DANISH MINISTRY
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Survey, migration and health evaluation of chemical substances in toys and childcare products produced from foam plastic

Pernille Borling, Birgit Engelund, Hanne Sørensen
and Karl-Heinz Cohr.

DTC
Health and Environment, a business unit of
DHI Water and Environment

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Preface

The project “Survey, migration and health evaluation of chemical substances in toys and childcare products produced from foam plastic“ was made on behalf of the Danish environmental protection agency. The project was a cooperation between The Danish Toxicology Centre, responsible for the survey and the health evaluation and Analytica AB, responsible for the chemical analysis.

The purpose of this project was to make a survey of toys and childcare articles produced from foam plastic in Denmark. Based on the survey the purpose was to select a number of products for analyses for content of chemical substances know to cause health problems in humans. Based on the analytical results chemical substances were chosen to the health assessment.

Summary

The objective of Phase 1 was to make a survey of toys and childcare articles on the Danish market produced from foam plastic, including their chemical composition.

Most wholesalers and distributors of toys and childcare articles have been very helpful providing lists of products of their assortment. It has however been difficult to obtain information on consumption and almost impossible to obtain information on the chemical composition of the products.

Foreningen af Legetøjsfabrikanter i Danmark (FLD) (The Association of Toy Manufacturers in Denmark), whose members count seven of the largest manufacturers in Denmark estimates that less than 1% of all toys (by number) are produced from foam plastic (1).

Based on data from the website "Danmarks statistik – www.statistikbanken.dk", an estimate on toys and childcare articles on the Danish market was made (2). The website contains information on imported and imported products in kilos. Since DTC did not find any toys or childcare articles made from plastic foam produced in Denmark, only the number of imported toys was estimated. As it was not possible to select data on specific materials, a data selection from the statistic base on a superior level was made based on which foam plastic products were specified. The estimated total of imported toys and childcare articles made from foam plastic in 2004 was 171.2 ton.

During the survey, it was not possible to obtain information on the complete chemical composition of the products. DTC obtained information on the use of two basic polymers, ethylene vinyl acetate (EVA) and polyurethane (PUR).

Based on the survey, the Danish Environmental Protection Agency (Danish EPA) has selected the following products for testing:

Product no.	Product	Argumentation
1	Sword	Swords represent a great part of the foam plastic toys on the market
2	Floor puzzle 1	Body contact. **For children of > 1 year**. May be used as nursing carpet
3	Surf board	Is shaped like a frog and therefore believed to attract attention to children < 3 years.
4	Activity carpet	Body contact. Children may spend a lot of time on it.
5	Mask	Face contact.
6	Book	Children are expected to mouth it.
7	Floor puzzle 2	Body contact when children are lying on the puzzle. **Marked for children > 3 years,** however, The Danish Safety Technology Authority has decided that the puzzle is for children < 3 years.
8	Ball	The diameter (< 20 cm) indicates use for children < 3 years.

The objective of Phase 2 is to determine the content of hazardous substances in the selected products. The selection of substances was based on knowledge of additives in plastic products as well as knowledge of substances that may be hazardous to humans.
The process of analyses was iterative and initiated with qualitative and quantitative analyses of eight products for bromated flame-retardants, TCEP, phthalates and metals. Testing for content of organic tin compounds and colorants was also performed as well as a screening for volatile organic compounds in selected products. The test results are shown in the following survey.

Product no.	Product	Phthalates	Bromated flame retardants + TCEP	Metals	Organic tin compounds	Azo colorants	Selected colorants, (specified in table 2.8)	Screening for volatile organic compounds < C_{14} - C_{16}
1	Sword	B	A	A		A	E	F
2	Floor puzzle 1	A	A	A		A	E	F
3	Swim board	A	A	A				
4	Activity Carpet	C	A	A	D			
5	Mask	A	A	A				F
6	Book	A	A	A	B			
7	Floor puzzle 2	C	A	A				
8	Ball	A	A	A				F

A Not measured in concentrations of concern
B Concentrations requiring safety assessment
C Concentrations exceeding the permitted limit
D Not assessed. The products were withdrawn from the Danish market because of the total content of phthalates)
E Assessment not possible. The detection limit is higher than the limit value due to the complexicity of the polymer materials
F The analyses was a screening without quantification or qualification of the substances. The GC-MS-spectrum of the ball contained a signal equal to C_{10}-C_{14} hydrocarbons.

The content of phthalates in two products (4 and 7) were higher than the limit value for phthalates in toys intended for children between 0-3 years of 0.05%, and the two products were ordered withdrawn from the Danish market (3). 5 chemical substances were selected for the safety assessment in phase 3; diisobutylphthalate (DIBP), di-n-butylphthalate (DBP), diisononylphthalate (DINP), monobutyltin (MBT) and dibutyltin (DBT).

The purpose of phase 3 was to set up toxicological profiles for the above 5 substances and perform an exposure assessment of MBT and DBT in product 6. Based on the safety assessment in phase 3, the below assessments were performed.

The highest DIBP measured in the remaining 6 products, was 6.5 mg/kg in product 5 (corresponding to 0.00065%). The amount is lower than the above limit value (3), and does not cause any health concern.

The highest DBP measured in the remaining 6 products was 11.9 mg/kg in product 6 (corresponding to 0.00119%). The amount is lower than the above limit value (3), and does not cause any health concern.

The highest amount of DINP measured in the remaining 6 products was 935 mg/kg in product 1 (corresponding to 0.0935%). The amount is higher than the above limit value (3), but as the product is intended for children > 3 years it was not withdrawn from the Danish market. The distributor of product 1 was informed of the content of DINP in the product and is working on eliminating the substance from the product.

Foamed toys and childcare products are mainly produced from EVA and PUR foam. Based on this survey, it is recommended to focus on the content of phthalates of these products, as 2 of 8 products contained concentrations above the permitted limit value for phthalates (0.05%) in toys intended for children between 0-3 years, (3). DEHP is furthermore contained in all products. DEHP, DBP and BBP, which have been identified as reproduction toxic substances, will be prohibited in concentrations above 0.1% of all softened toys and childcare articles. DINP, DIDP and DNOP will be prohibited in toys and childcare articles intended for mouthing (4). The prohibition comes into force one year after the proportion is agreed upon in the council.

2 products (4 and 6) were analysed for organic tin compounds. Product 4 was withdrawn from the Danish market and consequently it was not assessed. 1.95 g MBT/kg and 1.15 g DBT/kg was measured in product 6 (a fabric book with PUR stuffing intended for children under 3 years).

Sufficient data was not found on MBT and DBT's toxic effects in animals and humans. The substances were assessed based on a Tolerable Daily Intake (TDI) for the two substances recommended by the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) (4).

The assessment was based on a worst-case scenario under the assumption of a release of the total amount of MBT and DBT in one day and exposure of a newborn child and a child of 1.5 years of age. The average weight in Denmark of a newborn child is 3,450 g (5) and a child of 1.5 years weighs 9,850 g (6). An additive effect of the two substances is expected. A fraction sum < 1 means that the total content of MBT and DBT in the book does not cause any health concern.

Daily exposure, tin, child:

$$\frac{Exposure_{MBT}}{TDI_{MBT}} + \frac{Exposure_{DBT}}{TDI_{DBT}} < 1$$

The fraction sum of the exposure of a newborn child and a child of 1.5 years old is 0.08 and 0.03, respectively. This means that there is no reason for health concerns based on the content of MBT and DBT in the book.

The Margin of Safety (MoS) for the exposure of the two organic tin compounds from the book was calculated by dividing NOAEL with the exposure (under the

assumption that the entire amount of MBT (1.95 µg/kg book) and DBT (1.15 µg/kg book) is released in one day. A NOAEL for DBT of 2.5 mg/kg bw/day was used for both MBT and DBT.

MoS, MBT + DBT, child:

$$\frac{NOAEL}{Exposure_{MBT} + Exposure_{DBT}} > 1000$$

A MoS of 86000 and 250000 was calculated for a newborn child and a child of 1.5 years old, respectively, which is assumed to be sufficient for the protection of children. The used NOAEL for MBT and the assumption of a release of the total content of the organic tin compounds in one day underestimates the MoS. DTC estimates that exposure to organic tin compounds from the book does not cause any health concerns. Because of the large amount of organic tin compounds found in dust from European households, and the potential to ingest organic tin compounds through breast milk and food and from a number of other consumer products, DTC recommends that the contribution from other sources is calculated. An estimation of how large an amount of TDI that could be allocated to consumer products is then possible.

Introduction

Toys and childcare articles produced from plastic are predominating in nurseries. Many of these products may contain chemicals that may be potentially hazardous to human health and the environment.

Since the central nervous system, the immune system and the reproductive ability of children are more vulnerable than those of adults (7), it is important to assess whether these products contain chemicals that may cause adverse effects on children playing with them.

In this project, DTC has been requested to make a survey on toys and childcare articles specifically produced from foam plastic – phase 1.

Based on the survey, a number of products to be tested by the analysis laboratory, Analytica AB were selected – phase 2. The test programme is based on knowledge of additives in plastic products as well as of substances that may be hazardous to humans.

1 Survey of toys

The objective of Phase 1 is to make a survey of toys and childcare articles produced from foam plastic on the Danish market, including their chemical composition.

