	34500 mg/m ³	IPCS 1993
Acute inhalation, rat	LC ₅₀ (8 h)	23600 mg/m ³	IPCS 1993
Acute inhalation, rat	LC ₅₀ (90 d)	>5000 ppm * (14750 mg/m ³)	IUCLID 2000

*: 1 ppm = 2.95 mg/m³

The substance is irritating to the eyes and mildly to moderately irritating to the skin in rabbits (NCM 1999).

Skin irritation studies in rabbit showed a moderately irritation but not enough for a classification. However, the substance was highly irritating in a Draize eye irritating test on rabbits, where the substance had a maximum Draize score at between 1 hour and up to 14 days of exposure. The substance was not sensitising in a guinea pig maximisation test (IUCLID 2000).

In humans several case reports and occupational studies indicate neurological effects such as polyneuropathy, after prolonged exposure to 2-butanone vapours. This is supported by the acute exposure studies (NCM 1999).

In a repeated dose toxicity test on rats exposed to 0, 1250, 2500 or 5000 ppm 2-butanone via inhalation (vapours) 6 hours/day, 5 days/week for 90 days. After 90 days exposure via inhalation, a depression of mean body weight gain in the 5000 ppm exposure group was observed. The group also had a slight but significant increase in liver weight. LOAEL was 5000 ppm and NOAEL 2500 ppm (equivalent to 7500 mg/m³) (IUCLID).

In a mouse developmental study with exposure via inhalation (Schwetz *et al.* 1991) based on development of skeletal parts after exposure by inhalation for 7 hours/day on days 6-15 of gestation was observed a lowest effect concentration, LEC, of 5202 mg/m³. The study was used for the calculation of RfC (cf. below).

In a multigeneration reproductive developmental study, where rats were given 2-butanol in drinking water, was observed based on decreased pup body weight a NOAEL of 594 mg/kg bw/day (0.3% 2-butanol solution) and a LOAEL of 1771 mg/kg bw/day (1% 2-butanol solution) (Cox *et al.* 1975).

Recalculating from the test substance 2-butanol to 2-butanone the 21-day lower 95% confidence interval on the effective dose associated with 5% decrease in body weight (LED_{05}) was 639 mg/kg bw/day. The study was used to calculate the oral RfD, cf. below.

Cox *et al.* (1975) conducted a multigeneration reproductive and developmental toxicity study of 2-butanol. The identification of the critical effect for 2-butanone is based on its metabolic precursor, 2-butanol. Other available pharmacokinetic and toxicological data support the use of 2-butanol as an appropriate surrogate for 2-butanone. The rationale for using 2-butanol is that orally administered 2-butanol almost completely (96%) is converted to 2-butanone and its metabolites within 16 hours (IRIS 2003).

No studies examining the subchronic or chronic effects of oral exposure to 2-butanone in humans or experimental animals were identified.

Threshold limit values

The threshold limit value for the working environment is 50 ppm equivalent to 145 mg/m³ with skin notation, i.e. the substance can be absorbed through the skin (AT 2002).

The C-value is 1 mg/m³ (B-værdilisten, Miljøstyrelsen 2002).

Inhalation RfC: 5 mg/m³ cf. above.

In a developmental study on mice (Schwetz *et al.* 1991) was observed a lowest effect concentration LEC: 5202 mg/m³, which was recalculated / adjusted to $LEC_{(ADI)} = 5202 \text{ mg/m}^3 \times 7 \text{ h}/24 \text{ h} = 1517 \text{ mg/m}^3$ or adjusted to human equivalent concentration, LEC(HEC): 1517 mg/m³. Using a safety factor of 300 (3 for interspecies, 10 for intraspecies and 10 for data deficiencies) derived an oral RfC 5 mg/m³ (IRIS 2003).

Oral RfD: 0.6 mg/kg bw/day

In a multigeneration reproductive developmental rat drinking water study was observed a NOAEL of 594 mg/kg/day (0.3% 2-butanol solution) (Cox *et al.* 1975). Recalculating from the test substance 2-butanol to 2-butanone the lower 95% confidence interval associated with 5% decrease in body weight LED_{05} was 639 mg/kg bw/day. Using a safety factor of 1000 (10 inter, 10 intraspecies and 10 for data deficiencies) derived at a chronic oral RfD 0.6 mg/kg bw/day (IRIS 2004).

Absorption

Absorption studies in humans and animals have demonstrated that 2-butanone can be absorbed via the lungs, the skin, and the gastrointestinal system. Pulmonary absorption values range from 41.1% to 55.8% (IPCS 1993). The relative uptake through the lungs by humans was about 53% through a 4 hour exposure at 200 ppm (HSDB, WHO 1993).

Oral studies in rats have demonstrated that the peak blood level of 2-butanone (0.95 mg/ml blood) was reached in 4 hours following oral administration of the chemical in water (1690 mg/kg) (US-EPA 1994).

2-Butanone can also be absorbed through intact human skin. A steady state concentration in expired air was reached in 2-3 hours following exposure of the palmar surface of the forearm of volunteers (Krasavage *et al.* 1982).

Absorption is more rapid through moist skin than through dry skin, and the rate of percutaneous absorption has been estimated to range from 5 to 10 micrograms/cm²/min (IPCS 1993).

Assessment

The assessment of inhalation is based on short term exposure with 1 m³ air in the breathing zone and exposure for 1 hour, and a long-term exposure scenario using exposure in a 20 m³ room for 1 hour per day. Both scenarios using exposure to a child of 10 kg body weight (bw). The absorption by inhalation is set to 53%.

Calculation example

(The calculation example is only included for the first substance but the same calculation procedure is used for the remaining substances):

Evaporation of 2-butanone was measured to 2.3% corresponding to 184 ng from the toy (184 ng in 1 L rilsan bag corresponding to 0.079 mg/m³). The exposure in the breathing zone will be smaller corresponding to a dilution on 1000 compared to the concentration in the rilsan bag. The concentration in the breathing zone is 0.079 µg/m³.

Short term exposure will be: 0.079 µg/m³ × 0.53 (absorption) × IH short-term 1.2 m³/h or 8.3 m³/day / 10 kg / 20 m³), i.e.:

Short-term exposure: (0.079/1000) × 0.53 × 1.2 / 10 / 1

Long-term exposure: (0.079/1000) × 0.53 × 8.3 / 10 / 20

Table 6.1. Uptake via inhalation of 2-butanone

ID no.	Lab. no.	Content %	Total, ng	Breathing zone concentration, µg/m ³ *	Acute uptake via inhalation, µg/kg/day	Chronic uptake via inhalation, µg/kg/day
TI-01, exterior	30396-16A	2.3	184	0.079	0.0050	0.0017
TI-01, liquid	30396-16B	9.0	114.3	0.098	0.0062	0.0022

*: Note that the air concentration in the room used for the chronic exposure estimation is 5% (1/20) of the concentration in the tabulated breathing zone

2-Butanone was only found to evaporate from 1 slimy toy but from both the exterior part and the interior liquid.

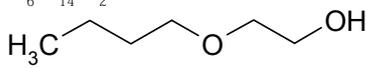
2-Butanone was not detected in saliva or perspiration (sweat) extracts.

Conclusion

The concentration of 2-butanone was far below the RfC value of 5 mg/m³ and the C-value of 1 mg/m³. The RfD value of 0.6 mg/kg bw/day was not exceeded either. The margin of safety (MOS) is above (594/2.2×10⁻⁶ =) 2.7×10⁸. It is therefore concluded that the exposure to 2-butanone does not present any health risk to the consumer.

6.3.2 2-Butoxyethanol

Identification

Name	2-Butoxyethanol
CAS no.	111-76-2
EINECS no.	203-905-0
Molecular formula	C ₆ H ₁₄ O ₂
Molecular structure	
Molecular weight	118.20 g/mol
Synonyms	ethylene glycol n-butyl ether EGBE Butylglycol

The melting point is -74.8°C . The boiling point is 168.4°C (DOW 1990). The vapour pressure is 117 Pa at 25°C (0.88 mmHg) (DOW 1990). The water solubility is 1 kg/l at 25°C (miscible, DOW 1990). The partition coefficient log Kow is experimentally determined to 0.83 (Hansch *et al.* 1995).

Use

2-Butoxyethanol is used as a solvent in surface coatings and in vinyl and acrylic paint (CICAD 1998). Further is mentioned the use as solvent in printing inks and colorants in the EU risk assessment report, draft 2004 (ECB 2004).

Classification

2-Butoxyethanol is classified in the List of dangerous substances (Miljøministeriet 2002):

Xn;R20/21/22	Harmful. Harmful by inhalation, in contact with skin and if swallowed
Xi;R36/38	Irritant. Irritating to eyes and skin

Effects on health

2-Butoxyethanol is moderately acute toxic, irritating to eyes and skin (but not a skin sensitizer). Eye irritation examinations showed that 30 and 70% concentrations of the substances were irritating to the eyes with increasing irritation with corresponding increasing time of exposure. The skin irritation was mild at 4 hours of exposure of rabbit skin, but the irritation increased with increasing time of exposure (CICAD 1998).

The effects have mostly been registered as a haemolytic activity of butoxyethanol. The effect was dependent on age with older rats as the most sensitive (CICAD 1998).

Acute toxicity:

Acute oral, rat	LD ₅₀	1480 mg/kg	Budavari 1996
Acute oral, mouse	LD ₅₀	1400 mg/kg	CICAD 1998
Acute oral, rabbit	LD ₅₀	320 mg/kg	CICAD 1998
Acute dermal, guinea pig	LD ₅₀	208 mg/kg	ECB 2004
Acute dermal, rabbit	LD ₅₀ (8 h)	100 mg/kg	ECB 2004
Acute inhalation, rat	LC ₅₀ (4 h)	2380 mg/m ³	ECB 2004

In a subchronic 90 days inhalation study, rats were exposed to 2-butoxyethanol at concentrations of 0, 5, 25, or 77 ppm for 6 hours/day, 5 days/week

for 13 weeks. Based on haematotoxic effects, the NOAEL and LOAEL were 25 ppm (121 mg/m³) and 77 ppm (372 mg/m³), respectively (Dodd *et al.* 1983).

In a study on developmental effects, pregnant rats were exposed to 2-butoxyethanol at 0, 25, 50, 100 or 200 ppm (35 per group) for 6 hours/day on days 6-15 of gestation. Based on haematotoxic effects the NOAEL and LOAEL were 50 ppm (242 mg/m³) and 100 ppm (483 mg/m³), respectively (Tyl *et al.* 1984).

In a 13 weeks study with rats groups of 10 of each sex were exposed through the drinking water. Based on the water consumption, the male rats were exposed to 0, 69, 129, 281, 367 or 452 mg/kg/day and female rats to 0, 82, 151, 304, 363 or 470 mg/kg/day. Based on effects of the blood parameter and liver, which were observed at even the lowest concentration, LOAEL was 69 mg/kg/d for males and 82 mg/kg/d for females. When water consumption and body weight from the last week of the exposure is used, LOAEL is converted into 55 mg/kg/d for males and 59 mg/kg/d for females. NOAEL could not be determined in the examination (NTP 1993, IRIS 1999). The result is still used by US-EPA to derive a RfD value of 0.5 mg/kg bw/day (IRIS 2004).

2-Butoxyethanol has been evaluated as potential human carcinogen, Group C (IRIS 2003).

Threshold limit values

The threshold limit value for the working environment is 20 ppm corresponding to 98 mg/m³ with skin notation, i.e. the substance may penetrate the skin (AT 2002).

The C-value is 0.04 mg/m³ (B-værdivejledningen, Miljøstyrelsen 2002).

Inhalation RfC value is 13 mg/m³.

The value is based on sub-chronic rat inhalation study (Tyl *et al.* 1984, cf. above). The value is based on NOAEL 242 mg/m³ and calculated with a safety factor 10, 6/24 in order to convert 6 hours' exposure to 24 hours per day, a conversion from rat to human (inhalation rate for rat 0.16 m³/d and for human 22 m³/d, the body weight of rat 0.215 kg and for human 64 kg) (CICAD 1998). The RfC calculated using the mentioned variables is then:
$$\text{RfC} = (242/10) \times (6/24) \times [(0.16/0.215)/(22/64)] = 13.1 \text{ mg/m}^3$$

Oral RfD value is 0.5 mg/kg bw/day.

The value is based on a 13-week of subchronic study where haematological effects were found as the most sensitive endpoint with a LOAEL of 55 to 59 mg/kg/day for rats (NTP 1993, cf. above). US-EPA converted the value into 5.1 mg/kg bw/day for humans and used a safety factor of 10 for intraspecies sensitivity (US-EPA 1999).

Absorption

2-Butoxyethanol is easily absorbed after inhalation, or by oral or dermal exposure (CICAD1998). Consequently, an absorption of 100% has been used.

In the ECB (2004), Risk Assessment Report draft is used 61% for absorption via inhalation and 30% dermal absorption.

Assessment

The evaluation of inhalation is based on short term exposure with 1 m³ air in the breathing zone and exposure for 1 hour, and a long-term exposure scenario using exposure in a 20 m³ room for 1 hour per day. Both scenarios using exposure to a child of 10 kg body weight (bw). The absorption by inhalation is set to 100%.

Table 6.2. Uptake via inhalation of 2-butoxyethanol

ID no.	Lab. no.	Content %	Total, ng	Breathing zone concentration, µg/m ³ *	Acute uptake via inhalation, µg/kg/day	Chronic uptake via inhalation, µg/kg/day
DK-02	30396-2	0.6	39	0.017	0.0020	0.00071
DK-03	30396-3	0.1	28.3	0.012	0.0014	0.00050
F-01	30396-8	1.8	558	0.240	0.0288	0.0100
TO-03A	30396-11 gel	0.7	39.9	0.017	0.0020	0.00071
G-01	30396-12	0.6	39.6	0.017	0.0020	0.0007
R-01	30396-17A	0.8	371.2	0.160	0.0192	0.0066
	30396-17B	66	118.8	0.102	0.0122	0.0042

*: Note that the air concentration in the room used for the chronic exposure estimation is 5% (1/20) of the concentration in the tabulated breathing zone

2-Butoxyethanol was detected released from 6 slimy toys. The estimated concentrations are more than 1000 times below the RfC value and the estimated uptakes significantly less than the RfD value of 500 µg/kg bw/day.

2- Butoxyethanol was not detected in saliva or sweat extracts.

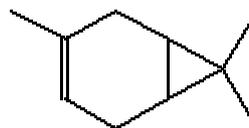
Conclusion

From the tables above can be derived that none of the amounts taken up by the use of slimy toys results in a dosage above the RfD value. Neither the inhalation reference value (RfC) of 13.5 mg/kg/day nor the C-value of 40 µg/m³ have been exceeded, as the concentration in the breathing zone was max. 0.24 µg/m³ and the room concentration was max. 0.24/20 = 0.012 µg/m³. The margin of safety MOS is more than (500/0.01=) 50000. Therefore, this substance is evaluated not to provide any health risk.

6.3.3 3-Carene

Identification

Name	3-Carene
CAS no.	13466-78-9
EINECS no.	236-719-3
Molecular formula	C ₁₀ H ₁₆
Molecular structure	



Molecular weight	136.23 g/mol
Synonyms	3,7,7-trimethyl bicyclohep-3-ene 3,7,7-trimethylbicyclo[4.1.0]hept-3-ene <i>delta</i> -3-carene

The melting point is <25°C. The boiling point is 170°C. The vapour pressure is estimated to 280 Pa at 25°C (2.09 mmHg). The water solubility is esti-

mated to 4.6 mg/l at 25°C (EPI 2000). The partition coefficient log Kow is measured to 4.38 (EPI).

Use

3-Carene belongs to the chemical group terpenes. Terpenes exist in ethereal oils. Terpenes may arise from the use of vegetable oils and resins in products and as solvent in colorants.

Classification

3-Carene is not classified. 3-Carene belongs to the group of terpenes. Terpenes or vegetable turpentine (CAS no. 9006-64-2) is classified in the List of dangerous substances (Miljøministeriet 2002):

R10	Flammable.
Xn;R20/21/22-65	Harmful by inhalation, in contact with skin and if swallowed Harmful: may cause damage to the lungs if swallowed
Xi;R36/38	Irritating to eyes and skin
R43	May cause sensitization by skin contact
N;R51/53	Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

Effects on health

Only few data have been available for 3-carene. Most of the available data were based on acute effects.

Acute toxicity:
Acute oral, rat LD₅₀ 4800 mg/kg Söderkvist 1987

Exposure of pigs and rats to 3-carene at 5000 mg/m³ for 10-20 minutes induced a marked bronchi-constriction in isolated, perfused and ventilated lungs (Falk-Filipsson 1995).

An oxidation product of 3-carene (probably a hydroperoxide) is thought to be the causal factor of the observed irritative and sensitising effects. 3-Carene induces contact allergy in pigs and sensitise guinea pigs. In case studies 3-carene has been found to be the specific sensitiser in the terpenes (Söderkvist 1987, Falk-Filipsson 1995).

In humans, a concentration of 450 mg/m³ 3-carene caused discomfort in the eyes experimentally. No effects were found at 225 mg/m³ (Falk-Filipsson 1995).

Because the substance is a terpene, the evaluation is based on a general knowledge on terpenes.

The terpenes are generally irritants to the mucous membranes. Turpentine from coniferous trees are skin sensitisers. The sensitization, however, is not confirmed for the individual terpenes with the exception of 3-carene (ASS 2000).

Monoterpenes, which include among others D-limonene, pinenes and carenes, are described under the common name "turpentine" with CAS no. 8006-64-2. Turpentine consists chemically of 58 to 65% *alpha*-pinene and *beta*-pinene and other isomere terpenes. Turpentine from wood extracted from

waste wood or sawdust contains 80% *alpha*-pinene, 15% monocyclic terpenes, 1.5% terpene-alcohols and other terpenes (Bingham *et al.* 2001).

Already in 1939 was demonstrated that Swedish painters more often suffered dermatitis from turpentine compared to French painters. The difference could be traced to the turpentine's content of 3-carene that was considerably higher in Swedish than in French manufactured turpentine. An oxidation product of 3-carene was later identified as the probable cause to these effects (Söderkvist 1978).

Effects on health

Vapours are irritating by contact to eyes and respiratory tracts. If vapours are inhaled, they may cause headache, vomiting, dizziness and faintness. The liquid irritates the skin, and if ingested may cause irritation to the total digestion system and possibility of kidney lesions. If the liquid substance reaches the lungs, it may cause severe pneumonia (Prager 1996).

The lethal dose of turpentine may by ingestion be as low as 110 g. However, survival after ingestion of 120 g has been observed. As little as 15 g has been shown fatal to a child (Bingham *et al.* 2001).

In an experiment with male and female volunteers, the following observations have been reported. Persons with an average age of 35 years were exposed to 0 or 450 mg/m³ of a mixture consisting of 10 parts *alpha*-pinene, 1 part *beta*-pinene and 5 parts 3-carene (synthetic turpentine) for 12 hours 4 times over a two-week period. Acute damages to the lungs were observed. Male volunteers exposed for two hours with 450 mg/m³ during easy workout experienced their respiratory passages were influenced by the exposure, and they had breathing difficulties after the termination of the exposure (Bingham *et al.* 2001).

Threshold limit values

The threshold limit value for the working environment is 25 ppm equivalent to 140 mg/m³, corresponding to high-boiling aromatic hydrocarbons (terpenes, turpentine) (AT 2002).

LCI (Lowest Concentration of Interest) is 0.25 mg/m³ for most terpenes (Larsen *et al.*, 1999).

The C-value for turpentine is 1 mg/m³ (C-value guidance, Miljøstyrelsen 2002).

Absorption

No information has been found on uptake of 3-carene but as turpentine and *alpha*- and *beta*-pinene are easily absorbed through lungs, skin and gastrointestinal canal (Clayton and Clayton 1983) the absorption for 3-carene is set to 100%.

Assessment

The evaluation of inhalation is based on short term exposure with 1 m³ air in the breathing zone and exposure for 1 hour, and a long-term exposure scenario using exposure in a 20 m³ room for 1 hour per day. Both scenarios using exposure to a child of 10 kg body weight (bw). The absorption by inhalation is set to 100%.

Table 6.3. Uptake via inhalation of 3-carene

ID no.	Lab. no.	Content, %	Total, ng	Breathing zone concentration, $\mu\text{g}/\text{m}^3$	Acute uptake via inhalation, $\mu\text{g}/\text{kg}/\text{day}$	Chronic uptake via inhalation, $\mu\text{g}/\text{kg}/\text{day}$
DK-02	30396-2	1.4	91	0.039	0.00468	0.0016
DK-03	30396-3	0.4	113.2	0.049	0.00588	0.0020
BR-01	30396-7A	0.2	55.4	0.024	0.00288	0.0010
F-01	30396-8	0.1	31	0.013	0.00156	0.00054
TO-03	30396-11	2.3	36.8	0.016	0.00192	0.00066
G-01	30396-12	0.3	19.8	0.009	0.00108	0.00037
TI-01	30396-16A	0.6	48	0.021	0.00252	0.00087

Carene was detected in 7 samples of slimy toys analysed for volatile organic compounds (headspace) at the concentrations between 9 and $49 \mu\text{g}/\text{m}^3$. The calculated uptake via inhalation is summarised in the table above.

Carene was not detected in the sweat or saliva extractions.

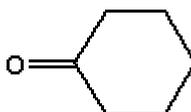
Conclusion

By comparison of the maximum measured concentration of $49 \mu\text{g}/\text{m}^3$ with the found LCI value of $250 \mu\text{g}/\text{m}^3$ is observed a factor of 5 in difference. Using NOAEL $225 \text{ mg}/\text{m}^3$ the margin of safety (MOS) is $225/2 \times 10^{-6} = 1,1 \times 10^8$. This means that the amount released does not imply any health risk.

6.3.4 Cyclohexanone

Identification

Name	Cyclohexanone
CAS no.	108-94-1
EINECS no.	203-631-1
Molecular formula	$\text{C}_6\text{H}_{10}\text{O}$
Molecular structure	



Molecular weight	98.15 g/mol
------------------	-------------

The melting point is -31°C . The boiling point is 155°C (Budavari 1996). The vapour pressure is 577 Pa at 25°C (4.3 mmHg) (Daubert and Danner 1985). The water solubility is 25 g/l at 25°C (Yalkowsky and Dannenfeler 1992). The partition coefficient log Kow is measured to 0.81 (Hansch *et al.* 1995).

Use

Cyclohexanone is used in the chemical industry for organic synthesis, particularly in the production of adipic acid and caprolactam (ca. 95%), polyvinyl chloride and its copolymers, and methacrylate ester polymers.

Classification

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

R10	Flammable
Xn;R20	Harmful. Harmful by inhalation

Effects on health

Acute toxicity:

Acute oral, rat	LD ₅₀	1296 mg/kg bw	SIDS 1996
Acute oral, mouse	LD ₅₀	1400 mg/kg bw	SIDS 1996
Acute inhalation, rat	LC ₅₀ (4 h)	32080 mg/m ³ (8000 ppm)	SIDS 1996
Acute inhalation, mouse	LD ₅₀ (4 h)	1235 mg/m ³ (308 ppm)	SIDS 1996
Acute dermal, rabbit	LD ₅₀	948 mg/kg bw	SIDS 1996

For humans was observed that the threshold for irritation to the nasal mucous membranes was 0.28 mg/l of air (280 mg/m³ or about 70 ppm). The value was seconded by irritation of eye, nasal, and throat at 0.362 mg/l of air (362 mg/m³ or about 90 ppm). A second exposure 2 weeks after the initial series indicated an increase in the sensory irritation threshold. In this series, the only response recovered was throat irritation at 0.547 mg/l of air (547 mg/m³ or about 136 ppm) (SIDS 1996).

Humans exposed for 3-5 minutes found 50 and 75 ppm (200-301 mg/m³ air) irritating to the eyes, nose and throat. A concentration of 25 ppm was unobjectionable (Nelson *et al.* 1994).

Cyclohexanone exhibits low to slight acute toxicity by the oral and inhalation routes and is moderately toxic by the dermal route. Cyclohexanone is an eye and skin irritant; but does not induce skin sensitisation.

Upon repeated administration to rats of cyclohexanone in drinking water, the NOAEL was 4700 ppm after 25 weeks, and the LOAEL was 3300 ppm after 2 years. Effects at higher concentrations were primarily body weight decreases.

The NOAEL in published repeated dose inhalation studies was 100-900 ppm. Those values were based on either gray mottling of the lungs or ocular irritation and degenerative changes in the liver and kidney at higher concentrations. However, the NOAEL in those studies was not confirmed in later and better inhalation studies, where for reproductive and developmental effects NOAEL values of 650-1000 ppm were observed. In a two-generation reproduction study, decreased fertility was observed in rats exposed via inhalation at 1400 ppm but not at 500 ppm. The effect was found to be reversible following a post-exposure recovery period. (IRIS 2004).

In a chronic rat oral study, where rats in groups of 52 animals per dose were exposed to cyclohexanone in drinking water at 3300, 6500, 13000 and 25000 ppm. Based on mortality and decrease in body weight a LOAEL of 6500 ppm corresponding to 910 mg/kg bw/day was found. NOAEL was 3300 ppm corresponding to 462 mg/kg bw/day (Lijinski and Kovatch 1986).

Threshold limit values

The threshold limit value (TLV) is 10 ppm equivalent to 40 mg/m³ with skin notation (H), i.e. the substance may penetrate the skin (AT 2002)

TCA (tolerable concentration in air) is 136 µg/m³ (Baars *et al.* 2001).

The C-value is 0.1 mg/m³ (B-værdivejledningen, Miljøstyrelsen 2002)

The oral RfD value is 5 mg/kg bw/day. In a chronic oral rat study was found a NOAEL of 462 mg/kg bw/day (cf. Lijinski and Kovatch 1986 above). Applying a safety factor of 100 (10 for inter- and 10 for intraspecies extrapolation) derived an oral RfD value of 5 mg/kg bw/day.

TDI (tolerable daily intake) value is 4.6 mg/kg bw/day (Baars *et al.* 2001).

Assessment

The evaluation of inhalation is based on short term exposure with 1 m³ air in the breathing zone and exposure for 1 hour, and a long-term exposure scenario using exposure in a 20 m³ room for 1 hour per day. Both scenarios using exposure to a child of 10 kg body weight (bw). The absorption by inhalation is set to 100%.

Table 6.4 Uptake via inhalation of cycl ohexanone

ID no.	Lab. no.	Content %	Total, ng	Breathing zone concentration, µg/m ³	Acute uptake via inhalation, µg/kg/day	Chronic uptake via inhalation, µg/kg/day
DK-01	30396-1	0.2	92	0.040	0.0048	0.0017
DK-02	30396-2	2.8	182	0.078	0.0093	0.0032
DK-03	30396-3	0.4	113.2	0.049	0.0059	0.0020
K-01, exterior	30396-5A	2.9	321.9	0.139	0.0167	0.0058
K-01, gel	30396-5B	24	139.2	0.120	0.0144	0.0050
F-01, exterior	30396-8	0.4	124	0.053	0.0064	0.0022
TO-01	30396-9	63	10773	4.637	0.5564	0.1924
TO-02	30396-10	30	1440	0.620	0.0744	0.0257
TO-03	30396-11 lip	2.3	36.8	0.016	0.0019	0.00066
TO-03	30396-11 gel	3.3	188.1	0.081	0.0097	0.0034
G-01	30396-12	3.9	257.4	0.111	0.0133	0.0046
K-03	30396-13	2.5	42.5	0.018	0.0022	0.00075
TI-01	30396-16B	1	12.7	0.011	0.0013	0.00046
R-01	30396-17	6	10.8	0.009	0.0011	0.00037

The TDI value of 4.6 mg/kg bw/day was not exceeded. A factor of >8000 to the highest estimated concentration in the breathing zone (1 m³) at acute exposure and a factor of >24000 to the highest estimated concentration in the 20 m³ room at chronic exposure was observed.

Cyclohexanone was detected in the sweat extractions from 4 slimy toys. The uptake is calculated below.

Table 6.5 Uptake of cycl ohexanone by dermal exposure

ID no.	Lab.no.	Weight, g	Measured migration, µg/g	Total migration, µg	Dermal uptake, µg/kg bw/day
DK-03, exterior	30396-3	8.2	1.0	8.22	0.21
TO-01, exterior	30396-9	14.7	430	6311.54	157.8
TO-02, exterior	30396-10	9.4	6.9	64.78	1.62
G-01, exterior	30396-12	102.7	0.5	51.33	1.28

The TDI value was not exceeded: the difference was approx. a factor of 30 to the TDI value of 4.6 mg/kg bw/day and the RfD value of 5 mg/kg bw/day. Using the NOAEL value of 462 mg/kg bw/day the margin of safety (MOS) is >2900.

Cyclohexanone was detected in the saliva extractions from 3 slimy toys. The calculated uptake by oral exposure is summarised in the table below.

Table 6.6 Uptake of cyclohexanone by oral exposure

ID no.	Lab.no.	Weight, g	Measured migration, µg/g	Total migration, µg	Oral uptake, µg/kg bw/day
DK-03, exterior	30396-3	8.2	0.6	4.93	0.12
TO-01, exterior	30396-9	14.7	160	2348.5	58.71
TO-02, exterior	30396-10	9.4	7.6	71.36	1.78
G-01, exterior	30396-12	102.7	<0.05	<5.1	<0.1

The TDI value was not exceeded. The difference was approx. 80 to the TDI value of 4.6 and the RfD value of 5 mg/kg bw/day.

Using the NOAEL value of 462 mg/kg bw/day the margin of safety (MOS) is >7800.

Conclusion

The maximum total uptake of cyclohexanone was from toy TO-01 at 216 µg/kg bw/day (cf. table below). This uptake was below the TDI value of 4.6 mg/kg bw/day.

