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PAHs in toys and childcare products

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Content

Preface

Based on a German study of toys and childcare articles that found high concentrations of Polycyclic Aromatic Hydrocarbons (PAHs), the Danish Environmental Protection Agency initiated this survey of PAHs in toys and childcare articles on the Danish market. The project consists of a literature survey and a chemical screening of selected articles.

The project has been performed by National Environmental Research Institute (NERI) at Aarhus University by Leif Hoffmann, Marianne Thomsen, Charlotte Dahl Schiødt and Pia Lassen as project leader.

The project has been performed for the Danish Environmental Protection Agency (DEPA).

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Summary and conclusions

Polycyclic Aromatic Hydrocarbons (PAHs) have been detected in consumer products as well as toys and childcare articles in a number of German investigations; the general tendency being that these products are characterised by being primarily made from natural rubber and synthetic rubber as well as plastics.

The known sources to PAHs in consumer products are extender oils and carbon black. These additives are mainly known to be used in production of tyres and the function is well described in the technical literature. In other consumer products the necessity and function of these additives is not well described, however, it must be expected that the function and purpose is more or less the same. Furthermore, no information about the use, amount and type of extender oils and black carbon in toys and childcare articles are available at present as such information is not required for by existing regulations. Therefore, it has not been possible to estimate the PAH content in toys and childcare articles from the use of different types and amounts of extender oils in the production of these products.

The knowledge on the content of PAHs in toys and childcare product are relatively limited. However, BfR (Bundesinstitut für Risikobewertung) in Germany has conducted several investigations of PAHs in consumer products and toys which have shown that PAHs are common in products.

There is no specific regulation on PAHs in toys and childcare articles at the present but the EU toy directive (88/378/EC) regulates in general the content of chemicals in toys. In the EU Regulation REACH (**R**egistration, **E**valuation, **A**uthorisation and Restriction of **Ch**emical substances) (EC) No 1907/2006 the content of PAHs in tyres is regulated on the extender oils used in the rubber for tyres. The oil content of benzo(a)pyrene must not exceed 1 mg/kg and the content of the sum of the 8 REACH PAHs must not exceed 10 mg/kg oil.

20 different toys and childcare articles were analysed. As this is a screening project the results are given in concentration ranges. However, the estimates within the concentration ranges are fairly precise due to the analytical method. The analytical method used a German standard method for analysing PAHs in consumer products. The method was further developed in order to achieve lower detection limits compared to the German method as well as low uncertainty on the measurements. The results showed that PAHs were found in all analysed samples. It can therefore be concluded that PAHs are common in toy and childcare articles on the Danish market. However, it is likely that the low detection limits in the present study have lead a higher number of samples with detectable PAHs compared to the German investigations, which have higher detection limits. The results also showed that it was mainly the small molecular size PAH (compared to Benzo(a)pyrene) which were found. This indicates that mainly lighter mineral oils were used in the materials. In general, the toxicity for PAHs increases with increasing molecular size.

55% of the samples contained <1 mg/kg sum of the 16 EPA PAHs; 40% contained 1-10 mg/kg and 5% (one sample) contained 100-1000 mgt/kg. Considering the sum of the eight REACH PAHs 90% of the samples were below 1 mg/kg and 5% were at 1-10 mg/kg and 10-100 mg/kg, respectively. Benzo(a)pyrene were below detection limit in 75% of the samples.

Two products were produced within EU. One of the product have concentration level between 10-100 mg/kg whereas the other were <1 mg/kg. This means that products produced in Europe also can have detectable amounts of PAHs.

Two baby articles were included in the study; both at concentration levels <1 mg/kg. For products with expected high skin contact four products have levels of 1-10 mg/kg, the rest were below 1 mg/kg.

Only one product exceeded the regulations limits there is for car tyres within REACH Regulation. This was a tyre from a bicycle which, due do its size, was not regulated as a toy. If estimating that the tyre contains relatively high amount of extender oil (40%) this product has a concentration of the sum of 8 REACH PAHs of 17 times higher than the regulations. For Benzo(a)pyrene the result exceeded 9 times the regulation limit. The bicycle tyre is not regulated under the limits for car tyres in REACH.

The German authorities have suggested a limit of 0.2 mg/kg in consumer products of the 8 PAHs which is regulated within REACH. If the suggested limits are compared to the results in the present study two products exceed. In tyre from a child bicycle the suggested limit is exceeded for all eight PAHs and whereas the limit in the scooter grip is exceeded for benzo(e)pyrene.