Phase 1 includes the following sub-activities:

- Definition of products
- Survey of Toys and Childcare articles produced from foam plastic
- Chemical composition of Toys and Childcare articles produced from foam plastic.
- Estimate of consumption
- Selection of products for analysis.

1.1 Definition of products

In the project description the Danish Environmental Protection Agency (DEPA) presented the following examples of toys and childcare articles produced from foam plastic: Floor puzzles and disguise items, such as masks, swords, and shields for role-playing. Most of the products intended for the formalized form of role-playing are made from latex and therefore excluded from this project. Apart from the product groups mentioned above, cuddly and soft-toys, handgrips on vehicles, support in rollers, protection equipment, soft balls, swim equipment, crowns and picture books were included in the survey, if they contained foam plastic. Mattresses and furniture containing foam plastics were excluded, as they are considered outside the target group of this project.

1.2 Survey of toys and childcare articles for children produced from foam plastic

The product survey of toys and childcare articles for children produced from foam plastic on the Danish marked was based on:

- Contact with 24 wholesalers. The list of potential wholesalers was generated from www.zapp-online.dk. Only 9 out of 24 wholesalers distributed this kind of toys. See table 1.1.
- Based on a list generated from www.nnerhverv.dk, 10 distributors of toys and childcare articles were contacted. 5 shops were selected either because they were among the largest distributors of toys or part of multiple shops. Jalsøe was chosen because of the large selection of childcare articles and the 4 minor shops were chosen because the represented other brands of toys than the large shops. See table 1.2.
- A search on Danish websites was performed in April 2005 via www.google.dk and www.yahoo.dk. The expressions searched on were: ”legetøj og skumplast” (toys and foam plastic), ”EVA skum sværd” (EVA foam sword) and “PUR skum legetøj” (PUR foam

toys). The search also included the enterprises ”Visiodan” og ”Metrodan”, names that were found on foam products in a shop for childcare articles. References containing information on foam products in Denmark is listed in table 1.3.

DTC estimates that the above activities adequately illustrate the Danish market for toys and childcare articles produced from foam plastic. A list of products on the Danish marked is presented in table 1.4.

Table 1.1 Contacted wholesalers of toys (in bold), references from wholesalers to other distributors (not in bold)

No.	Wholesalers	Address
1	**Aage Mottlau A/S**	**3520 Farum**
2	**B.K.H. Sport & Leg***	**2610 Rødovre**
2.1	Select *	2600 Glostrup
2.2	Tress*	8660 Skanderborg
3	**Best Buy Toys**	**6580 Vamdrup**
4	**Captoy**	**2860 Søborg**
5	**CK Team Trading Aps**	**8783 Hornsyld**
6	**Cova Collection Aps**	**7400 Herning**
7	**Danimals Educational Toys**	**8752 Østbirk**
8	**Dansk Supermarked***	**8270 Højbjerg**
9	**Electronic Fun I/S**	**8464 Galten**
10	**FDB***	**2620 Albertslund**
11	**G.A. Import***	**2770 Kastrup**
11.1	Tatic	
12	**Hasbro Nordic**	**2600 Glostrup**
13	**Joy Toy**	**2680 Solrød Strand**
14	**K.E. Mathiasen A/S***	**8220 Brabrand**
15	**Krea A/S***	**8200 Århus N**
16	**Leico Aps**	**8700 Horsens**
17	**Maki Aps***	**3500 Vørløse**
18	**Mattel Northern Europe A/S**	**2605 Brøndby**
19	**Mega Trading**	**8240 Risskov**
20	**Nikko Scandinavia Filial A/S**	**2670 Greve**
21	**Ran-Play Gruppen A/S***	**8900 Randers**
22	**TOP TOY A/S***	**4000 Roskilde**
23	**Toys & Company**	**3000 Helsingør**
24	**VN Legetøj A/S**	**8361 Hasselager**

* Distributor of toys and childcare articles produced from foam plastic.

Table 1.2 Stores distributing toys and childcare articles

No.	Name	Address
1	Absalon	1620 København V
2	Børne Shoppen*	2970 Hørsholm
3	BR*	3450 Allerød
4	Gk Legetøj Aps Herning Centret	7400 Herning
5	Jalsøe*	2500 Valby
6	Lego/Legoland*	7190 Billund
7	Magasin	2800 Kgs. Lyngby
8	Narnia*	3050 Humlebæk
9	Skagen Legecenter	9990 Skagen
10	Toys R'us*	2610 Rødovre

*Stores distributing toys and childcare articles produced from foam plastic.

Table 1.3 References from Danish websites containing information on foam plastic products

No.	Website
1	www.a-sport.dk
2	www.legehuset.dk
3	www.metrodan.dk
4	www.visiodan.dk

Table 1.4 Products produced from foam plastic found on the Danish market.

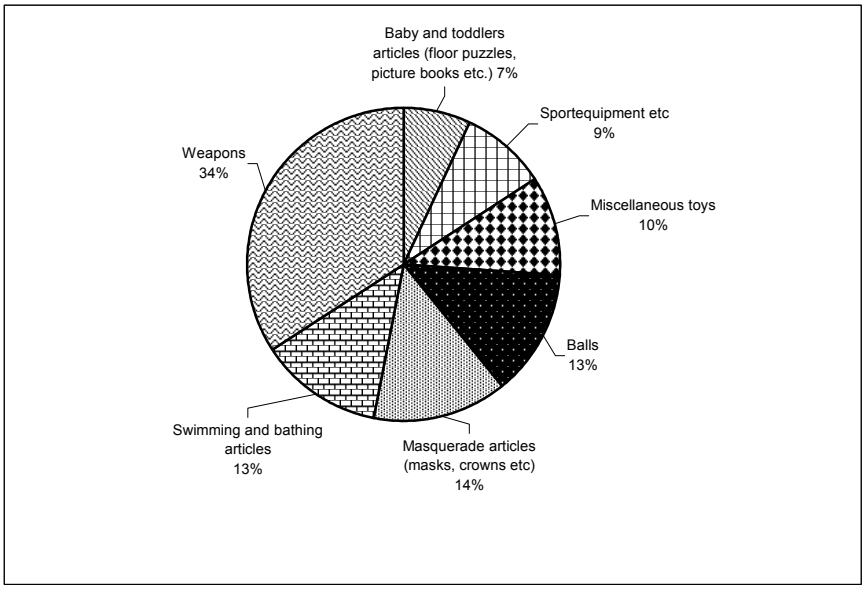
Products	Number	Age
3-D activity book	1	> 6 months
Activated toy	1	> 7 months
Activated toy	1	> 5 months
Axe	4	> 3
Baby activity Gym	2	> 0
Baby book	2	< 3
Bathing book	4	< 3
Bike helmet	12	> 3
Blackboard sponge	2	< 3
Body board	2	> 3
Car wash	1	< 1.5
Claw	2	> 3
Copter ball	1	> 3
Crowns	15	> 3
Crowns and feathers	8	> 3
Disc launcher	2	> 3
Dolls pram (handgrip)	12	< 3
Eye patch	1	< 3
Floor puzzle	6	> 2
Floor puzzle, puzzle mats	6	< 3
Floor puzzle, puzzle mats	2	> 3
Foam ball (unspec)	3	> 3
Foam ball (unspec)	4	< 3
Foam ball (Ø15 cm)	1	< 3
Foam ball (Ø18 cm)	3	< 3
Foam ball (Ø21 cm)	4	> 3
Foam ball (Ø27 cm)	3	> 3

Products	Number	Age
Foam ball (Ø36 cm)	2	> 3
Foam ball (Ø46 cm)	1	> 3
Foam ball (Ø48 cm)	1	> 3
Foam ball (Ø54 cm)	1	> 3
Foam ball (Ø65 cm)	1	> 3
Foam rocket	1	> 3
Foam tennis ball	5	< 3
Football	3	> 3
Football	1	< 3
Goal keeper gloves	1	> 3
Hammer	1	> 3*
Hand ball	3	< 3
Hand ball	1	> 3
Hat	1	> 3*
Helmet	3	> 3*
Indian feather	1	> 3
Kids mobile	1	> 6
Knife	1	> 3*
Mask	10	> 3
Mirror	1	< 3
Mirror (foam edges)	2	> 3
Picture book	1	> 3*
Pirate hook	1	> 3*
Play to car	1	> 3*
Police badge	1	> 3*
Rifle	1	>3*
Road cone	1	3*
Roller skates	9	> 3
Roller protector	1	> 3
Sabre	1	> 3*
Scimitar	1	> 3
Sheriff badge, pistols, guns etc	11	> 3
Shield	37	> 3
Skater helmet	1	> 3
Skipping (hand grip)	2	> 3
Soft bricks	2	> 3*
Softball bat	2	> 3
Swim board	7	> 3
Swim board	8	> 3*
Swimming belt	2	0-6
Swimming belt	2	6-12
Swimming belt	11	Depending on child's weight
Swimming board	8	> 3*
Swimming collar	2	> 3
Swim-safe	1	2-6
Sword	51	> 3
Tiara	1	> 3*
Tomahawk	1	> 3*
Tool	2	> 3*
Volleyball	1	> 6
Volleyball	2	> 3

Products	Number	Age
Walki Talki	1	> 3*
Toa Torso Top Wakama	1	> 3*
Wand Princess Light Up	1	> 3*
Vahki EVA Tool Light Up	1	> 3*
Water wings	2	> 3*
Total	317	

* Estimated by DTC

Figure 1 Distribution on different types of toys and childcare articles produced from foam plastic based on present survey



1.3 Chemical composition of toys and childcare articles produced from foam plastic

Experience shows that it is often difficult to obtain information on complete chemical composition from manufacturers. Since most of the products relevant for this project are made in the Far East, the elaboration of the survey of the chemical composition was complicated and the available information very sparse. It was not possible to obtain full chemical composition of any of the products. Only two manufacturers returned partial information on the chemical composition of the products. As this information is given in confidence, we have abstained from presenting this information to prevent transparency in the product information.