Table 6.7 Total uptake of cyclohexanone by exposure to slimy toys

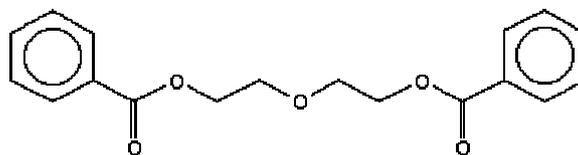
ID no.	Lab. no.	Uptake via inhalation, µg/kg/day	Dermal uptake, µg/kg bw/day	Oral uptake, µg/kg w/day	Total uptake, µg/kg w/day
DK-01	30396-1	0.0017			0.0017
DK-02	30396-2	0.0032			0.0032
DK-03	30396-3	0.0020	0.21	0.12	0.332
K-01	30396-5A	0.0058			0.0058
	30396-5B	0.0050			0.0050
F-01	30396-8	0.0022			0.0022
TO-01	30396-9	0.1924	157.8	58.71	216.70
TO-02	30396-10	0.0257	1.62	1.78	3.43
TO-03A	30396-11 lip	0.00066			0.00066
TO-03B	30396-11 gel	0.0034			0.0034
G-01	30396-12	0.0046	1.28	<0.1	1.28
K-03	30396-13	0.00075			0.00075
TI-01	30396-16B	0.00046			0.00046
R-01	30396-17	0.00037			0.00037

The total uptake by the three exposure routes is below the TDI value of 4.6 mg/kg bw/day. Besides, the total margin of safety is (MOS: $462/0.217 =$) > 2000. The release of cyclohexanone is therefore not considered to pose a health problem.

6.3.5 Diethylglycol dibenzoate

Identification

Name	Diethylglycol dibenzoate
IUPAC name	Oxydiethylene dibenzoate (EINECS name)
CAS no.	120-55-8
EINECS no.	204-407-6
Molecular formula	C ₁₈ H ₁₈ O ₅
Molecular structure	



Molecular weight	314.34 g/mol
Synonyms	2,2'-oxybis-ethanol dibenzoate (CA name) Diethylene glycol dibenzoate

The melting point is 28°C. The boiling point is 225°C (Budavari 1996). The vapour pressure is 573 Pa at 25°C (4.3 mmHg) (Daubert and Danner 1985). (1.7x10⁻⁵ Pa, Velsicol 2001). The water solubility is 38.3 mg/l at 30°C (Velsicol 2001). The partition coefficient log K_{ow} is measured to 3.2 (Velsicol, OPPT 2001).

Use

Diethylglycol dibenzoate is used as plastisiser in polymers and may be recovered in vinyl floors, adhesives and sealants. Diethylglycol dibenzoate is mentioned in the INCI list with a function as emollient.

Classification

Diethylglycol dibenzoate is not classified.

Effects on health

The acute toxicity is low:

Acute oral, rat	LD ₅₀	Male: 4800 mg/kg bw, Female: 3500 mg/kg bw, combined: 4200 mg/kg bw	OPPT 2001
Acute dermal, rat	LD ₅₀	>2000 mg/kg bw	OPPT 2001

In a repeated dose toxicity study, where diethylglycol dibenzoate was dietary administered for 13 weeks at the concentration 0, 250, 1000, 1700 or 2500 mg/kg/day, was observed a NOAEL 1000 mg/kg bw/day (OPPT 2001).

In a study on developmental toxicity to rat foetuses the test substance was given as oral (gavage) administration at 0, 250, 500 and 1000 mg/kg/day. The exposure period was days 6-19 of gestation inclusively. Maternal toxicity resulted in a NOAEL 1000 mg/kg/day. Prenatal development showed a NOAEL 500 mg/kg/day. Foetal growth and developmental had a NOAEL of 250 mg/kg/day (OPPT 2001).

In a study on reproductive toxicity for two-generations, rats were exposed for 38 weeks by dietary administration at 0, 1000, 3300 or 10000 ppm. NOAEL for the developing offspring is considered to be 300 ppm. NOEL for reproductive parameters is considered to be 10000 ppm (OPPT 2001).

In a skin sensitisation test on guinea pig, no evidence of skin sensitisation in any of twenty test animals. Evidence of skin sensitisation was produced by hexyl cinnamic aldehyde (HCA) in all ten positive controls thus confirming the sensitivity of the method (OPPT 2001).

Threshold limit values

No threshold limit values have been available.

Absorption

No values on absorption were available, therefore, the absorption is set to 100%.

Assessment

Diethylglycol dibenzoate was not detected as volatile substance in the head-space analyses but as migrated substance in the sweat and saliva extractions.

Table 6.8 Uptake of diethylglycol dibenzoate by dermal exposure

ID no.	Lab. no.	Weight, g	Migration to sweat, µg/g	Total migration, µg	Dermal uptake, µg/kg bw/day
TO-01, exterior	30396-9	14.7	118	1732.0	43.3
TO-02, exterior	30396-10	9.4	26	244.1	6.1

Table 6.9 Uptake of diethylglycol dibenzoate by oral exposure

ID no.	Lab. no.	Weight, g	Migration to saliva, µg/g	Total migration, µg	Oral uptake, µg/kg bw/day
TO-01, exterior	30396-9	14.7	65	954.1	23.85
TO-02, exterior	30396-10	9.4	38	356.8	8.92

As no threshold limit values are found, the margin of safety to NOAEL from a rat development toxicity study is used (OPPT 2001). The lowest NOAEL observed is 250 mg/kg bw/day and the total uptake from dermal and oral exposure is $43.3+23.9 = 67.2$ µg/kg bw/day, i.e. the margin of safety (MOS) is >3700.

Thus it is concluded that no health risk from the exposure to diethylglycol dibenzoate existed.

Components homologous to diethylglycol dibenzoate

Chemical components homologous to diethylglycol dibenzoate were observed even if they could not be specifically identified. However, they could be detected in the sweat and saliva extractions.

Measurements of components homologous to diethylglycol dibenzoate resulted in the following uptakes (cf. tables below):

Table 6.10 Uptake by dermal exposure

ID no.	Lab. no.	Weight, g	Measured migration, µg/g	Total migration, µg	Dermal uptake, µg/kg bw/day
TO-01, exterior	30396-9	14.7	103	1511.8	37.8
TO-02, exterior	30396-10	9.4	4	37.6	0.94

Table 6.11 Uptake by oral exposure

ID no.	Lab. no.	Weight,	Measured	Total	Oral
--------	----------	---------	----------	-------	------

		g	migration, µg/g	migration, µg	uptake, µg/kg bw/day
TO-01, exterior	30396-9	14.7	69	1012.8	25.3
TO-02, exterior	30396-10	9.4	7	65.7	1.64

The homologues substances were detected at approximately the same concentrations as the corresponding diethylglycol dibenzoate. Assuming that their toxicity are of a comparable character and level the measured concentrations can be added (cf. table below):

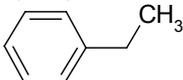
Table 6.12 Total Uptake by oral exposure

Substance	Diethylglycol dibenzoate		Diethylglycol dibenzoate homologues		Total uptake, µg/kg bw/day
	Dermal uptake, µg/kg bw/day	Oral uptake, µg/kg bw/day	Dermal uptake, µg/kg bw/day	Oral uptake, µg/kg bw/day	
TO-01, exterior	43.3	23.85	37.8	25.3	130.3
TO-02, exterior	6.1	8.92	0.94	1.64	17.6

Based on a margin of safety (MOS) of at least $250/0.130 = 1920$ was assessed that they do not pose a health risk to the consumer.

6.3.6 Ethylbenzene

Identification

Name	Ethylbenzene
CAS no.	100-41-4
EINECS no.	202-849-4
Molecular formula	C_8H_{10}
Molecular structure	

Molecular weight 106.17 g/mol

The melting point is $-95^{\circ}C$. The boiling point is $136.2^{\circ}C$ (Budavari 1996). The vapour pressure is 1280 Pa at $25^{\circ}C$ (9.6 mmHg, Daubert and Danner 1985). The water solubility is 169 mg/l at $25^{\circ}C$ (Sanemase *et al.* 1982; EPI). The partition coefficient log Kow is measured to 3.15 (Hansch *et al.* 1995).

Use

Ethylbenzene is used as solvent of resins in printing inks and lacquers. Ethylbenzene is a component of oil products.

Classification

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

F;R11	Highly flammable
Xn;R20	Harmful. Harmful by inhalation

Effects on health

Ethylbenzene has a low acute and chronic toxicity. The acute threshold values are 430 to 860 mg/m^3 (100-200 ppm) (IPCS 1996). Ethylbenzene is moderately toxic by oral administration (Lewis 1992).

Acute toxicity:			
Acute oral, rat	LD ₅₀	3500 mg/kg	IPCS 1996
Acute dermal, rabbit	LD ₅₀	77400 mg/kg	IPCS 1996
Acute inhalation, rat	LCL ₀	9370 mg/m ³ (2180 ppm)	IPCS 1996
Chronic data:			
Oral, rat	NOAEL	136 mg/kg/d	Vermeire <i>et al.</i> 1996
Inhalation, rat	NOAEL	430 mg/m ³	Vermeire <i>et al.</i> 1996
Inhalation, rat	NOEL	2150 mg/m ³ (500 ppm)	IPCS 1996

Ethylbenzene is an irritant to skin, eyes and mucous membranes and may affect the central nervous system (Budavari 1996, IPCS 1996).

The main part of toxicity studies on ethylbenzene is inhalation studies. Inhalation of 434 mg/m³ may cause irritation. The lowest published toxic concentration for humans is 434 mg/m³ (8 hours exposure) causing irritation of the nose and eyes (Larsen *et al.* 1999).

Based on a 13 weeks inhalation study a NOAEL of 430 mg/m³ (100 ppm) has been derived (IPCS 1996, ATSDR 1999). The NOAEL 430 mg/m³ is based on 6 hours/day, 5 days a week. A back-calculation based on continuous exposure 24 hours/day and 7 days/week results in a concentration of 77 mg/m³. Using an uncertainty factor of 100 (10 for interspecies and 10 for intraspecies extrapolation) resulted in a TCA of 770 µg/m³ (Baars *et al.* 2001).

A recommended threshold limit value (TWA) of 22 mg/m³ (5 ppm) is derived from a 13 weeks inhalation animal study: $2150/(10 \times 5 \times 2) = 22 \text{ mg/m}^3$ (IPCS 1996).

In a 182 days oral rat study ethylbenzene was administered via gavage in olive oil to rats at the doses 13.6, 136, 408 and 680 mg/kg/day for 5 days/week. After examination of several toxic effects was set a LOAEL of 408 mg/kg/day based on histopathological changes. Recalculating from 5 days/week to 7 days/week the level was adjusted to $(408 \times 5/7 =)$ 291 mg/kg bw/day. Correspondingly was NOAEL of 136 mg/kg bw/day recalculated to 97 mg/kg bw/day (Wolf *et al.* 1956).

Ethylbenzene has been evaluated by IARC who concluded that there was insufficient evidence of ethylbenzene being carcinogenic to humans but sufficient evidence for test animals. Ethylbenzene was therefore classified in group 2B: "possibly carcinogenic to humans" (IARC 2000).

Absorption

The most important exposure route was inhalation where 44 to 64% is absorbed via the lungs (IPCS 1996). In the assessment is used 100% absorption.

Threshold limit values

The threshold limit value for the working environment is 50 ppm corresponding to 217 mg/m³ (AT 2002).

The C-value is 0.5 mg/m³ (B-værdivejledningen 2002, Miljøstyrelsen 2002). TCA (tolerable concentration in air): 770 µg/m³ (Baars *et al.* 2001).

TDI (tolerable daily intake) value is 100 µg/kg/day (IPCS 1996).

The oral RfD value is 97 µg/kg bw/day.
 The RfD value was derived from a NOAEL in a 182 days oral rat study (Wolf *et al.* 1956) of 97 mg/kg bw/day. Using a safety factor of 1000 (10 for intraspecies, 10 for interspecies variation and 10 for extrapolating from sub-chronic to chronic) was derived a NOAEL of 97 µg/kg bw/day. The same study and methodology forms the basis for WHO derivation in the Drinking water programme of a TDI of 97 µg/kg bw/day (IPCS 1996).

Assessment

Ethylbenzene was detected in the screening test but was quantified together with xylenes in the headspace analyses. In the assessment of inhalation ethylbenzene, therefore, is included in the assessment of xylenes.

Ethylbenzene is separated in the qualitative analyses of migration to sweat and saliva. The results are presented below.

Table 6.13 Uptake by dermal exposure

ID no.	Lab. no.	Weight, g	Measured migration, µg/g	Total migration, µg	Dermal uptake µg/kg bw/day
K-01, exterior	30396-5	22.2	<0.05	<1.11	<0.028
BR-01, exterior	30396-7	25.2	0.56	14.1	0.35
F-01, exterior	30396-8	20.6	<0.05	<1.0	<0.026
F-01, interior	30396-8C	6.1	<0.05	<1.0	<0.026
G-01, exterior	30396-12	102.7	<0.05	<5.1	<0.13
A-01, exterior	30396-18	12.2	0.06	0.73	0.018

Table 6.14 Uptake by oral exposure

ID no.	Lab. no.	Weight, g	Measured migration, µg/g	Total migration, µg	Oral uptake, µg/kg bw/day
K-01, exterior	30396-5	22.2	<0.05	<1.11	<0.028
BR-01, exterior	30396-7	25.2	0.64	16.1	0.40
F-01, exterior	30396-8	20.6	<0.05	<1.0	<0.025
F-01, interior	30396-8C	6.1	<0.05		
G-01, exterior	30396-12	102.7	<0.05	<5.1	<0.13
A-01, exterior	30396-18	12.2	0.06	0.73	0.018

By adding the uptakes from sweat and saliva from the toy with the highest migration of ethylbenzene, BR-01, is reached $0.35+0.40 = 0.75$ µg/kg bw/day. This value does not exceed the TDI value 100 µg/kg bw/day. The margin of safety (MOS) is calculated to: $97/0.00075 = >10000$.

Therefore, it is concluded that ethylbenzene does not imply a health risk by handling or placing the toy in the mouth.

Relating to inhalation cf. the section on xylene.

6.3.7 2-Hexanone

Identification

Name	2-Hexanone
CAS no.	591-78-6
EINECS no.	209-731-1
Molecular formula	C ₆ H ₁₂ O
Molecular structure	
Molecular weight	100.16 g/mol
Synonyms	hexan-2-one (EINECS name) butyl methyl ketone methyl butyl ketone methyl-n-butyl ketone MBK propyl acetone

The melting point is -55.5°C. The boiling point is 127.6°C (Budavari 1996). The vapour pressure is 1146 Pa at 25°C (11.6 mmHg, Daubert and Danner 1985). The water solubility is 17500 mg/l at 25°C (EPI). The partition coefficient log K_{ow} is measured to 1.38 (Hansch *et al.* 1995).

Use

2-Hexanone is as pure substance a clear, colourless liquid with a sharp odour. The substance dissolves very easily in water, and can evaporate easily into the air as a vapour. The substance is used in paint and paint thinner, to make other chemical substances, and to dissolve oils and waxes. It is used in drying and curing of coatings in which it is contained as a solvent.

Classification

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

R10	Flammable
T;R48/23	Toxic: danger of serious damage to health by prolonged exposure through inhalation
Repr. Cat. 3; R62	Possible risk of impaired fertility
R67	Vapours may cause drowsiness and dizziness

Effects on health

Acute toxicity:			
Acute oral, rat	LD ₅₀	2590 mg/kg	ATSDR 1992
Acute inhalation, rat	LD ₅₀ (4 h)	8000 ppm	ATSDR 1992
Acute dermal, rabbit	LD ₅₀	4800 mg/kg	ATSDR 1992

Most studies concern exposure via inhalation.

In a 90-day study, hens were exposed continuously to 2-hexanone. At 200 ppm 1 of 5 hens died after 72 days. At 400 ppm, 2 of 5 hens died by day 27. The cause of death was not stated. No deaths were observed in the groups exposed to 100 ppm and below. The highest NOAEL value (approx. 10 ppm) and a reliable LOAEL value of 50 ppm are recorded in comparable studies (ATSDR 1992).

Studies using oral administration of the substances are usually of low quality. However, two studies are presented below and used in the evaluation.

The lowest NOAEL was observed in a study on effects following oral administration by gavage in rats. The rats were dosed 5 days/week for 40 weeks. Based on the effects on kidney and liver NOAEL was 400 mg/kg/day (Eben *et al.* 1979).

In a study on hens 2-hexanone was administered orally via gavage 7 days/week for 90 days at doses from 100 mg/kg bw/day and more. Based on neurotoxic symptoms such as ataxia (disturbance of co-ordination or dyssynergy, i.e. movements are badly co-ordinated because they cannot be properly controlled from the brain) and histopathological changes is set a LOAEL of 100 mg/kg bw/day (Abou-Donia *et al.* 1982).

Threshold limit values

The threshold limit value for the working environment is 1 ppm corresponding to 4 mg/m³ with skin notation (H), i.e. the substance may penetrate the skin (AT 2002).

The C-value is 0.3 mg/m³ (Hexanones in the C-value guidance document (B-værdivejledningen, Miljøstyrelsen 2002)).

Absorption

2-Hexanone is easily absorbed after administration via the inhalation route. An analysis of the expired breath from humans who had inhaled 2-hexanone at 10 and 50 ppm for 7.5 hours or 100 ppm for 4 hours indicate that 75 to 95% of the inhaled amount of vapours was absorbed by the lungs and respiratory tract (DiVincenzo *et al.* 1978).

2-Hexanone also appears to be easily absorbed after oral administration. Humans who ingested a single capsule containing ¹⁴C-2-hexanone at 0.1 mg/kg excreted about 40% of the ¹⁴C in breath and 26% in urine during the next 8 days (DiVincenzo *et al.* 1978). This indicates that the excreted and with that absorbed amount averaged at least 40+26=66% of the administered dose.

Oral administration of ¹⁴C-2-hexanone at doses of 20 or 200 mg/kg by gavage to rats resulted in excretion of about 1.2% of the administered radioactivity in the feces, about 44% in the breath, 38% in urine, and 16% remaining in the carcass (DiVincenzo *et al.* 1977). The results were similar at either dosage level. These findings suggest that about 98% of the administered dose was absorbed.

2-Hexanone is also absorbed after dermal application. The excretion of ¹⁴C in the breath and urine of two human volunteers was measured after a 60-minute occlusive application of ¹⁴C-2-hexanone to their shaved forearms (DiVincenzo *et al.* 1978). Calculated skin absorption rates were 4.8 and 8.0 pg/min/cm²; however, the fraction of 2-hexanone that was absorbed was not calculated. ¹⁴C-Hexanone was also applied to the clipped thorax of beagle dogs, and absorption was observed to be slow at first but increased dramatically after 20 minutes. At 60 minutes, 77 mg of 2-hexanone had penetrated the skin (DiVincenzo *et al.* 1978). The fraction of applied 2-hexanone that was absorbed was not calculated.

Assessment

The evaluation of inhalation is based on short term exposure with 1 m³ air in the breathing zone and exposure for 1 hour, and a long-term exposure scenario using exposure in a 20 m³ room for 1 hour per day. Both scenarios using exposure to a child of 10 kg body weight (bw). The absorption by inhalation is set to 100%.

Table 6.15 Uptake by exposure via inhalation of 2-hexanone

ID no.	Lab. no.	Content, %	Total, ng	Breathing zone concentration, µg/m ³	Acute uptake via inhalation, µg/kg/day	Chronic uptake via inhalation, µg/kg/day
TI-01	30396-16A	2.7	216	0.093	0.011	0.0039
	30396-16B	8	101.6	0.087	0.010	0.0036

2-Hexanone was detected in 2 slimy toys. The estimated uptake via inhalation is 3.8 and 3.6 ng/kg body weight.

Using the C-value for hexanones of 300 µg/m³ the value is far more (>3000 times) than the estimated inhalation concentration of 0.09 µg/m³ in the breathing zone (1 m³) and the room concentration of 0.09/20 = 0.0045 µg/m³.

By comparing the LOAEL from the 90-day rat oral study of 100 mg/kg bw/day the margin of safety (MOS) is $100/3.9 \times 10^{-6} = >2.6 \times 10^8$.

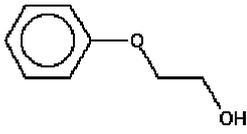
2-Hexanone was not detected as migrated substance in the sweat or saliva extractions.

Conclusion

2-Hexanone is a volatile substance that evaporates fast which is confirmed by the detection of the substance in the headspace analyses only. Because no ADI or similar values were found, the validated C-value and MOS are used for the assessment. As the measured concentrations were above the C-value and MOS is very high, it is considered that no health problems to the consumer are expected by exposure to 2-hexanone.

6.3.8 2-Phenoxyethanol

Identification

Name	2-Phenoxyethanol
CAS no.	122-99-6
EINECS no.	204-589-7
Molecular formula	C ₈ H ₁₀ O ₂
Molecular structure	

Molecular weight 138.17 g/mol

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

Use

2-Phenoxyethanol is used as solvent in many industrial products.

Classification

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

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

Effects on health

Acute toxicity:

Acute oral, rat	LD ₅₀	1260 mg/kg bw	IUCLID 2000
Acute oral, rat	LD ₅₀	2740 mg/kg bw	IUCLID 2000
Acute inhalation, rat	LC ₅₀ (8 h)	saturated atmosphere	IUCLID 2000
Acute dermal, rat	LD ₅₀	14422 mg/kg bw	IUCLID 2000
Acute dermal, rabbit	LD ₅₀	3660 mg/kg bw	IUCLID 2000

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

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

Threshold limit values

The threshold limit value for the working environment (TLV) is 20 ppm corresponding to 110 mg/m³ with skin notation (H), i.e. the substance may penetrate the skin (DF 2001).

The C-value is 0.1 mg/m³ (Miljøstyrelsen 2002).

Absorption

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

Assessment

The evaluation of inhalation is based on short term exposure with 1 m³ air in the breathing zone and exposure for 1 hour, and a long-term exposure scenario using exposure in a 20 m³ room for 1 hour per day. Both scenarios using exposure to a child of 10 kg body weight (bw). The absorption by inhalation is set to 100%.

Table 6.16 Uptake by exposure via inhalation of 2-phenoxy-ethanol

ID no.	Lab. no.	Content, %	Total, ng	Breathing zone concentration, µg/m ³	Acute uptake via inhalation, µg/kg/day	Chronic uptake via inhalation, µg/kg/day
TO-03	30396-11	3.9	222.3	0.096	0.01152	0.003984

2-Phenoxyethanol was detected in 1 slimy toy. The calculated uptake via inhalation was 3.9 ng/kg bw/day.

2-Phenoxyethanol was detected in the sweat extractions of 4 slimy toys. By intake it is assumed that a child uses the toy for 1 hour/day. The weight of the child is 10 kg and the absorption is 100%. Based on this the amount of uptake of the substance is calculated (cf. table below).

Table 6.17 Uptake by dermal exposure to 2-phenoxyethanol

ID no.	Lab no.	Weight, g	Measured migration $\mu\text{g/g}$	Total migration, μg	Dermal uptake $\mu\text{g/kg bw/day}$
F-01, exterior	30396-8	20.6	53	1090.1	27.3
F-01, interior	30396-8C	6.1	60	1234.1	30.9
TO-03, glitter gel	30396-11	3.8	16000	60592	1514.8
R-01, exterior	30396-17	23.1	120	2775.5	69.4

Because no TDI value is available the NOAEL value of 200 mg/kg bw/day is used. By comparing the NOAEL to the estimated values the margin of safety (MOS) for dermal uptake was >130.

2-Phenoxyethanol was detected in the saliva extractions of 3 slimy toys.

Table 6.18 Uptake by oral exposure to 2-phenoxyethanol

ID no.	Lab no.	Weight, g	Measured migration, $\mu\text{g/g}$	Total migration, μg	Oral uptake $\mu\text{g/kg bw/day}$
F-01, exterior	30396-8	20.6	44	905.0	22.6
F-01, interior	30396-8C	6.1	17	349.7	8.7
R-01, exterior	30396-17	23.1	80	1850.3	46.3

Because no TDI value is available the NOAEL value of 200 mg/kg bw/day is used. By comparing the NOAEL to the estimated values the margin of safety (MOS) for oral uptake was >4300.

Conclusion

Since no limit values are available the margin of safety to NOAEL from a 90 days rat repeated dose toxicity test is used (IUCLID 2000). The lowest NOAEL found was 200 mg/kg bw/day and the highest total uptake from inhalation, dermal and oral exposure was 1514 $\mu\text{g/kg bw/day}$, i.e. margin of safety (MOS) is >130.

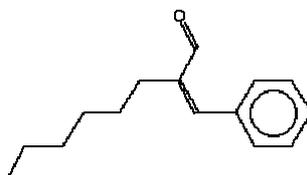
It is assessed that no health risk from the exposure to 2-phenoxyethanol exists.

6.3.9 2-Phenylmethylenooctanal (*alpha*-Hexylcinnamaldehyd)

Identification

Name	2-Phenylmethylenooctanal *
IUPAC name	α -Hexylcinnamaldehyd
CAS no.	101-86-0
EINECS no.	202-983-3
Molecular formula	C ₁₅ H ₂₀ O

Molecular structure



Molecular weight	216.33 g/mol
Synonyms	Octanal, 2-(phenylmethylene)- <i>alpha</i> -hexylcinnamaldehyde (EINECS name) alfa-hexylkanelaldehyd 2-Benzylideneoctanal

* The substance is probably better known as *alpha*-hexylcinnamaldehyde, therefore, that name is used below.

The melting point is 4°C. The boiling point is 304°C. The vapour pressure is 0.027 Pa at 20°C (0.0002 mmHg). The water solubility is estimated to 1.8 mg/l at 25°C (also found estimated to 2.75 mg/l at 25°C based on an estimated log Kow 4.82). The partition coefficient log Kow is measured to 5.3. All data are based on studies or estimates presented in FFHPVC (2000).

Use

alpha-Hexylcinnamaldehyde is often added as fragrance or flavour in food and cosmetics.

Classification

alpha-Hexylcinnamaldehyde is not adopted on the List of dangerous substances (Miljøministeriet 2002):

Effects on health

Acute toxicity:

Acute oral, rat	LD ₅₀	3100 mg/kg bw	RTECS 1998
Acute dermal, rabbit	LD ₅₀	>3000 mg/kg bw	FFHPVC 2000
Acute inhalation, rat	LC ₅₀	>5000 mg/m ³	FFHPVC 2000

Of subchronic tests, only a 90 days dermal test was found. The test material was applied percutaneously to the shaved dorsals of 10 male rats at dose levels of 0.125, 0.25, 0.50 and 1.0 g/kg bw/day for 90 consecutive days. Based on multisystemic toxicity in the examined parameters LOAEL was 0.125 g/kg bw/day. Because effects were observed at the lowest applied dose level no NOAEL could be derived (FFHPVC 2000). Thus, LOAEL was 125 mg/kg bw/day.

In a similar 90 days test with daily dermal application to the clipped backs of 10 rats, only 1 dose level at 25 mg/kg bw/day was used. No evidence of toxic-

ity induced by treatment was observed. Thus NOAEL was 25 mg/kg bw/day (FFHPVC 2000).

In an Ames test, no mutagenic activity was determined with any of the *Salmonella typhimurium* strains tested (FFHPVC 2000).

Contact sensitisation due to exposure with *alfa*-hexylcinnamaldehyde is rare (De Groot *et al.* 1994).

Still, *alfa*-hexylcinnamaldehyde is used as positive control for the Local Lymph Node Assay (LLNA). LLNA is used as *in vivo* confirmation of sensitisation potential of chemical substances (Klink and Meade 2003).

In the OECD guideline on skin sensitisation, hexylcinnamaldehyde is mentioned as one of three preferred substances for reliability check of the tests sensitivity, as it is known to have mild-to-moderate skin sensitisation properties (OECD 1993).

In vivo geno toxicity was tested in a BASC test on the fruit fly *Drosophila melanogaster* after oral administration of the test substance. No mutagenic activity was demonstrated (FFHPVC 2000, Wild *et al.* 1983). The same result was observed in a micronucleus test on mice. Thus NOEL was 756 mg/kg which was the highest dosage used (FFHPVC 2000, Wild *et al.* 1983).

alfa-Hexylcinnamaldehyde is one of the fragrances that according to the Scientific Committee on cosmetic products and non-food products intended for consumers (SCCNFP) is evaluated as allergenic by skin contact, i.e. allergenic (List of undesirable substances Miljøstyrelsen 2004).

alfa-Hexylcinnamaldehyde (CAS no. 101-86-0) is a common fragrance allergenic according to the survey by the EU Scientific Committee. The substance is included in the SCCNFP list of the 26 substances there are most often reported as allergenic. The substance belongs to the substances that the EU Parliament in 2002 suggested obligatory to be declared on cosmetic products. From March 11 2005, the substance must be declared in the ingredients list on cosmetic products in the EU, if the concentration exceeds 0.001% (1 mg per 100 gram) in products to remain on the skin (leave-on products) or 0.01% (10 mg per 100 gram) in products that are washed off (rinse-off products) (Directive 2003/15/EC, EC 2003).

Threshold limit values

No threshold limit values are found.

Absorption

No values for the absorption via the different exposure routes were available. Thus, an absorption of 100% is assumed.

Assessment

alfa-Hexylcinnamaldehyde was not detected as volatile substance in the head-space analyses.

alfa-Hexylcinnamaldehyde was detected in the sweat extractions in 1 slimy toy.

Table 6.19 Uptake by dermal exposure to *alpha*-hexylcinnamaldehyde

ID no.	Lab no.	Weight, g	Measured migration, µg/g	Total migration, µg	Dermal uptake µg/kg bw/day
TO-03, gel	30396-11	3.8	8.6	32.6	0.81

Since no limit values are available, the uptake through skin is assessed by a comparison to NOAEL of 25 mg/kg bw/day from a 90 days dermal rat test. The margin of safety (MOS) was $25/0.00081 = 30800$.

alpha-Hexylcinnamaldehyde was not detected in the saliva extractions. The effect of oral uptake is thus not assessed.

Conclusion

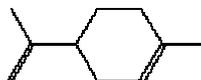
alpha-Hexylcinnamaldehyde was found migrated only to sweat with a MOS of 30800. *alpha*-Hexylcinnamaldehyde, therefore, is assessed not to imply a health risk to the consumer.

However, it should be noted that *alpha*-hexylcinnamaldehyde is used as positive control in studies on skin sensitising. Thus, a risk for skin sensitising can not be excluded.