Based on the investigation it must be concluded that PAHs are common in toys and childcare articles in Denmark. The concentration levels of PAHs are low and only two of the investigated products showed a PAH content above the limit suggested by the German Authorities.

1 Introduction

A report published by the German risk assessment institute BfR (Bundesinstitut für Risikobewertung) in 2009 concluded that children are not sufficient protected in the new toy safety Directive 2009/48/EC as the classification limits for Polycyclic Aromatic Hydrocarbons (PAHs) will be too high. However, the new EU toy safety Directive 2009/48/EC, which for the chemistry part will be in force by July 2013, regulates the content of CMR classified substances; substances which are carcinogenic, mutagenic or toxic for reproduction and these compounds must not according to the new directive be present in toys in concentrations above the classification limits. REACH has only limits for the PAH content in extender oils used in tyres. The Danish EPA has previously investigated tyres used in playgrounds and concluded that there were no risk of using tyres for that purpose.

However, as BfR have found PAHs in consumer products the Danish EPA has therefore decided to make a screening investigation of PAHs in toys. The objective of the study is thus to verify to which extent PAHs are present in toys and childcare articles on the Danish market.

This report presents a screening survey of the PAH content in 20 selected pieces toys and childcare articles. The project is divided in two phases: An initial literature survey on information on the use of PAH-containing extender oils and carbon black in the production of toys and childcare articles and selection of representative products of soft rubber or plastic materials. In the second phase the selected toys and childcare articles were subjected to analytical chemical screening for PAHs. As the present project is a screening study no risk assessment have been made on the basis of the results.

2 Literature survey of PAH in products

2.1 PAHs included in the survey

Polycyclic Aromatic Hydrocarbons (PAHs) are a large group of compounds which consist of two or more aromatic rings attached to each other. More than 100 PAHs are known. They are in general "heavy" compounds with low volatility and high boiling point. In nature they are generally regarded as persistent. Several of the PAHs are identified as carcinogenic and genotoxic, and PAHs are considered as the largest single group of carcinogenic compounds. The PAHs included in the present investigation is presented in table 2.1. The selection of the PAHs is based on 8 PAHs which are covered by the REACH Regulation (EC) No 1907/2006 as well as the 16 PAHs in the US EPA list of PAHs[1], often called the 16 EPA PAHs. The table also present the classification of the individual substances according to the Dangerous Substances Directive 67/548/EEC and the new regulation on the classification, labelling and packaging of substances and mixtures; i.e. Regulation EC No. 1272/2008.

Table 2.1. Classifications and TEF[3] values of PAHs in the present study

		CAS no.	Classification according to 67/548/EEC	Classification according to 1272/2008	TEF[3]
1	Acenaphthene[2]	83-32-9	-	-	-
2	Acenaphthylene[2]	208-96-8	-	-	-
3	Anthracene[2]	120-12-7	-	-	-
4	Benzo(a)anthracene[1,2]	56-55-3	CARC2;R45 N;R50/53	Carc. 1B; Aquatic Acute 1; Aquatic Chronic 1	0,1
5	Benzo(b)fluoranthene[1,2]	205-99-2	CARC2;R45 N;R50/53	Carc. 1B; Aquatic Acute 1; Aquatic Chronic 1	0,1
6	Benzo(k)fluoranthene[1,2]	207-08-9	CARC2;R45 N;R50/53	Carc. 1B; Aquatic Acute 1; Aquatic Chronic 1	0,1
7	Benzo(j)fluoranthene[1,2]	205-82-3	CARC2;R45 N;R50/53	Carc. 1B; Aquatic Acute 1; Aquatic Chronic 1	0,1
8	Benzo(g,h,i)perylene[2]	191-24-2	-	-	-

[1] PAHs covered by REACH (EC, 2006).
[2] EPA PAHs.
[3] Toxicity Equivalence Factors (BfR, 2009b).
"-" indicates that to that no values exists. This means that there is not sufficient documentation of the effects for these PAHs. E.g. indeno(1,2,3-cd)pyrene is in US EPAs IRIS database classified as B2, possible carcinogen, meaning that the compounds has been tested positive in animal tests but there are no data on humans which document the effect(http://www.epa.gov/iris/).

[1] In the late seventies the United States Environmental Protection Agency (EPA) published at list of priority pollutants including 16 PAHs. This list of the 16 EPA priority PAHs has become a standard for measurement of PAHs.