1.4 Estimated consumption

DTC received information on sales numbers from very few distributors of toys and childcare articles produced from foam plastic. The Association of Toy Manufacturers in Denmark that counts seven of the largest manufacturers of toys in Denmark evaluates that less than 1% of the total amount of toys is produced from foam plastic (1).

From the website "Danmarks statistik – www.statistikbanken.dk" information on imported products stated in either kilos or Danish crones was retrieved (2).

DTC estimated that there are four main groups of toys primarily made from plastic foam. The four main groups are toy weapons, puzzles, balls, and swim equipment. The remaining products are more isolated examples. e.g. a blackboard with a sponge made from foam, doll's pram with handgrips made from foam or rollers with foam insertion. As the scope of this project does not admit a thorough investigation of the different products, we have decided to focus on the main groups described in table 1.5.

It is not possible to select data on specific materials. Therefore data from the statistic base on a superior level have been selected followed by an estimate from DTC specified on foam plastic products.

Data have been selected as follows: The names of the four main groups in the statistics database are "toy weapons", "puzzles except from wooden puzzles", "balls except from balls for golf, table tennis, tennis, cricket, polo and inflatable balls" and "swim equipment including swimming- and paddling pools and childcare articles for outdoor play". DTC found neither toys nor childcare articles made from plastic foam, which have been produced in Denmark. Therefore, only imported numbers are included in the below estimate (Table 1.5).

Table 1.5 Estimated amount of toys and childcare articles for children composed of foam plastic imported in 2004. The estimate is based on 4 main groups of toys.

Childcare articles	Imported amount in 2004 (ton)[1]	Percentage produced from foam (%)*	Estimated amount produced from foam in 2004 (ton)*
Toy weapons	727.4	5	36.4
Puzzles, except puzzles made from wood	429.6	5	21.5
Balls, except balls for golf, table tennis, tennis, cricket, polo and inflatable balls	451.9	5	22.6
Swimming equipment including swimming- and paddling pools and childcare articles for outdoor play	9067.9	1	90.7
Total	**10,676.8**		**171.2**

* Estimated by DTC

1. Danmarks statistik – www.statistikbanken.dk provided information on imported products stated in tons (2).

The total amount of toys and childcare products imported to Denmark in 2004 is estimated to be 171.2 tons.

1.5 Selection of products for analysis

The Danish EPA has selected the products stated in table 1.6 for testing.

Table 1.6 Products for testing

Product	No.	Argumentation
Sword	1	Swords represent a great part of the toys made from foam plastic on the market and are therefore believed relevant to test.
Floor puzzle 1	2	Appearance and shape of foam floor puzzles means that they are often used as a soft playground for children of less than 3 years old. They may also be used as nursing carpet, which involves full body contact. This puzzle is marked "**for children of one year or more**". Is furthermore chosen based on a consumer alert notification from the Czech Republic on another floor puzzle produced in China.
Surf board	3	The surfboard is shaped like a frog and therefore believed to attract attention to children less than three years old. Furthermore there is much focus on bathing toys of softened polymers and it is relevant to test the alternative made from foam plastic.
Activity carpet	4	Is recommended for children from birth. The use of the activity carpet involves full body contact and children may spend a lot of time on it. Children are also expected to mouth the product.
Mask	5	Full-face contact and potential migration of chemicals through sweat.
Book	6	Is recommended for children under three years, which are expected to suck on it with a potential migration of chemicals through saliva.
Floor puzzle 2	7	This puzzle is marked "only to be used by children more than 3 years old". The Danish Safety Technology Authority has however decided that it is for children below 3 years old. Appearance and shape of foam floor puzzles means that they are often used as a soft playground for children of less than 3 years old. They may also be used as nursing carpet, which involves full body contact. Is furthermore chosen based on a consumer alert notification from the Czech Republic on another floor puzzle produced in China.
Ball	8	The name of the ball indicated use for children less than three years. Furthermore the diameter of the ball is less than 20 cm and therefore addresses children of less than three years old.

2 Analyses

2.1 Objective

The objective of phase 2 is to determine the content of hazardous substances in selected products, as it is not easily obtained from importers or producers.

From the survey results of phase 1, The Danish Environmental Protection Agency and DTC selected a number of products to be analysed for certain chemical substances (Table 2.1). The products were selected to cover the most sold products on the marked and ages below and above 3 years.

The three new toy standards EN71-9: 2005, Final draft PrEN71-10: 2004 and Final draft prEN71-11: 2005 contain recommended testing of 26 product types, which however of the 8 selected products only include the mask: "***Toys worn over the mouth or nose***".

The selection of the chemical substances was based on knowledge of additives in polymers and knowledge of substances hazardous to humans. Phase 2 was an iterative process that was initiated with qualitative and quantitative analyses of 8 products for bromated flame-retardants, TCEP, phthalates and metals. Based on the test for metals where two products were found to contain tin, these two products were furthermore tested for content of organic tin compounds. Two products representing a product with printed colours and a product with dyed colours were chosen for analysis for content of colorants. 4 Products were selected for a screening of volatile organic compounds, partly based on a RAPEX notification (Rapid Alert System for Non-Food Products) on an EVA product, witch contained organic solvents - and for one of the products also because of a chemical scent from the product. Table 2.2. shows a the performed tests. Analytica AB performed the analyses.

Table 2.1 Selected products

Product No.	Product
1	Sword
2	Floor puzzle 1
3	Swim board
4	Activity carpet
5	Mask
6	Book
7	Floor puzzle 2
8	Ball

2.2 Analysis Programme

Each section contains a description of the used analysis method, including detection limits and analysis uncertainties. All analyses are based on double determinations.

Table 2.2 Performed tests

Product no.	Product	Phthalates	Bromated flame retardants +TCEP	Metals	Organic tin compounds	Azo colorants	Selected colorants, (specified in table 2.8)	Screening for volatile organic compounds < C_{14} - C_{16}
1	Sword	B	A	A		A	E	F
2	Floor puzzle 1	A	A	A		A	E	F
3	Swim board	A	A	A				
4	Activity Carpet	C	A	A	D			
5	Mask	A	A	A				F
6	Book	A	A	A	B			
7	Floor puzzle 2	C	A	A				
8	Ball	A	A	A				F

A Not measured in concentrations of concern
B Concentrations requiring safety assessment
C Concentrations exceeding the permitted limit
D Not assessed. The products were withdrawn from the Danish market because of the total content of phthalates)
E Assessment not possible. The detection limit is higher than the limit value due to the complexicity of the polymer materials
F The analyses was a screening without quantification or qualification of the substances. The GC-MS-spectrum of the ball contained a signal equal to C_{10}-C_{14} hydrocarbons.

2.3 Analysis methods

A weighed sample (approx. 30 – 50 g) was taken from the foam matrices of all products and fractionized into particles with surfaces of maximally 6 mm. The colours of the products with different colours were equally distributed to make the sample representative for the complete product. From product no. 1 sample material was taken from the handle, as the handle is the most used contact surface of the product. The products containing several different materials (e.g. textile, elastic and foam), only partial samples of the foam material were taken (product no. 4, 5 and 6).

2.3.1 Flame retardants

The method for testing the content of bromated flame-retardants and TCEP is Soxhlet extraction of 1 – 2 g material with toluene (4-5 hours). By Soxhlet extraction the test sample is heated and the chemical substances is trapped in

a closed system. GC-MS-measurements were made. The uncertainty of the analysis for pentabromodiphenyle ether (PeBDE) and octabromodiphenyl ether (OBDE) is < 15% and for the remaining decabromodiphenyl ether (DeBDE) tetrabromobisphenol A (TBBPA), hexabromocyclododecan (HBCD) og tris(2-chloroethyl)phosphate (TCEP) < 25%. The internal standards used for PeBDE, OBDE, DeBDE, HBCD, and TCEP were: DBOFB (Dibromooctafluoro biphenyl) for "retrieve control" and PCB209 for “injectioncontrol”. For TBBPA the internal standard was: Tribromophenol. For external standards, the compounds tested for was used.

2.3.2 Phthalates

A Soxhlet-extraction (6 hours) with hexane is used for testing the content of phthalates. By Soxhlet extraction the test sample is heated and the chemical substances are trapped in a closed system. GC-MS measurements were performed. The analysis uncertainty of the determinations is 20-30%. The detection limits of the phthalate analyses stated below are for standard analyses in solid (not foamed) matrices with a fixed test quantity (10-20 g). The standardised amount of test material cannot be used for testing in foam matrices, because the large volume and surface would interfere with the analysis. 1-2 g test material is used for the analyses, and the detection limit is thus 10 times lower than the reported minimum values. Internal standards were hexaclorobenzene and deuteriummarked-DEHP. For external standards, the compounds tested for was used.