6.3.10 D-Limonene

Identification

Name	D-Limonene
CAS no.	5989-27-5
EINECS no.	227-813-5
Molecular formula	C ₁₀ H ₁₆
Molecular structure	



Molecular weight	136.24 g/mol
Synonyms	(R)-1-methyl-4-(1-methylethenyl)-cyclohexene 4-Isopropenyl-1-methylcyclohexene p-Mentha-1,8-diene (EINECS name) Citrene Cinene

The melting point is -74.35°C (Lide 1992). The boiling point is 176°C (Budavari 1996). The vapour pressure is 192 Pa at 25°C (1.44 mmHg) (Riddick *et al.* 1986). The water solubility is 13.8 mg/l at 25°C (Massaldi and King 1973). The octanol/water distribution coefficient log Kow is measured to 4.57 (Li and Perdue 1995).

D-Limonene has a high vapour pressure indicating that limonene can be expected to evaporate from dry and wet surfaces

Use

D-Limonene is used as solvent, in the production of resins and as wetting and dispersing agent.

Classification

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

R10	Flammable
Xi;R38 R43	Irritant. Irritating to skin. May cause sensitization by skin contact
N;R50/53	Dangerous for the environment. Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

Effects on health

D-Limonene is irritating to the skin and may be a sensitizer (Budavari 1996, Karlberg and Lindell 1993). D-Limonene is a moderate oral toxicant (Lewis 1992). Examples of effect levels are presented below.

D-Limonene is readily oxidised by the air oxygen. Experimental studies show that limonene in itself is not allergenic, but allergenic compounds are formed from limonene by autooxidation (Karlberg *et al.* 1992, Karlberg and Lindell 1993).

Acute toxicity:

Acute oral, rat	LD ₅₀	4400 mg/kg	Lewis 1992
Acute oral, mouse	LD ₅₀	5600 ml/kg (4710 mg/kg)	HSDB 2004
Acute dermal, rabbit	LD ₅₀	>5000 mg/kg	Karlberg and Lindell 1993
Oral rat, 13 weeks	NOEL	10 mg/kg/d	Falk-Filipsson 1998

In a 13 weeks study on rats, the rats were administered orally at a dosage of 0, 2, 5, 10, 30, and 75 mg/kg bw/day 5 days/week. Based on histological examination changes in the kidneys were observed. On that basis was set a NOEL of 5 mg/kg bw/day. The LOEL for increased liver and kidney weight was 75 mg/kg bw/day. The NOEL for effects in the liver was 10 mg/kg bw/day. The NOAEL for effects in the liver was 30 mg/kg bw/day (Webb *et al.* 1989, CI-CAD 1998).

In a 13 weeks study on rats, the rats were orally administered 0, 150, 300, 600, 1200 or 2400 mg/kg/day. Based on a dose-related decrease in body weight gain from 600 mg/kg/day NOAEL was 300 mg/kg bw/day (IRIS 2004).

In a 2-year study, rats were orally by gavage administered D-limonene 5 days/week at the dosages 0, 300 and 600 mg/kg/day. The mortality was significantly increased at 600 mg/kg/day. Thus, NOAEL was 300 mg/kg bw/day (IRIS 2004).

In a 2-year study on mice with oral administration 5 days/week at the dosage 0, 250 and 500 mg/kg/day (male mice); or 0, 500 and 1000 mg/kg/day (female mice). Based on histopathological observations in the liver (multinucleated hepatocytes and cytomegaly) a LOAEL was set at 500 mg/kg bw/day and NOAEL 250 mg/kg bw/day (NTP 1990, IRIS 2004).

In the studies, effects on the liver appear to be the effect observed at the lowest dose. Therefore, this effect forms the basis for deriving the TDI value.

D-limonene (CAS no. 5989-27-5) is a common fragrance allergenic. The substance is included in the SCCNFP list of the 26 substances there are most

often reported as allergenic. From March 11 2005, the substance must be declared in the ingredients list on cosmetic products in the EU, if the concentration exceeds 0.001% (1 mg per 100 gram) in products to remain on the skin (leave-on products) or 0.01% (10 mg per 100 gram) in products that are washed off (rinse-off products) (Directive 2003/15/EC, EC 2003).

Threshold limit values

Threshold limit values for the working environment (TLV) is 25 ppm corresponding to 140 mg/m³, which is equivalent to high-boiling aromatic carbohydrates such as terpenes and turpentine (AT 2002).

In Sweden the threshold limit value NGV (niveaugränsvärde) is 150 mg/m³ (25 ppm) with the remark skin sensitiser (Karlberg and Lindell 1993).

The TDI value 0.1 mg/kg bw/day is based on a 13 weeks oral rat study with the lowest level of observed effects on the liver. NOAEL was 10 mg/kg bw/day (Webb *et al.* 1989). Using a safety factor of 100 (10 for interspecies and 10 for intraspecies variation) derives a TDI at 0.1 mg/kg bw/day (CICAD 1998).

D- Limonene is on the List of undesirable substances, because it is suspected to be allergenic (Miljøstyrelsen 2000).

Absorption

D-Limonene is easily taken up from the lungs after inhalation. Short-time exposure studies show 58 to 70% absorbed after 2 hours of exposure (Karlberg and Lindell 1993, Falk-Filipsson *et al.* 1993, 1998). Due to the high absorption, the absorption is set at 100% in this study.

Assessment

The evaluation of inhalation is based on short term exposure with 1 m³ air in the breathing zone and exposure for 1 hour, and a long-term exposure scenario using exposure in a 20 m³ room for 1 hour per day. Both scenarios using exposure to a child of 10 kg body weight (bw). The absorption by inhalation is set to 100%.

Table 6.20 Uptake by exposure via inhalation of D-limonene

ID no.	Lab. no.	Content %	Total, ng	Breathing zone concentration, µg/m ³	Acute uptake via inhalation, µg/kg/day	Chronic uptake via inhalation, µg/kg/day
DK-02	30396-2	0.9	58.5	0.025	0.0030	0.0010
DK-03	30396-3	0.2	56.6	0.024	0.0029	0.0010
TO-03B	30396-11 gel	0.4	22.8	0.010	0.0012	0.00041
G-01	30396-12	0.4	26.4	0.011	0.0013	0.00046

D-Limonene was detected in 4 slimy toys with a calculated uptake via inhalation between 1 and 3 ng/kg body weight at short-term exposure and between 0.4 and 1 ng/kg bw/day at prolonged exposure.

The TDI value of 0.1 mg/kg bw/day was not exceeded, and the margin of safety (MOS) was 10 x 10⁶.

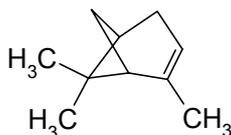
D-Limonene was not detected in the sweat or saliva extractions.

Conclusion

D-Limonene was measured as volatile substance in 4 slimy toys. NOAEL was 10 mg/kg/day in a 90 days rat study. Thus, the margin of safety is above $>1 \times 10^7$, and D-limonene is considered not to present a health problem at prolonged exposure related to the used scenarios. However, it is noted that it is known that D-limonene may oxidise to allergenic compounds.

6.3.11 *alpha*-Pinene

Identification

Name	<i>alpha</i> -Pinene
CAS no.	80-56-8
EINECS no.	201-291-9
Molecular formula	C ₁₀ H ₁₆
Molecular structure	
Molecular weight	136.24 g/mol
Synonyms	2,6,6-trimethyl-bicyclo[3.1.1]hept-2-ene 2,6,6-trimethyl-bicyclo[3.1.1]-2-heptene Pinene 2-Pinene

The melting point is -62.5°C. The boiling point is 156°C (Furia and Bellanca 1975). The vapour pressure is 633 Pa at 25°C (4.75 mmHg, Daubert and Danner 1989). The water solubility is 0.65 mg/l at 25°C (FFHPVC 2002). The partition coefficient log Kow measured to 4.83 (Li and Perdue 1995).

Pinene has a high vapour pressure indicating that pinene can evaporate from dry and wet surfaces.

Use

alpha-Pinene belongs to the chemical group terpenes (cf. further details at 3-carene). Terpenes exist in ethereal oils. Terpenes may arise from the use of vegetable oils and resins in products and as solvent in colorants.

Classification

alpha-Pinene is not classified under its own name or CAS no. If pinene is considered analogues to vegetable turpentine the classification is (Miljøministeriet 2002):

R10	Flammable.
Xn;R20/21/22-65	Harmful by inhalation, in contact with skin and if swallowed Harmful: may cause damage to the lungs if swallowed
Xi;R36/38	Irritating to eyes and skin
R43	May cause sensitization by skin contact
N;R51/53	Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

Effects on health

alpha-Pinene is moderately oral toxic but very toxic by inhalation (Lewis 1992) and strongly irritating to eyes, mucous membranes and skin (Budavari

1996, Lewis 1992). Examples on effect levels are presented below. *alpha*-Pinene is known as contact allergen (Thomsen 1990).

Acute toxicity:

Acute oral, rat	LD ₅₀	3700 mg/kg	Lewis 1992
Acute dermal, rat	LD ₅₀	>5000 mg/kg	FFHPVC 2002
Acute inhalation, rat	LC ₁₀ (6 h)	0.625 mg/m ³	Lewis 1992
Acute inhalation, mouse	LC ₁₀	0.364 mg/m ³	Lewis 1992

Most studies available are based on exposure via inhalation. However, a few studies on the effect on reproduction in rats (1-generation) have been found. All studies are performed by using turpentine containing approx. 20% *alpha*-pinene. The test substance was administered orally by gavage. In each study, NOAEL was the highest administered dosage, i.e. NOAEL varied between 260 and 600 mg/kg bw/day (FFHPVC 2002). Three examples are presented below:

One generation reproduction study on mice. The mice were orally administered by gavage the test material, which was a mixture of 85-90% terpene hydrocarbons and <10% oxygenated terpene hydrocarbons. The major bicyclic terpene hydrocarbon constituents of the formula C₁₀H₁₆ are *alpha*-pinene (20-25%), *beta*-pinene (15-18%) and sabinene (38-42%). The animals were exposed on days 6 to 15 of gestation. The doses given were 0 (control), 6, 26, 120, or 560 mg/kg bw/day. NOAEL was 560 mg/kg bw/day (FFHPVC 2002).

The same test material was used in hamsters in a 1-generation reproduction study on adult hamsters with oral administration (gavage) on day 6 to 15 of gestation at the dosages 0 (control), 6, 28, 130 or 600 mg/kg bw/day. NOAEL was 600 mg/kg bw/day (FFHPVC 2002).

The same test material was used in rats in a 1-generation reproduction study on adult rats with oral administration (gavage) up to day 14 of gestation with the dosages 0 (control), 3, 12, 56 or 260 mg/kg bw/day. NOAEL was 260 mg/kg bw/day (FFHPVC 2002).

Threshold limit values

TLV is 25 ppm corresponding to 140 mg/m³. The same as high boiling aromatic hydrocarbons (terpenes, turpentine) (AT 2002).

The C-value is 0.05 mg/m³ (Miljøministeriet 2002).

Assessment

The evaluation of inhalation is based on short term exposure with 1 m³ air in the breathing zone and exposure for 1 hour, and a long-term exposure scenario using exposure in a 20 m³ room for 1 hour per day. Both scenarios using exposure to a child of 10 kg body weight (bw). The absorption by inhalation is set to 100%.

Table 6.21 Uptake by exposure via inhalation of *alfa*-pinene

ID no.	Lab. no.	Content, %	Total, ng	Breathing zone concentration, $\mu\text{g}/\text{m}^3$	Acute uptake via inhalation, $\mu\text{g}/\text{kg}/\text{day}$	Chronic uptake via inhalation, $\mu\text{g}/\text{kg}/\text{day}$
DK-01	30396-1	0.1	46	0.020	0.0024	0.00083
DK-02	30396-2	3.4	221	0.095	0.0114	0.0039
DK-03	30396-3	0.7	198.1	0.085	0.0102	0.0035
K-01	30396-5A	3.8	421.8	0.182	0.0218	0.0076
F-01	30396-8	0.3	93	0.040	0.0048	0.0017
TO-03A	30396-11 lip	1.1	17.6	0.008	0.00096	0.00033
TO-03B	30396-11 glitter gel	0.4	22.8	0.010	0.0012	0.00042
G-01	30396-12	0.7	46.2	0.020	0.0024	0.00083
TI-01	30396-16A	1.2	96	0.041	0.0049	0.0017

alfa-Pinene was detected in 9 slimy toys. Using the NOAEL 260 mg/kg bw/day, the margin of safety (MOS) was $>3.2 \times 10^7$.

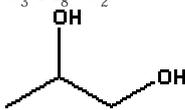
alfa-Pinene was not detected in the sweat or saliva extractions.

Conclusion

alfa-Pinene was measured in 9 out of 17 slimy toys. The MOS was very high and *alfa*-pinene, therefore, is not considered a potential health problem at prolonged exposure duration. However, it is noted that *alfa*-pinene is known as contact allergenic.

6.3.12 1,2-Propanediol

Identification

Name	1,2-Propanediol
CAS no.	57-55-6
EINECS no.	200-338-0
Molecular formula	$\text{C}_3\text{H}_8\text{O}_2$
Molecular structure	

Molecular weight	76.10 g/mol
Synonyms	Propan-1,2-diol (EINECS name) Propylene glycol Methylethylene glycol (S)-(+)-propane-1,2-diol = CAS no. 4254-15-3 (not on the EINECS list)

The melting point is -60°C . The boiling point is 187.6°C (Budavari 1996). The vapour pressure is 17.2 Pa at 25°C (0.129 mmHg, Daubert and Danner 1989). The water solubility is high, i.e. miscible at 25°C (EPI). The partition coefficient log Kow is measured to -0.92 (Hansch *et al.* 1995).

Use

1,2 Propanediol is a synthetic liquid substance that absorbs water. The substance is also known as propylene glycol, which is used to make polyester compounds, and as a base for de-icing solutions. The substance is used in chemical, food and pharmaceutical industries. The substance is used to absorb extra water and maintain moisture in certain medicines, cosmetics, or

food products. It is used as a solvent for food colours and flavours, and in the paint and plastics industries (Clayton and Clayton 1982, IRIS 2004).

Classification

The substance is not adopted on the List of dangerous substances and, therefore, not classified (Miljøministeriet 2002).

Effects on health

1,2-Propanediol is not especially acute toxic. For instance it has been found that a lethal dosis for humans is given as 15 g/kg body weight (Gosselin *et al.* 1976).

Acute toxicity:

Acute oral, rat	LD ₅₀	20000 mg/kg	Lewis 1999
Acute oral, mouse	LD ₅₀	24000 mg/kg	Lewis1999
subacute, human (child)	LOEL (56 weeks)	79000 mg/kg	Lewis1999

However, studies of humans and animals show that repeated eye, skin, nasal, or oral exposures to 1,2-propanediol for a short time may develop some irritation (ATSDR 1997).

Studies indicate that exposure to 1,2-propanediol for a prolonged period may lead to haemolysis of red blood cells (ATSDR 1997).

In a 13-week study the effect by exposure of rats via inhalation 6 hours/day, 5 days/week using aerosol concentrations at 0, 51, 321 and 707 ppm is studied. Based on nasal haemorrhaging was set a LOAEL of 51 ppm, which was the lowest concentration used (Suber *et al.* 1989).

In rhesus monkeys and rats, exposed to 1,2-propanediol continuously via inhalation at concentrations in air up to 112 ppm for 13 to 18 months, no adverse effects were observed in the hepatic system (Robertson *et al.* 1947).

In studies on rats exposed via the food for 2 years, no adverse hepatic effects were observed at the highest level of 2500 mg/kg bw/day (Gaunt *et al.* 1972).

Threshold limit values

A threshold limit value for the working environment is not set in Denmark: An American value of 50 ppm corresponding to 170 mg/m³ has been found (ACGIH, ATSDR 1997).

The C-value is 1 mg/m³ (Miljøstyrelsen 2002).

The American MRL (Minimal risk Level) corresponding to RfC is 0.009 ppm corresponding to 0.03 mg/m³. The MRL was based on the LOAEL of 51 ppm for nasal haemorrhaging in rats (Suber *et al.* 1989). The MRL was obtained by dividing the LOAEL value by 1000 (10 for inter and 10 for intravariability and 10 to extrapolation to NOAEL) and multiplying by factors to adjust the exposure from 6 hours per day (6 or 24) and 5 days per week (5 of 7) to continuous exposure (ATSDR 1997).

The ADI value is 25 mg/kg bw/day according to FAO/WHO (1974).

RfD_{subchronic} is 30 mg/kg bw/day. The oral reference dose is based on a NOEL of 6% after oral administration in the diet over 20 weeks to rats. The value is based on adverse effects to the liver and using a safety factor of 100 (10 for

intra and 10 for interspecies variation): Oral RfD subchronic 30 mg/kg bw/day (US-EPA 1997).

RfD_{chronic} is 20 mg/kg bw/day. The oral reference dose is based on NOEL 50000 ppm administered orally over 2 years in the diet to dogs. The value is based on decreased erythrocyte counts, decreased hematocrit and haemoglobin content in the blood and a safety factor of 100: Oral RfD chronic 20 mg/kg bw/day (US-EPA 1997).

Absorption

Propylene glycol is readily absorbed by the gastro-intestinal tract (US-EPA 1997). Thus, the absorption is set to 100%.

Assessment

The evaluation of inhalation is based on short term exposure with 1 m³ air in the breathing zone and exposure for 1 hour, and a long-term exposure scenario using exposure in a 20 m³ room for 1 hour per day. Both scenarios using exposure to a child of 10 kg body weight (bw). The absorption by inhalation is set to 100%.

Table 6.22 Uptake via inhalation by exposure to 1,2-propanediol

ID no.	Lab. no.	Content %	Total, ng	Breathing zone concentration, µg/m ³	Acute uptake via inhalation, µg/kg/day	Chronic uptake via inhalation, µg/kg/day
BR-01	30396-7	7	238	0.205	0.0246	0.0085
TO-03B	30396-11 gel	66	3762	1.619	0.1943	0.0672

1,2-Propanediol was detected as volatile substance from 2 slimy toys. The uptake is calculated to max. 67 ng/kg bw/day. The ADI value of 25 mg/kg bw is not exceeded. Using NOAEL 2500 mg/kg bw/day the margin of safety (MOS) is more than 3.6 x 10⁷.

1,2-Propanediol was not detected in the sweat or saliva extractions.

Conclusion

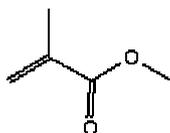
1,2-Propanediol is assessed not to imply a health problem to the consumer.

6.3.13 2-Propenoic acid 2-methyl-methylester (methyl methacrylate)

2-Propenoic acid 2-methyl-methylester is better known under the name methyl methacrylate which is used below.

Identification

Name	Methyl methacrylat
CAS no.	80-62-6
EINECS no.	201-297-1
Molecular formula	C ₅ H ₈ O ₂
Molecular structure	



Molecular weight	100.12 g/mol
Synonyms	Methyl methacrylate (EINECS name) 2-methyl-propenoic acid, methyl ester (IUPAC name) 2-Propenoic acid 2 methyl-methylester (CA name)

The melting point is -48°C. The boiling point is 100°C. The vapour pressure is 3600-4700 Pa at 20°C. The water solubility is 16000 mg/l at 20°C. The partition coefficient log K_{ow} is measured to 1.38 at 20°C. (All values from ECB 2002).

Use

The substance is mainly used as an intermediate in production of polymers, copolymers, adhesives, reactive resins, as well as in other polymers used for consumer products (ECB 2002, RAR vol 22).

Classification

Methyl methacrylate is adopted on the List of dangerous substances and classified (Miljøministeriet 2002):

F; R11	Highly flammable
Xi; R37/38	Irritant. Irritating to respiratory system and skin
R43	May cause sensitization by skin contact

Effects on health

Acute toxicity:

Acute oral, rat	LD ₅₀	8420-10000 mg/kg	SIDS 2003
Acute oral, mouse	LD ₅₀	5200 mg/kg	SIDS 2003
Acute inhalation, rat	LC ₅₀ (4 h)	7093 ppm (29.8 mg/l =29800 mg/m ³)	SIDS 2003
Acute inhal., mouse	LC ₅₀ (3 h)	33 mg/l	SIDS 2003
Acute dermal, rabbit	LD ₅₀	5000-7500 mg/kg	SIDS 2003

The acute toxicity is low regardless of exposure route as based on the available values. However, the substance is an irritant and classified as such.

For irritating effects a NOAEC of 100 ppm corresponding to 410 mg/m³ (ECB 2002) is found.

The substance has a moderate to strong sensitising potential in experimental animals. Cases of contact dermatitis have been reported for workers exposed to the substance (SIDS 2003).

The main effect caused by inhalation is a degeneration of the olfactory region of the nose. For this effect in a two-year inhalation study in rats a NOAEC of 25 ppm corresponding to 104 mg/m³ was identified (SIDS 2003). Based on the results from the same study by Lomax *et al.* (1997) US-EPA derives a RfC of 0.7 mg/m³ (IRIS 2004).

Oral administration to rats resulted in a NOAEL of 200 mg/kg bw/day (SIDS 2003).

In a 2-year oral rat study, the rats were administered via the drinking water at the doses 6, 60 and 2000 mg/l. The highest exposure level was recalculated to animal body weight: 2000 mg/l × 0.0313 l/rat/day divided with the rat body weight. A NOAEL of 146 mg/kg bw/day for females, while NOAEL was 121 mg/kg bw/day for males, which was the highest concentration tested on males (Borzelleca *et al.* 1964).

Absorption

Methyl methacrylate is rapidly absorbed after inhalatory or oral administration. Besides, the substance can easily be absorbed through skin (SIDS 2003, ECB 2002).

Threshold limit values

The threshold limit value for the working environment is 25 ppm corresponding to 102 mg/m³ with skin notation H, i.e. the substance may penetrate the skin (AT 2002).

The C-value is 0.03 mg/m³ (B-værdivejledningen, Miljøstyrelsen 2002). The RfC value is 0.7 mg/m³ (cf. above).

TDI (tolerable daily intake) is 1.2 mg/kg/day. The lowest NOAEL value from the 2-year rat study by Borzelleca *et al.* (1964) is used to derive a TDI using a safety factor of 100 (10 for intra and 10 for interspecies variation), i.e. TDI is 121/100 = 1.2 mg/kg bw/day (CICAD 1998).

The RfD value is 1.4 mg/kg bw/day. The RfD value is derived from the same study used for TDI. However, an average body weight of the rats of 0.462 kg is used. Thus, the combined NOAEL is 136 mg/kg bw/day and the RfD 1.4 mg/kg bw/day (IRIS 2004).

Assessment

The evaluation of inhalation is based on short term exposure with 1 m³ air in the breathing zone and exposure for 1 hour, and a long-term exposure scenario using exposure in a 20 m³ room for 1 hour per day. Both scenarios using exposure to a child of 10 kg body weight (bw). The absorption by inhalation is set to 100%.

Table 6.23 Uptake by exposure via inhalation of methyl methacrylate

ID no.	Lab. no.	Content, %	Total, ng	Breathing zone concentration, µg/m ³	Acute uptake via inhalation, µg/kg/day	Chronic uptake via inhalation, µg/kg/day
TO-03B	30396-11 gel	7.2	410.4	0.177	0.0212	0.0073

Methyl methacrylate was detected as evaporated substance from 1 slimy toy. The uptake was calculated to 7 ng/kg bw/day. Thus the TDI value of 1.2 mg/kg bw is not exceeded. Using NOAEL 121 mg/kg bw/day the margin of safety (MOS) is 1.6×10^7 .

Methyl methacrylate was not detected in the sweat or saliva extractions.

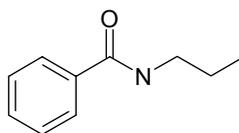
Conclusion

Methyl methacrylate was assessed not to imply a health risk to the consumer.

6.3.14 N-Propylbenzamide

Identification

Name	N-Propylbenzamid
CAS no.	10546-70-0
EINECS no.	



Molecular formula	C ₁₀ H ₁₃ N O
Molecular structure	
Molecular weight	163.22 g/mol

The melting point is 100°C. The boiling point is 328°C (Budavari 1996). The vapour pressure is estimated to 0.01 Pa at 25°C (7.8×10^{-5} mmHg). The water solubility is estimated to 2247 mg/l at 25°C (EPI). The partition coefficient log Kow is measured to 1.72 (Hansch *et al.* 1995).

Classification

N-Propylbenzamide is not adopted on the List of dangerous substances (Miljøministeriet 2002).

Effects on health

No information to describe the effects to humans of the substance was available.

Threshold limit values

No threshold limit values are found.

Assessment

N-Propylbenzamide and N-acetylbenzamide were not detected in the head-space as volatile substances.

N-Propylbenzamide and N-acetylbenzamide were not determined quantitatively in sweat and saliva extracts. Therefore, the somewhat more uncertain qualitative measurements from 2 products are used in the assessment.

Table 6.24 Uptake by exposure to N-propyl benzamide + N-acetyl benzamide based on the results from the screening of sweat and saliva extracts

ID no.	Lab. no.	Weight, g	Measured migration, µg/g	Total migration, µg	Dermal uptake µg/kg bw/day
TO-01, exterior	30396-9	14.7	2.4	35.2	0.88
TO-02, exterior	30396-10	9.4	0.7	6.6	0.16

ID no.	Lab. no.	Weight, g	Measured migration, µg/g	Total migration, µg	Oral uptake µg/kg bw/day
TO-01, exterior	30396-9	14.7	36	528	13.2
TO-02, exterior	30396-10	9.4	1.6	15	0.38

Conclusion

No data were available for an evaluation of effects and thereby a conclusion.

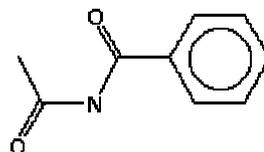
The analyses results show that the substance is detected as migrated at concentrations between 1 and 36 µg/g and the estimated uptake to maximum $13.2 + 0.88 = 14.1$ µg/kg bw/day. The missing toxicological data mean that it is not possible to assess potential risk to the consumers of the toy.

However, the substances are not expected to pose an immediate potential health risk at such low concentrations.

6.3.15 N-Acetylbenzamide

Identification

Name	N-Acetylbenzamide
CAS no.	1575-95-7
EINECS no.	
Molecular formula	$C_9H_9NO_2$
Molecular structure	



Molecular weight	163.18 g/mol
------------------	--------------

The estimated melting point is 172°C. The boiling point is estimated to 400°C (Budavari 1996). The vapour pressure is estimated to 1.5×10^{-5} Pa at 25°C (Daubert and Danner 1985). The water solubility is estimated to 17400 mg/l at 25°C (EPI). The partition coefficient log Kow is estimated to 0.68.

Classification

N-Acetylbenzamide is not adopted on the List of dangerous substances (Miljøministeriet 2002):

Effects on health

No information to describe the effects to humans of the substance was available.

Threshold limit values

None found.

Assessment

Both benzamides are considered above under N-propylbenzamide.

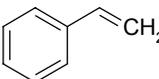
N-Acetylbenzamide was not detected in the headspace as volatile substance. N-Acetylbenzamide was not determined quantitatively in sweat and saliva extracts. Therefore, the somewhat more uncertain qualitative measurements from 2 products are used in the assessment.

Conclusion

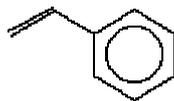
Cf. N-propylbenzamide

6.3.16 Styrene

Identification

Name	Styrene
CAS no.	100-42-5
EINECS no.	202-851-5
Molecular formula	C ₈ H ₈
Molecular structure	

Molecular structure



Molecular weight	104.15 g/mol
Synonyms	Benzene, ethenyl Ethenylbenzene Phenylethylene Vinylbenzene

The melting point is -30.6°C. The boiling point is 145.2°C. The water solubility is 300 mg/l at 25°C. The vapour pressure is 867 Pa at 25°C. The octanol/water partition coefficient is measured to log Kow 3.02 (ECB 2002).

Use

Styrene is used to a large extent in the plastic (polystyrene) and rubber industry but also in many other products.

Classification

Styrene is classified in the List of dangerous substances (Miljøministeriet 2002):

R10	Flammable
Xn;R20	Harmful: Harmful by inhalation
Xi;R36/38	Irritant: Irritating to eyes and skin
Conc. >=12.5%:	Xn;R20 Xi;R36/38

Effects on health

Styrene is not acute toxic based on acute toxicity data. Of these are mentioned:

Acute oral rat	LD ₅₀	5000 mg/kg	IPCS 26, 1983
Acute inhalation, rat	LC ₅₀ , 4 h	41000 mg/m ³	Koch 1984

The problematic health effect is that styrene is considered neurotoxic. Affecting the neurological development seems to be the most sensitive endpoint

observed. In young rats exposed to 260 mg/m³ effects were observed on behaviour and biochemical parameters in the brain (Kishi *et al.* 1992 in WHO 2000).

In occupationally exposed humans, minor effects were observed such as effects on verbal abilities and disturbances to the vision at air concentrations of 107-213 mg/m³. Using the lowest value for precautionary reasons and recalculated from working hours to continuous exposure with a factor 4.2 and apply a further safety factor of 10 for inter-individual variation and 10 for extrapolating from LOAEL to NOAEL a value of $107/(4.2 \times 10) = 0.26$ mg/m³ (weekly average) is derived (WHO 2000).

Mutti *et al.* (1984) examined in a cross-sectional study the neuropsychological function in 50 workers whose mean duration of styrene exposure was 8.6 (SD of 4.5) years. Styrene exposure was assessed by the authors to correspond to air concentrations ranging from 10-300 ppm as a mean daily exposure. This was based on the concentration-response relationship between urinary metabolite concentration (mandelic acid and phenylglyoxylic acid levels normalised to creatinine in "morning-after" urine). There were observed a significant effect level in the subgroup whose urine contained 150-299 mmole urinary metabolites/mole creatinine. Workers with metabolite concentrations of up to 150 mmoles/mole appeared to have no significant effects. This level is therefore designated as the NOAEL in this study. The authors state that this level of urinary metabolites corresponds to a mean daily 8-hour exposure to air styrene of 25 ppm (106 mg/m³). 95% confidence interval is calculated for an 8-hour exposure at 100 ppm, and the lower limit of the confidence calculation was 88% of the mean styrene exposure. This factor is applied to the correction of NOAEL: $25 \text{ ppm} \times 0.88 = 22 \text{ ppm}$ (94 mg/m³).