Table 2.2. Continued. Classifications and TEF[3] values of PAHs in the present study

		CAS no.	Classification according to 67/548/EEC	Classification according to 1272/2008	TEF[3]
9	Benzo(a)pyrene[1,2]	50-32-8	CARC2;R45 MUT2;R46 REP2;R60-61 R43 N;R50/53 2.5%≤C<25%: CARC2;R45 MUT2;R46 REP2;R60-61 R43 N;R51/53 1%≤C<2.5%: CARC2;R45 MUT2;R46 REP2;R60-61 R43 R52/53 0.5%≤C<1%: CARC2;R45 MUT2;R46 REP2;R60-61 R52/53 0.25%≤C<0.5%: CARC2;R45 MUT2;R46 R52/53 0.1%≤C<0.25%: CARC2;R45 MUT2;R46 0.01%≤C<0.1%: CARC2;R45	Carc. 1B; Muta. 1B; Repr. 1B; Skin Sens. 1; Aquatic Acute 1; Aquatic Chronic 1	1
10	Benzo(e)pyrene[1]	192-97-2	CARC2;R45 N;R50/53	Carc. 1B; Aquatic Acute 1; Aquatic Chronic 1"	-
11	Chrysene[1,2]	218-01-9	CARC2;R45 MUT3;R68 N;R50/53	Carc. 1B; Muta. 2; Aquatic Acute 1; Aquatic Chronic 1"	0,01
12	Dibenzo(a,h)-anthracene[1,2]	53-70-3	CARC2;R45 N;R50/53	Carc. 1B; Aquatic Acute 1; Aquatic Chronic 1"	1
13	Fluoranthene[2]	206-44-0	-	-	-
14	Fluorene[2]	86-73-7	-	-	-
15	Indeno(1,2,3-cd)pyrene[2]	193-39-5	-	-	-
16	Naphthalene[2]	91-20-3	XN;R22 CARC3;R40 N;R50/53	Carc. 2; Acute Tox. 4; Aquatic Acute 1; Aquatic Chronic 1"	0,001
17	Phenanthrene[2]	85-01-8	-	-	-
18	Pyrene[2]	129-00-0	-	-	-

[1] PAHs covered by REACH (EC, 2006).
[2] EPA PAHs.
[3] Toxicity Equivalence Factors (BfR, 2009b).
"-" indicates that to that no values exists.

2.2 Origin of sources to PAHs

PAHs are natural constituents of mineral oil (petrogenic PAHs) or are generated during combustion (pyrogenic PAHs). More or less the same PAHs will be present weather the source is pyrogenic or petrogenic, but the relative composition of the mixture of PAHs are different depending on the source.

In the present study the focus is on two types of additives, i.e. extender oils and carbon black, which are found in rubber and plastic products and are known to contain PAHs. Extender oils are mineral oil products which are derived from crude oil (petrogenic PAHs) whereas carbon black is a material produced by the incomplete combustion or thermal decomposition of heavy petroleum such as e.g. coal tar (mainly pyrogenic PAHs). Carbon black is used as a pigment and reinforcement in rubber and plastic products.

PAHs are present as a natural ingredient of crude oil, which the producer afterwards process and separate in order to convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oils to more valuable gasoline, olefinic gases and other products. In the process the PAHs

are being concentrated in the heavier fractions, e.g. aromatic oils and tar, whereas they have little affinity for the lighter fractions, e.g. gasoline. Mainly heavier mineral oils are used as additives in materials for the production of e.g. toys and childcare articles and can therefore be expected to be a source for PAHs in the products.

However, processes to extract the PAHs from the oil have been developed; producing "cleaner" oil products for e.g. consumer products in general (BAuA 2010). Also carbon black with reduced content of PAHs can be found on the market (see section 2.4).

Therefore, the amount of PAHs in the mineral oils and carbon black will depend on the origin and the production process (see section 2.3 and 2.4).

2.3 Sources of PAHs in rubber and plastic materials

For consumer products the main source of PAHs is considered to be different mineral oils which are used in the productions of the used materials, mainly as additives.

Consumer products consisting of the following materials or additives are considered to have potential PAH contamination[2]:

- Rubber and flexible plastics (e.g. PVC): Softening oils and carbon black as e.g. pigment
- Plastics. Black carbon used as e.g. black pigment

The present study focus on toys and childcare articles where materials, that may contain PAHs, are applied; that are toys and childcare articles made of rubber or plastics of different kinds.