2.3.3 Metals

The method for testing migration of metals is governed by The Toy Standard EN 71-3:1994. Besides the 8 metals in the Toy Standard, testing for tin and nickel is also performed. The sample is fractionized into particles with a surface of maximum 6 mm. The particles are placed in a 37°C hydrochloric acid solution (0.07 mol/l) – equal to 50 times the sample weight, shaked for 1 hour and filtrated and centrifuged before analysis. The analysis uncertainty of the metals given in table 2.6 is for the individual metal and not for the method in particular. The analyses methods for tin and nickel are not accredited and consequently their uncertainties are not stated.

2.3.4 Organic tin compounds

The method used for testing the content of organic tin compounds is an extraction (2-3 hours) of 1-2 g material with a sodium diethyldithiocarbamate solution in ethanol, alkylated with sodium tetraethyborate and transferred to organic phase by extraction with hexane. The uncertainty of the analysis is 10-20%.

2.3.5 Colorants

The method used for testing the content of aromatic amines was extraction of 2-5 g material at 70o C in a buffer solution with pH=6 followed by reduction for 30 min. and dredging by liquid/liquid extraction. GC-MS-measurements were performed.

The method used for testing of content of the carcinogenic, allergenic and supplementary 4 colorants was extraction at 70 °C in methanol in 30 minutes and clean -p by filtration. LC-MS-measurements were performed. The

reported results are the extractable parts of the colorants. The uncertainty of the analyses were
< 20%.

2.3.6 Screening for volatile organic solvents

The method for screening for volatile organic compounds (VOC) was a fractionization into particles of approx. 0.5 – 4g material were To screen for organic volatile substances the samples were fractioned, whereupon 0,6 µg internal standard per sample was added (deuterated toluene, deuterated C2-aromates, deuterated decane, deuterated C3 aromates). The screening for VOC was in a mass area of 30 -.700 amu. The GC-MS headspace measurement method (at 80° C) was used. The screening approximately last for 30 minutes and the detection limit is estimated to be approximately 0.5 ug/sample. As the analysis was a screening for VOC without quantification or qualification of the substances, the uncertainty of the analysis is not indicated. If there had been more time in the project, analysis could have been made, that identified and quantified chemical substances present in the products.

2.4 Analyses results

2.4.1 Flame retardants

The content of flame-retardants above the detection limit has not been measured. EU has assigned a limit value of 0.1% for content of PeBDE and OBDE. Marketing of products containing one of these two substances above this limit value is not legal in the EU. The detection limit of all tested flame-retardants is below this limit value, and DTC evaluates that the results do not imply further testing.

Table 2.3 Content of flame-retardants (mg/kg). The values are averages of duplicate determinations. The uncertainty of the analysis for pentabromodiphenyle ether (PeBDE) and octabromodiphenyl ether (OBDE) is < 15% and for the remaining decabromodiphenyl ether (DeBDE) tetrabromobisphenol A (TBBPA), hexabromocyclododecan (HBCD) og tris(2-chloroethyl)phosphate (TCEP) < 25%.

Flame-retardant	CAS-No.	No. 1	No. 2	No. 3	No. 4	DL*
PeBDE	32534-81-9	< 10	< 10	< 10	< 10	10
OBDE	32536-52-0	< 50	< 50	< 50	< 50	50
DeBDE	1163-19-5	< 100	< 100	< 100	< 100	100
TBBPA	79-94-7	< 50	< 50	< 50	< 50	50
HBCD	25637-99-4	< 200	< 200	< 200	< 200	200
TCEP	115-96-8	< 50	< 50	< 50	< 50	50
Flame-retardant	**CAS-No.**	**No. 5**	**No. 6**	**No. 7**	**No. 8**	**DG***
PeBDE	32534-81-9	< 10	< 10	< 10	< 10	10
OBDE	32536-52-0	< 50	< 50	< 50	< 50	50
DeBDE	1163-19-5	< 100	< 100	< 100	< 100	100
TBBPA	79-94-7	< 50	< 50	< 50	< 50	50
HBCD	25637-99-4	< 200	< 200	< 200	< 200	200
TCEP	115-96-8	< 50	< 50	< 50	< 50	50

DL*: Detection limit

2.4.2 Phthalates

Phatalates have been found in all products. The products 4 and 7 both exceed the permitted limit (0.05%) for phthalates in toys intended for children between 0-3 years (3). On the packaging of product no. 7 is indicated that the product is intended for children of more than 3 year. However, as The Danish Safety Technology Authority has decided that the product because of appearance and shape also appeals to children of less than three years. The

Danish EPA has decided that the limit value for phthalates in toys for children between 0-3 years should be observed.

Product 4 contains totally 1867.8 mg/kg (corresponding to 0.19%), diisobutylphthalate (DIBP) (1800 mg/kg) being the absolutely largest quantity. Product 7 contains totally 1451.8 mg/kg (corresponding to 0.15%) with di-n-butylphthalate (DBP) (780 mg/kg) as the greatest quantity. The two products (4 and 7) were therefore withdrawn from the Danish market.

All 8 products also contain di-2-(ethylhexyl)phthalate (DEHP).

Table 2.4 Content of phthalates (mg/kg) in all 8 products. The results are averages of duplicate determinations. The analysis uncertainty of the determinations is 20-30%.

Product	CAS-No.	No. 1	No. 2	No. 3	No. 4	DL*
Dimethylphthalate (DMP)	131-11-3	4.85	< 0.5	< 0.5	0.84	0.05
Diethylphthalate (DEP)	84-66-2	< 0.5	< 0.5	< 0.5	1.5	0.05
Di-n-propylphthalate (DPP)	131-16-8	< 0.5	< 0.5	< 0.5	< 0.5	0.05
Diisobutylphthalate (DIBP)	84-69-5	2.85	3.1	5.75	1800	0.05
Di-n-butylphthalate (DBP)	84-74-2	1.8	7.95	2.0	23	0.05
Di-n-pentylphthalate (DNPP)	131-18-0	< 0.5	< 0.5	< 0.5	< 0.5	0.05
Butylbenzylphthalate (BBP)	85-68-7	< 0.5	< 0.5	< 0.5	< 0.5	0.05
Di-2-(ethylhexyl)phthalate (DEHP)	117-81-7	76	45	0.89	42.5	0.05
Dicyclohexylphthalate (DCP)	84-61-7	< 0.05	< 0.5	< 0.5	< 0.5	0.05
Di-n-octyl-phthalate (DNOP)	117-84-0	4.9	< 0.5	< 0.5	< 0.5	0.05
Total		90.4	56.1	8.64	**1867.8**	
Product	**CAS-No.**	**No. 5**	**No. 6**	**No. 7**	**Nor. 8**	**DL***
DMP	131-11-5	< 0.5	< 0.5	< 0.5	< 4	0.05
DEP	84-66-2	< 0.5	< 0.5	< 0.5	< 3	0.05
DPP	131-16-8	< 0.5	< 0.5	< 0.5	< 3	0.05
DiBP	84-69-5	6.5	3.4	315	< 4	0.05
DBP	84-74-2	2.6	11.9	780	< 2.5	0.05
DNPP	131-18-0	< 0.5	< 0.5	< 0.5	< 2.5	0.05
BBP	85-68-7	< 0.5	< 0.5	< 0.5	< 2.5	0.05
DEHP	117-81-7	1.9	9.4	355	17.7	0.05
DCP	84-61-7	< 0.05	< 0.5	< 0.5	< 0.5	0.05
DNOP	117-84-0	4.9	< 0.5	1.8	< 0.5	0.05
Total		15.9	24.7	**1451.8**	17.7	

* DL: Detection Limit

In the process of evaluating the above results, DTC realized that tests were not performed for diisodecylphthalate (DIDP) and diisononyl phthalate (DINP), and testing for these phthalates was performed. Product 4 and 7 were not tested, because they had been withdrawn from the Danish market.

Table 2.5 Content of phthalates (mg/kg) in the selected products. The results are averages of duplicate determinations. The analysis uncertainty of the determinations is 20-30%.

Phthalates	Cas no.	1	2	3	5	6	8	DL*
DIDP	26761-40-0	25.5	< 0.5	< 0.5	< 0.5	< 0.5	< 5.0	0.5
DINP	28553-12-0	935	18.5	< 0.5	< 5.0	5.1	9.5*	0.5
* Average of a value indicated as < 5.0 estimated at 5.0 and a value of 14								

* DL: Detection limit

Based on the above analyses, DIBP, DBP and DINP were selected for toxicological assessment in Phase 3.

2.4.3 Metals

There is no migration of metals in concentrations above the migration limits as stipulated in DS/IN 71-3. There is a migration of tin compounds from product 4 and 6 45 mg/ and 21 mg/kg), which is calculated as the average of two determinations. As the products are produced from polyurethane (PUR), the tin present may be from organic tin compounds, which are used catalyst in the production of PUR.

Table 2.6 Migration of metals in mg/kg. The values are averages of duplicate determinations.