In a subchronic oral study on dogs, where the effect of styrene on red blood cells and the liver was studied after oral administration for 560 days, LOAEL was observed at 400 mg/kg/day and NOAEL set to 200 mg/kg/day (Quast *et al.* 1979).

In a 2-year three-generation rat study, rats were exposed to 125 mg/l (corresponding to 7.7 mg/kg/day for males and 12 mg/kg/day for females) and 250 mg/l (corresponding to 14 mg/kg/day for males and 21 mg/kg/day for females) in drinking water. The body weight was affected at 21 mg/kg/day, while male and female reproduction was not affected. Therefore, NOAEL was 14 mg/kg/day for males and 12 mg/kg/day for females (Van Appeldoorn *et al.* 1986).

There are only weak indication that styrene should be carcinogenic. However, IARC has evaluated the substance as possible carcinogenic to humans and placed the substance in group 2B (*inadequate evidence in humans and limited evidence in experimental animals for the carcinogenicity of styrene*: IARC 1994, WHO 2000). Apparently, the carcinogenicity potential of styrene is related to the metabolite styrene oxide, which is quickly transformed into styrene glycols (WHO 2000).

Threshold limit values

The threshold limit value for the working environment is 25 ppm equivalent to 105 mg/m³ with notation LHK. L means that the threshold limit value is a ceiling value, which at no time must be exceeded. H means that the substance

can penetrate the skin. K means that the substance is adopted on the list of substances that may be carcinogenic (AT 2002).

WHO has given a 24 hours air quality guideline value of 800 µg/m³ (IPCS 1983) and for continued exposure 260 µg/m³ air (WHO 2000).

The C-value is 0.2 mg/m³ (Miljøstyrelsen 2002).

The inhalation RfC value is set on basis of effects to the central nervous system (Mutti *et al.* 1984) with a NOAEL 94 mg/m³ (cf. above). The value is calculated to continuous exposure and assuming that 10 m³ air was the respiration rate during the working hours: 94 mg/m³ × 10/20 m³/day × 5/7 days = 34 mg/m³ (NOAEL HEC, human equivalent concentration). The safety factor of 30 was based on the application of 10 for intraspecies variation and 3 for data deficiencies, thus, RfC = 34/30 = 1 mg/m³ (IRIS).

The oral RfD value is based on a subchronic oral study on dogs for 560 days, where NOAEL was observed to 200 mg/kg/day (Quast *et al.* 1979). Applying a safety factor of 1000 (10 for inter-, 10 for intraspecies variation and 10 for extrapolation subchronic to chronic effects the resulting RfD is: 200/1000 = 0.2 mg/kg bw/day (IRIS).

TDI is 120 µg/kg bw/day. A Dutch value (Van Appeldoorn *et al.* 1986, cf. above) is based on a 2-year rat study with a safety factor of 100 (Baars *et al.* 2001).

Absorption

Styrene is absorbed easily from the lungs. In different studies uptake has been measured to vary between 45 and 93% (IPCS 1983).

Assessment

The evaluation of inhalation is based on short term exposure with 1 m³ air in the breathing zone and exposure for 1 hour, and a long-term exposure scenario using exposure in a 20 m³ room for 1 hour per day. Both scenarios using exposure to a child of 10 kg body weight (bw). The absorption by inhalation is set to 100%.

Table 6.25 Uptake via inhalation by exposure to styrene

ID no.	Lab. no.	Content %	Total, ng	Breathing zone concentration, µg/m ³	Acute uptake via inhalation, µg/kg/day	Chronic uptake via inhalation, µg/kg/day
TO-02	30396-10	5.1	244.8	0.105	0.0126	0.0044
TO-03	30396-11 gel	2	114	0.049	0.0059	0.0020

Considering inhalation the concentrations are below the RfC value of 1 mg/m³ and below the WHO air quality guideline value of 0.26 mg/m³.

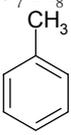
Considering the amount taken up the RfD is 0.2 mg/kg bw/day. The calculated values are a factor of 1×10⁶ lower. The calculated values are below the found TDI value of 0.12 mg/kg bw/day. Using NOAEL 12 mg/kg bw/day the margin of safety (MOS) is more than 2.7×10⁶.

Conclusion

Based on the calculated scenarios no health risks to the consumers are expected due to the presence of styrene in slimy toys.

6.3.17 Toluene

Identification

Name	Toluene
CAS no.	108-88-3
EINECS no.	203-625-9
Molecular formula	C ₇ H ₈
Molecular structure	
Molecular weight	92.15 g/mol
Synonyms	Methylbenzene Phenylmethane

The melting point is -95°C. The boiling point is 111°C. The vapour pressure is 3800 Pa at 25°C. The water solubility is 515 mg/l. The partition coefficient log Kow is experimentally determined to 2.65 (ECB 2003).

Classification

Toluene is classified in the List of dangerous substances (Miljøministeriet 2002):

F;R11	Highly flammable
Repr.Cat.3; R63	Possible risk of harm to the unborn child.
Xn;R48/20-65	Harmful: danger of serious damage to health by prolonged exposure through inhalation, may cause lung damage if swallowed.
Xi;R38	Irritant. Irritating to skin
R67	Vapours may cause drowsiness and dizziness

Effects on health

Toluene is irritating to the skin and harmful to the health. Toluene is suspected to be toxic to reproduction, i.e. possible risk of harm to the unborn child.

Acute toxicity

Of acute data several have been found. Of those are mentioned:

Acute oral, rat	LD ₅₀	5500 mg/kg	Kimura <i>et al.</i> 1971
Acute dermal, rabbit	LD ₅₀	12400 mg/kg	Smyth <i>et al.</i> 1969
Acute inhalation, rat	LC ₅₀ (6 h)	22 mg/l (22 g/m ³)	Bonnet <i>et al.</i> 1982
Acute inhalation, mouse	LC ₀ (6 h)	24 mg/l (24 g/m ³)	Bonnet <i>et al.</i> 1982

Data on acute toxicity via inhalation was between 22 and 24 g/m³, which do not present any immediate reason to concern. However, it was also observed that toluene even at low concentrations (from 285 mg/m³) may induce headaches, dizziness, irritation and sleeplessness (ECB 2003).

An inhalation value for humans with a LOEL 25 mg/m³ has been found (Lewis 1999).

In humans experimentally exposed to toluene a concentration at and above 75 ppm (285 mg/m³) resulted in headache, dizziness, a feeling of intoxication, irritation and sleeplessness. A NOAEC of 40 ppm (150 mg/m³) is set for these effects (ECB 2003).

A study concerns the neurological effects in occupationally exposed persons. No NOAEL could be established. LOAEL was observed to be 332 mg/m³ (88 ppm). LOAEL adjusted to continuous exposure was: $332 \times 10/20 \times 5/7 = 119$ mg/m³ (Foo *et al.* 1990).

In a 2-year rat study with chronic inhalation a degeneration of the nasal epithelium was observed (NTP, 1990). NOAEL could not be established. LOAEL was 2261 mg/m³ (600 ppm). Recalculating LOAEL to 24 hour/day and 7 days a week results in: $2261 \text{ mg/m}^3 \times 6.5/24 \text{ hours} \times 5/7 \text{ days} = 437 \text{ mg/m}^3$. Adjusting the effect in the extra-thoracic region assuming that the respiration rate for rats was 0.27 m³/day and that the epithelium in rats was 11.6 cm² and 177 cm² in humans, a resulting value would be: $437 \times (0.24/20 \text{ m}^3/\text{day}) \times (177/11.6 \text{ cm}^2) = 79 \text{ mg/m}^3$.

In humans, toluene is a known respiratory irritant with central nervous system (CNS) effects. Available studies could not provide a NOAEL concentration for either of these effects that should have been used in the evaluation of a potential basis for the RfC calculation. Consequently, the study of Foo *et al.* (1990) was used for the CNS effects, and that of the National Toxicology Program (NTP, 1990) for the irritant effects. Because the CNS effect was judged to be a more severe and relevant endpoint, the LOAEL for this effect was used for deriving the RfC. Further, this effect is supported by a number of other occupational studies that show effects around 100 ppm.

In a 13 week study on mice a LOAEL of 312 mg/kg/day was observed (WHO 2000). The result is based on a subchronic study (NTP 1989), where 10 rats/sex/group were orally gavage administered toluene dissolved in corn oil at dosage levels of 0, 312, 625, 1250, 2500, or 5000 mg/kg for 5 days/week for 13 weeks. All animals receiving 5000 mg/kg died within the first week. One female and 8 males in the 2500 mg/kg group died, but 2 of these were due to gavage errors. No deaths occurred at lower doses. Based on liver and kidney weight changes in male rats at 625 mg/kg the NOAEL was 312 mg/kg/day. The toxicological significance of these organ weight changes is strengthened by the occurrence of histopathologic changes in both the liver and kidney at higher doses. Because the exposure was for 5 days/week, LOAEL is recalculated to 7 days: $(625 \times 5/7 =)$ 446 mg/kg/day and NOAEL correspondingly $325 \times 5/7 = 223$ mg/kg/day (IRIS 2004).

A 90 days oral rat study with NOAEL of 625 mg/kg/day and a 2-year rat inhalation study with a NOAEC 300 ppm (1125 mg/m³) (ECB 2003).

Toluene is classified as reproduction toxic category 3 (Dir. 2004/74/EC, EC 2004), meaning that indications have been observed of possible risk of harm to the unborn child. Indication on repeated contact may cause allergic contact dermatitis has also been observed.

Absorption

Data have been found on the dermal exposure, and the uptake fraction is low. Dermal uptake at exposure to toluene vapours is measured to approx. 1% of

the amount of toluene taken up via inhalation at exposure to the same concentrations (Riihimäki and Pfäffli 1978, Piotrowski 1967).

Uptake via inhalation is studied in humans. The uptake after 3 hours of exposure when at rest was approx. 50% of the inhaled amount of toluene. During work the uptake may be significantly higher. It was concluded that toluene is fast taken up by inhalation and that the amount depended on the respiration rate.

Threshold limit values

The threshold limit value for the working is 94 mg/m^3 equivalent to 25 ppm (AT 2002).

The inhalation RfC value 0.4 mg/m^3 is based on the Foo *et al.* 1990 study mentioned above where a LOAEL was found and recalculated to 119 mg/m^3 . Applying a safety factor of 300 (10 for intraspecies variation, 10 for extrapolating from LOAEL to NOAEL and 3 due to data deficiencies) results in $\text{RfC} = 119/300 = 0.4 \text{ mg/m}^3$.

The C-value is 0.4 mg/m^3 (B-værdivejledningen 2002).

Oral RfD value is 0.2 mg/kg bw/day based on a 13 weeks oral rat study where styrene was administered by gavage. In the study changes in liver and kidney weight were observed. LOAEL was 625 mg/kg bw/day and NOAEL 312 mg/kg bw/day . Because the exposure was for 5 days/week NOAEL was adjusted to $312 \times 5/7 = 223 \text{ mg/kg bw/day}$. A safety factor of 1000 was applied (for inter and intraspecies variation, for subchronic to chronic extrapolation and for limited number of data on reproduction and development).

The TDI value $223 \text{ } \mu\text{g/kg bw/day}$ is based on LOAEL 312 mg/kg/day in a 13 week study on mice (WHO 2000).

Assessment

The evaluation of inhalation is based on short term exposure with 1 m^3 air in the breathing zone and exposure for 1 hour, and a long-term exposure scenario using exposure in a 20 m^3 room for 1 hour per day. Both scenarios using exposure to a child of 10 kg body weight (bw). The absorption by inhalation is set to 100%.

Table 6.26 Uptake via inhalation by exposure to toluene

ID no.	Lab. no.	Content, %	Total, ng	Breathing zone concentration, $\mu\text{g}/\text{m}^3$	Acute uptake via inhalation, $\mu\text{g}/\text{kg}/\text{day}$	Chronic uptake via inhalation, $\mu\text{g}/\text{kg}/\text{day}$
DK-01	30396-1	4.2	1932	0.832	0.0998	0.0345
DK-02	30396-2	18	1170	0.504	0.0605	0.0209
DK-03	30396-3	5.9	1670	0.719	0.0863	0.0298
K-01, exterior	30396-5A	66	7326	3.153	0.3784	0.1308
K-01, gel	30396-5B	70	406	0.350	0.0420	0.0145
BR-01	30396-7A	7.1	1967	0.847	0.1016	0.0352
BR-01	30396-7B	8	272	0.234	0.0281	0.0097
F-01	30396-8	6	1860	0.801	0.0961	0.0332
TO-01	30396-9	2.3	393.3	0.169	0.0203	0.0070
TO-02	30396-10	17	816	0.351	0.0421	0.0146
TO-03	30396-11 lip	20	320	0.138	0.0166	0.0057
TO-03	30396-11 gel	6.9	393.3	0.169	0.0203	0.0070
G-01	30396-12	10	660	0.284	0.0341	0.0118
K-03	30396-13	7.2	122.4	0.053	0.0064	0.0022
TI-01	30396-16A	10	800	0.344	0.0413	0.0143
TI-01	30396-16B	10	127	0.109	0.0131	0.0045
R-01	30396-17A	1	464	0.200	0.0240	0.0083
A-01	30396-18A	2.1	495.6	0.213	0.0256	0.0088

The RfD and TDI value of 223 $\mu\text{g}/\text{kg}$ bw/day is not exceeded.

Toluene was also observed in the analyses of migrated substances. The results are presented below.

Table 6.27 Uptake by dermal exposure to toluene

ID no.	Lab. no.	Weight, g	Measured migration, $\mu\text{g}/\text{g}$	Total migration, μg	Dermal uptake $\mu\text{g}/\text{kg}$ bw/day
DK-01	30396-1	23.7	0.20	4.734	0.1184
DK-02	30396-2	15.6	0.13	2.0238	0.0506
DK-03	30396-3	8.2	0.17	1.3969	0.0349
K-01, exterior	30396-5A	22.2	1.4	31.0716	0.7768
BR-01, exterior	30396-7	25.2	0.16	4.0254	0.1006
F-01, exterior	30396-8	20.6	0.14	2.8795	0.0720
F-01, interior	30396-8C	6.1	0.19	3.9079	0.0977
G-01	30396-12	102.7	0.06	6.1598	0.1540
K-03, exterior	30396-13	9.8	<0.05	<0.4884	<0.0122
TI-01, exterior	30396-16	3.7	<0.05	<0.1859	<0.0046
A-01	30396-18	12.2	0.05	0.6076	0.0152

Table 6.28 Uptake by oral exposure to toluene

ID no.	Lab. no.	Weight, g	Measured migration, µg/g	Total migration, µg	Oral uptake µg/kg bw/day
DK-01	30396-1	23.7	0.27	6.3909	0.1598
DK-02	30396-2	15.6	0.09	1.40112	0.0350
DK-03	30396-3	8.2	0.22	1.8077	0.0452
K-01, exterior	30396-5A	22.2	1.5	33.2910	0.8323
BR-01, exterior	30396-7	25.2	0.15	3.7739	0.0943
F-01, exterior	30396-8	20.6	0.16	3.2909	0.0823
F-01, interior	30396-8C	6.1	0.24	4.9363	0.1234
G-01	30396-12	102.7	0.05	5.1332	0.1283
K-03, exterior	30396-13	9.8	<0.05	<0.4884	<0.0122
TI-01, exterior	30396-16	3.7	<0.05	<0.1859	<0.0046
A-01	30396-18	12.2	<0.05	<0.6076	<0.0152

The total contribution from the three exposure routes is calculated below by addition of each contribution.

Table 6.29 The total contribution by exposure to toluene

	Slimy toy no.	Uptake via inhalation, µg/kg/day	Dermal uptake µg/kg bw/day	Oral uptake, µg/kg bw/day	Total uptake, µg/kg bw/day
DK-01	30396-1	0.0345	0.1184	0.1598	0.3127
DK-02	30396-2	0.0209	0.0506	0.0350	0.1065
DK-03	30396-3	0.0298	0.0349	0.0452	0.1099
K-01, exterior	30396-5A	0.1308	0.7768	0.8323	1.7399
K-01, gel	30396-5B	0.0145			0.0145
BR-01	30396-7A	0.0352	0.1006	0.0943	0.2301
BR-01	30396-7B	0.0097			0.0097
F-01	30396-8	0.0332	0.0720	0.0823	0.1875
F-01	30396-8C		0.0977	0.1234	0.2211
TO-01	30396-9	0.0070			0.0070
TO-02	30396-10	0.0146			0.0146
TO-03	30396-11 lip	0.0057			0.0057
TO-03	30396-11 gel	0.0070			0.0070
G-01	30396-12	0.0118	0.1540	0.1283	0.2941
K-03	30396-13	0.0022	<0.0122	<0.0122	<0.0266
TI-01	30396-16A	0.0143	<0.0046	<0.0046	<0.0235
TI-01	30396-16B	0.0045			0.0045
R-01	30396-17A	0.0083			0.0083
A-01	30396-18A	0.0088	0.0152	<0.0152	<0.0392

Conclusion

The toluene release from the tested slimy toys did not reach concentrations that could cause health problems to the consumer. The highest uptake was from K-01 where the uptake was 1.7 µg/kg bw/day. The TDI value is 223 µg/kg bw/day. Using the NOAEL 223 mg/kg bw/day the margin of safety is more than $(223/0.0017 =)$ 130000.

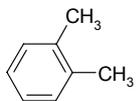
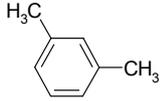
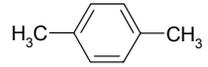
However, it should be noted the amount of toluene in air may also be caused by other sources than the studied toys. The actual indoor air concentration of toluene may therefore be higher than the estimated concentration.

6.3.18 Xylene

Xylene is used as solvent and in the production of colorants. Xylene consists of a mixture of the three isomers: o-, m-, and p-xylene with m-xylene as the dominant part (ratio approx. 20:40:20, respectively).

Identification

Name	Xylene
CAS no.	1330-20-7
EINECS no.	205-535-7
Molecular formula	C ₈ H ₁₀
Molecular structure	C ₆ H ₄ (CH ₃) ₂
Molecular weight	106,16 g/mol
Synonyms	Dimethylbenzene, (3 isomers o-, m-, og p-xylen) Methyltoluene Xylol

Name	CAS no.	EINECS no.	Structure
<i>ortho</i> -xylene (1,2-dimethylbenzene)	95-47-6	202-422-2	
<i>meta</i> -xylene (1,3-dimethylbenzene)	108-38-3	203-576-3	
<i>para</i> -xylene (1,4-dimethylbenzene)	106-42-3	203-396-5	

The boiling point of xylene (mixture) is 138.5°C. The vapour pressure is 1065 Pa at 25°C (7.99 mmHg, Daubert and Danner 1985). The water solubility is 106 mg/l at 25°C (Yalkowski and Dannenfelser 1992). The partition coefficient log Kow is experimentally determined to 3.12 (Hansch *et al.* 1995).

Classification

Xylene (and isomers) is adopted on the List of dangerous substances and classified (Miljøministeriet 2002):

R10	Flammable
Xn;R20/21	Harmful. Harmful by inhalation and in contact with skin
Xi;R38	Irritant. Irritating to skin

Effects on health

Of acute and chronic data are found:

Acute oral, rat	LD ₅₀	3608 mg/kg (<i>o</i> -xylene) 5011 mg/kg (<i>m</i> -xylene) 4029 mg/kg (<i>p</i> -xylene)	IPCS 1997
Acute dermal, rabbit	LD ₅₀	12180 mg/kg	IPCS 1997
Acute inhalation, rat	LC ₅₀ (6 h)	4330 ppm (<i>o</i> -xylene) 5796 ppm (<i>m</i> -xylene) 4591 ppm (<i>p</i> -xylene)	IPCS 1997
Chronic tests			
Oral rat,	NOEL	250 mg/kg	2 years, IPCS 1997
Inhalation, rat	LOAEL (6 h/d, 20 d)	870 mg/m ³ (200 ppm)	Hass and Jacobsen 1993

ATSDR (1995) points out that both animals and human data indicate that the mixtures of xylenes: m-, o- and p-xylene, all results in similar effects but that the single isomers not necessarily are equal potent relating to a specific effect. Therefore, the evaluation is based on xylene mixture.

Prolonged exposure to organic solvents may cause brain damage. Generally, concentrations around 100 ppm are observed to be the NOEL for brain damages. 10 mg/m³ is observed to be NOEL for teratogenic effects in animal studies (Hass and Jacobsen 1993).

Korsak *et al.* (1992) exposed groups of 12 rats to toluene, m-xylene, or a 1:1 mixture for 6 hours per day, 5 days per week at a concentration of 0 or 100 ppm for 6 months or 1000 ppm for 3 months. In a second study, Korsak *et al.* (1994) exposed groups of 12 rats by inhalation to 0, 50, or 100 ppm m-xylene, n-butyl alcohol or a 1:1 mixture for 6 hours per day, 5 days per week for 3 months and evaluated similar endpoints as in the earlier study (Korsak *et al.*, 1992). Sensitivity to pain was assessed by placing the animal on a hot plate (54°C) and measuring the time until the animal starts licking its paws. Rats exposed to 50 or 100 ppm m-xylene alone had statistically significantly increased sensitivity to pain at the end of the 3-month exposure period. LOAEL is set to 100 ppm and NOAEL 50 ppm.

Condie *et al.* (1988) has performed an oral rat study. A LOAEL of 150 mg/kg/day could be established, but the effects were minor, and there was no reason to believe that the NOAEL would be very different. The study is supported by NTP (1986), which in a chronic oral rat study observed a NOAEL of 179 mg/kg/day (cf. RfD below).

Xylenes are not classified for their carcinogenicity. IARC has placed xylenes in Group 3, i.e. "not classifiable as to its carcinogenicity to humans" (IARC 1999).

Threshold limit values

The threshold limit value for the working environment is 25 ppm equivalent to 109 mg/m³ with notation H, i.e. may penetrate the skin (AT 2002).

The C-value is 0.1 mg/m³ (B-værdivejledningen Miljøstyrelsen 2002).

The TCA (tolerable concentration in air): 870 µg/m³ (Baars *et al.* 2001). TCA is a guidance threshold limit value based on LOAEL 870 mg/m³ (200 ppm) observed in an inhalation study, where the critical endpoint was reproduction toxicity (Hass and Jacobsen 1993) and the application of a safety factor of 1000 (IPCS 1997).

The LCI value 100 µg/m³ is based on an animal study with a NOEL for teratogenic effect of 10 mg/m³ (LCI = NOEL/10×10×1) (Larsen *et al.* 1999).

The RfC: 0.1 mg/m³ is based on Korsak *et al.* (1992). In the study, impaired motor co-ordination was observed with a NOAEL 50 ppm equivalent to 217 mg/m³, which was recalculated to 217 mg/m³ × 6/24 hours × 5/7 days = 39 mg/m³. Applying a safety factor of 300 (10 for inter- and 10 for intraspecies variation and 3 for LOEL extrapolation to NOEL): 39/300 = 0.1 mg/m³.

The TDI (tolerable daily intake): 150 µg/kg bw/day (based on Condie *et al.* 1988).

The oral RfD value 0.2 mg/kg /day is based on a 2-year rat study where rats were administered xylene mixture daily for 5 days per week. A LOAEL was observed at 500 mg/kg/day and a NOAEL at 250 mg/kg/day (NTP 1986). Adjusted to chronic exposure the NOAEL value corresponded to $250 \times 5/7$ days = 179 mg/kg/day. Applying a safety factor of 1000 the RfD is derived at: $RfD = 179/1000 = 0.2$ mg/kg bw/day.

Absorption

Uptake via inhalation is found to be approx. 60% (ATSDR 1995, IPCS 1997). Because no further information was found, the evaluation is based on 100% absorption.

Assessment

The evaluation of inhalation is based on short term exposure with 1 m³ air in the breathing zone and exposure for 1 hour, and a long-term exposure scenario using exposure in a 20 m³ room for 1 hour per day. Both scenarios using exposure to a child of 10 kg body weight (bw). The absorption by inhalation is set to 100%.

Because xylene (= dimethylbenzene) and ethylbenzene were hardly separable in the screening analysis (headspace), they are considered together for the exposure via inhalation. However, they are separated in the quantitative analyses on migration to sweat and saliva.

Table 6.30 Uptake by exposure via inhalation of xylenes and ethylbenzene

ID no.	Lab. no.	Content, %	Total, Ng	Breathing zone concentration, µg/m ³	Acute uptake via inhalation, µg/kg/day	Chronic uptake via inhalation, µg/kg/day
DK-01	30396-1	1.3	598	0.257	0.0308	0.0107
DK-02	30396-2	11	715	0.308	0.0370	0.0128
DK-03	30396-3	2.2	622.6	0.268	0.03216	0.0111
K-01, exterior	30396-5A	13	1443	0.621	0.0745	0.0258
K-01, gel	30396-5B	6	34.8	0.030	0.0036	0.0012
BR-01	30396-7A	74	20498	8.823	1.0588	0.3662
	30396-7B	79	2686	2.312	0.2774	0.0959
F-01	30396-8	4.2	1302	0.560	0.0672	0.0232
TO-01	30396-9	0.5	85.5	0.037	0.0044	0.0016
TO-02	30396-10	10	480	0.207	0.0248	0.0086
TO-03	30396-11 lip	20	320	0.138	0.0166	0.0057
TO-03	30396-11 gel	2.7	153.9	0.066	0.0079	0.0027
G-01	30396-12	39	2574	1.108	0.1330	0.0460
K-03	30396-13	16	272	0.117	0.0140	0.0049
TI-01	30396-16A	14	1120	0.482	0.0578	0.0200
TI-01	30396-16B	9	114.3	0.098	0.0118	0.0041
R-01	30396-17A	0.8	371.2	0.160	0.0192	0.0066
A-01	30396-18A	45	10620	4.571	0.5485	0.1897
A-01	30396-18B	100	170	0.146	0.0175	0.0061

The uptake via inhalation is below the TDI value of 150 µg/kg bw/day.

Xylene was also detected in the analyses of migrated substance. The results are presented below.

Table 6.31 Uptake by dermal exposure to xylene

ID no.	Lab. no.	Weight, g	Measured migration, µg/g	Total migration, µg	Dermal uptake µg/kg bw/day
K-01, exterior	30396-5A	22.2	0.30	6.6582	0.1665
BR-01, exterior	30396-7	25.2	1.10	27.6749	0.6919
F-01, exterior	30396-8	20.6	0.26	5.3477	0.1337
F-01, interior	30396-8C	6.1	0.20	4.1136	0.1028
G-01	30396-12	102.7	0.27	27.7190	0.6930
A-01	30396-18	12.2	0.81	9.8431	0.2461

The dermal uptake is below the TDI value of 150 µg/kg bw/day.

Table 6.32 Uptake by oral exposure to xylene

ID no.	Lab. no.	Weight, g	Measured migration, µg/g	Total migration, µg	Oral uptake µg/kg bw/day
K-01, exterior	30396-5A	22.2	<0.05	<1.1097	<0.0277425
BR-01, exterior	30396-7	25.2	1.2	30.1908	0.75477
F-01, exterior	30396-8	20.6	0.31	6.37608	0.159402
F-01, interior	30396-8C	6.1	<0.05	<1.0284	<0.02571
G-01	30396-12	102.7	0.25	25.66575	0.64164375
A-01	30396-18	12.2	0.79	9.60008	0.240002

Oral uptake via the mouth cavity is below the TDI value of 150 µg/kg bw/day.

Even if the contribution from the two exposure routes dermal and oral are added, the largest calculated contribution of approx. 1.4 µg/kg/day is still below the TDI value.

The total contribution is made complicated, as the contribution from inhalation includes both xylene and ethylbenzene. Therefore, the total contribution from the three exposure routes is calculated by addition of each contribution from both xylene and ethylbenzene, cf. below.

Table 6.33 The total uptake by exposure to xylene and ethylbenzene

ID no.	Lab. no.	Uptake via inhalation, $\mu\text{g}/\text{kg}/\text{day}$	Dermal uptake $\mu\text{g}/\text{kg bw}/\text{day}$	Oral uptake $\mu\text{g}/\text{kg bw}/\text{day}$	Total uptake $\mu\text{g}/\text{kg bw}/\text{day}$
DK-01	30396-1	0.0107			0.0107
DK-02	30396-2	0.0128			0.0128
DK-03	30396-3	0.0111			0.0111
K-01, exterior	30396-5A	0.0258	0.1665 + <0.028	<0.0277 + <0.028	<0.2760
K-01, gel	30396-5B	0.0012			0.0012
BR-01	30396-7A	0.3662	0.6919 + 0.35	0.7548 + 0.40	2.5628
BR-01	30396-7B	0.0959			0.0959
F-01	30396-8	0.0232	0.1337 + <0.026	0.1594 + <0.025	<0.3673
F-01	30396-8C		0.1028	<0.0257	<0.1286
TO-01	30396-9	0.0015			0.0015
TO-02	30396-10	0.0086			0.0086
TO-03	30396-11 lip	0.0057			0.0057
TO-03	30396-11 gel	0.0027			0.0027
G-01	30396-12	0.0460	0.6930 + <0.13	0.6416 + <0.13	<1.6406
K-03	30396-13	0.0049			0.0049
TI-01	30396-16A	0.0200			0.0200
TI-01	30396-16B	0.0041			0.0041
R-01	30396-17A	0.0066			0.0066
A-01	30396-18A	0.1897	0.2461 + 0.018	0.2400 + 0.018	0.7118
A-01	30396-18B	0.0061			0.0061

Using the lowest TDI value of 100 $\mu\text{g}/\text{kg bw}/\text{day}$ (TDI for ethylbenzene) for the assessment, it is observed that the highest total uptake of 2.6 $\mu\text{g}/\text{kg bw}/\text{day}$ is from product BR-01. Thus, the amount is still below the TDI value. Using the NOAEL 179 $\text{mg}/\text{kg bw}/\text{day}$ the margin of safety (MOS) is more than: $179/0.00256 = 69000$.

Conclusion

The conclusion is that xylene (and ethylbenzene) is not released to an extent to pose a health risk to the consumer.

6.3.19 Boron

Identification

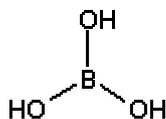
Name	Boron
CAS no.	7440-42-8
EINECS no.	231-151-2
Molecular formula	B
Atomic weight	10.81 g/mol

Boron has a melting point of 2300°C.