2.3.1 Natural rubber and synthetic rubber

Natural rubber is produced from latex of the rubber tree (***Hevea brasiliensis***). By use of different additives and production process the physical properties of the natural rubber can be altered and thereby manufactured to different end uses. Natural rubber is used within a range of different sectors (UNCTAD, 2010). Examples given below:

- Transport sector: pneumatic tyres and tyre products, inner tubes, automotive belts
- Industrial sector: conveyor and transmission belting, tyres for lift trucks, castors, seismic materials, hoses, belts, plates, packing and sealing devices, industrial gloves, automotive mats
- Consumer sector: threads, erasers, golf balls, inflatable articles, mats, toys and textiles
- Hygiene and medical sector: examination and surgical gloves, contraceptives (condoms, intrauterine devices), other biomaterials (blood bags, syringes, implantable devices).

[2] TÜV Rheinland Group. http://www.twn.tuv.com/images/banner/TR%20PAH%20Fact%20Sheet-English.pdf

The consumption of natural rubber for tyres constitute for about 50% of the total consumption of natural rubber worldwide (UNCTAD, 2010). Due to that most of the technical literature focuses on tyres.

The chemical composition of natural rubber and latex is ***cis***-Polyisoprene:

$$\left[-CH_2-C(CH_3)=CH-CH_2-\right]_n$$

Natural rubber is further processed before use. By adding sulphur and heat (vulcanization) cross-links are made between the polymer chains which results in a more stabilized polymer; a harder material.

Synthetic rubber is used in combination with or as alternative to natural rubber and can in many cases be used for the same purposes as natural rubber.
Synthetic rubber covers a group of different polymers:

- Polybutadiene rubber
- Butyl rubber/Isobutylene-isoprene rubber
- Hydrogenated nitrile butadiene rubber
- Polychloroprene
- Polyolefin elastomer
- Fluoro elastomer
- Acrylonitrile-butadiene rubber
- Styrenic block copolymers
- Styrene-butadiene rubber
- Ethylene-propylene-diene copolymer
- Polyisoprene

Natural rubber as well as synthetic rubbers is formulated together with a wide range of additives in order to achieve the optimal quality of the material. Examples of additives used for the production of natural rubber materials are listed below (UBA, 2003):

- vulcanisation agent (sulphur)
- vulcanisation accelerators
- anti ageing agents
- fillers and pigments
- plasticisers
- processing aids

Plasticisers (mainly softeners) are a group of additives that include extender oils. These extender oils are also referred to as Distillate Aromatic Extract (DAE) or Highly Aromatic (HA) oil and are described in section 2.3.3

Carbon black is also used as an additive and even though PAHs are removed to some extend during the production of carbon black, PAH residues is still expected to be present as further described in section 2.3.4.

2.3.2 Poly Vinyl Chloride - PVC

PVC is produced by polymerisation of vinyl chloride and the chemical composition is presented below (Allsopp & Vianello, 2005):

$$\left[-CH_2-CHCl-\right]_n$$

PVC can be manufactured by addition of different additives. The potential additives are

- heat stabilisers
- internal and external lubricants
- processing aids
- impact modifiers
- fillers
- pigments
- UV stabilisers
- primary and secondary plasticisers

The actual composition of the PVC product will depend on the individual manufacturer and the wanted material properties of the product. Extender oils can be used in PVC as a secondary plasticiser and are also a cheaper additive that can substitute part of the more expensive primary plasticisers (e.g. phthalates) in flexible PVC or as process aid in rigid PVC (Nynas, 2010). The Handbook of fillers, extenders and diluents (Ash & Ash 2007) mentions several extender oils which can be used as plasticisers in PVC.

Additives applied in PVC may therefore be a source to PAHs in consumer products.

2.3.3 Functional oils as additives

Extender oils in the rubber and plastic industry are mainly used by:

- manufacturers of soften polymers.
- manufacturers of finished rubber products in order to aid processing; that is mixing operation, reducing compounding time and improving process ability and modify the physical properties of the finished product

The main functions of extender oils are by swelling of the polymer and to function as lubricants between the stiff rubbery polymers and softeners. By adding extender oils the molecular weight, viscosity and solvency of the base polymers (the rubber) can be varied. Further, because of oil content more additional ingredients can be blended. A major use of extender oils is therefore as additives in rubber tyres where the additives add important rubber characteristics and properties to, e.g. winter and summer, tyres.

The content of PAH in extender oils may vary between mineral oil fractions as mentioned in section 2.2. An example of the composition of PAHs in extender oil is compiled and presented in table 2.2.

Table 2.2 An example of the PAH content and profile in an extender oil (Kemikalieinspektionen, 2003).