Sample	Nr. 1	Nr. 2	Nr. 3	Nr. 4	Nr. 5	Nr. 6	Nr. 7	Nr. 8	DL*	AU (%)**
As	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	44
Ba	34.6	9.54	<1	1.48	<1	<1	2.57	<1	<1	19
Cd	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	14
Cr	<3	<3	<3	<3	<3	<3	<3	<3	<3	17
Hg	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	26
Pb	0.882	1.24	<0.5	<0.5	<0.5	<0.5	1.46	<0.5	<0.5	17
Sb	<0.5	<0.5	<0.5	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	15
Se	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0,5	14
Ni	<1	<1	<1	<1	<1	<1	<1	<1	<1	-
Sn	<1	<1	<1	45.1	<1	20.9	2.3	<1	<1	-

DL: Detection limit
AU: Analysis Uncertainty

2.4.4 Summary of initial qualitative and quantitative analyses

The conclusion of the above results:

- Product no.3, 5 and 8 do not require further testing at present
- Product 4 and 6 may contain organic tin compounds
- The content of phthalates in product no. 4 and 7 is higher than the permitted value for toys intended for children of 0-3 years (0.05%) (3).

It was decided to analyse product 4 and 6 to clarify, if they contained organic tin compounds, and in the affirmative which.

2.4.5 Organic tin compounds

Monobutyltin (MBT) and dibutyltin (DBT) were measured above the detection limit in product no. 4 and 6.

Table 2.7 Content of organic tin compounds (g/kg) in the selected samples. The values are averages of duplicate determinations. The analysis uncertainty of the determinations is 10-20%.

Organotin compounds	Cas No.	No. 4	No. 6	DL*
Monobutyl tin	78763-54-9	1.95	1.95	0.3
Dibutyl tin	1002-53-5	<0.3	1.15	0.3
Tributyltin	56573-85-4	<0.3	<0.3	0.3
Tetrabutyltin	1461-25-2	<0.3	<0.3	0.3
Monooctyltin	-	<0.4	<0.4	0.4
Dioctyltin	-	<0.4	<0.4	0.4
Tricyclohexyltin	-	<0.3	<0.3	0.3
Monophenyltin	-	<0.3	<0.3	0.3
Diphenyltin	-	<0.3	<0.3	0.3
Triphenyltin	668-34-8	<0.3	<0.3	0,3

DL: Detection limit

Based on the data shown in table 2.7, MBT and DBT have been selected for assessment in phase 3.

2.4.6 Isocyanates

Products produced from polyurethan (PUR) foam may contain isocyanates, if they are packed prematurely in tight plastic. Testing for isocyanates was not performed, because the two products produced from PUR foam were not packed in air free packaging and their hardening process thus considered completed.

2.4.7 Colorants

Two products to be tested for colorants were selected. The products were selected from the remaining 6 products (1, 2, 3, 5, 6 and 8) were sword and floor puzzle (1 and 2), as they represent a product with printed colours and a product with many dyed colours. Testing was performed for azo colorants, colorants that are known as allergens or carcinogens, and 4 supplementary colorants from EN71-9. The specific colorants are listed in table 2.8.

Table 2.8 Tested colorants and detection limits. The analysis uncertainty of the determinations is < 20 %.

Azo colorants measured as aromatic amines (Split up from azo colorants)	**Detection limit (mg/kg)**
o-Anisidine	5
4-Aminobiphenyl	5
Benzidine	5
2-Naphthylamine	5
p-Chloraniline	5
4-Methoxy-m-phenylendiamine (2,4-Diaminoanisol)	5
4,4´-Diaminodiphenylmethane	5
3,3´-Dichlorbenzidine	5
3,3´-Dimethoxybenzidine	5
3,3´-Dimethylbenzidine	5
3,3´-Dimethyl-4,4´-diaminodiphenylmethane	5
4,4´-Methylen-bis-(2-chloraniline)	5
2-Amino-4-nitrotoluene	5
4,4´-Oxydianiline	5
4,4´-Thiodianiline	5
4-Methyl-1,3-phenylendiamine (2,4-Toluylendiamine)	5
2,4,5-Trimethylaniline	5
2-Methoxy-5-methylaniline (p-Kresidine)	5
o-Toluidine (2-Aminotoluene)	5
Carcinogenic colourants	
Acid Red 26	75
Basic Red 9	75
Basic Violet 14	75
Direct Black 38	75
Direct Blue 6	75
Direct Red 28	75
Disperse Blue 1	75
Disperse Orange 11	75
Disperse Yellow 3	75
Dispers-dyes, allergenic	75
Allergenic colourants	
Disperse Blue 1	75
Disperse Blue 3	75
Disperse Blue 35	75
Disperse Blue 106	75
Disperse Blue 124	75
Disperse Yellow 3	75
Disperse Orange 3	75
Disperse Orange 37/76	75
Disperse Red 1	75
Supplementary colourants from EN71-9	
Solvent Yellow 1	75
Solvent Yellow 2	75
Solvent Yellow 3	75
Basic Violet 1	75

No colorants above the detection limit have been measured in the two products.

According to the Toy Standard "Organic chemical compounds – requirements", EN71-9, the limit value of aromatic amines is the detection limit (5 mg/kg. As described in Section 2.1, this standard does not cover products such as the sword and the puzzle. However, judged from the limit value assigned for other product types, the content of azo colorants should not cause any concern. The detection limit of the carcinogenic, allergenic and supplementary 4 colorants are however markedly higher than the limit proposed in Final draft prEN71-11 of 10 mg/kg. As is the case for the phthalate analysis described in paragraph 2.3.2, this is caused by the smaller amount of sample material compared with the standard analyses in solid (not foam) matrices, because a larger amount of sample would interfere with the analyses in the test. Therefore, it is not possible to evaluate if the amount of colorants exceeds the limit values proposed in EN71-11. This assessment would require a test method to analyse the colorants with a lower detection limit in complex polymer matrices.

2.4.8 Screening for organic solvents

The last test was a screening for volatile organic solvents. The method detects the presence of volatile solvents ($< C_{14} – C_{16}$), but a qualification and quantification of the compounds were not carried out. 4 products were selected for the screening: Sword, floor puzzle 1, mask and ball (product no. 1, 2, 5 and 8). The products were selected on the basis of a RAPEX information (Rapid Alert System for Non-Feed Products) concerning an EVA product containing organic solvents – and for the ball also based on a chemical smell from the product. The puzzle and the ball were wrapped when purchased, and to perform a test with an optimal simulation of the exposure to a child, when opening a new product, it was decided to repurchase these two products. However, the ball was out of stock and only the puzzle was repurchased. Testing of the ball, the mask and the sword was performed in previously purchased products.

Table 2.9 Screening for volatile organic solvents in the selected samples ($C_{14} – C_{16}$).

Product			
1	2	5	8
*	**	*	***

* No signals of relevance were detected or identified
** Few signals were detected and identified as hydrocarbons.
*** 2 individual signals as C_2 aromatic and a pattern of hydrocarbons from C10 -C_{14} were identified

Only in product no. 2 and 8, signals for VOC were detected (C_{14} - C $_{16}$). Only in product 8, the signals were significant, and the analysis laboratory has identified the substances to be hydrocarbons with a carbonic chain length of C_{10} to C_{14}. Due to shortage in time, these signals were not further qualified or quantified. If there had been more time in the project, analysis could have been made, that identified the chemical substances and the concentration.

2.5 Summary of analysis results

Product no.	Product	Phthalates	Bromated flame-retardants + PCB	Metals	Organic tin compounds	Azo colorants	Selected colorants, (specified in table 2.8)	Screening for volatile organic compounds < C_{14} - C_{16}
1	Sword	B	A	A		A	E	F
2	Floor puzzle 1	A	A	A		A	E	F
3	Swim board	A	A	A				
4	Activity Carpet	C	A	A	D			
5	Mask	A	A	A				F
6	Book	A	A	A	B			
7	Floor puzzle 2	C	A	A				
8	Ball	A	A	A				F

A Not measured in concentrations of concern
B Concentrations requiring safety assessment
C Concentrations exceeding the permitted limit
D Not assessed. The products were withdrawn from the Danish market because of the total content of phthalates)
E Assessment not possible. The detection limit is higher than the limit value due to the complexicity of the polymer materials
F The analyses was a screening without quantification or qualification of the substances. The GC-MS-spectrum of the ball contained a signal equal to C_{10}-C_{14} hydrocarbons.

3 Health assessment

Based on the results of the analysis of diisobutylphthalate (DIBP), di-n-butylphthalate (DBP), diisononylphthalate (DINP), monobutyltin (MBT) and dibutyltin (DBT) were selected for assessment. The toxicological profiles for the 5 chemical substances are described in the following.

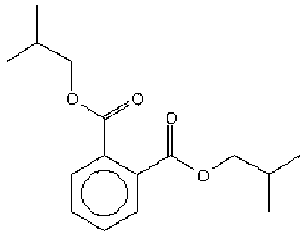
3.1 Toxicological profiles

3.1.1 Diisobutylphthalate

3.1.1.1 Use

Is used as softener in plastic, paint, lacquer, glue and die (8).

3.1.1.2 Identification

Chemical name	Diisobutylphthalate
Synonym	DIBP
CAS-No.	84-69-5
EINECS No.	201-553-2
Molecular formula	C_{16}-H_{22}-O_4
Molecular Structure	
Classification (9).	Not classified Based on new evaluations DK has suggested, a classification of Rep 2; R60-61 like DEHP
Limit value (10).	3 mg/m^3
The list of unwanted substances (11).	Not listed
ECB (European Chemicals Bureau) (12).	The substance has not been risk assessed by the EU and is not on the priority list on assessment and control regarding risk and control of existing substances.
Synoptic document (13)	Listed as an additive permitted in packaging for feedstuffs with a [2]group-R: 0.05 mg/kg bw[3].