Boric acid

Identification

Name	Boric acid	
CAS no.	10043-35-3	11113-50-1
EINECS no.	233-139-2	234-343-4
Molecular formula	H_3BO_3	



Atomic weight	61.83 g/mol
---------------	-------------

Boric acid has a melting point of 171°C. The water solubility is 47.2 g/l at 20°C (IUCLID 2000) and 63.5 g/l at 30°C (WHO 1998). The vapour pressure is very low (9.9 μ Pa, ECB 2004). The partition coefficient is -0.757 at 25°C (IUCLID 2000).

Classification

Neither boron nor boric acid is classified currently (Miljøministeriet 2002). However, a new EU classification is suggested for boric acid, borax and other boron compounds (Miljøstyrelsen 2004):

Repr.Cat.3;R62	Possible risk of impaired fertility
Repr.Cat.3;R63	Possible risk of harm to the unborn child

According to the draft of 30th ATP (Adaptation to Technical Progress of Directive 67/548/EEC, draft, Jan. 2005) the later proposal is even more rigorous:

Repr.Cat.2;R60	May impair fertility
Repr.Cat.2;R61	May cause harm to the unborn child

Use

Boric acid and sodium salts of boron (primarily borax, or disodium tetraborate decahydrate) are used for the manufacture of glass, fibreglass insulation, polymers, laundry products, etc. (Woods 1994). Elemental boron has only limited applications.

Effects on health

Boron is a non-metallic element. Because boric acid is a weak acid with a pKa value of 9.2 the substance exists primarily as the undissociated acid (H_3BO_3) in aqueous solutions as do the borate salts. Therefore, the toxicity associated with these compounds is expected to be similar based on boron equivalents (US-EPA 2004). Most data on effects of boron are found in studies using boric acid and then recalculating to boron.

Acute toxicity:			
Acute oral, rat	LD ₅₀	550 mg B/kg bw	WHO 1998
Acute, inhalation, rat	LC ₅₀	890 mg/m ³	WHO 1998
Inhalation, rat, mouse	LC _{LO}	24 mg/m ³	WHO 1998

Boric acid is slightly irritating to the skin and to the eyes but not to a degree that requires classification (IUCLID 2000).

The data regarding developmental and reproductive toxicity show that lower foetal body weights in rats is the critical effect.

In a study on rat foetal development the female rats were administered boric acid from mating to 20 days later in the diet. The doses are calculated to 0, 78, 163, or 330 mg boric acid/kg/day (0, 13.6, 28.5 or 57.7 mg B/kg/day). Among several examined parameters the foetal weight was the most sensitive. LOAEL for decreased foetal weight was 13.6 mg B/kg bw/day (Heindel *et al.* 1992).

A similar study performed in the same way but using the doses 19, 36, 55, 76, and 143 mg boric acid/kg/day (3.3, 6.3, 9.6, 13.3, and 25 mg B/kg/day). In the study was observed that for the foetal weight gain LOAEL was 76 mg boric acid/kg bw/day (13.3 mg B/kg bw/day) and NOAEL 55 mg boric acid/kg bw/day corresponding to 9.6 mg B/kg bw/day (Price *et al.* 1996).

It is noted that boric acid is undergoing risk assessment in the EU with Austria as the Member State responsible.

Threshold limit values

The threshold limit value for the working environment is 10 mg B/m³ (AC-GIH, boric acid as nuisance dust).

The C-value is administratively set to 0.003 mg B/m³ (B-værdilisten Miljøstyrelsen 2002).

The RfD value is 0.2 mg/kg bw/day (IRIS 2004, cf. - below).

Based on the studies by Heindel *et al.* (1992) and Price *et al.* (1996) US-EPA has calculated a "Benchmark Dose Level" with effect in the foetal weight decrease of 59 mg boric acid/kg bw/day (10.3 mg B/kg bw/day) and using a safety factor of 66 derived a RfD value of 0.2 mg B/kg bw/day (IRIS 2004).

The TDI is 0.4 mg B/kg bw/day (WHO 1998).

The recommended TI (Tolerable Intake) is 0.4 mg/kg bw/day (9.6/25), where it is also recommended that consumer products are allocated 5% of this value = 0.02 mg/kg bw/day (IPCS 1998).

Absorption

Boron is absorbed during inhalation exposure (US-EPA 2004).

Boron apparently is not absorbed across intact skin. However, there is evidence that boron can be absorbed through damaged skin, especially from an aqueous vehicle (Nielsen 1970).

Boron is well absorbed from the gastro-intestinal tract in humans. Schou *et al.* (1984) observed that after oral administration of boric acid in both water and water-emulsifying ointment an average of 92-94% of administered boron was excreted in the urine within 96 hours (US-EPA 2004).

Assessment

Boron was determined as total substance (cf. section 5). The results are presented below.

Table 6.34 Content of boron in positive screening analysis (remaining samples below detection limit of 1 µg/g)

ID no.	Lab. no.	Weight G	Measured content µg B/g
DK-01, exterior	30396-1	23.7	30
DK-01, liquid	30396-1	0.5	5800
K-01, liquid	30396-5	22.2	1.7
TO-01, exterior	30396-9	14.7	520
TO-02, exterior	30396-10	9.4	920
TO-03, lip gloss	30396-11	1.0	2.5
A-01, stars	30396-18	0.1	5.4

Table 6.35 Content of boric acid in positive quantitative analysis (remaining samples below the detection limit of 0.5-1 µg/g)

ID no.	Lab. no.	Weight g	Measured content µg B/g	Total, µg	Dermal uptake µg B/kg bw/day	Oral uptake µg B/kg bw/day
DK-01, liquid	30396-1	0.5	8400	4200	0.097	4.2
TO-01, exterior	30396-9	14.7	653	9320	0.21	0.93
TO-02, exterior	30396-10	9.4	1170	10985	0.25	1.10

The estimates of uptake from the interior (liquid) part of the slimy toy DK-01 is based on the assumption that the liquid may come into contact with the skin or as worst case directly into the mouth. The absorption is set to 23% via the skin (contact fraction 0.001) and 100% absorption via the mouth with a contact fraction estimated to 1%. Thus, the dermal uptake is: $0.5 \times 8400 \times 0.23 \times 0.001/10 = 0.097 \mu\text{g B/kg bw/day}$ and oral uptake: $0.5 \times 8400 \times 1.0 \times 0.01/10 = 4.2 \mu\text{g B/kg bw/day}$.

The estimates of the uptake from the analysed exterior part of the slimy toy are based on 1 o/oo migration and 23% uptake via the skin and 100% absorption orally.

The RfD value of boron is 0.2 mg B/kg bw/day. Because the value is based on boric acid in the study, the value is considered valid. This means that if more than 1% of the liquid in the toy is swallowed, there may be a risk of a harmful effect. Using the NOAEL 9.6 mg B/kg bw/day the margin of safety (MOS) is more than: $9.6/0.0043 = 2230$.

The highest concentration found was 8400 µg/g equivalent to 8400 mg/kg or 0.8% of the product.

Boric acid is regulated by the Statutory Order on Cosmetics according to which it is not to be used in products to children under 3 years of age. In mouthwash products maximum is 0.1% calculated boric acid, mass/mass and in other products max. 3%, both calculated as boric acid (Statutory Order no. 74 of 14/01/2005). This means that if the consumer by accident (release the liquid inside the toy) may "wash his mouth" with the content before spitting it out, the consumer has been exposed to a concentration of boron higher than allowed in mouthwash products.

Conclusion

The content of boron may potential pose a health problem to the consumer. Especially by contact to or by swallowing the liquid inside the toy, where the highest concentration of boron was measured.

6.3.20 Nickel

Identification

Name	Nickel
CAS no.	7440-02-0
EINECS no.	231-111-4
Molecular formula	Ni
Atomic weight	58.69

The melting point of nickel is 1455°C.

Classification

Nickel is classified in the List of dangerous substances (Miljøministeriet 2002):

Carc.3;R40	Limited evidence of carcinogenic effects
R43	May cause sensitization by skin contact

Most nickel compounds are classified for sensitisation potentials as R43, May cause sensitization by skin contact.

Effect on health

Skin contact with nickel is essential, as most nickel compounds may cause allergic reactions by sensitised persons. An assessment of skin contact would therefore be relevant. However, it has not been possible to find relevant data for such an assessment. EU has included nickel in the risk evaluation programme for existing substances but this has not yet been completed (ECB 2002).

Oral RfD is based on the results from a 2-year rat study (Ambrose *et al.* 1976), where the rats were exposed to 0, 100, 1000 or 2500 ppm nickel in the food (estimated to 0, 5, 50 and 125 mg/kg bw). A significant reduction of body weight was observed and in the females a significant higher heart to body weight ratio and a lower liver to body weight ratio than in controls both in 1000 and 2500 ppm groups. No significant effects were observed in the 100 ppm group. LOAEL was therefore set to 1000 ppm (50 mg Ni/kg bw) while NOAEL was 100 ppm (5 mg Ni/kg bw). The study was supported by a subchronic study performed later (1986), which also finds a NOAEL of 5 mg Ni/kg bw/day (IRIS 2004).

Threshold limit values

The threshold limit value for the working environment is 0.05 mg/m³ (AT 2002).

The TCA (tolerable concentration in air) is 0.05 µg/m³ (Baars *et al.* 2001). The C-value is 0.0001 mg/m³ (B-værdivejledningen 2002).

The tolerable daily intake by oral ingestion (TDI) has been calculated to 5 µg/kg bw/day (WHO 1996).

However, a Dutch assessment on nickel suggests 0.05 mg/kg bw/day i.e. 50 µg/kg bw/day based on a NOAEL of 5 mg/kg/day from a chronic rat study, where rats were exposed to nickel sulphate in the food and using a safety factor of 100 (Baars *et al.* 2001).

The RfD value 0.02 mg/kg bw/day is based on a 2-year rat study by Ambrose *et al.* (1976). A safety factor of 300 was used (IRIS 2004).

Absorption

The bioavailability by oral intake is estimated to 5% (Baars *et al.* 2001). By dermal uptake the absorption is shown to be 0.2% for humans (MST 2003).

Assessment

Nickel was measured as total nickel in the screening. The quantitative measurements resulted only in a small increase. The results are presented below.

Table 6.36 Content of nickel in the screening analyses with a positive result (remaining samples had nickel below the detection limit of 1 µg/g)

ID no.	Lab. no.	Weight, g	Measured content, µg Ni/g
TO-01, exterior	30396-9	14.7	0.72
A-01, gel	30396-18	12.2	2.6

The uptake is estimated based on the fact that all nickel is bioavailable.

Calculation example (assuming that all nickel migrates):

Dermal uptake: $2.96 \times 12.2 \times 0.002 / 10 = 0.0072$ µg/kg bw/day

Oral uptake: $2.96 \times 12.2 \times 0.05 / 11 = 0.1798$ µg/kg bw/day

Table 6.37 Content of nickel in quantitative analyses with positive result (remaining samples had nickel below the detection limit of 1 µg/g)

ID no.	Lab. no.	Weight, g	Measured content µg Ni/g	Total, µg	Dermal uptake µg/kg bw/day	Oral uptake µg/kg bw/day
TO-01, exterior	30396-9	14.7	0.83	12.18	0.0024	0.06
A-01, gel	30396-18	12.2	2.96	35.97	0.0072	0.18

This means that the total uptake (dermal and oral) is at maximum 0.2 µg/kg bw/day. The calculation demonstrates that even by the unrealistic assumption of total release the amounts will be below the TDI value.

The highest concentration was 2.96 µg Ni/g equivalent to 3×10^{-4} %. The WHO derived TDI value was 5 µg/kg body weight as the lowest of the two available TDI values.

From the calculation in the table above is observed that none of the amount intakes or uptakes result in a dose above 5 µg/kg bw/d. Using the NOAEL 5 mg/kg bw/day the margin of safety (MOS) is more than: $5 / 0.00018 = 28000$. Thus it is assessed that nickel does not imply any health risk.

Conclusion

Nickel does not pose a health risk by uptake at the amounts determined by analyses of the selected toys to most consumers.

Nickel is a known allergen. No information was found as to the levels necessary to exclude the possibility as it is individual and depends of the sensitivity of the exposed person. Therefore, a reservation is made relating to particularly sensitive persons.

6.4 Conclusion of health assessment

For the health assessments, parameters relating to small children are used in the scenarios, as the consumers in this context especially is related to children.

For the selected chemical substances, the table below summarises the released concentrations in the breathing zone (1 m³), migration to artificial sweat and saliva, the calculated uptakes, the used NOAEL, margin of safety (MOS) and conclusions. It should be noted that the room air concentration used to estimate uptake and compared to NOAEL is 5% (1/20) of the tabulated concentration in the breathing zone.

Table 6.38 Summary of conclusions for the evaluated substances

Name	N	Release to the breathing zone (ng/m ³), sweat and saliva (µg/g)	Uptake µg/kg bw/day	NOAEL mg/kg bw/day	MOS	Conclusion
Organic substances:						
2-Butanone	2	Air: 79-98 ng/m ³	0.0017-0.0022	594	≥2.7×10 ⁶	No health risk
2-Butoxyethanol	6	Air: 12-240 ng/m ³	0.0005-0.010	5	≥5.1×10 ⁵	No health risk
3-Carene	7	Air: 9-49 ng/m ³	0.0003-0.002	225	≥1.1×10 ⁸	No health risk (NB allergenic)
Cyclohexanone	14 4 4	Air: 9-4637 ng/m ³ Sweat: 0.5-43 µg/g Saliva: <0.05-160 µg/g	0.0004-0.192 0.21-158 <0.1-59 Total: 0.0004-217	462	≥2.4×10 ⁶ ≥2.9×10 ³ ≥7.8×10 ³ Total: ≥2000	No health risk
Diethylglycol di-benzoate	2	Sweat: 26-118 µg/g Saliva: 38-65 µg/g	6.1-43.3 8.9-23.9 Sum: 15-67 Total incl homologues: 17.6-130	250	≥5770 ≥10480	No health risk
Homologues	2	Sweat: 4-103 µg/g Saliva: 7-69 µg/g			Total incl homologues: ≥1920	
Ethylbenzene	6	Sweat: <0.05-0.56 µg/g Saliva: <0.05-0.64 µg/g	0.018-0.35 0.018-0.4 Total: <0.036-0.75	97	≥2.8×10 ⁵ ≥2.4×10 ⁵ Total: ≥10000	No health risk
2-Hexanone	1	Air: 87-93 ng/m ³	0.004	100	≥2.6×10 ⁸	No health risk
d-Limonene	4	Air: 10-25 ng/m ³	0.00046-0.001	10	≥1.0×10 ⁷	No health risk (NB allergenic oxidation products)
2-Phenoxyethanol	1 4 3	Air: 96 ng/m ³ Sweat: 53-16000 µg/g Saliva: 17-80 µg/g	0.004 27.3-1515 8.7-46 Total: 40-1515	200	5×10 ⁷ ≥130 ≥4300 Total ≥130	No health risk
2-Phenylmethylen-oktanal	1	Sweat: 8.6 µg/g	0.81	25	30800	No health risk (NB allergenic)
<i>alpha</i> -Pinene	9	Air: 8-182 ng/m ³	0.0003-0.022	260	≥3.2×10 ⁷	No health risk (NB allergenic)
1,2-Propanediol	2	Air: 205-1619 ng/m ³	0.008-0.067	2500	≥3.6×10 ⁷	No health risk
2-Propenoic acid 2 methyl-methylester =methylmethacrylate	1	Air: 177 ng/m ³	0.0073	121	1.6×10 ⁷	No health risk
N-Propylbenzamide + N-acetylbenzamide	2	Sweat: 0.7-2.4 µg/g Saliva: 1.6-36 µg/g	0.16-0.88 0.38-13.2 Total: 0.54-14.1	?		No health risk expected

N = Number of discoveries over the detection limit

Name	N	Release to the breathing zone (ng/m ³), sweat and saliva (µg/g)	Uptake µg/kg bw/day	NOAEL mg/kg bw/day	MOS	Conclusion
Styrene	2	Air: 49-105 ng/m ³	0.002-0.004	12	≥2.7×10 ⁶	No health risk
Toluene	17 11 11	Air: 53-3153 ng/m ³ Sweat: 0.05-1.4 µg/g Saliva: 0.05-1.5 µg/g	0.002-0.13 <0.005-0.78 <0.005-0.83 Total: <0.02-1.74	223	≥1.3×10 ⁵	No health risk
Xylene	15	Air: 37-8823 ng/m ³ Sweat: 0.20-1.1 µg/g Saliva: 0.31-1.2 µg/g	0.0016-0.37 0.13-0.69 <0.03-0.75 Total (sweat+saliva): 0.17-1.4	179	Saliva + sweat: ≥128000	No health risk
Xylene + ethylbenzene	16 6 6		Air: 0.006-0.37 Sweat: 0.1-1.14 Saliva: 0.02-1.15 Total: 0.0012-2.56	179 and 97 (used 97)	Total: ≥37900	No health risk
Inorganic substances:						
Boron	3	Total: 635-8400 µg B/g	Dermal: 0.10-0.25 Oral: 0.93-4.2 Total: 1.14-4.3	9.6	≥38400 2≥286 Total: ≥2230	No health risk at intended use, cf. remarks below and the evaluation of the substance
Nickel	2	Total: 0.83-2.96 µg Ni/g	Dermal: 0.0024-0.0072 Oral: 0.06-0.18 Total: 0.06-0.187	9.6	≥1.3×10 ⁵ ≥1.4×10 ⁵ Total: 51280	No health risk (NB allergenic)

N = Number of discoveries over the detection limit

The strong odour was observed from a few products. It can not be excluded that they may result in acute effects such as irritation of eyes, nose and throat. For a few substances a prolonged exposure, the possibility of contact allergy can not be excluded for specifically sensitive individuals.

The Scientific Committee on Cosmetic Products has identified 26 substances as known contact allergens (SCCNFP 1999). The substances have been regulated later by Directive 2003/15/EC (EC 2003). Of these, 2 of the 26 substances were detected in this study:

Table 6.37 Contact allergens from the SCCNFP list detected in the analyses of slimy toys

Names in the analysis	Name in SCCNFP 1999	CAS no.
2-(phenylmethylene)-octanal	Hexyl cinnamaldehyde	101-86-0
D-Limonene	D-Limonene	5989-27-5

D-Limonene was detected in 3 products and hexylcinnamaldehyde in 1 product.

Of other substances that are potentially allergenic, 3-carene, *alfa*-pinene and nickel were detected.

All 3 terpenes: D-limonene, 3-carene (7 products) and *alfa*-pinene (8 products), were only detected in the headspace analyses. Whether the effect from contact allergenes is the same by exposure via inhalation as by dermal contact is somewhat uncertain but the substances may also be found in aerosols, which potentially also may reach skin areas.

Boron was detected in 3 products at maximum 0.8% of the product. It is evaluated that by exposure to the liquid inside one of the products a health risk could not be excluded.

Nickel was detected in 2 products at maximum of 0.0003% of the toy. It is evaluated that the nickel content poses no immediate concern, unless the consumer is specifically sensitive (nickel allergy).

For the remaining substances were found that none was detected neither as volatile nor as migrated to sweat or saliva at such concentrations that uptake would cause any concern to let children play with the products.

However, it should be noted that the consumer (child) may handle more than one slimy toy simultaneously or at intervals, thus increasing the exposure to one or more chemical substances correspondingly. Other sources of the same chemicals may also be present in the surroundings of the play activity. This may also contribute to the total exposure.

7 Health assessment of two additional products

7.1 Introduction

The Danish Consumer Council has tested 80 pcs. of toy purchased in 10 European countries in collaboration with other European consumer organisations (Forbrugerrådet 2004a). The analysis results have been published on the Internet (Forbrugerrådet 2004b).

As a consequence of the examination, the Danish Environmental Protection Agency decided to have 2 slimy toy products, which were included in the test, analysed and assessed together with the slimy toy products, which were included in the survey project.

7.2 Screening and quantitative analyses

Based on the results of the study of the Danish Consumer Council an analysis of boron is performed by ICP-AES and headspace analysis by GC-MS for VOC, including aliphatic hydrocarbons and styrene. These analyses were performed similar to the analyses of the remaining pieces of slimy toy mentioned in chapter 5. The Danish Environmental Protection Agency has decided not to carry out migration analyses (sweat- and saliva extractions) on the 2 pcs. of slimy toy.

7.3 Identified substances

The substances in the 2 additional slimy toy products have been identified, and the results are presented in Enclosure J and K. The volatile substances detected at headspace (organic substances) are presented below together with the amount of boron detected in a total analysis (inorganic substances).

Table 7.1 Identified volatile substances in the headspace analysis of the 2 products

ID. no.		EX-01	EX-02
Component	CAS no.	% m/m	% m/m
Organic substances			
2-n-Butylacrolein	1070-66-2	4.2	
Cyclohexanone	108-94-1	0.9	
Ethanol	64-17-5		0.1
Heptanal	111-71-7	0.8	
cis-Hept-2-enal	57266-86-1	0.9	
Hexanal	66-25-1	13	
1-Methoxy-2-propanol	107-98-2	7.9	
1-Methoxy-2-propanone	5878-19-3		incl. in 2-propanol
2-Methyl-2-propanol	75-65-0	12	
Nonanal	124-19-6	1.7	
Octanal	124-13-0	1.8	
2-Octene-1-ol	26001-58-1	0.8	
2-Phenoxy ethanol	122-99-6		8.1
1-Propanol	71-23-8	14	
2-Propanol	67-63-0	15	0.3
Propylene glycol	57-55-6		28
Styrene	100-42-5		3.3
Xylenes			2.3
C9H12 aromatic hydrocarbons			17
C10H14 aromatic hydrocarbons			3.2
C9H18 aliphatic hydrocarbons		2.8	
C6 - C7 aliphatic hydrocarbons		26	
C12 - C16 aliphatic hydrocarbons			37

From the above table follows that only one organic substance (2-propanol) is in common. Otherwise, the products have different compositions.

Table 7.2 Quantitative measurements of inorganic substances (mg/kg)

Element	CAS no.	EX-01	EX-02
		mg/kg	mg/kg
Boron	7440-42-8	729	1100
Copper	7440-50-8	2.4 *	-
Nickel	7440-02-0	1.0 *	-
Selenium	7782-49-2	1.4 *	-
Zinc	7440-66-6	13000 *	-

* Values from the Danish Consumer Council (2004b)

-: below the limit of detection

7.4 Classification of identified substances

The classification of the identified substances are mentioned in tables below for the volatile organic compounds and the inorganic substances respectively.

Table 7.3 Classification of identified volatile substances

Chemical name	CAS no.	EINECS no.	Classification	Text
2-n-Butylacrolein (=2-Methylen hexanal)	1070-66-2	213-978-0		
Cyclohexanone	108-94-1	203-631-1	R10 Xn;R20	Flammable Harmful. Harmful by inhalation (conc. >=25% class.: Xn;R20)
Ethanol	64-17-5	200-578-6	F;R11	Highly flammable
Heptanal	111-71-7	203-898-4		
cis-2-Heptenal	57266-86-1			
Hexanal	66-25-1	200-624-5		

Chemical name	CAS no.	EINECS no.	Classification	Text
1-Methoxy-2-propanol	107-98-2	203-539-1	R10	Flammable
1-Methoxy-2-propanone (= methoxy-acetone)	5878-19-3	227-549-0		
2-Methyl-2-propanol (= EU: <i>tert</i> -butyl alcohol)	75-65-0	200-889-7	F;R11 Xn;R20	Highly flammable. Harmful. Harmful by inhalation (conc.>=25% class.: Xn;R20)
Nonanal	124-19-6	204-688-5	Self class.: N;R50	Very toxic to aquatic organisms
Octanal	124-13-0	204-683-8		
2-Octene-1-ol	26001-58-1			
2-Phenoxy ethanol	122-99-6	204-589-7	Xn;R22 Xi;R36	Harmful. Harmful if swallowed. Irritant: irritating to eyes
1-Propanol	71-23-8	200-746-9	F;R11 Xi;R41 R67	Highly flammable. Irritant. Risk of severe eye damage. Vapours may cause lethargy and dizziness
2-Propanol	67-63-0	200-661-7	F;R11 Xi;R36 R67	Very inflammable. Irritant. Irritating to eyes. Vapours may cause drowsiness and dizziness
Propylene-glycol	57-55-6	200-338-0		
Styrene	100-42-5	202-851-5	R10 Xn;R20 Xi;R36/38	Flammable. Harmful. Harmful by inhalation. Irritant. Irritating to eyes and skin conc.>=12.5% class.: Xn;R20 Xi;R36/38
Xylene (isomers)	1330-20-7	205-535-7	R10 Xn;R20/21 Xi;R38	Flammable. Harmful. Harmful by inhalation and in contact with skin conc.>=20% class.: Xn;R20/21 Xi;R38 12.5%<=conc.<20% class.: Xn;R20/21
C ₉ H ₁₂ aromatic hydrocarbons				
C ₁₀ H ₁₄ aromatic hydrocarbons				
C ₉ H ₁₈ aliphatic hydrocarbons				
C ₆ – C ₇ aliphatic hydrocarbons				
C ₁₂ – C ₁₆ aliphatic hydrocarbons				

Table 7.4 Classification of inorganic substances

Chemical name	CAS no.	EINECS no.	Classification	Text
Boron	7440-42-8	231-151-2		According to Miljøstyrelsen 2004 a proposal to classify boron the same as boric acid has been submitted. According to the 30th ATP, draft, boric acid, CAS no. 10043-35-3, is proposed classified Repr.Cat.2;R60 - 61, i.e. May impair fertility, May cause harm to the unborn child
Copper	7440-50-8	231-159-6		
Nickel	7440-02-0	231-111-4	Carc3;R40 R43	Limited evidence of carcinogenic effects May cause sensitization by skin contact
Selenium	7782-49-2	231-957-4	T; R23/25 R33 R53	Toxic by inhalation and if swallowed. Danger of cumulative effects. May cause long-term adverse effects in the aquatic environment
Zinc	7440-66-6	231-175-3	N; R50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

Subsequently, the substances have been evaluated based on the chemical substances selected in the other slimy toy products.

7.5 Assessment of 2 additional products

For the sake of comparability the assessments have been carried out in the same way as on the other slimy toy products. In consideration of the readability the used limit values are mentioned again.

Cyclohexanone

Cyclohexanone has previously been detected in 11 out of 20 products. Effect data are presented in section 6.3.4.

Threshold limit values

The threshold limit value is 40 mg/m³ with skin notation (H), i.e. the substance may penetrate the skin (AT 2002).

TCA (tolerable concentration in air): 136 µg/m³ (Baars *et al.* 2001).

The C-value is 0.1 mg/m³ (C-value guidelines, Miljøstyrelsen 2002).

The oral RfD value is 5 mg/kg bw/day (IRIS 2004).

The TDI value is 4.6 mg/kg/day (Baars *et al.* 2001).

Assessment

The assessment of inhalation is based on short-term exposure with 1 m³ air in the breathing zone and one hour of exposure, and also a long-term scenario with exposure in 20 m³ room for one hour daily, both for child with 10 kg body weight (bw). The absorption by inhalation has been set at 100%.

Table 7.5 Absorption via inhalation of cyclohexanone

ID no.	Lab. no.	Content %	Total, ng	Breathing zone concentration µg/m ³	Acute uptake via inhalation µg/kg/day	Chronic uptake via inhalation µg/kg/day
EX-01	31396-19	0.9	10	0.004	0.0005	0.00017

The TDI value of 4.6 mg/kg bw/day was not exceeded. The estimated concentration in the breathing air (1 m³) at acute exposure is 9.2x10⁶ times lower than the TDI value, and the estimated concentration in the air in 20 m³ room (chronic exposure) is 2.7x10⁶ times lower than the TDI value.

Using the NOAEL 462 mg/kg bw/day the margin of safety (MOS) is:
 $462/0.00000017 = 2.7 \times 10^8$.

Conclusion

Consequently, the release of cyclohexanone is not considered to constitute a health problem.

2-Phenoxyethanol

2-Phenoxyethanol has previously been detected as a volatile substance in 1 product. Effect data are stated in section 6.3.8.

Threshold limit values

The threshold limit value is 110 mg/m³ with skin notation (H), i.e. the substance may penetrate the skin (DF 2001).

The C-value is 0.1 mg/m³ (Miljøstyrelsen 2002).

Assessment

The assessment of inhalation is based on short-term exposure with 1 m³ air in the breathing zone and one hour of exposure, and also a long-term scenario

with exposure in 20 m³ room for one hour daily, both for child with 10 kg body weight (bw). The absorption by inhalation has been set at 100%.

Table 7.6 Uptake via inhalation by exposure to 2-phenoxyethanol

ID no.	Lab. no.	Content, %	Total, ng	Breathing zone concentration, µg/m ³	Acute uptake via inhalation, µg/kg/day	Chronic uptake via inhalation, µg/kg/day
EX-02	30396-20	8.1	2680	1.152	0.138	0.048

The calculated absorption via inhalation was 138 ng/kg bw/day in the short-term scenario and 48 ng/kg bw/day in the chronic scenario.

Since no TDI value is available, the NOAEL value of 200 mg/kg bw/day has been used. When comparing with this the margin of safety (MOS) for absorption via inhalation was 40×10⁶.

It should be noted that the headspace concentration, which has been measured in 1 litre of air, must be diluted by a factor 1000 to 1 m³, i.e. the concentration in breathing zone is 1.152 µg/m³ air. Thus, this value is approx. 100 times lower than the C-value.

Conclusion

It is assessed not to be a health risk from the exposure of 2-phenoxyethanol.

Styrene

Styrene has previously been detected in 2 products.

Threshold limit values

The threshold limit value for the working environment is 105 mg/m³ with notation LHK. **L** means that the threshold limit value is a ceiling value, which at no time must be exceeded. **H** means that the substance can penetrate the skin. **K** means that the substance is adopted on the list of substances that may be carcinogenic(AT 2002).

WHO has given a 24 hours air quality guideline value of 800 µg/m³ (IPCS 1983) and for continued exposure 260 µg/m³ air (WHO 2000).