PAH	CAS-nr.	Content (mg/kg)
Fluoranthene	206-44-0	11.0
Pyrene	129-00-0	25.6
Benzo(a)fluorine	238-84-6	0.9
Benzo(a)anthracene[1]	56-55-3	34.2
Chrysene[1]	218-01-9	395.3
Benzo(b)fluoranthene[1]	205-99-2	72.9
Benzo(e)pyrene[1]	192-97-2	113.2
Benzo(a)pyrene[1]	50-32-8	13.4
Dibenzo(a,j)anthracene	224-41-9	4.6
Dibenzo(a,h)anthracene[1]	53-70-3	5.7
Indono(1,2,3-c,d)pyrene	193-39-5	6.2
Benzo(g,h,i)perylene	191-24-2	17.9
Anthracene	191-26-4	6.6
Total		707.5

[1] PAHs regulated by REACH (EC, 2006).

Table 2.2 presents an example of the content of PAHs in extender oil. It should be noted that the PAH content of this extender oil exceeds the limit values included in the REACH Regulation (Benzo(***a***)pyrene < 1 mg/kg and sum of 8 PAHs < 10 mg/kg).

However, the amount of extender oils used in the production of toys and childcare articles is unknown and can vary significantly according to the designed properties of the rubber and plastic material and the use of other additives. A survey on producers and patents showed that the content of extender oils ranged from 2 to 50 w/w% in the material. For comparison a Swedish investigation found that the content of extender oils in tyres range from 10-40 w/w% (Kemikalieinspektionen, 2003).

There is only very little information in the literature on the amount of PAHs in the different oils and further, no information on the PAH content and specific type of oil used in the products are available. It was therefore not possible to correlate different extender oils, their content of PAHs and the different products.

Still, it is known that the lower molecular weight PAHs have highest affinity for being present in light mineral oils, whereas high molecular weight PAHs have highest affinity for being present in heavy mineral oils.

In addition, toys and childcare articles may be produced by use high quality extender oil with low PAH content (see section 2.4).

2.3.4 Carbon black

Carbon black (CAS no.: 1333-86-4) is also an additive which is used in tyres, rubber and plastic products, printing inks and coatings (ICBA, 2010).

Carbon black is virtually pure elemental carbon in the form of colloidal particles that are produced by incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions.

Its physical appearance is that of a black, finely divided pellet or powder. Its use in tires, rubber and plastic products, printing inks and coatings is related to properties of specific surface area, reinforcement of the material, particle

size, structure, conductivity and colour. Due to the source and production method carbon black may contain residues of PAHs.

Carbon black is classified as a Group 2B carcinogen by IARC (2006). However, carbon black is not adopted on the list of harmonised classification and labelling of hazardous substances (Annex VI to the Classification Directive 2008/1272/EC).

Tsai et al. (2001) have investigated the amounts of PAHs and the mass balance during the production of carbon black. Examples on the concentrations of PAHs in the crude oil used for production and in different carbon black products produced at different temperatures are presented in table 2.3.

Table 2.3 PAH concentration in carbon black products and crude oil (Tsai et al., 2001)

		Carbon black	
Substance	Crude oil mg/l (n=3)	Manufacturing at 1780 °C[1] mg/kg (n=9)	Manufacturing at 1950 °C[2] mg/kg (n=9)
Naphthalene	925	2.3	8.68
Acenaphthylene	159	2.11	15.2
Acenaphthene	52.9	0.526	0.870
Fluorene	115	0.457	0.194
Anthrecene	555	4.86	4.92
Phenanthrene	4.61	0.455	0.215
Fluoranthene	96.4	10.6	8.74
Pyrene	459	73.2	11.4
Cyclopenta(cd)pyren	79.9	6.19	5.91
Benzo(a)anthracene	56.0	4.67	7.74
Chrysene	22.3	0.083	0.032
Benzo(b)fluoranthene	34.0	0.026	0.057
Benzo(k)fluoranthene	24.3	0.026	0.001
Benzo(e)pyrene	69.5	0.718	0.774
Benzo(a)pyrene	62.1	0.238	0.366
Perylene	11.4	0.086	0.042
Indeno(1,2,3-cd)pyrene	4.79	0.155	0.112
Dibenzo(ah)anthracene	96.0	0.002	0.008
Benzo(b)chrysene	55.4	0.223	0.185
Benzo(ghi)perylene	77.9	1.06	1.04
Coronene	20.1	0.531	0.392
Total PAHs	2980	109	66.9

[1] Average for three types of carbon black: N-550, N-660, and N-774.
[2] Average for three types of carbon black: N-220, N-330, and N-339

In the process a significant amount of the PAHs is removed. For most of the PAHs only 0-5% of the incoming PAHs are present in the carbon black products compared to the crude oil, but still in high amounts for certain PAHs. Further, it can be noticed that the production temperature has an influence on the content of the PAHs in carbon black, but the effect vary for the different PAHs.