[2] Group: Quantitative restrictions for migration in feedstuffs
[3] bw: Body weight

Physical-chemical properties (14).

Physical state	Liquid
Mol weight (g/mol)	278.35
Melting point, °C	- 64
Boiling point, °C	296.5
Evaporation rate (Pa)	0.89 at 25 °C
Octanol-water partition coefficient	Log Pw = 4.11
Water solubility (mg/l)	20.3 at 20 °C

Acute toxicity	Oral [4]LD_{50} = 15 g/kg body weight for rats (15). Dermal LD_{50} = 10 g/kg bw for guinea pigs (15).
Irritation	Testing for irritation of skin and eyes in rabbits according to the [5]OECD guideline 404 and 405 did not show signs of irritation on skin and eyes (16).
Allergy	No data have been found on the skin sensitizing effect of DIBP. DIBP can be compared with linear DIBP, which has no sensitizing effect on skin and is thus not expected to cause skin sensibilization. (17).
Short-term exposure	A NOEL[6] of 50 mg DIBP/kg bw based on liver effects was proposed. The NOEL was based on a test with female rats, which were administered orally 50 mg DIBP/kg bw for fourteen days. No data on other tested doses (17).
Long-term/ repeated exposure	Rats administered 5% DIPB in the feed for several months showed no increased mortality. Total dose and number of months not indicated (8). Dogs administered 2 g of DIBP/kg bw in the feed for several months (total not indicated) did not show increased mortality and no toxic effect was observed. (8).
Cancer	No data were found on the carcinogenic properties of DIBP. Long-term studies of the carcinogenic properties of other phthalates with rodents demonstrate that tumors are mainly induced by an peroxisome proliferation mechanism. However, this mechanism is not found in humans, and indication of carcinogenic properties in rodents does not prove that it is carcinogenic to humans.
Mutagenicity	DIBP showed a negative effect in the *Salmonella typhimurium* mutagenicity test (18)
Reproduction	Groups of 5 gestated rats were administered DIBP corresponding to 0.390 0.779 or 1.299 ml/kg bw on day 4, 5, 10 and 15 of the period of gestation. In this study the highest dose was calculated to be one third of LD_{50} for intraperitoneal administration (3.9 g/kg bw). This value is lower than the oral LD_{50} found by DTC of 15 g/kg bw. The occurrence of resorption was 26.6% in the highest dosage group compared to 0% in the control group. The birth weight of all three dosage groups was lower than that of the control group. Abnormal skeletal formations were found in all three dosage groups (19). Intake of 2% of DIPB through the feed for 7 days caused decreased zinc concentrations in the testicles of mouse and an increase of the relative weight of the testicles. The total dose is not indicated (20).
Critical effect	A NOEL of 50 mg DIBP/kg bw based on effect of the liver was stated. No other dose levels are mentioned (17).

[4] LD_{50}: The lethal dose for 50% of a given population
[5] OECD: Organization for Economic Co-operation and Development
[6] NOEL: No Observed Effect Level

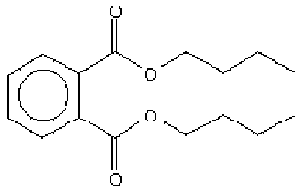
The highest amount of DIBP measured in the 6 products (product 4 and 7 are not included as they were withdrawn from the Danish market) was 6.5 mg/kg in product 5 (corresponding to 0.00065%). The amount is markedly lower than the permitted limit for phthalates in toys intended for children between 0-3 years of 0.05% (3) and the substance is not further assessed.

3.1.2 Di-n-butylphthalate

3.1.2.1 Use

Is used as softener in plastic, paint, lacquer, glue and die (8).

3.1.2.2 Identification

Chemical name	Di-n-butylphthalate
Synonym	DBP
CAS-No.	84-74-2
EINECS No.	201-557-4
Molecular formula	C_{16}-H_{22}-O_4
Molecular Structure	
Classification (9).	Repr. Cat. 2; R61, Repr. Cat. 3; R62, N; R50
Limit value (10).	3 mg/m^3
The list of unwanted substances (11).	Listed
ECB (European Chemicals Bureau).	Risk assessed by EU in 2003. Addendum published in 2004 .
Synoptic document (13)	Listed as an additive permitted in packaging for foodstuffs with a TDI[7] = 0.1 mg/kg bw.

Physical chemical properties (14).

Physical state	Liquid
Molecular weight (g/mol)	278.35
Melting point, °C	- 35
Boiling point °C	340
Evaporation rate (Pa)	0.0027 at 25 °C
Octanol-water partition coefficient,	Log Pow = 4.9
Water solubility (mg/l)	13 at 20 °C

Acute toxicity	Oral LD_{50} = 6,3-8,0 g/kg bw for rats (21). Dermal LD_{50} > 20 g/kg bw for rabbits (21). A 23-year old man, who accidentally ingested 10 g DBP, showed symptoms of nausea, vomiting and dizziness, and a few hours later lacrimation, photophobia and pain in the eyes. The cornea was severely damaged. Urinalysis showed microhaematuria, oxalate crystals and pathological leucocyte counts. Recovery occurred within 14 days after treatment (21).

[7] TDI: Tolerable Daily Intake

Irritation	Test for irritation of skin and eyes with rabbits in accordance with OECD guideline 404 and 405 did not show any sign of irritation of skin and eyes (21).
Allergy	DBP did not show skin sensitisation effects in two maximization tests in guinea pigs. (21)
Short-term exposure	In a two-week dietary study with rats, a NOAEL[8] for induction of peroxisomally associated enzymes were estimated to be 200 mg/kg of the feed (corresponding to 19.9 mg/kg bw (21). In a four-week dietary study with rats, a NOAEL value for increased enzyme activity was estimated at 104 mg/kg bw. However it should be mentioned that the liver weight of the animals significantly increased significantly at all dose levels: (51.5; 104; 515; 1,040 and 2,600 mg/kg bw (21).
Long-term /repeated exposure	Based on a 3 months dietary study, an oral NOAEL of 152 mg/kg bw has been established (21). A NOAEL of 19.9 mg/kg bw has been established for peroxisomal proliferation in rats (21). In an inhalation study performed in accordance with OECD Guideline no. 412, rats were exposed for 6 hours/day, 5 days/week during 4 weeks at concentrations of 0; 1.18; 5.57; 49.3 or 509 mg DBP /m^3. The exposure by repeated inhalation caused no systemic effects at the highest concentration, 509 mg DBP/m^3. NOAEC[9] could not be established, as even the lowest exposure effected the upper respiratory tract. A LOAEC[10] for rats of 1.18 mg/m^3 was established for local effects in the upper respiratory tract (21).
Carcinogenicity	Sufficient data on DBP's carcinogenic properties are not available. Long-term studies of the carcinogenicity of other phthalates in rodents demonstrate that tumours are mainly provoked by an peroxisomal proliferation mechanism. However, This mechanism is not found in humans, and indication of carcinogenicity in rodents does not prove that it is carcinogenic in humans.
Mutagenicity	DBP was positive in *Salmonella typhimurium* mutagenicy test (18). Based on tests with other phthalates and *in vitro/in vivo* studies of DBP's genotoxic effects the substance is assessed to be non-genotoxic by the EU (21)
Reproduction	In an extensive 2-generation reproduction study in rats with continuous breeding and exposure of both female and male animals, the animals were administered 0; 0.1; 0.5; and 1.0% in the feed, 0.1% in the feed (corresponding to 52 mg/kg bw for males and 80 mg/kg bw for females) corresponds to the LOAEL[11] in the study. Several determinations of NOAEL-values are shown in other studies, but as the above test has incorporated a number of more sensitive endpoints, it takes into account fx. endocrine disrupting effects. Therefore, the EU risk assessment uses the LOAEL-value of 52 mg/kg bw for further assessment (21).

[8] NOAEL: No Observed Adverse Effect Level
[9] NOAEC: No Observed Adverse Effect Concentration
[10] LOAEC: Lowest Observed Adverse Effect Concentration
[11] LOAEL: Lowest Observed Adverse Effect Level

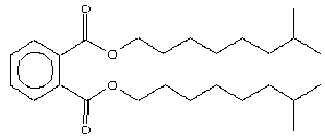
Critical effect	The critical effect is assessed to be reduced weight of offspring in litter no. 2 corresponding to a LOAEL of 52 mg/kg bw (21). A worst-case exposure of children of 0.81 µg/kg bw/day was estimated for DBP. The estimate was based on a maximal migration rate of 259 µg/dm^2/day (measured in a Danish investigation) converted to a daily DBP dose, under the assumption of a child weighing 8 kg mouthing 10 cm^2 of the toy for 6 hours a day (21). In the EU risk assessment of DBP, the assumed worst-case infant exposure of 0.81 µg/kg bw and the LOAEL value of 52 mg/kg bw/day was compared resulting in a MoS[12] of approx. 65,000, which is assumed to be sufficient for the protection of children (21).

The highest amount of DIBP measured in the remaining 6 products was 11.9 mg/kg in product 6 (corresponding to 0.00119%) The amount is considerably lower than the permitted limit for phthalates in toys intended for children between 0-3 years of 0.05% (3) and the substance is not further assessed.

3.1.3 Diisononyl Phthalate

Use
Used as softener in plastic (8).