The C-value is 0.2 mg/m³ (Miljøstyrelsen 2002).

The RfC value is 1 mg/m³ (IRIS).

The RfD value is 0.2 mg/kg bw/day (IRIS).

TDI is 120 µg/kg bw/day (Baars *et al.* 2001).

Assessment

The assessment of inhalation is based on short-time exposure with 1 m³ air in the breathing zone and one hour of exposure, and also a long-term scenario with exposure in 20 m³ room for one hour daily, both for child with 10 kg body weight (bw). The absorption by inhalation has been set at 100%.

Table 7.7 Uptake via inhalation by exposure to styrene

ID no.	Lab. no.	Content, %	Total, ng	Breathing zone concentration, µg/m ³	Acute uptake via inhalation, µg/kg/day	Chronic uptake via inhalation, µg/kg/day
EX-02	30396-20	3.3	1090	0.467	0.056	0.019

It should be noted that the uptake from this product is 5 times higher than for the previous 2 products, where styrene was detected.

Regarding inhalation the estimated concentration of $0.467 \mu\text{g}/\text{m}^3$ in the breathing zone is below the RfC value of $1 \text{ mg}/\text{m}^3$ and below WHO's air quality value of $0.8 \text{ mg}/\text{m}^3$.

Regarding uptake the chronic RfD is $0.2 \text{ mg}/\text{kg bw}/\text{day}$. The calculated value is a factor 10500 lower. The calculated value is below the stated TDI- value of $0.12 \text{ mg}/\text{kg bw}/\text{day}$.

Using the NOAEL $12 \text{ mg}/\text{kg bw}/\text{day}$ the margin of safety (MOS) is:
 $12/0.000019 = 631000$.

Conclusion

Based on the calculated scenarios no health problems are expected due to the presence of styrene in the mentioned toy.

Xylene

Xylene was detected as volatile substance in almost all the examined slimy toys.

Threshold limit values

The threshold limit value for working environment is $109 \text{ mg}/\text{m}^3$ with notation H (can penetrate the skin) (AT 2002).

The C-value is $0.1 \text{ mg}/\text{m}^3$ (Miljøstyrelsen 2002).

TCA (tolerable concentration in air): $870 \mu\text{g}/\text{m}^3$ (Baars *et al.* 2001).

The RfC value is $0.1 \text{ mg}/\text{m}^3$ (IRIS 2004).

TDI (tolerable daily intake): $150 \mu\text{g}/\text{kg bw}/\text{day}$ (based on Condie *et al.* 1988).
 The RfD value is $0.2 \text{ mg}/\text{kg}/\text{day}$ (IRIS 2004).

Assessment

The assessment of inhalation is based on short-term exposure with 1 m^3 air in the breathing zone and with exposure for one hour, and also a long-term scenario with exposure in 20 m^3 room for one hour daily, both for child with 10 kg body weight (bw). The absorption by inhalation has been set at 100%.

Table 7.8 Uptake via inhalation by exposure to xylenes and ethylbenzene

ID no.	Lab. no.	Content, %	Total, Ng	Breathing zone concentration, $\mu\text{g}/\text{m}^3$	Acute uptake via inhalation, $\mu\text{g}/\text{kg}/\text{day}$	Chronic uptake via inhalation, $\mu\text{g}/\text{kg}/\text{day}$
EX-02	30396-20	2.3	770	0.331	0.0397	0.0137

The concentration in the breathing zone is $0.33 \mu\text{g}/\text{m}^3$, corresponding to 300 times lower than the RfC value.

The uptake via inhalation is below the TDI- value of $150 \mu\text{g}/\text{kg bw}/\text{day}$.

Using the NOAEL $179 \text{ mg}/\text{kg bw}/\text{day}$ the margin of safety (MOS) is:
 $179/0.0000137 = 1.3 \times 10^7$.

Conclusion

Consequently, xylene and ethylbenzene are not released to an extent that constitute a health problem to the consumer.

Aliphatic hydrocarbons

The aliphatic hydrocarbons may be linear or branched.

The alkanes C₆₋₇ and C₁₂₋₁₆ (hexane, heptane and dodecane, tridecane, tetradecane, pentadecane, hexadecane) have been grouped in the measurements.

Effects on health

For many of the aliphatic hydrocarbons dermatitis, irritation, influences on the central nervous system and anaesthesia have been observed. The effects are increased by increased molecular weight. In general, aliphatic mixtures have a neurotoxic effect at approx. 100 ppm corresponding to 200-600 mg/m³ (Larsen *et al.* 1999).

The lowest toxic dose (TD₀₁) for tetradecane on mice exposed for 20 weeks is 9600 mg/kg according to Clayton and Clayton (1981), who state that C₁₃-C₁₆ alkanes at inhalation have the same effects as C₆-C₁₀, but with a slower mortality rate.

Classification

Alkanes, C₆₋₁₂-branched and linear, are adopted on the List of dangerous substances (Miljøministeriet 2002) with the classification:

Carc2;R45 May cause cancer

Threshold limit values

The threshold limit value for C₉-C₁₃: 180 mg/m³ (AT 2002).

LCI for C₇₋₁₂ is based on a general neurotoxic effect at 200 to 600 mg/m³ in humans, i.e. LCI = NOEL/1×10 = 20 to 60 mg/m³ is suggested in Larsen *et al.* (1999).

Other limit values detected for the substances or related substances:

Substance	Threshold limit value mg/m ³	LCI, mg/m ³	C-value, mg/m ³
Heptane	820	8	
Octane	930		
Nonane	180	10	
Decane	180	2	
Undecane	180		1
Dodecane	180		
Tridecane	180		1

In the analyses in 1 product (lab no. 31396-20) for the group of C₁₂₋₁₆ was detected at a concentration that was recalculated to 5.324 mg/m³ in the head-space container of 1 litre. Diluting this concentration to 1 m³ (the breathing zone), the concentration in the breathing zone is 5.3 µg/m³.

Conclusion

The aliphatic hydrocarbons could not be separated in the chemical analysis and must be considered as a group. Based on the subjective assessment when purchasing the samples the presence of hydrocarbons could be smelled as an oily smell, which is characteristic of hydrocarbons.

The measurements of the evaporated concentrations do not reach the 200 mg/m³, which cause neurotoxic damages according to Larsen *et al.* (1999). The LCI value of 20 mg/m³ (which is the lowest concentration that can cause irritant effects by inhalation), can only be exceeded by placing the nose very close to the recently purchased product. The data basis is too small in order to give a unambiguous conclusion. However, if the classification is valid for the detected substances, they may be carcinogenic.

Boron

Boron has been detected in 6 of the previously examined slimy toys.

Threshold limit values

The threshold limit value for the working environment is 10 mg B/m³ (AC-GIH, boric acid as nuisance dust).

The C-value is administratively set to 0.003 mg B/m³ (Miljøstyrelsen 2002).

The RfD value is 0.2 mg/kg bw/day (IRIS 2004).

The recommended TI (Tolerable Intake) is 0.4 mg/kg bw/day (9.6/25) where it is also recommended that consumer products are allocated 5% of this value = 0.02 mg/kg bw/day (IPCS 1998).

Assessment

Boron was determined as total substance. The results are presented below.

Table 7.9 Content of boron in µg B/g

ID nr.	Lab. nr.	Weight, g	Measured content, µg B/g	Total, µg	Dermal uptake µg/kg/dag	Oral uptake µg/kg/dag
EX-01	30396-19	27,9	729	20339	0,4678	20,3
EX-02	30396-20	17,8	1100	19580	0,4503	19,6

The %RSD presents the percentage relative standard deviation made as common estimate based on the relative standard deviation from duplicate determinations.

The highest measured concentration was 1100 µg/g equivalent to 1100 mg/kg or 0.11% of the product.

The estimates of the uptake from the liquid inside the slimy toys are based on the assumption that the liquid may come into contact with the skin or as worst case directly into the mouth. The estimates of the uptake from the exterior parts of slimy toys are based on 1 o/oo migration and 23% uptake via the skin and 100% absorption orally. The uptake via inhalation is estimated to be insignificant from a slimy product.

Thus, the calculations are (example):

dermal uptake: $17.8 \times 1100 \times 0.23 \times 0.001 / 10 = 0.45 \mu\text{g/kg/day}$

oral uptake: $17.8 \times 1100 \times 1.0 \times 0.01 / 10 = 19.6 \mu\text{g/kg/day}$

Comparing the total uptake of approx. 20 µg/kg bw/day with the chronic RfD value of 0.2 mg/kg bw/day, no immediate health risks exist.

Using the NOAEL 9.6 mg B/kg bw/day the margin of safety (MOS) is approx.: $9.6/0.020 = 480$.

However, it should be remembered that according to Miljøstyrelsen (2004) a proposal to classify boron the same as boric acid. This would result in a classification of at least: Reproduction toxic category 3;R62 and R63, i.e. "Possi-

ble risk of impaired fertility” and ”Possible risk of harm to the unborn child”. Since then the proposed classification is made more rigorous to: Reproduction toxic category 2;R60 and R61, i.e. ”May impair fertility” and ”May cause harm to the unborn child”.

Boric acid is under the EU risk assessment of existing chemical substances but the assessment is not finalised.

Conclusion

Based on the available information it is assessed that the content of boron does not constitute a health problem to the consumer.

7.6 Conclusion

A further 2 products were included in the study. The exposure to most of the volatile substances was assessed not to cause a health risk to the consumer. A rather high concentration of the group of aliphatic hydrocarbons was detected, which are classified carcinogenic.

8 References

- Abdo KM, Graham DG, Timmons PR (1982): Neurotoxicity of continuous (90 days) inhalation of technical grade methyl butyl ketone in hens. *J. Toxicol. Environ. Health* 9:199-215.
- Abou-Donia MB, Makkawy H-AM, Graham DB (1982): The relative neurotoxicities of n-hexane, methyl n-butyl ketone, 2,5-hexanediol, and 2,5-hexanedione following oral or intraperitoneal administration in hens. *Toxicol. Appl. Pharmacol.* 62: 369-389.
- ACGIH (1991). Documentation of the Threshold Limit Values and Biological Exposure Indices. 6th Edition. Vol. 2. American Conference of Governmental Industrial Hygienists Inc., Cincinnati (OH), 1063-1066.
- Ambrose AM, Larson DS, Borzelleca JR, Hennigar GR, Jr. (1976): Long-term toxicologic assessment of nickel in rats and dogs. *J. Food Sci. Technol.* 13: 181-187.
- ASS (2000): Hygieniska gränsvärden och åtgärder mot luftföroreningar. Arbetskyddsstyrelsen, Solna, Sverige.
- AT (2002): Grænseværdier for stoffer og materialer. At-vejledning. C.0.1, Oktober 2002. Arbejdstilsynet, København.
- ATP (2003): Revision of the 29th Adaptation to Technical Progress of Dir. 67/548/EEC on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances. European Commission, European Chemicals Bureau. *NB revisio- nen godkendt i Dir. 2004/73/EC (EC 2004) men endnu ikke implementeret i dansk lovgivning " bekg. af listen over farlige stoffer " (Miljøministeriet 2002)*
- ATSDR (1992): Toxicological profile for hexanone. Agency for Toxic Substances and Disease Registry. U.S. Department of Health and Human Services, Public Health Service, Atlanta (GA), USA.
- ATSDR (1995): Toxicological profile for xylenes. Agency for Toxic Substances and Disease Registry. U.S. Department of Health and Human Services, Public Health Service, Atlanta (GA), USA.
- ATSDR (1997): Toxicological profile for ethylene glycol and propylene glycol. US Department of Health and Human Services. Agency for Toxic Substances and Disease Registry, Georgia, USA.
- Baars AJ, Theelen RMC, Janssen PJCM, Hesse JM, van Apeldoorn ME, Meijerink MCM, Verdam L, Zeilmaker MJ (2001): Re-evaluation of human-toxicological maximum permissible risk levels. RIVM report 711701025. National Institute of Public Health and the Environment, Bilthoven, The Netherlands.

Bingham E, Cohrssen B, Powell CH (2001): Turpentine. *Patty's Toxicology*, 5th ed., Vol.4: 209-212. John Wiley and Sons, New York, NY.

Statutory Order 74 (2005): Statutory Order on Cosmetics. Statutory Order no. 74 of 14/01/05. The Ministry of Health.

Bonnet P, Morele Y, Raoult G, Zissu D, Gradiski D (1982). Détermination de la concentration létale₅₀ des principaux hydrocarbures aromatiques chez le rat. *Arch. Mal. Prof.* 34: 261-65.

Borzelleca JF, Larson PS, Hennigar GR, Hluf EG, Crawford EM, Blackwell Smith R (1964): Studies on the chronic oral toxicity of monomeric ethyl acrylate and methyl methacrylate. *Toxicol. Appl. Pharmacol.* 6: 29-36.

Bremmer HJ, van Veen MP (2002): Children's toys fact sheet. To assess the risks for the consumer. RIVM report 612810012/2002. National Institute of Public Health and the Environment, Bilthoven, The Netherlands.

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

CICAD (1998): Methyl methacrylate. The Concise International Chemical Assessment Document No. 4. The International Programme on Chemical Safety (IPCS), World Health Organization, Geneva.

CICAD (1998): Limonene. The Concise International Chemical Assessment Document No. 5. The International Programme on Chemical Safety (IPCS), World Health Organization, Geneva.

CICAD (1998): 2-Butoxyethanol. Concise International Chemical Assessment Document No. 10. International Programme on Chemical Safety. WHO, Geneva.

Clayton GD, Clayton FE, eds. (1981): *Patty's Industrial Hygiene and Toxicology: Volume 2: Toxicology*. 3rd ed. John Wiley Sons, 1981-1982. New York.

Cox GE, Bailey DE, Morgareidge K (1975): Toxicity studies in rats with 2-butanol including growth, reproduction and teratologic observations. Food and Drug Research Laboratories, Inc., Waverly, NY. Report No. 91MR R 1673 (IRIS 2004).

Condie LW, Hill JR, Borzelleca JF (1988): Oral toxicity studies with xylene isomers and mixed xylenes. *Drug Chem. Toxicol.* 11: 329-354.

Daubert TE, Danner RP (1989); *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*. Design Inst Phys Prop Data, Amer Inst Chem Eng NY: Hemisphere Pub Corp, NY.

De Groot AC, Bos JD, Jagtman BA, Bruynzell DP, van Joost T, Weyland JW (1986): Contact allergy to preservatives – II. Contact Dermatitis 15: 218-222.

De Heer C, Wilschut A, Stevenson H, Hakkert BC (1999): Guidance document on the estimation of dermal absorption according to a tiered approach.

An update. TNO report No. V98.1237. TNO Nutrition and Food Research Institute, Zeist, The Netherlands.

DF (2001): Maximale Arbeitsplatzkonzentrationen und Biologische Arbeitsstofftoleranzwerte. Deutsche Forschungsgemeinschaft, Senatskommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe. Mitteilung 37. MAK und BAT Werte Liste 2001. Weinheim, Wiley-VCH.

DF (2001): MAK- und BAT- Werte-Liste 2001. Maximale Arbeitsplatzkonzentrationen und Biologische Arbeitsstofftoleranzwerte. Senatskommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe. Mitteilung 37. Deutsche Forschungsgemeinschaft. Wiley-VCH.

DiVincenzo GD, Hamilton ML, Kaplan CJ, et al. (1977): Metabolic fate and disposition of ¹⁴C-labeled methyl n-butyl ketone in the rat. *Toxicol Appl Pharmacol* 41:547-560.

DiVincenzo GD, Hamilton ML, Kaplan CJ, et al. (1978): Studies on the respiratory uptake and excretion and the skin absorption of methyl n-butyl ketone in humans and dogs. *Toxicol Appl Pharmacol* 44:593-604.

Dodd DE, Snelling WM, Maronpot RR (1983) Ethylene glycol monobutyl ether. Acute, 9-day and 90-day vapor inhalation studies in Fisher 344 rats. *Toxicol. Appl. Pharmacol.* 68: 405-414.

DOW (1990): The Glycol Ethers Handbook. The Dow Chemical Company, Midland, MI.

Eben A, Flucke W, Mihail F (1979): Toxicological and metabolic studies of methyl n-butylketone, 2,5-hexanedione, and 2,5-hexanediol in male rats. *Ecotoxicol. Environ. Safety* 3: 204-217.

EC (2003): Technical Guidance Document on Risk Assessment in support of Commission Directive 93/67/EEC on Risk assessment for new notified substances, Commission Regulation (EC) 1488/94 on Risk assessment for existing substances and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market. Parts 1-4. European Commission (EC), Joint Research Centre, EUR 20418 EN, Office for Official Publications of the EC, Luxembourg.

EC (2003): Europa Parlamentets og Rådets direktiv 2003/15/EF af 27. februar 2003 om ændring af Rådets direktiv 76/768/EØF om indbyrdes tilnærmelse af medlemsstaternes lovgivning om kosmetiske midler. *Den Europæiske Unions Tidende*, 11.3.2003, L 66: 26-35.

EC (2004): Commission Directive 2004/73/EC of 29 April 2004 adapting to technical progress for the 29th time Council Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances. *Official Journal of the European Union*, 16.6.2004, L 216; 3-310.

ECB (2002): Risk Assessment Report on Methyl methacrylate, CAS#: 80-62-6, EINECS#: 201-297-1. Risk-Assessment Report Vol. 22, EUR 19832 EN. European Commission – Joint Research Centre. Institute for Health and Con-

sumer Protection. European Chemicals Bureau (ECB). Office for official publications of the European Communities. Luxembourg.

ECB (2002): Risk Assessment Report on Styrene, CAS#: 100-42-5, EINECS#: 202-851-5. Risk-Assessment Report, environment only Vol. 27, EUR 20541 EN. European Commission – Joint Research Centre. Institute for Health and Consumer Protection. European Chemicals Bureau (ECB). Office for official publications of the European Communities. Luxembourg.

ECB (2003): Risk Assessment Report on Toluene, CAS#: 108-88-3, EINECS#: 203-625-9. Risk-Assessment Report Vol. 30, EUR 20539 EN. European Commission – Joint Research Centre. Institute for Health and Consumer Protection. European Chemicals Bureau (ECB). Office for official publications of the European Communities. Luxembourg.

ECB (2004); Risk Assessment Report on 2-Butoxyethanol, CAS No.: 111-76-2, EINECS No: 203-905-0. Draft of August 2004. Prepared by France for the European Commission – Joint Research Centre. Institute for Health and Consumer Protection. European Chemicals Bureau (ECB).

ECB (2004): Risk Assessment Report on zinc metal, CAS#: 7440-66-6, EINECS#: 231-175-3. Risk Assessment Report Vol. 42, 2004: EUR 21169 EN. European Commission – Joint Research Centre. Institute for Health and Consumer Protection. European Chemicals Bureau (ECB). Office for official publications of the European Communities. Luxembourg.

EU (1997): Evaluation of VOC Emissions from Building Products. Report no. 18. European Commission.

Fairhurst S, Minty CA (1989): The toxicity of chromium and inorganic chromium compounds. Toxicity Review 21. Health and Safety Executive, Her Majesty's Stationary Office, London.

Falk-Filipsson A (1995): Toxicokinetics and acute effects of inhalation exposure to monoterpenes in man. Arbete och Hälsa 1995: 3. Arbetsmiljövinstutetet (National Institute of Occupational Health), Solna, Sweden.

Falk-Filipsson A, Löf A, Hagberg M, Wigaeus Hjelm E, Wang Z (1993): d-Limonene exposure to humans by inhalation: Uptake, distribution, elimination and effects on the pulmonary function. J. Toxicol. Environ. Health 38: 77-88.

Falk Filipsson A, Bard J, Karlsson S (1998): Limonene. Concise International Chemical Assessment Document (CICAD) No. 5, International Programme on Chemical Safety, World Health Organization, Geneva.

FAO/WHO (1974). Toxicological evaluation of certain food additives with a review of general principles and of specifications. In: 17th Report of the Joint FAO/WHO Expert Committee on Food Additives, Geneva, Switzerland, June 25-July 4, 1973. Geneva, Switzerland: Food and Agricultural Organization of the United Nations/World Health Organization.

FFHPVC (2000): Test plan for cinnamyl derivatives. Submitted to US-EPA under the HPV Challenge Program by The Flavor and Fragrance High Production Volume Consortia, The Aromatic Consortium, Washington DC.

FFHPVC (2002): Robust summaries for bicyclic terpene hydrocarbons. The Flavour and Fragrance High Production Volume Consortia, The Terpene Consortia. Submitted to the US-EPA under the HPV challenge program. (www.epa.gov/opptintr).

Foo S, Jeyaratnam J, Koh D (1990): Chronic neurobehavioral effects of toluene. *Br. J. Ind. Med.* 47(7): 480-484.

Forbrugerrådet (2004a): Legetøj – Kemiske stoffer kaster skygge over børns leg. Tænk og test nr. 49/2004: 16-23 . Forbrugerrådet, København.

Forbrugerrådet (2004b): Test of toys for presence of chemical compounds. Udført af Teknologisk Institut for Forbrugerrådet, København, Danmark. Oktober 2004 (http://www.miljoeogsundhed.dk/rapport/TI_report.pdf)

Furia TE, Bellanca N (1975): Fenaroli's Handbook of Flavor Ingredients. Volume 2. Edited, translated, and revised by T.E. Furia and N. Bellanca. 2nd ed. The Chemical Rubber Co., Cleveland.

Gaunt IF, Carpanin FMB, Grasso P(1972) Long-term toxicity of propylene glycol in rats. *Food Cosmet Toxicol* 10(2):151-162.

Gosselin RE, Smith RP and Hodge HC (1984). *Clinical Toxicology of Commercial Products*. 5th ed. Williams and Wilkins, London.

Green MA (2002): Mouthing times among young children from observational data. Division of Hazard Analysis, US Consumer Product Safety Commission (www.cpsc.gov). Washington DC, USA.

Groot ME, Lekkerkerk MC, Steenbekkers LPA (1998): Mouthing behaviour of young children - an observational study. *Household and Consumer Studies*, report no. 3. Wageningen Agricultural University, Wageningen, The Netherlands.

Hansch C, Leo A, Hoekman D (1995): *Exploring QSAR - Hydrophobic, Electronic, and Steric Constants*. American Chemical Society, Washington, DC.

Hass U, Jacobsen BM (1993): Prenatal toxicity of xylene inhalation in the rat: a teratogenicity and postnatal study. *Pharmacol. Toxicol.* 73: 20-23.

Heindel JJ, Price CJ, Field EA (1992): Developmental toxicity of boric acid in mice and rats. *Fund. Appl. Toxicol.* 18: 266-277.

HSDB (2004): Hazardous Substances Databank, a database of the National Library of Medicine's TOXNET system (<http://toxnet.nlm.nih.gov>).

IARC (1978): *Monographs on the evaluation of the carcinogenic risk of chemicals to man*. Vol 16. World Health Organization, International Agency for Research on Cancer. Geneva.

IARC (1994): Styrene. *Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man*. Vol 60: 297. International Agency for Research on Cancer.

IARC (1999): Xylenes. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Vol. 71: 1189. International Agency for Research on Cancer.

IPCS (1983): Styrene. Environmental Health Criteria 26. International Programme on Chemical Safety. World Health Organization, Geneva.

IPCS (1993): Methyl Ethyl Ketone. Environmental Health Criteria No. 143. International Programme on Chemical Safety. World Health Organization, Geneva.

IPCS (1994): Assessing human health risks of chemicals: derivation of guidance values for health-based exposure limits. Environmental Health Criteria 170. International Programme on Chemical Safety. World Health Organization, Geneva.

IPCS (1996): Ethylbenzene. Environmental Health Criteria 186. International Programme on Chemical Safety. World Health Organization, Geneva, Switzerland.

IPCS (1997): Xylenes. Environmental Health Criteria 190. International Programme on Chemical Safety. World Health Organization, Geneva, Switzerland.

IPCS (1998): Boron. Environmental Health Criteria 204. International Programme on Chemical Safety. World Health Organization, Geneva, Switzerland.

IRIS (2004): Integrated Risk Information System. US Environmental Protection Agency (www.epa.gov/iris).

IRIS (1998): Methyl methacrylate CAS no. 80-62-6. Last update 03/02/98. Integrated Risk Information System (IRIS), U.S. Environmental Protection Agency.

IUCLID (2000) International Uniform Chemical Information Database. A database on 'Existing Chemicals' compiled by the European Chemicals Bureau (ECB), Ispra, Italy. (CD-rom).

IUCLID: International Uniform Chemical Information Database. A database on 'Existing Chemicals' compiled by the European Chemicals Bureau (ECB), Ispra, Italy. (on line <http://ecb.jrc.it>).

JECFA (1999) Safety evaluation of certain food additives. WHO Food Additives Series 42. 51st meeting of the Joint FAO/WHO Expert Committee on Food Additives. WHO Geneva

Karlberg AT, Lindell B (1993): Limonen. Nordiska Expertgruppen för Gränsvärdesdokumentation, 107 Limonen. Arbete och Hälsa 1993:14. Arbetsmiljövinstutet, National Institute of Occupational Health, Solna, Sweden.

Karlberg AT, Magnusson K, Nilsson U (1992): Air oxidation of d-limonene (the citrus solvent) creates potent allergens. Contact Dermatitis 26(5): 332-340.

- Kimura ET, Ebert DM, Dodge PW (1971): Acute toxicity and limits of solvent residue for sixteen organic solvents. *Toxicol. Appl. Pharmacol.* 19: 699-704.
- Kirk-Othmer (1978): *Encyclopedia of Chemical Technology*. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.
- Kishi R, et al. (1992): Neurochemical effects in rats following gestational exposure to styrene. *Toxicol. Letters* 63(2): 141-146.
- Kiss CT (2001): A mouthing observation study of children under 6 years of age. Division of human factors. US Consumers Product Safety Commission (www.cpsc.gov).
- Klink KJ, Meade BJ (2003): Dermal exposure to 3-amino-5-mercapto-1,2,4-triazole (AMT) induces sensitization and airway hyperactivity in BALB/c mice. *Toxicological Science* 75: 89-98.
- Korsak Z, Sokal JA, Górny R (1992): Toxic effects of combined exposure to toluene and m-xylene in animals. III. Subchronic inhalation study. *Polish J Occup Med Environ Health* 5:27-33.
- Korsak Z, Wisniewska-Knypl J, Swiercz R (1994): Toxic effects of sub-chronic combined exposure to n-butyl alcohol and m-xylene in rats. *Int J Occup Med Environ Health* 7:155-166.
- Krasavage WJ, O'Donoghue JL, Divincenzo GD (1982): Ketones. In: Clayton GD, Clayton FE. 1981-1982. *Patty's Industrial Hygiene and Toxicology*, 3rd ed., Vol. 2C. John Wiley & Sons, New York, pp. 4747-4751.
- Larsen A, Frost L, Funch LW, Hansen MK, Jensen LK, Knudsen BB, Mølhave L (1999): Emission af flygtige forbindelser fra træ, træbaserede materialer, møbler og inventar. Miljøprojekt nr. 501. Miljøstyrelsen.
- Larsen A, Frost L, Funch LW (1999): Emission of volatile organic compounds from wood and wood-based materials. Working Report no. 15/1999. Danish Environmental Protection Agency, Copenhagen, Denmark.
- Lewis R.J (1999): *Sax's Dangerous Properties of of Industrial Materials*. 10th ed. Volumes 1-3 New York, NY: John Wiley & Sons Inc.
- Li J, Perdue EM; Physicochemical Properties of Selected Monoterpenes. Preprint Extended Abstract, Presented Before The Division of Environmental Chemistry, Amer Chem Soc, Anaheim, Ca: April 2-7 (1995)
- Lijinsky W, Kovatch M (1986): A chronic toxicity study of cyclohexanone in rats and mice (NCI study). *J. Natl. Cancer Inst.* 77(4): 941-949.
- Lomax LG, Krivanek N, Frame SR (1997): Chronic inhalation toxicity and oncogenicity of methyl methacrylate in rats and hamsters. *Food Chem. Toxicol.* 35: 393-407.
- Massaldi HA, King CJ (1973): Simple technique to determine solubilities of sparingly soluble organics: solubility and activity coefficients of *d*-limonene,

n-butylbenzene, and *n*-hexyl acetate in water and succrose solutions. J. Chem. Eng. Data. 18(4): 393-397.

Miljøministeriet (2002): Bekendtgørelse om listen over farlige stoffer. Bekendtgørelse nr. 439 af 3. juni 2002. Miljøministeriet, Miljøstyrelsen. (In Danish: Statutory Order no. 439 of 3 June 2002 on Dangerous substances. Implementation of 28th amendment to EU directive 67/548/EEC)

Miljøstyrelsen (2000): Listen over uønskede stoffer. Orientering fra Miljøstyrelsen nr. 9. Miljøstyrelsen, København.

Miljøstyrelsen (2001): Report on the Advisory list for selfclassification of dangerous substances. Environmental Project no, 636. Can be obtained together with search function and excell file on the Danish EPA homepage, chemicals, www.mst.dk/chemi/01050000.htm.

Miljøstyrelsen (2002): B-værdivejledningen. Oversigt over B-værdier. Vejledning nr. 2, 2002. Miljøstyrelsen, København.

Miljøstyrelsen (2004): Listen over uønskede stoffer 2004. Orientering fra Miljøstyrelsen nr. 8/2004. Miljøstyrelsen, København. (English version: List of undesirable substances 2004. Environmental review no. 15 2004. Danish Environmental Protection Agency.

MST (2003): Risk assessment report of nickel compounds prepared in relation to Council Regulation (EEC) 793/93. Draft of August 2003. Chapter 4: Human Health – only. Draft prepared by the Danish Environmental Protection Agency for the European Commission.

Mutti A, Mazzucchi A, Rusticelli P, Frigeri G, Arfini G, Franchini I (1984): Exposure-effect and exposure-response relationships between occupational exposure to styrene and neuropsychological functions. Am. J. Ind. Med. 5: 275-286.

NCM (1999): Butanone. Health Effects of Selected Chemicals Vol 1-5. Nord 1999:5, p. 45-61. Nordic Council of Ministers. Copenhagen, Denmark.

Nelson KW et al. (1943): Journal of Industrial Hygiene and Toxicology, 25, 282-285. I OECD/SIDS. Screening Information Data Set (SIDS) of OECD High Production Volume Chemicals Programme, (1994)

Nielsen FH (1970): Percutaneous absorption of boric acid from boron-containing preparations in rats. Acta Pharmacol. Toxicol. 28: 413-424.

NTP (1989): Toxicology and Carcinogenesis Studies of toluene in F344/N rats and B6C3F1 mice. Technical Report Series No. 371. United States National Toxicology Program, Research Triangle Park, NC.

NTP (1990): Toxicology and carcinogenesis studies of d-limonene in F344/N rats and B6C3F1 mice. NTP Technical Report No. 347. US Department of Health and Human Services, National Institutes of Health, National Toxicology Program. Springfield, VA.

NTP (1993): Technical report on toxicity studies of ethylene glycol ethers 2-methoxyethanol, 2-ethoxyethanol, 2-butoxyethanol administered in drinking water to F344/N rats and B6C3F1 mice. National Toxicology Program

Technical Report No. 26. US Department of Health and Human Services, National Institutes of Health, Research Triangle Park, NC.

NTP (2003): United States National Toxicology Program. Chemical Status Report. NTP Chemtrack System. Research Triangle Park, NC. (<http://ntp-server.niehs.nih.gov>).

OECD (1993): Occupational and consumer exposure assessment. Environment Monograph no. 70. Organisation for Economic Co-operation and Development. Paris.

OECD (1993b): Skin sensitisation. Guideline for testing of chemicals No. 406. OECD Guidelines for the Testing of Chemicals. Organisation for Economic Co-operation and Development)

OPPT (2001): Diethylene glycol dibenzoate robust summary in the HPV chemical challenge program. Report AR201-13271. Velsicol to OPPT, 2001. Office of Pollution Prevention & Toxics, US Environmental Protection Agency.
(www.epa.gov/chemrtk/diglydib/c13271tc.htm)

Piotrowski J (1967). Quantitative estimate of the absorption of toluene in people (In Polish with English summary). Med. Pracy. 18; 213-223.

Prager JC (1996): Environmental Contaminant Reference Handbook, Vol. 2 1067. Van Nostrand Reinhold New York, NY.

Price CJ, Strong PL, Marr MC, Myers CB, Murray FJ (1996): Developmental toxicity NOAEL and postnatal recovery in rats fed boric acid during gestation. Fund. Appl. Toxicol. 32: 179-193.

Quast JF, Humiston CG, Kalnins RY (1979): Results of a toxicity study of monomeric styrene administered to beagle dogs by oral intubation for 19 months. J. Work Environ. Health. 4(suppl.2): 127-135.

Riddick JA, Bunger WB, Sakano TK (1985): Techniques of Chemistry 4th ed., Volume II. Organic Solvents. New York, NY: John Wiley and Sons.

Riihimäki V, Pfäffli P (1978). Percutaneous absorption of solvent vapors in man. Scand J Work Environ Health, 4, 73-85.

Sanemasa I, Araki M, Deguchi T, Nagai H (1982): Solubility measurements of benzene and the alkylbenzenes in water by making use of solute vapor. Bull. Chem. Soc. Jpn 55: 1054-1062.

SCCNFP (1999): Fragrance allergy in consumers: A review of the problem, analysis of the need for approximate consumer information and identification of consumer allergens. SCCNFP/0017/98 Final. The Scientific Committee on Cosmetic Products and Non-food Products Intended for Consumers. Brussels.

Schou JS, Jansen JA, Aggerbeck B (1984): Human pharmacokinetics and safety of boric acid. Arch. Toxicol. 7: 232-235.

- Schwetz BA, Mast TJ, Weigel RJ, Dill JA, Morrisey RE (1991): Developmental toxicity of inhaled methyl ethyl ketone in mice. *Fund. Appl. Toxicol.* 16: 742-748.
- SIDS (1996): Cyclohexanone. OECD/SIDS. Screening Information Data Set (SIDS) of OECD High Production Volume Chemicals Programme, (1994) vol 3/II, July 1996
- Smyth HF, Carpenter CP, Weil CS, Pozzani UC, Striegel JA, Nycum JS (1969): Range-finding toxicity data: List VII. *American Industrial Hygiene Association Journal*, 30: 470-476.
- Suber RL, Deskin R, Nikiforov I, et al. 1989. Subchronic nose-only inhalation study of propylene glycol in Sprague-Dawley rats. *Food Chem. Toxicol.* 27(9): 573-584.
- Söderkvist S (1987): Kriteriedokument för gränsvärden: Terpentin/terpener (alfa-pinen, beta-pinen, delta-3-careen). *Arbete och Hälsa* 1987:23. Arbetsmiljöinstitutet, Solna, Sverige.
- Thomsen KG (1990): Allergi- og overfølsomhedfremkaldende stoffer i arbejdsmiljøet. AMI rapport nr. 34/1990. Arbejdsmiljøinstitutet, Arbejdstilsynet.
- Tyl TR, Millicovsky G, Dodd DE, Pritts IM, France KA, Fisher LC (1984): Teratologic evaluation of ethylene glycol monobutyl ether in Fisher 344 rats and New Zealand white rabbits following inhalation exposure. *Env. Health. Perspectives* 57:47-68
- US-EPA (1994): Chemical summary for methyl ethyl ketone. EPA 749-F-94-015a. Office of Pollution and Prevention and Toxics, US-Environmental Protection Agency.
- US-EPA (1997): Exposure factors handbook. Update to exposure factors handbook 1989. EPA/600/P-95/002Fa. U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment. Washington DC.
- US-EPA (1997): Health effects assessment summary tables. FY-1997 update. Office of Research and Development, Office of Emergency and Remedial Responses. EPA 540/R-97-036, PB97-921 199. US Environmental Protection Agency.
- US-EPA (1999): Toxicological review of ethylene glycol monobutyl ether (EGBE), CAS no. 111-76-2, in support of summary information on the Integrated Risk Information System (IRIS), October 1999. U.S. Environmental Protection Agency. Washington DC, USA
- US-EPA (2004): Toxicological review of boron and compounds. EPA 635/04/052. US Environmental Protection Agency, Washington DC.)
- Van Apeldoorn ME (1986): Criteriadocument Styreen. , RIVM report no. 738513003. National Institute of Public Health and the Environment, Bilthoven, The Netherlands.

Vermeire TG, Van der Poel P, Van de Laar RTH, Roelfzema H (1993): Estimation of consumer exposure to chemicals: application of simple models. *Sci. Total Environ.* 136: 155-176.

Webb DR, Ridder GM, Alden CL (1989): Acute and subchronic nephrotoxicity of d-limonene in Fischer 344 rats. *Food and Chemical Toxicology* 27: 639-649.

WHO (1993): Methyl Ethyl Ketone. Environmental Health Criteria no. 143. World Health Organisation, Geneva, Switzerland.

WHO (1996): Guidelines for Drinking water quality. Second edition, Vol. 2. Health criteria and other supporting information. World Health Organization, Geneva, Switzerland.

WHO (2000): Air quality guidelines for Europe. 2nd edition. WHO Regional Publications, European Series No. 91. World Health Organisation Regional Office for Europe, Copenhagen.

Wild D, King MT, Gocke E, Eckhardt K (1983): Study of artificial flavouring substances for mutagenicity in the Salmonella / Microsome, BASC and Micronucleus tests. *Food and Chem. Toxicol.* 21(6): 707-719.

Wolf MA, Rowe VK, McCollister DD, Hollingsworth RL, Oyen F (1956): Toxicological studies of certain alkylated benzenes and benzene. *Arch. Ind. Health.* 14: 387-398.

Woods WG (1994): An introduction to boron: history, sources, uses, and chemistry. *Environ. Health Perspect.* 102(Suppl 7): 5-11.

Yalkowsky SH, Dannenfelser RM; The Aquasol Database of Aqueous Solubility. Fifth Ed, Tucson, AZ: Univ Az, College of Pharmacy (1992)

Enclosure A: List of purchased slimy toys

Identification No.	Description	Place of purchase
DK-01	Approx. 10 cm multicoloured rubbery saurian	Petrol station
DK-02	Approx. 4 cm blue and soft octopus	Petrol station
DK-03	Approx. 4 cm lilac and soft fish	Petrol station
BO-01	Pink rubber hose. Approx. 20 cm long	Automatic machine
K-01	Yellow, transparent ball with insect inside	Supermarket
K-02	Lilac spiked pig space hopper with light-emitting diode, approx. 10 cm in diameter	Supermarket
K-03	Pink rubbery hand	Supermarket
BR-01	Pink transparent liquid-filled softball with insect inside. Approx. 5 cm in diameter. Made in China	Toyshop
F-01	Transparent liquid-filled egg with "yolk". Approx. 5 cm long	Toyshop
TO-01	Green slime with insects inside	Toyshop
TO-02	Hard plastic container with green slime inside	Toyshop
TO-03	Blue gel for hair, skin and lips	Toyshop
G-01	Multicoloured octopus approx. 20 cm long with tiny balls inside	Toyshop
TI-01	Green 10 cm liquid-filled stick. Made in China	10 DKr.'s market
B-01	Red tomato. Approx. 5 cm in diameter	Supermarket
B-02	Green slime with figure inside	Supermarket
R-01	Green liquid-filled ball with spikes	Huckster's market
A-01	Transparent liquid-filled disc with stars inside	Accessories in weekly magazine
EX-01	Green slime	Forbrugerrådet
EX-02	Slime with cola scent	Forbrugerrådet

Enclosure B: FTIR Analysis results from screening

No.	Exterior product	Content (most frequently liquid)	Accessories
DK-01	Hydrocarbon with a small aromatic content	Hydro gel, primarily water and glycerol	
DK-02	Hydrocarbon with a small aromatic content		
DK-03	Hydrocarbon with a small aromatic content		
BO-01	Hydrocarbon with a small aromatic content		
K-01	Hydrocarbon with a small aromatic content	Yellow liquid cannot be unambiguously identified by FTIR	Fish is made of SBS (styrene-butadiene-styrene) elastomer
K-02	Hydrocarbon with a small aromatic content	There is no liquid	Transparent ball is made of PS (polystyrene)
BR-01	Hydrocarbon with a small aromatic content	Liquid cannot be unambiguously identified by FTIR	Spiders are made of an SBS (styrene-butadiene-styrene) elastomer
F-01	Hydrocarbon with a small aromatic content	The liquid might be water with preservative agent (Na benzoic acid salt)	Yellow ball is made of hydrocarbon with a small aromatic content
TO-01	Hydro gel with a content of "parabene"		Animals are made of LDPE, low density polyethylene
TO-02	Hydro gel with a content of "parabene"		
TO-03	Water-glycerol gel		
G-01	Hydrocarbon with a small aromatic content		Small balls are made of PS (polystyrene)
K-03	Pink rubbery hand		
B-01	Hydrocarbon with a small aromatic content	The liquid is aqueous and seems to be thickened with an acrylic polymer	
B-02	Hydro gel with a content of "parabene"		Animals are made of phthalate plasticised PVC with chalk
TI-01	Hydrocarbon with an aromatic content	The liquid is aqueous with a small content of a component, which cannot be unambiguously identified by FTIR	
R-01	Hydrocarbon with an aromatic content	The liquid is aqueous with a small content of a component, which cannot be unambiguously identified by FTIR	
A-01	Hydrocarbon with an aromatic content	The liquid contains water, but also a considerable amount of a component, which might be a modified glycerol	

Enclosure C: Headspace analysis results from screening

Analysis results from headspace analysis at 20°C

ID no.	DK-01, exterior	
Chemical Technology label	30396-1	
Component	CAS no.	% m/m
Toluene	108-88-3	4.2
Hexanal	66-25-1	< 0.1
Ethylbenzene	100-41-4	1.3
m-, p-Xylene	108-88-3/106-42-3	
o-Xylene	95-47-5	
Cyclohexanone	108-94-1	0.2
α -Pinene	80-56-8	0.1
C10H14-aromatic hydrocarbons	-	0.5
C11-C14 aliphatic hydrocarbons + Decahydro naphthalenes methyl decahydronaphthalenes dimethyl decahydronaphthalenes	-	94

Comments

The stated % m/m is equivalent to the percentage part of totally collected VOC-content of the component, assuming that all detected components have the same response for the same amount.

ID no.	DK-02, exterior	
Chemical Technology label	30396-2	
Component	CAS no.	% m/m
Toluene	108-88-3	18
Hexanal	66-25-1	0.6
Ethylbenzene	100-41-4	11
m-, p-Xylene	108-88-3/106-42-3	
o-Xylene	95-47-5	
Cyclohexanone	108-94-1	2.8
2-Butoxy-ethanol	111-76-2	0.6
α -Pinene	80-56-8	3.4
β -Pinene	127-91-3	0.6
3-Carene	13466-78-9	1.4
2-Ethyl-1-hexanol	104-76-7	0.6
d-Limonene	5989-27-5	0.9
Aliphatic hydrocarbons etc.	-	60

Comments

The stated % m/m is equivalent to the percentage part of totally collected VOC-content of the component, assuming that all detected components have the same response for the same amount.

ID no.	DK-03, exterior	
Chemical Technology label	30396-3	
Component	CAS no.	% m/m
Toluene	108-88-3	5.9
Hexanal	66-25-1	0.1
Ethylbenzene	100-41-4	2.2
m-, p-Xylene	108-88-3/106-42-3	
o-Xylene	95-47-5	
Cyclohexanone	108-94-1	0.4
2-Butoxy-ethanol	111-76-2	0.1
α -Pinene	80-56-8	0.7
β -Pinene	127-91-3	0.1
3-Carene	13466-78-9	0.4
2-Ethyl-1-hexanol	104-76-7	0.2
d-Limonene	5989-27-5	0.2
C11-C14 aliphatic hydrocarbons + decahydro naphthalenes methyl decahydronaphthalenes dimethyl decahydronaphthalenes	-	90

Comments

The stated % m/m is equivalent to the percentage part of totally collected VOC-content of the component, assuming that all detected components have the same response for the same amount.

ID no.	K-01, exterior	
Chemical Technology label	30396-5 A	
Component	CAS no.	% m/m
C7H14 and C7H16 aliphatic hydrocarbons	-	1.8
Toluene	108-88-3	66
C8 + C9 aliphatic hydrocarbons	-	8.1
Ethylbenzene	100-41-4	13
m-, p-Xylene	108-88-3/106-42-3	
o-Xylene	95-47-5	
Cyclohexanone	108-94-1	2.9
α -Pinene	80-56-8	3.8
C9H12 + C10H14 aromatic hydrocarbons	-	3.3
Eucalyptol (C10H18O)	470-82-6	0.2
C10H16	-	1.0

ID no.	K-01, liquid	
Chemical Technology label	30396-5 B	
Component	CAS no.	% m/m
Toluene	108-88-3	70
Ethylbenzene	100-41-4	6
m-, p-Xylene	108-88-3/106-42-3	
o-Xylene	95-47-5	
Cyclohexanone	108-94-1	24

Comments

The stated % m/m is equivalent to the percentage part of totally collected VOC-content of the component, assuming that all detected components have the same response for the same amount.

ID no.	BR-01, exterior	
Chemical Technology label	30396-7 A	
Component	CAS no.	% m/m
Toluene	108-88-3	7.1
Hexanal	66-25-1	0.3
C8H16	e.g. 1678-91-7	1.3
m-, p-Xylene	108-88-3/106-42-3	74
o-Xylene	95-47-5	
C9H12 aromatic hydrocarbons	-	5.9
3-Carene	80-56-8	0.2
C11-C14 aliphatic hydrocarbons	-	10.8

ID no.	BR-01, liquid	
Chemical Technology label	30396-7 B	
Component	CAS no.	% m/m
1.2-Propandiol	4254-15-3	7
Toluene	108-88-3	8
Ethylbenzene	100-41-4	79
m-, p-Xylene	108-88-3/106-42-3	
o-Xylene	95-47-5	
C9H12 aromatic hydrocarbons	-	3
C10-C14 aliphatic hydrocarbons	-	3

Comments

The stated % m/m is equivalent to the percentage part of totally collected VOC-content of the component, assuming that all detected components have the same response for the same amount.

ID no.	F-01, exterior	
Chemical Technology label	30396-8	
Component	CAS no.	% m/m
2-Ethylbutanal	97-96-1	0.2
Butanal	123-72-8	0.2
Butanol	71-36-3	0.2
Toluene	108-88-3	6.0
C8H16 aliphatic hydrocarbons	-	0.4
Ethylbenzene	100-41-4	4.2
m-, p-Xylene	108-88-3/106-42-3	
o-Xylene	95-47-5	
Cyclohexanol	108-93-0	0.3
Cyclohexanone	108-94-1	0.4
2-Butoxy-ethanol	111-76-2	1.8
α -Pinene	80-56-8	0.3
C9H12-aromatic hydrocarbons		0.6
3-Carene	13466-78-9	0.1
C10H14-aromatic hydrocarbons	-	0.6
C11-C14 aliphatic hydrocarbons	-	85
C10H16O	e.g. 5948-04-9	0.2

Comments

The stated % m/m is equivalent to the percentage part of totally collected VOC-content of the component, assuming that all detected components have the same response for the same amount.

ID no.	TO-01, exterior	
Chemical Technology label	30396-9	
Component	CAS no.	% m/m
2-Ethylbutanal	97-96-1	2.4
Butanal	123-72-8	0.6
3-Methylbutanal	590-86-3	0.3
1-Methoxy-2-propanol	107-98-2	1.0
Toluene	108-88-3	2.3
Hexanal	66-25-1	2.6
C9H20 aliphatic hydrocarbons	-	5.3
m-, p-Xylene	108-88-3/106-42-3	0.5
o-Xylene	95-47-5	
Cyclohexanone	108-94-1	63
2-Cyclohexen-1-one	930-68-7	0.1
2-Heptenal	18829-55-5	0.5
2-Okten-1-ol	18409-17-1	0.6
Octanal	124-13-0	1.2
2-Ethyl-1-hexanol	104-76-7	3.6
C10-C14 aliphatic hydrocarbons	-	16

Comments

The stated % m/m is equivalent to the percentage part of totally collected VOC-content of the component, assuming that all detected components have the same response for the same amount.

ID no.	TO-02, exterior	
Chemical Technology label	30396-10	
Component	CAS no.	% m/m
1-Propanol	71-23-8	1.1
Butanal	123-72-8	0.7
Toluene	108-88-3	17
N,N-Dimethyl formamide	68-12-2	0.4
Octane	111-65-9	1.1
Hexanal	66-25-1	1.5
Ethylbenzene	100-41-4	10
m-, p-Xylene	108-88-3/106-42-3	
o-Xylene	95-47-5	
n-Butyl ether	142-96-1	1.5
Styrene	100-42-5	5.1
Cyclohexanone	108-94-1	30
C9H12-aromater	-	7.7
Octanal	124-13-0	0.7
2-Ethyl-1-hexanol	104-76-7	7.7
C10H14-aromatic hydrocarbons	-	15

Comments

The stated % m/m is equivalent to the percentage part of totally collected VOC-content of the component, assuming that all detected components have the same response for the same amount.

ID no.	TO-03, lip-gloss	
Chemical Technology label	30396-11	
Component	CAS no.	% m/m
2-Propanol	67-63-0	20
2-Methyl-1-propanol	78-83-1	6.9
Toluene	108-88-3	30
Ethylbenzene	100-41-4	16
m-, p-Xylene	108-88-3/106-42-3	
o-Xylene	95-47-5	
Cyclohexanone	108-94-1	2.3
α -Pinene	80-56-8	1.1
3-Carene	13466-78-9	2.3
3.3.5-Trimethylcyclohexen-1-ol	e.g. 78-59-1	5.7
C10+C11+C12+C13 aliphatic hydrocarbons	-	16

Comments

The stated % m/m is equivalent to the percentage part of totally collected VOC-content of the component, assuming that all detected components have the same response for the same amount.

ID no.	TO-03, gel	
Chemical Technology label	30396-11	
Component	CAS no.	% m/m
1-Propanol	71-23-8	0.7
2-Methyl-1-propanol	78-83-1	1.3
1-Butanol	71-36-3	2.6
1-Methoxy-2-propanol	107-98-2	0.4
2-Propenoic acid 2 methyl-methyl ester (methyl-methacrylate)	80-62-6	7.2
Toluene	108-88-3	6.9
1.2-Propandiol	4254-15-3	66
Ethylbenzene	100-41-4	0.7
m-, p-Xylene	108-88-3/106-42-3	1.0
o-Xylene	95-47-5	1.0
Styrene	100-42-5	2.0
Cyclohexanone	108-94-1	3.3
2-Butoxy-ethanol	111-76-2	0.7
α -Pinene	80-56-8	0.4
D-Limonene	5989-27-5	0.4
3.3.5-Trimethylcyclohexen-1-ol	e.g. 78-59-1	2.3
2-Phenoxy ethanol	122-99-6	3.9

Comments

The stated % m/m is equivalent to the percentage part of totally collected VOC-content of the component, assuming that all detected components have the same response for the same amount.

ID no.	G-01, exterior	
Chemical Technology label	30396-12	
Component	CAS no.	% m/m
Butandiol + alcohol e.g. ethanol, 2-propanol	110-63-4 + e.g. 64-17-5, 67-63-0	35
Butanal	123-72-8	2.8
Butanol		1.0
Toluene	108-88-3	10
Hexanal	66-25-1	0.4
Ethylbenzene	100-41-4	39
m-, p-Xylene	108-88-3/106-42-3	
o-Xylene	95-47-5	
Cyclohexanone	108-94-1	3.9
2-Butoxy-ethanol	111-76-2	0.6
α -Pinene	80-56-8	0.7
Benzaldehyde	100-52-7	1.3
3-Carene	13466-78-9	0.3
D-Limonene	5989-27-5	0.4
C ₁₀ H ₁₄ -aromatic hydrocarbons	-	3.8
Nonanal	124-19-6	0.5

Comments

The stated % m/m is equivalent to the percentage part of totally collected VOC-content of the component, assuming that all detected components have the same response for the same amount.

ID no.	K-03, exterior	
Chemical Technology label	30396-13	
Component	CAS no.	% m/m
Butandiol + alcohol, e.g. ethanol, 2-propanol	110-63-4+ e.g. 64-17-5, 67-63-0	55
Ethyl acetate	141-78-6	1.9
Tetrahydrofuran	109-99-9	3.4
Toluene	108-88-3	7.2
Hexanal	66-25-1	1.8
Ethylbenzene	100-41-4	16
m-, p-Xylene	108-88-3/106-42-3	
o-Xylene	95-47-5	
Cyclohexanone	108-94-1	2.5
C10-C13 aliphatic hydro carbons	-	15

Comments

The stated % m/m is equivalent to the percentage part of totally collected VOC-content of the component, assuming that all detected components have the same response for the same amount.

ID no.	TI-01, exterior	
Chemical Technology label	30396-16	
Component	CAS no.	% m/m
Butandiol + alcohol, e.g. ethanol, 2-propanol	110-63-4+ e.g. 64-17-5, 67-63-0	4.3
2-Butanon	78-93-3	2.3
Tetrahydrofuran	109-99-9	0.4
Butanol	71-36-3	3.0
2-Pentanon	107-87-9	1.1
C7+C8+C9 aliphatic hydrocarbons		29
Toluene	108-88-3	10
2-Hexanon	591-78-6	2.7
Hexanal	66-25-1	0.7
Ethylbenzene	100-41-4	14
m-, p-Xylene	108-88-3/106-42-3	
o-Xylene	95-47-5	
n-Butyl ether	142-96-1	2.2
2-Heptanon	110-43-0	3.3
Heptanal	111-71-7	1.3
α -Pinene	80-56-8	1.2
C9H12-aromatoc compounds (sum)		4.5
2-Oktanon	111-13-7	2.4
Octanal	124-13-0	2.1
3-Carene	13466-78-9	0.6
Nonanol	143-08-8	1.1
C11H22		5.0
Nonanal	124-19-6	1.3
3.5.5-Trimethylcyclohexen-1-one	78-59-1	1.2
2-Decanon	693-54-9	0.4
Decanal	112-31-2	0.4
Undecanal	112-44-7	0.9
Dodecanal	112-54-9	0.8

Comments

The stated % m/m is equivalent to the percentage part of totally collected VOC-content of the component, assuming that all detected components have the same response for the same amount.

ID no.	TI-01, liquid	
Chemical Technology label	30396-16,B	
Component	CAS no.	% m/m
Dichloromethane	75-09-2	3
1.1-Dimethoxypropan	4744-10-9	5
2-Butanon	78-93-3	9
Tetrahydrofuran	109-99-9	1
2-Pentanon	107-87-9	9
Toluene	108-88-3	10
2-Hexanone	591-78-6	8
Ethylbenzene	100-41-4	9
m-, p-Xylene	108-88-3/106-42-3	
o-Xylene	95-47-5	
n-Butyl ether	142-96-1	2
3-Heptanon	106-35-4	1
2-Heptanon	110-43-0	10
Cyclohexanone	108-94-1	1
Heptanal	111-71-7	3
Heptanol	53535-33-4	3
2-Oktanon	111-13-7	6
Octanal	124-13-0	5
Nonanol	143-08-8	1
C11H22	-	7
Nonanal	124-19-6	3
3.5.5-Trimethylcyclohexen-1-one	78-59-1	3
Decanal	112-31-2	1

Comments

The stated % m/m is equivalent to the percentage part of total VOC-content of the component, assuming that all detected components have the same response for the same amount.

ID no.	R-01, exterior	
Chemical Technology label	30396-17	
Component	CAS no.	% m/m
Ethanol	64-17-5	0.2
2,6-Dimethyl-1,4-dioxan (C ₆ H ₁₂ O ₂)	e.g. 10138-17-7	0.9
Toluene	108-88-3	1.0
Ethylbenzene	100-41-4	0.8
m-, p-Xylene	108-88-3/106-42- 3	
o-Xylene	95-47-5	
2-Butoxy-ethanol	111-76-2	0.8
C11-C14-aliphatic hydrocar- bons	-	96

ID no.	R-01, liquid	
Chemical Technology label	30396-17 B	
Component	CAS no.	% m/m
Ethanol	64-17-5	27
Cyclohexanone	108-94-1	6
2-Butoxy-ethanol	111-76-2	66

Comments

The stated % m/m is equivalent to the percentage part of totally collected VOC-content of the component, assuming that all detected components have the same response for the same amount.

ID no.	A-01, exterior	
Chemical Technology label	30396-18	
Component	CAS no.	% m/m
C6H12O2	e.g. 21460-36-6 + 10138-17-7	1.7
Toluene	108-88-3	2.1
Ethylbenzene	100-41-4	45
m-, p-Xylene	108-88-3/106-42- 3	
o-Xylene	95-47-5	
C9H12 aromatic hydrocarbons	-	3.2
1-Propenylbenzen	873-66-5	
C10 - C16 aliphatic hydrocarbons	-	46

ID no.	A-01, liquid	
Chemical Technology label	30396-18	
Component	CAS no.	% m/m
Ethylbenzene	100-41-4	100
m-, p-Xylene	108-88-3/106-42- 3	
o-Xylene	95-47-5	

Comments

The stated % m/m is equivalent to the percentage part of totally collected VOC-content of the component, assuming that all detected components have the same response for the same amount.

Enclosure D: GC-MS Analysis results from screening

Analysis results for sweat-extracts stated in µg/g sample

ID no. DK-01, exterior	Sample amount: 1.83 g	
Chemical Technology label 30396-1		
Component	CAS no.	µg/g
Toluene	108-88-3	0.25
Naphthalene	91-20-3	0.02
Ethanol-2-(butoxy ethoxy)acetate	112-15-2	0.2

Analysis results for saliva-extracts stated in µg/g sample

ID no. DK-01, exterior	Sample amount: 1.98 g	
Chemical Technology label 30396-1		
Component	CAS no.	µg/g
Toluene	108-88-3	0.31
Naphthalene	91-20-3	0.02
Ethanol-2-(butoxy ethoxy)acetate	112-15-2	0.2

Comments

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

The stated amounts are calculated according to response for internal standards assuming that all detected components have same response for same amount and same recovery.

Analysis results for sweat-extracts stated in $\mu\text{g/g}$ sample

ID no. DK-02, exterior	Sample amount: 1.30 g	
Chemical Technology label 30396-2		
Component	CAS no.	$\mu\text{g/g}$
Toluene	108-88-3	0.10

Analysis results for saliva-extracts stated in $\mu\text{g/g}$ sample

ID no. DK-02, exterior	Sample amount: 1.97 g	
Chemical Technology label 30396-2		
Component	CAS no.	$\mu\text{g/g}$
Toluene	108-88-3	0.09

Comments

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

The stated amounts are calculated according to response for internal standards assuming that all detected components have same response for same amount and same recovery.

Analysis results for sweat-extracts stated in µg/g sample

ID no. DK-03, exterior	Sample amount: 1.14 g	
Chemical Technology label 30396-3		
Component	CAS no.	µg/g
Toluene	108-88-3	0.15
Cyclohexanone	108-94-1	0.2

Analysis results for saliva-extracts stated in µg/g sample

ID no. DK-03, exterior	Sample amount: 1.17 g	
Chemical Technology label 30396-3		
Component	CAS no.	µg/g
Toluene	108-88-3	0.26
Cyclohexanone	108-94-1	0.2

Comments

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

The stated amounts are calculated according to response for internal standards assuming that all detected components have same response for same amount and same recovery.

Analysis results for sweat-extracts stated in µg/g sample

ID no. K-01, exterior	Sample amount: 2.34 g	
Chemical Technology label 30396-5		
Component	CAS no.	µg/g
Toluene	108-88-3	1.8

Analysis results for saliva-extracts stated in µg/g sample

ID no. K-01, exterior	Sample amount: 1.90 g	
Chemical Technology label 30396-5		
Component	CAS no.	µg/g
Toluene	108-88-3	1.9

Comments

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

The stated amounts are calculated according to response for internal standards assuming that all detected components have same response for same amount and same recovery.

Analysis results for sweat-extracts stated in µg/g sample

ID no. K-01, gel	Sample amount: 2.31 g	
Chemical Technology label 30396-5		
Component	CAS no.	µg/g
Aliphatic hydrocarbon >C14		0.1

Analysis results for saliva-extracts stated in µg/g sample

ID no. K-01, gel	Sample amount: 1.57g	
Chemical Technology label 30396-5		
Component	CAS no.	µg/g
Aliphatic hydrocarbon >C14		0.9

Comments

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

The stated amounts are calculated according to response for internal standards assuming that all detected components have same response for same amount and same recovery.