Identification

Chemical name	Diisononylphthalate
Synonym	DINP
CAS-No.	28553-12-0
EINECS No.	249-079-5
Molecular formula	C_{26}-H_{42}-O_4
Molecular Structure	
Classification (9).	Not classified
Limit value (10).	3 mg/m^3
The list of unwanted substances (11).	Not listed
ECB (European Chemicals Bureau)(12).	Risk assessed by EU in 2003. Addendum published in 2004.
Synoptic document (13)	Listed as an additive permitted in packaging for feedstuffs

Physical-chemical properties (14), (22)

Physical state	Viscous liquid
Molecular weight (g/mol)	418.62
Melting point, °C	-54 - -42
Boiling point, °C	244-274
Evaporation rate(Pa)	7.2 * 10 ¯5 at 25 °C
Octanol-water partition coefficient	Log Pow = 8.8
Water solubility (mg/l)	0.2 at 20 °C

[12] Margin of Safety

Acute Toxicity	Intake of up to 40 g DINP/kg bw caused respiratory trouble but no deaths in rats. Oral LD_{50} > 40 g/kg bw for rats (22). Dermal LD_{50} > 3.2 g/kg bw for rabbits (22).
Irritation	DINP causes slight irritation to skin and eyes. Irritating effects cease shortly. (22).
Allergy	A toy producer has reported five cases of allergy due to misuse of a toy produced from a material containing DINP. None of these cases, however, could be directly related to DINP. A patch test with repeated human exposure showed not positive reactions. Totally, the various cases only indicate that DINP may cause allergy in humans (22). Two tests of DINPs sensitizing properties in guinea pigs have shown that DINP is slightly sensitizing and not sensitizing respectively (22).
Short-term exposure	Single-dose tests to determine a LD^{50} value have been performed, but not multiple-dose tests for a short period of time. The tests for determination of LD^{50} values have been performed before the guidelines were established for which reason DINP is assessed to have low toxicity at short-term exposure, however they are not consistent (22).
Long-term/repeated exposure	Groups of rats were orally administered 500, 1,500; 6,000 or 12,000 mg/kg through the feed for 2 years. Based on this test, a NOAEL value of 88 mg/kg bw (corresponding to 1,500 mg/kg/feed) was proposed with respect to negative effects on both liver and kidneys (22).
Carcinogenicity	Sufficient data on DINPs carcinogenic properties in humans have not been identified. Long-term studies of DINPs carcinogenic properties in rodents demonstrate that tumours are mainly induced by a peroxisome proliferation mechanism. However, This mechanism is not found in humans, and indication of carcinogenic properties in rodents does not prove that it is carcinogenic in humans.
Mutagenicity	Based on *in vitro* and *in vivo* studies of DINPs genotoxic effects, EU has assessed the compound to be non-genotoxic. (22).
Reproduction	By repeated exposure of mice for 104 weeks by ingestion, DINP causes reduced testis weight. Due to the effects on testis weight, a NOAEL of 276 mg/kg/day was set in this study (22). In a one generation study with rats, the dams were exposed to DINP by oral ingestion in the gestation period. A reduced number of live-born pups and congenital malformations were observed at doses, which were toxic for the dams. NOAEL for reduced number of live-born pups was 622 mg/kg bw/day, and NOAEL for congenital malformation was 500 mg/kg bw/day (22). DINP demonstrates a slight estrogenic effect on cells *in vitro*. In the EU risk assessment, the above does not justify a classification of DINP as toxic to reproduction (22).
Critical effect	Based on animal studies, the critical organs by long-term DINP exposure are liver and kidneys. The NOAEL for liver and kidney effects has been established at 88 mg/kg bw/day for rats. This NOAEL protects from the toxic effects on reproduction mentioned above (22).

The highest amount of DIBP measured in the 6 remaining products was 935 mg/kg in product 1 (corresponding 0.0935%.) The amount is higher than the permitted limit for phthalates in toys intended for children between 0-3 years of 0.05% (3) However, as the product is intended for children > 3 years, it has not been withdrawn from the Danish market. The distributor of product 1 has

been informed of the content of DINP in the substance and is working on eliminating the substance from the product.

3.1.4 Monobutyltin

Use

Is used as catalyst in the production of PUR foam. Organic tin compounds are also used in other kinds of polymers (e.g. PVC), packaging for foodstuff, pesticides and paints (23).

Identification

Chemical name	Monobutyltin
Synonym	-
CAS-No.	78763-54-9
EINECS No.	-
Molecular formula	C_4-H_9-Sn^{3+}
Molecular structure	
Classification (9).	Not classified
Limit value (10).	0.1 mg/m^3 (Tin compounds, organic calculated as Sn)
The list of unwanted substances (11).	Not listed
ECB (European Chemicals Bureau) (12).	Not assessed by ECB
Synoptic document (13)	Not listed

Physical-chemical properties

Physical state	-
Molecular weight (g/mol)	175.83
Melting point, °C	-
Boiling point, °C	-
Evaporation (Pa)	-
Octanol-water partition coefficient, (log Pow)	-
Water solubility (mg/l)	-

No data were found on the toxic effects of monobutyltin in animals and humans, by searching toxicological databases (Micromedex[13] and TOXNET[14]) and standard literature at DTC. The compound is assessed in section 3.1.7.

[13] Micromedex includes the following databases: MEDITEXT®, HAZARDTEXT®, CHRIS, Dolphin MSDS, HSDB®, IRIS, LOLI®, New Jersey Hazardous Substance Fact Sheets, NIOSH Pocket Guide (TM), OHM/TADS, RTECS®, REPROTEXT®, REPROTOX®, Shepard's Catalog of Teratogenic Agents, TERIS, - Teratogen Information System og Martindale.

[14] TOXNET includes the following databases: CCRIS, ChemIDplus Lite, ChemIDplus Advanced, DART/ETIC, DIRLINE, GENE-TOX, Haz-Map, Household Products, HSDB, IRIS, ITER, TOXLINE, TOXMAP, TRI.

3.1.5 Dibutyltin

Use

Is used as catalyst in the production of PUR foam. Organic tin compounds are also used in other kinds of polymers (e.g. PVC), packaging for foodstuff, pesticides and paints (23).

Identification

Chemical name	Dibutyltin
Synonym	-
CAS-No.	1002-53-5
EINECS No.	-
Molecular formula	C_8-H_{20}-Sn
Molecular structure	-
Classification (9).	Ikke klassificeret
Limit Value (10).	0.1 mg/m^3 (tin compounds organic, calculated as Sn)
List of unwanted substances (11).	Not listed
ECB (European Chemicals Bureau) (12).	Not assessed by ECB
Synoptic document (13)	Not listed

Physical-chemical properties

Physical state	-
Molecular weight (g/mol)	234.97
Melting point, °C	-
Boiling point, °C	-
Evaporation (Pa)	-
Octanol-water partition coefficient, (log Pow)	-
Water solubility (mg/l)	-

Acute toxicity	Oral LD50 = 800 mg/kg bw for rats (24).
NOAEL	NOAEL = 2.5 mg/kg/day (teratogenicitet) (25). NOAEL = 5.0 mg/kg/day (maternal toksicitet) (25). There is no description of or reference to the studies that the NOAELs are based on.

Sufficient data has not been found on the toxic effects of DBT in animals and humans. Literature has been searched for in toxicological databases (Micromedex and TOXNET) and standard literature at DTC. The substance is assessed in section 3.1.7.

3.1.6 Tin compounds generally

Tin can combine with other chemicals to form compounds. Combinations with chemicals like chlorine, sulfur, or oxygen are called inorganic tin compounds. These are used in toothpaste, perfumes, soaps, food additives and dyes. Tin also can combine with carbon to form organic tin compounds like the compounds above, monobutyltin and dibutyltin (23).

Tin metal is used to line cans for food and beverages. Exposure to inorganic tin compounds can occur by eating food or drinking liquids from tin-lined cans (today greater than 90% of tin-lined cans used for food are protected with lacquer).

Metallic tin is not very toxic due to its poor gastrointestinal absorption. Human and animal studies show that ingestion of large amounts of inorganic tin compounds can cause stomachache, anemia, and liver and kidney problems (23).

Exposure to some organic tin compounds can occur by eating seafood from coastal waters (23) or from contact with consumer products i.e. toys produced from PVC or PUR, supports in shoes, biker's pants, foot spray and silicon coated cooking paper (26). Inhalation of dust can also cause exposure to organic tin compounds from floor- and wall covers that releases organic tin compounds due to wear and tear. Levels of MBT and DBT have been found in dust from European households of respectively 2.8 and 1.3 mg/kg dust (27). Breathing or swallowing, or skin contact with some organotins, such as trimethyltin and triethyltin compounds, can interfere with the way the brain and nervous system work. In severe cases, it can cause death. Some organic tin compounds, have been shown to affect the immune system in animals and to affect the reproductive system. This has not been examined in people (23).

Inorganic or organic tin compounds placed on the skin or in the eyes can produce skin and eye irritation. There is no evidence that tin or tin compounds cause cancer in humans. Studies in animals have not shown evidence of carcinogenicity for inorganic tin. A study in rats and another in mice showed that a specific organic tin compound, triphenyltin hydroxide, could produce cancer in animals after long-term oral administration. There is conflicting evidence as to whether tin compounds can be transferred to offspring through breast milk (23). Data from a study of women in Zaire and Guatemala has shown tin levels in the breast milk of respectively 0.24 and 2.81 g/l breast milk. There is no mention of whether the tin originates from inorganic or organic tin compounds (28).