Analysis results for sweat-extracts stated in µg/g sample

ID no. BR-01, exterior	Sample amount: 2.39 g	
Chemical Technology label 30396-7		
Component	CAS no.	µg/g
Toluene	108-88-3	0.14
o-, m-, p-Xylene, ethylbenzene	95-47-5, 108-38-3, 106-42-3, 100-41- 4	2.3

Analysis results for saliva-extracts stated in µg/g sample

ID no. BR-01, exterior	Sample amount: 2.23 g	
Chemical Technology label 30396-7		
Component	CAS no.	µg/g
Toluene	108-88-3	0.17
o-, m-, p-Xylene, ethylbenzene	95-47-5, 108-38-3, 106-42-3, 100-41- 4	2.4

Comments

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

The stated amounts are calculated according to response for internal standards assuming that all detected components have same response for same amount and same recovery.

Analysis results for sweat-extracts stated in µg/g sample

ID no. F-01, exterior	Sample amount: 2.69 g	
Chemical Technology label 30396-8A		
Component	CAS no.	µg/g
Toluene	108-88-3	0.16
3,5,5-Trimethyl-2-cyclohexen-1-one	78-59-1	0.06
2-Phenoxy ethanol	122-99-6	0.4

Analysis results for saliva-extracts stated in µg/g sample

ID no. F-01, exterior	Sample amount: 2.23 g	
Chemical Technology label 30396-8A		
Component	CAS no.	µg/g
Toluene	108-88-3	0.21
3,5,5-Trimethyl-2-cyclohexen-1-one	78-59-1	0.05
2-Phenoxy ethanol	122-99-6	0.5

Comments

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

The stated amounts are calculated according to response for internal standards assuming that all detected components have same response for same amount and same recovery.

Analysis results for sweat-extracts stated in µg/g sample

ID no. F-01, interior (yellow egg yolk)	Sample amount: 3.37 g	
Chemical Technology label 30396-8C		
Component	CAS no.	µg/g
Toluene	108-88-3	0.23
3,5,5-Trimethyl-2-cyclohexen-1-one	78-59-1	0.05
2-Phenoxy ethanol	122-99-6	0.5

Analysis results for saliva-extracts stated in µg/g sample

ID no. F-01, interior (yellow egg yolk)	Sample amount: 2.64 g	
Chemical Technology label 30396-8C		
Component	CAS no.	µg/g
Toluene	108-88-3	0.29
3,5,5-Trimethyl-2-cyclohexen-1-one	78-59-1	0.03
2-Phenoxy ethanol	122-99-6	0.3

Comments

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

The stated amounts are calculated according to response for internal standards assuming that all detected components have same response for same amount and same recovery.

Analysis results for sweat-extracts stated in µg/g sample

ID no. TO-01, exterior	Sample amount: 2.16 g	
Chemical Technology label 30396-9		
Component	CAS no.	µg/g
Cyclohexanone	108-94-1	57
Methyl parabene	99-76-3	3.9
1,2-Propandion-1-phenyl-2-oxim	119-51-7	5.8
Propyl parabene	94-13-3	5.3
Benzoic acid-propylester	2315-68-6	12
Benzoic acid-butylester	136-60-7	10
Benzoic acid-phenylester	93-99-2	0.3
N-Propyl benzamide + N-acetyl benzamide	10546-70-0 + 1575-95-7	2.4
Diethylglycol dibenzoate etc.	e.g. 120-55-8	127
Diethylglycol dibenzoate etc.		99

Analysis results for saliva-extracts stated in µg/g sample

ID no. TO-01, exterior	Sample amount: 2.41 g	
Chemical Technology label 30396-9		
Component	CAS no.	µg/g
Cyclohexanone	108-94-1	14
Methyl parabene	99-76-3	1.8
1,2-Propandion-1-phenyl-2-oxim	119-51-7	3.0
Propyl parabene	94-13-3	3.3
Benzoic acid-propylester	2315-68-6	6.9
Benzoic acid-butylester	136-60-7	5.1
Benzoic acid-phenylester	93-99-2	0.2
N-Propyl benzamide + N-acetyl benzamide	10546-70-0 + 1575-95-7	36
Diethylglycol dibenzoate etc.	e.g. 120-55-8	115
Diethylglycol dibenzoate etc.		114

Comments

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

The stated amounts are calculated according to response for internal standards assuming that all detected components have same response for same amount and same recovery.

Analysis results for sweat-extracts stated in µg/g sample

ID no. TO-02, exterior	Sample amount: 2.31 g	
Chemical Technology label 30396-10		
Component	CAS no.	µg/g
Cyclohexanone	108-94-1	0.6
Methyl parabene	99-76-3	2.2
1,2-Propandion-1-phenyl-2-oxim	119-51-7	0.2
Propyl parabene	94-13-3	1.9
Benzoic acid-propylester (etc.)	2315-68-6	0.8
Benzoic acid-butylester (etc.)	136-60-7	0.7
Benzoic acid-phenylester (etc.)	93-99-2	1.1
N-Propyl benzamide + N-acetyl benzamide	10546-70-0 + 1575-95-7	0.7
Diethylglycol dibenzoate etc.	e.g. 120-55-8	25
Diethylglycol dibenzoate etc.		4.1

Analysis results for saliva-extracts stated in µg/g sample

ID no. TO-02, exterior	Sample amount: 1.97 g	
Chemical Technology label 30396-10		
Component	CAS no.	µg/g
Cyclohexanone	108-94-1	0.2
Methyl parabene	99-76-3	0.6
1,2-Propandion-1-phenyl-2-oxim	119-51-7	0.8
Propyl parabene	94-13-3	1.2
Benzoic acid-propylester (etc.)	2315-68-6	0.5
Benzoic acid-butylester (etc.)	136-60-7	0.4
Benzoic acid-phenylester (etc.)	93-99-2	0.2
N-Propyl benzamide + N-acetyl benzamide	10546-70-0 + 1575-95-7	1.6
Diethylglycol dibenzoate etc.	e.g. 120-55-8	16
Diethylglycol dibenzoate etc.		3.7

Comments

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

The stated amounts are calculated according to response for internal standards assuming that all detected components have same response for same amount and same recovery.

Analysis results for sweat-extracts stated in µg/g sample

ID no. TO-03, gel	Sample amount: 2.10 g	
Chemical Technology label 30396-11		
Component	CAS no.	µg/g
3,5,5-Trimethyl-2-cyclohexen-1-one	78-59-1	0.3
2-Phenoxy ethanol	122-99-6	145
Methyl parabene	99-76-3	1.6
Ethyl parabene	120-47-8	2.2
Propyl parabene	94-13-3	0.6
Methyldihydrojasmonat	24851-98-7	0.2
Butyl parabene	94-26-7	0.9
Benzoic acid-propylester (etc.)	2315-68-6	1.5
2-Phenylmethylenoctanal (= Hexylcinnamaldehyde) Allergenic odorant	101-86-0	0.3

Analysis results for saliva-extracts stated in µg/g sample

ID no. TO-03, lip-gloss	Sample amount: 0.64 g	
Chemical Technology label 30396-11		
Component	CAS no.	µg/g
3,5,5-Trimethyl-2-cyclohexen-1-one	78-59-1	1.4
Propyl parabene	94-13-3	23
Component not identified		12
Component not identified		5.8
Component not identified		4.2
Component not identified		4.2
Component not identified		5.2

Comments

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

The stated amounts are calculated according to response for internal standards assuming that all detected components have same response for same amount and same recovery.

Analysis results for sweat-extracts stated in µg/g sample

ID no. G-01, exterior	Sample amount: 2.98 g	
Chemical Technology label 30396-12		
Component	CAS no.	µg/g
Toluene	108-88-3	0.05
o-, m-, p-Xylene, ethylbenzene	95-47-5, 108-38-3, 106-42-3, 100-41-4	0.1
Cyclohexanone	108-94-1	0.1

Analysis results for saliva-extracts stated in µg/g sample

ID no. G-01, exterior	Sample amount: 3.13 g	
Chemical Technology label 30396-12		
Component	CAS no.	µg/g
Toluene	108-88-3	Trace <0.05
o-, m-, p-Xylene, ethylbenzene	95-47-5, 108-38-3, 106-42-3, 100-41-4	0.08
Cyclohexanone	108-94-1	Trace <0.05

Comments

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

The stated amounts are calculated according to response for internal standards assuming that all detected components have same response for same amount and same recovery.

Analysis results for sweat-extracts stated in µg/g sample

ID no. K-03, exterior	Sample amount: 2.26 g	
Chemical Technology label 30396-13		
Component	CAS no.	
Toluene	108-88-3	Trace <0.02
Hydrocarbons > C14		2

Analysis results for saliva-extracts stated in µg/g sample

ID no. K-03, exterior	Sample amount: 1.96 g	
Chemical Technology label 30396-13		
Component	CAS no.	µg/g
Toluene	108-88-3	Trace <0.02
Hydrocarbons > C14		3

Comments

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

The stated amounts are calculated according to response for internal standards assuming that all detected components have same response for same amount and same recovery.

Analysis results for sweat-extracts stated in µg/g sample

ID no. TI-01, exterior	Sample amount: 1.29 g	
Chemical Technology label 30396-16		
Component	CAS no.	µg/g
Toluene	108-88-3	Trace <0.05
3,5,5-Trimethyl-2-cyclohexen-1-one	78-59-1	0.8

Analysis results for saliva-extracts stated in µg/g sample

ID no. TI-01, exterior	Sample amount: 1.35 g	
Chemical Technology label 30396-16		
Component	CAS no.	µg/g
Toluene	108-88-3	Trace <0.05
3,5,5-Trimethyl-2-cyclohexen-1-one	78-59-1	0.7

Comments

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

The stated amounts are calculated according to response for internal standards assuming that all detected components have same response for same amount and same recovery.

Analysis results for sweat-extracts stated in µg/g sample

ID no. R-01, exterior	Sample amount: 2.67 g	
Chemical Technology label 30396-17		
Component	CAS no.	µg/g
5-Methyl-2-(1-methylethylcyclohexanol)	23283-97-8	0.1
2-Phenoxy ethanol	122-99-3	1.8

Analysis results for saliva-extracts stated in µg/g sample

ID no. R-01, exterior	Sample amount: 1.84 g	
Chemical Technology label 30396-17		
Component	CAS no.	µg/g
5-Methyl-2-(1-methylethylcyclohexanol)	23283-97-8	0.2
2-Phenoxy ethanol	122-99-3	1.6

Comments

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

The stated amounts are calculated according to response for internal standards assuming that all detected components have same response for same amount and same recovery.

Analysis results for sweat-extracts stated in µg/g sample

ID no. A-01, exterior	Sample amount: 2.02 g	
Chemical Technology label 30396-18		
Component	CAS no.	µg/g
Toluene	108-88-3	Trace <0.05
o-, m-, p-Xylene, ethylbenzene	95-47-5, 108-38-3, 106-42-3, 100-41-4	0.90

Analysis results for saliva-extracts stated in µg/g sample

ID no. A-01, exterior	Sample amount: 2.05 g	
Chemical Technology label 30396-18		
Component	CAS no.	µg/g
Toluene	108-88-3	Trace <0.05
o-, m-, p-Xylene, ethylbenzene	95-47-5, 108-38-3, 106-42-3, 100-41-4	0.86

Comments

The components were identified by comparing the respective mass spectra with mass spectra from NIST library.

The stated amounts are calculated according to response for internal standards assuming that all detected components have same response for same amount and same recovery.

Enclosure E: ICP analysis results from screening

Mark	DK-01		DK-02	DK-03	K-01			BR-01			F-01			DL
	Exterior	Liquid	Exterior	Exterior	Exterior	Liquid	Accessories	Exterior	Liquid	Accessories	Exterior	Liquid	Accessories	
30396-	1	1	2	3	5	5	5	7	7	7	8	8	8	DL
Analyt	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Li	-	-	0.13	-	-	-	7.5	-	-	4.2	-	-	-	0.1
Be	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5
B	30	5800	-	-	-	1.7	-	-	-	-	-	-	-	1
Na	34	7200	-	61	-	-	10	-	260	17	-	74	-	10
Mg	-	25	-	-	-	15	-	1.1	37	31	-	-	-	10
Al	-	44	65	58	-	-	49	-	13	25	-	-	-	10
K	-	40	36	10	-	-	-	-	17	21	18	-	-	5
Ca	370	820	8.4	9	-	-	35	20	-	1400	16	-	8	5
Sc	-	0.12	-	-	-	-	-	-	-	-	-	-	-	0.1
Ti	-	-	9.2	0.86	-	-	0.95	-	1.2	1.3	-	-	-	0.5
V	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5
Cr	-	0.94	-	-	-	-	-	-	-	-	-	-	-	0.5
Mn	-	0.13	-	-	-	-	-	-	-	0.19	-	-	-	0.1
Fe	-	-	-	-	-	-	-	-	-	6.6	-	-	-	5
Co	-	-	-	-	-	-	-	-	-	-	-	-	0.29	0.1
Ni	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5
Cu	-	-	8.7	-	-	-	5.3	-	-	0.68	-	-	-	0.5
Zn	-	-	-	1.1	0.79	-	1.9	1.2	-	210	0.61	-	1.9	0.5
Ga	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
As	-	-	-	-	-	-	-	-	-	-	-	-	-	1
Se	-	-	-	-	-	-	-	-	-	-	-	-	-	1
Rb	-	0.17	0.3	-	-	-	-	-	0.13	-	-	-	-	0.1
Sr	-	0.5	-	-	-	-	-	-	-	1.3	-	-	-	0.5
Y	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Zr	-	-	-	-	-	-	0.23	-	-	-	-	-	-	0.1
Nb	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Mo	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Ru	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Pd	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Ag	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Cd	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
In	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Sn	-	-	0.61	-	-	-	-	-	-	-	-	-	-	0.5
Sb	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Te	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Cs	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Ba	11	0.49	0.2	0.1	0.1	-	28	-	-	7.9	0.13	-	-	0.1
La	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Ce	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Pr	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Nd	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Sm	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Eu	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Gd	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Tb	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Dy	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Ho	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Er	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Tm	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Yb	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Lu	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Hf	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Ta	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
W	-	0.21	-	-	-	-	-	-	-	-	-	-	-	0.1
Os	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Ir	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Pt	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Au	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Hg	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5
Tl	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Pb	-	-	-	-	-	-	-	-	-	0.13	0.12	-	0.12	0.1
Bi	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Th	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
U	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1

	TO-01	TO-02	TO-03		G-01	K-03	TI-01		R-01		A-01			DL
	Exterior	Exterior	Lip-gloss	gel	Exterior	Gel	Gel	Liquid	Exterior	Liquid	Gel	Liquid	Stars	
30396-	9	10	11	11	12	13	16	16	17	17	18	18	18	
Analyt	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Li	-	-	0.15	-	-	-	-	-	-	-	0.1	-	-	0.1
Be	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5
B	520	920	2.5	-	-	-	-	-	-	-	-	-	5.4	1
Na	440	800	17	32	-	-	-	130	14	100	10	-	40	10
Mg	24	36	-	-	-	-	-	-	-	-	-	-	-	10
Al	-	-	120	16	-	-	-	-	11	-	12	-	-	10
K	82	140	-	-	-	5.1	-	-	16	-	4	22	24	5
Ca	120	250	8.7	-	22	14	7.7	-	74	-	18	12	330	5
Sc	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Ti	-	-	-	-	-	-	-	-	-	-	-	-	2.3	0.5
V	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5
Cr	0.1	-	-	0.52	-	-	-	-	-	-	0.61	-	-	0.5
Mn	-	-	2	-	-	-	-	-	0.43	-	0.17	-	-	0.1
Fe	-	-	-	-	-	-	-	-	12	-	-	-	15	5
Co	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Ni	0.72	-	-	-	-	-	-	-	-	-	2.6	-	-	0.5
Cu	-	0.56	4	-	-	-	0.75	0.61	0.82	-	0.73	-	0.92	0.5
Zn	-	14	-	-	2.6	0.68	-	-	2.8	-	1.5	-	2.2	0.5
Ga	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
As	-	-	-	-	-	-	-	-	-	-	-	-	-	1
Se	-	-	-	-	-	-	-	-	-	-	-	-	-	1
Rb	-	0.1	-	-	-	-	-	-	-	-	-	-	-	0.1
Sr	0.59	1.1	-	-	0.69	-	-	-	0.34	-	-	-	-	0.5
Y	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Zr	0.1	0.1	-	-	-	-	-	-	-	-	-	-	0.04	0.1
Nb	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Mo	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Ru	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Pd	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Ag	-	-	-	-	-	0.01	-	-	0.01	-	-	-	-	0.1
Cd	-	-	-	-	-	-	-	-	0.02	-	-	-	0.07	0.1
In	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Sn	0.53	-	-	-	-	-	-	-	-	-	-	-	39	0.5
Sb	-	-	1.8	3.8	-	-	-	-	-	-	-	-	0.23	0.1
Te	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Cs	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Ba	-	0.21	0.64	0.16	-	-	-	-	0.38	-	0.69	-	8	0.1
La	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Ce	-	-	-	-	-	-	-	-	-	-	0.03	-	-	0.1
Pr	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Nd	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Sm	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Eu	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Gd	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Tb	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Dy	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Ho	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Er	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Tm	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Yb	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Lu	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Hf	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Ta	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
W	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Os	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Ir	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Pt	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Au	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Hg	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5
Tl	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Pb	-	-	-	-	-	-	0.1	-	0.17	-	0.29	-	0.9	0.1
Bi	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
Th	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
U	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1

Enclosure F: Analysis results from boric acid determination by ICP-AES

Lab mark 30396-	Sample mark	Intermediate sample	B µg/g	%RSD	DL µg/g
1	DK-01	Exterior	-		1
1	DK-01	Liquid	8400	1.2	1
2	DK-02	Exterior	-		1
3	DK-03	Exterior	-		1
5	K-01	Exterior	-		1
5	K-01	Liquid	-		0.5
5	K-01	Accessories	-		1
7	BR-01	Exterior	-		1
7	BR-01	Liquid	-		0.5
7	BR-01	Accessories	-		1
8	F-01	Exterior	-		1
8	F-01	Liquid	-		0.5
8	F-01	Accessories	-		1
9	TO-01	Exterior	653	0.94	1
10	TO-02	Exterior	1170	4.7	1
11	TO-03	Lip-gloss	-		0.5
11	TO-03	Glitter	-		1
12	G-01	Exterior	-		1
13	K-03	Gel	-		1
16	TI-01	Gel	-		1
16	TI-01	Liquid	-		1
17	R-01	Exterior	-		1
17	R-01	Liquid	-		1
18	A-01	Gel	-		1
18	A-01	Liquid	-		0.5
18	A-01	Stars	-		1

%RSD indicates the percentage relative standard deviation based on repeat determinations.

"-" indicates less than the limit of detection listed in the rightmost column.

DL indicates the limit of detection.

Enclosure G: Analysis results for headspace analyses stated in mg/m³

ID no.		DK-01	DK-02	DK-03	K-01 exterior	K-01 liquid
Chemical Technology label		30396-1	30396-2	30396-3	30396-5A	30396-5B
Component	CAS no.	mg/m ³				
2-Butoxy-ethanol	111-76-2	-	0.017	0.012	-	-
Cyclohexanone	108-94-1	0.040	0.078	0.049	0.139	0.120
Dichloromethane	75-09-2	-	-	-	-	-
N,N-Dimethyl formamide	68-12-2	-	-	-	-	-
2-Hexanone	591-78-6	-	-	-	-	-
1,2-Propandiol	4254-15-3	-	-	-	-	-
2-Propenoic acid 2 methyl-methyl ester	80-62-6	-	-	-	-	-
Toluene	108-88-3	0.832	0.504	0.719	3.153	0.350
Xylenes, ethylbenzene	-	0.257	0.308	0.268	0.621	0.030
<i>Alfa</i> -Pinene	80-56-8	0.020	0.095	0.085	0.182	-
Styrene	100-42-5	-	-	-	-	-
3-Carene	13466-78-9	-	0.039	0.049	-	-
D-Limonene	5889-27-5	-	0.025	0.024	-	-
2-Phenoxy ethanol	122-99-6	-	-	-	-	-
2-Butanone	78-93-3	-	-	-	-	-

ID no.		BR-01 exterior	BR-01 liquid	F-01	TO-01	TO-02
Chemical Technology label		30396-7A	30396-7B	30396-8	30396-9	30396-10
Component	CAS no.	mg/m ³				
2-Butoxy ethanol	111-76-2	-	-	0.240	-	-
Cyclohexanone	108-94-1	-	-	0.053	4.637	0.620
Dichloromethane	75-09-2	-	-	-	-	-
N,N-Dimethyl formamide	68-12-2	-	-	-	-	0.008
2-Hexanone	591-78-6	-	-	-	-	-
1,2-Propandiol	4254-15-3	-	0.205	-	-	-
2-Propenoic acid 2 methyl-methyl ester	80-62-6	-	-	-	-	-
Toluene	108-88-3	0.847	0.234	0.801	0.169	0.351
Xylenes, ethylbenzene	-	8.823	2.312	0.560	0.037	0.207
<i>alfa</i> -Pinene	80-56-8	-	-	0.040	-	-
Styrene	100-42-5	-	-	-	-	0.105
3-Carene	13466-78-9	0.024	-	0.013	-	-
D-Limonene	5889-27-5	-	-	-	-	-
2-Phenoxy ethanol	122-99-6	-	-	-	-	-
2-Butanone	78-93-3	-	-	-	-	-

"-": means not detected

Analysis results for headspace analyses stated in mg/m³

ID no.		TO-03 Lip-gloss	TO-03 gel	G-01	K-03	TI-01 exterior
Chemical Technology label		30396-11	30396-11	30396-12	30396-13	30396-16A
Component	CAS no.	mg/m ³	mg/m ³	mg/m ³	mg/m ³	mg/m ³
2-Butoxy-ethanol	111-76-2	-	0.017	0.017	-	-
Cyclohexanone	108-94-1	0.016	0.081	0.111	0.018	-
Dichloromethane	75-09-2	-	-	-	-	-
N,N-Dimethyl formamide	68-12-2	-	-	-	-	-
2-Hexanone	591-78-6	-	-	-	-	0.093
1,2-Propandiol	4254-15-3	-	1.619	-	-	-
2-Propenoic acid 2 methyl-methyl ester (Methyl methacrylate)	80-62-6	-	0.177	-	-	-
Toluene	108-88-3	0.138	0.169	0.284	0.053	0.344
Xylenes, ethylbenzene	-	0.138	0.066	1.108	0.117	0.482
<i>alpha</i> -Pinene	80-56-8	0.008	0.010	0.020	-	0.041
Styrene	100-42-5	-	0.049	-	-	-
3-Carene	13466-78-9	0.016	-	0.009	-	0.021
D-Limonene	5889-27-5	-	0.010	0.011	-	-
2-Phenoxy ethanol	122-99-6	-	0.096	-	-	-
2-Butanone	78-93-3	-	-	-	-	0.079

ID no.		TI-01 liquid	R-01 exterior	R-01 liquid	A-01 exterior	A-01 liquid
Chemical Technology label		30396-16B	30396-17A	30396-17B	30396-18A	30396-18B
Component	CAS no.	mg/m ³				
2-Butoxy-ethanol	111-76-2	-	0.160	0.102	-	-
Cyclohexanone	108-94-1	0.011	-	0.009	-	-
Dichloromethane	75-09-2	0.033	-	-	-	-
N,N-Dimethyl formamide	68-12-2	-	-	-	-	-
2-Hexanone	591-78-6	0.087	-	-	-	-
1,2-Propandiol	4254-15-3	-	-	-	-	-
2-Propenoic acid 2 methyl-methyl ester (Methyl methacrylate)	80-62-6	-	-	-	-	-
Toluene	108-88-3	0.109	0.200	-	0.213	-
Xylenes, Ethylbenzene	-	0.098	0.160	-	4.571	0.146
<i>alpha</i> -Pinene	80-56-8	-	-	-	-	-
Styrene	100-42-5	-	-	-	-	-
3-Carene	13466-78-9	-	-	-	-	-
D-Limonene	5889-27-5	-	-	-	-	-
2-Phenoxy ethanol	122-99-6	-	-	-	-	-
2-Butanone	78-93-3	0.098	-	-	-	-

"-": means not detected

Enclosure H: GC-MS quantitative analysis results

Quantitative analysis of selected components in sweat- and saliva-extracts ($\mu\text{g/g} = \text{mg/kg}$)

Component	CAS no.	DK-01, exterior	DK-02, exterior	DK-03, exterior	K-01, exterior	BR-01, exterior	F-01, exterior	F-01, interior	TO-01, exterior	TO-02, exterior	TO-03, gel	G-01, exterior	K-03, exterior	TI-01, exterior	R-01, exterior	A-01, exterior
		1	2	3	5	7	8	8 C	9	10	11	12	13	16	17	18
Cyclohexanone	108-94-1			1.0					430	6.9		0.5				
Diethylglycol dibenzoate	120-55-8								118	26						
Component corresponding to diethylglycol dibenzoate									103	4						
2-Phenoxy ethanol	122-99-6						53	60			16000				120	
2-Phenylmethylene octanal (=Hexylcinnamaldehyde)	101-86-0										8.6					
N-Propyl benzamide + N-acetyl benzamide	10546-70-0, 1575-95-7								*	*						
Toluene	108-88-3	0.20	0.13	0.17	1.4	0.16	0.14	0.19				0.06	<0.05	<0.05		0.05
o-, m-, p-Xylene	95-47-5, 108-38-3, 106-42-3				0.30	1.1	0.26	0.20				0.27				0.81
Ethylbenzene	100-41-4				< 0.05	0.56	< 0.05	< 0.05				< 0.05				0.06

Quantitative analysis of selected components in saliva-extracts ($\mu\text{g/g} = \text{mg/kg}$)

Component	CAS no.	DK-01, exterior	DK-02, exterior	DK-03, exterior	K-01, exterior	BR-01, exterior	F-01, exterior	F-01, interior	TO-01, exterior	TO-02, exterior	G-01, exterior	K-03, exterior	TI-01, exterior	R-01, exterior	A-01, exterior
		1	2	3	5	7	8	8 C	9	10	12	13	16	17	18
Cyclohexanone	108-94-1			0.6					160	7.6	<0.5				
Diethylglycol dibenzoate	120-55-8								65	38					
Component corresponding to diethylglycol dibenzoate									69	7					
2-Phenoxy ethanol	122-99-6						44	17						80	
N-Propyl benzamide + N-acetyl benzamide	10546-70-0, 1575-95-7								*	*					
Toluene	108-88-3	0.27	0.09	0.22	1.5	0.15	0.16	0.24			0.05	<0.05	<0.05		<0.05
o-, m-, p-Xylene	95-47-5, 108-38-3, 106-42-3				< 0.05	1.2	0.31	< 0.05			0.25				0.79
Ethylbenzene	100-41-4				< 0.05	0.64	< 0.05	< 0.05			< 0.05				0.06

*These organic compounds have not been determined quantitatively, as the standards were not commercially available.

Enclosure I: ICP quantitative analysis results

Analysis UT015

Lab mark	Sample mark	Ni $\mu\text{g/g}$	% RSD
31519-14	TO-01	0.83	4.0
31519-24	A-01	2.96	2.5

Enclosure J: Boron determination by ICP-AES

Lab mark	Sample mark	B $\mu\text{g/g}$	% RSD
30396-19	EX-01	729	0.97
30396-20	EX-02	1100	20

%RSD indicates the percentage relative standard deviation based on repeat determinations

Enclosure K: Supplementary tests - Analysis results for headspace analyses stated in mg/m³

ID no.		EX-01
Chemical Technology label		30396-19
Component	CAS no.	mg/m ³
2-Propanol	67-63-0	0.063
2-Propanol, 2-methyl-	75-65-0	0.053
1-Propanol	71-23-8	0.065
2-Propanol, 1-methoxy-	107-98-2	0.036
C6-C7 aliphatic hydrocarbons		0.119
Hexanal	66-25-1	0.061
2,4-Dimethyl-1-heptene	19549-87-2	0.013
2-n-Butylacrolein	1070-66-2	0.019
Cyclohexanone	108-94-1	0.004
Heptanal	111-71-7	0.004
cis-Hept-2-enal	57266-86-1	0.004
2-Octen-1-ol, (Z)-	26001-58-1	0.004
Octanal	124-13-0	0.008
Nonanal	124-19-6	0.008

ID no.		EX-02
Chemical Technology label		30396-20
Component	CAS no.	mg/m ³
Ethanol	64-17-5	0.019
2-Propanol	67-63-0	0.000
2-Propanone, 1-methoxy-	5878-19-3	0.037
Acetic acid		*
Propylene glycol	57-55-6	4.039
Xylenes	-	0.331
Styrene	100-42-5	0.467
C9H12 aromatic hydrocarbons	-	2.410
C10H14 aromatic hydrocarbons	-	0.451
C12-C16 aliphatic hydrocarbons	-	5.324
2-Phenoxy ethanol	122-99-6	1.152

"*": means detected

Enclosure L: Quantitative determination of phthalate by GC-MS

Sample mark	Lab mark	Component	µg/g	% (m/m)
DK-01	30396-1	Di-iso-nonyl phthalate (DINP)	1800	0.18
F-01 (white)	30396-8	Diethyl hexyl phthalate (DEHP)	20	0.0020
F-01 (yellow)	30896-8	Diethyl hexyl phthalate (DEHP)	21	0.0021
R-01	30896-17	Diethyl hexyl phthalate (DEHP)	17	0.0017
A-01	30896-18	Diethyl hexyl phthalate (DEHP)	27	0.0027
EX-02	30896-20	Diethyl hexyl phthalat (DEHP)	81	0.0081

Sample mark	Lab mark	Comments
DK-02	30396-2	No content of phthalates above the mentioned limits of detection was detected
DK-03	30396-3	
K-01	30396-5	
BR-01	30396-7	
TO-03, gel	30396-11	
G-01	30396-12	
K-03	30396-13	
EX-01	30396-19	