Children under 6 months are mainly expected to ingest breast milk or milk substitute (29). If the measured concentrations of tin in breast milk originate from organic tin compounds, food can be a source of exposure for infants (28). Furthermore exposure from inhalation of dust containing organic tin compounds can also be a source of exposure (27).

Children of more 6 months are mainly exposed to tin through the feed, by eating contaminated soil, and by inhalation of dust containing organic tin compounds. A 7-day study of 1.75 – 2.2 year-old children illustrated that the daily intake of tin through feedstuff was 1.78 mg/kg bw and the daily exposure through intake of contaminated soil was 1-200 g Sn (23). There is no specification of whether the measured tin levels originate from inorganic or organic tin compounds (23).

3.1.7 Assessment of organic tin compounds in product no. 6

Testing was performed for organic tin compounds in 2 products (4 and 6). As product 4 had been withdrawn from the Danish market, it was not included in the assessment. In product 6 (a fabric book with PUR-stuffing intended for children under 3 years) was measured 1.95 g MBT/kg and 1.15 g DBT/kg.

The exposure route of the fabric book with PUR-stuffing is mainly oral, as children are expected to mouth things. By contact with saliva, the external fabric layer may be soaked and possible chemical substances in the PUR-stuffing may be available for ingestion. Testing for release of organic tin

compounds to sweat and saliva has not been performed and the below assessment is therefore based on a worst-case scenario.

Table 3.1 Concentration of MBT and DBT in product no. 6. The values are averages of duplicate determinations. CSTEE's recommended TDI for MBT and DBT.

Organotincompound	Average concentration i no. 6 (μg/kg)	Average Sn concentration i no. 6 (g Sn/kg)	Average amount Sn per book* (g Sn)	**Recommended TDI of CSTEE (30) g Sn/kg bw/day
MBT	1.95	1.32	0.04	0.5
DBT	1.15	0.585	0.019	0.1

* Weight of product no. 6: 32 g
** There are no available data on the critical effects of MBT and the TDI is therefore very conservative. The DBT value is based on TDI for tributyltin, which is also a very conservative method.

The average weight of a newborn child in Denmark is 3,450 g (5), and of a child of 1.5 years 9,850 g (6). It is assumed that the measured total amount of MBT and DBT is released in one day and that the substances have an additive effect. The following form is used to calculate the total effect of MBT and DBT. A fraction sum < 1 means that the total content of MBT and DBT in the book do not cause any health concern.

Daily exposure, tin, child:

$$\frac{Exposure_{MBT}}{TDI_{MBT}} + \frac{Exposure_{DBT}}{TDI_{DBT}} < 1$$

Daily exposure, tin, newborn:

$$\frac{(0.04\ \mu g\ Sn/day)\ /3.45\ kg\ bw}{0.5\ \mu g\ Sn/kg\ bw./day} + \frac{(0.019\ \mu g\ Sn/day)\ /\ 3.45\ kg\ bw}{0.1\ \mu g\ Sn/kg\ bw/day} = 0{,}08$$

Daily exposure, tin, 1.5 years:

$$\frac{(0.04\ \mu g\ Sn/day)\ /9.85\ kg\ bw}{0.5\ \mu g\ Sn/kg\ bw./day} + \frac{(0.019\ \mu g\ Sn/day)\ /9.85\ kg\ bw}{0.1\ \mu g\ Sn/kg\ bw/day} = 0{,}03$$

The above calculation shows that the content of MBT and DBT in the book does not cause reason for health concern.

The Margin of Safety (MoS)[15] for the exposure of the two organic tin compounds from the book is calculated by dividing NOAEL with the exposure (under the assumption that the entire amount of MBT (1.95 μg/kg book) and DBT (1.15 μg/kg book) is released in one day. A NOAEL for DBT of 2.5 mg/kg bw/day was used for both MBT and DBT.

MoS, MBT + DBT, child:

$$\frac{NOAEL}{Exposure_{MBT} + Exposure_{DBT}} > 1000$$

MoS, MBT + DBT, newborn:

$$\frac{2500\ \mu g/kg\ bw/day}{} = 86000$$

[15] Margin of Safety (MoS) expresses the factor, that NOAEL is higher than the estimated exposure level. A high MoS means a smal risk.

$$\frac{}{0{,}018\ \mu g/kg\ bw/day + 0{,}011\ \mu g/kg\ bw/day}$$

MoS, MBT + DBT, 1,5 year:

$$\frac{2500\ \mu g/kg\ bw/day}{0{,}006\ \mu g/kg\ bw/day + 0{,}004\ \mu g/kg\ bw/day} = 250000$$

A MoS of 86000 and 250000 was calculated for a newborn child and a child of 1.5 years old, respectively. A high MoS means a good protection of the consumer. In this case it is recommended that the MoS is at least 1000, corresponding to 10 in order to account for sensitive individuals, 10 to account for difference between animals and humans, and 10 in order to account for quality and relevance of the data that NOAEL is based on. Furthermore the used NOAEL for MBT and the assumption of a release of the total content of the organic tin compounds in one day underestimates the MoS. DTC estimates that exposure to organic tin compounds from the book does not cause any health concerns. Because of the large amount of organic tin compounds found in dust from European households, and the potential to ingest organic tin compounds through breast milk and food and from a number of other consumer products, DTC recommends that the contribution from other sources is calculated. An estimation of how large an amount of TDI that could be allocated to consumer products is then possible.

4 Summary and Conclusions

Based on the survey phase the Danish Environmental Protection Agency selected the following products for testing:

Product No.	Product
1	Sword
2	Floor puzzle 1
3	Swim board
4	Activity carpet
5	Mask
6	Book
7	Floor puzzle 2
8	Ball

The analysis part, which was an iterative process, was initiated with qualitative and quantitative analyses of 8 products for bromated flame-retardants, TCEP, phthalates and metals. Performed were also tests for content of organic tin compounds, content of colorants and screening for volatile organic compounds in selected products.

Only concentrations of phthalates and organic tin compounds above the detection limit were measured. Based on the phthalate analyses, two products were withdrawn (4 and 7) from the Danish market because the contained amount was higher than the permitted limit value for phthalates in toys intended for children between 0-3 years (0.05%) (3).

5 chemical substances were selected for the health assessment to be performed in phase 3; diisobutylphthalate (DIBP), di-n-butylphthalate (DBP), diisononylphthalate (DINP), monobutyltin (MBT) og dibutyltin (DBT).

The highest amount of DIBP and DBP (0,05%) in the remaining 6 products was measured in product 5 and 5 respectively. The amount was considerably lower than the permitted limit value for phthalates in toys intended for children between 0-3 years (3) and does not give reason for health concern.

The highest amount of DINP (0.05%) in the remaining 6 products was measured in product 1. The amount was higher than the permitted limit value for phthalates in toys intended for children between 0-3 years. However, as the product is intended for children of more than 3 years, it was not withdrawn from the Danish market. The distributor of product 1 has been informed about the content of DINP in the product and is working on eliminating the substance completely from the product.

Foamed toys and childcare products are mainly produced from EVA and PUR foam. Based on this survey, it is recommended to focus on the content of phthalates of these products, as 2 of 8 products contained concentrations above the permitted limit value for phthalates (0.05%) in toys intended for children between 0-3 years, (3). DEHP is furthermore contained in all products. DEHP, DBP and BBP, which have been identified as reproduction

toxic substances, will be prohibited in concentrations above 0.1% of all softened toys and childcare articles. DINP, DIDP and DNOP will be prohibited in toys and childcare articles intended for mouthing (4). The prohibition comes into force one year after the proportion is agreed upon in the council.

Testing for organic tin compounds was performed in 2 products (4 and 6). Product 4 has been withdrawn from the Danish market and is not included in the assessment. In product 6 (a fabric book with PUR-stuffing intended for children under 3 years) was measured 1.95 g MBT/kg and 1.15 g DBT/kg. An exposure assessment based on a worst-case scenario was made: A newborn child and a child of 1.5 years were exposed and the total concentration of MBT and DBT was released and ingested in one day. As sufficient data was not found on the toxic effects of MBT and DBT in animals and humans, the assessment was based on the content of tin and a Tolerable Daily Intake (TDI) for the two substances which is recommended by Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) (30). The additive effect of MBT and DBT was calculated. A fraction sum < 1 means that the total MBT and DBT in the book do not cause reason for health concern. The additive effect of the substances was calculated to be 0.08 and 0.03 for a newborn child and a child of 1.5 years, respectively. Based on this calculation the content of MBT and DBT in the book should not cause any health concern.

The Margin of Safety (MoS) for the exposure of the two organic tin compounds from the book was calculated by dividing NOAEL with the exposure (under the assumption that the entire amount of MBT (1.95 µg/kg book) and DBT (1.15 µg/kg book) is released in one day. A NOAEL for DBT of 2.5 mg/kg bw/day was used for both MBT and DBT.

A MoS of 86000 and 250000 was calculated for a newborn child and a child of 1.5 years old, respectively. DTC estimates that exposure to organic tin compounds from the book does not cause any health concerns. DTC recommends however that the contribution from other sources is calculated. An estimation of how large an amount of TDI that could be allocated to consumer products would then be possible.

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