2.4 Alternative products or additives with low or no content of PAHs

2.4.1 Extender oil with low content of PAHs

There are alternative oils with low content of PAHs which can be and are used in consumer products. Kemikalieinspektionen (2003) and BAuA (2010) have listed a number of alternatives to the traditional extender oils which contain significant lower content of PAHs:

- Treated Distillate Aromatic Extract (TDAE), e.g. CAS: 90641-09-1 is produced from distilled aromatic extracts (DAE) which are further treated by a solvent extraction to remove the aromatic components with three rings and higher.
- Treated Residual Aromatic Extract (TRAE) is produced from residual aromatic extract (RAE), a heavy oil fraction produced from the de-asphalting of heavy petroleum residues, by solvent extraction of aromatic components.
- Mild Extract Solvate (MES) consists mainly of paraffinic oils, i.e. linear alkanes, which result from the lube base oil production and where aromatic components with two and more rings have been removed by extraction.
- Hydrotreated Paraffinic Distillate (HPD) consists mainly of paraffinic oils, i.e. linear alkanes, which have been treated with hydrogen in the presence of a catalyst of heavy petroleum distillates.
- Hydrotreated Naphthenic Distillate (HND) consists mainly of cyclic alkanes. It is produced by hydro-treatment of heavy vacuum petroleum distillates.

As several of these oils have gone through an additional treatment for removing the PAHs, they are expected to be more expensive than traditionally extender oils, and it is possible that these alternative oils may only be used in the more expensive toys and childcare articles.

Substitution of the traditional extender oils with these alternative oils has mainly been investigated for tyres, where there are specific demands for the properties of the rubber material. Bowman et al. (2004) have investigated the effect of substituting HA oil in Styrene butadiene rubber with two alternative extender oils containing less PAHs; TDAE or MES. They concluded that substitution was possible with respect to the physical properties; however, the best results were obtained by using TDAE. The long term service life performances were not clarified.

2.4.2 Carbon black with low content of PAHs

The amount of PAHs in carbon black can further be reduced by certain extraction procedures: e.g. soxhlet extraction with organic solvents under high temperatures (ICBA, 2010) or by thermal treatment under vacuum or inert gas atmosphere at temperatures >300°C and solvent extraction (BAuA 2010).

2.4.3 Alternative materials that do not contain extender oils

Another option is a substitution of natural rubber or synthetic rubber with thermoplastic elastomers (TPE) (BAuA, 2010). PTS (2007) presented a number of thermoplastic elastomers based on DIN ISO 18064 definitions:

- TPE-S: Block copolymers based on styrene, butylene, ethylene, propylene and modifications hereof
- TPE-U: Block copolymers based on polyurethane
- TPE-E: Block copolymers based on polyesters and polyethers
- TPE-A: Block copolymers based on polyamides
- TPE Silicone: Block copolymers based on silicone
- TPE-O: Olefin based thermoplastic elastomers
- TPE-V: Dynamic vulcanisates
- TPE radiation crosslink-able

Thermoplastic elastomers contain a hard, thermoplastic compound and a soft, elastomeric compound which are physically bound to each other to form the final elastic polymer.

These alternative polymers do not need to contain extender oil in order to obtain the right material properties which has been verified by the German survey (BAuA, 2010), as the study concludes that thermoplastic elastomers do not contain PAHs. Thermoplastic elastomers can be produced with different material properties and they are therefore capable of replacing a range of rubber products. The thermoplastic elastomers have therefore not been investigated any further in the present study.

2.5 PAH in specific consumer products

It has not been possible to correlate different kind of extender oils and their PAH content with the different rubber and plastic materials used and neither to correlate this information to the different toys and childcare articles. The reason is that there are no precise data on the content of PAHs in the different extender oils. Further, it has not been possible to correlate the different extender oils to different rubber and plastic materials. This situation appeared also for the carbon black products as there are no specifications of these additive materials or in which products they are used as well as in what amounts.

Due to the lack of specific information on additives in toys and childcare articles the focus has been laid on products of soft plastic and rubber materials. Hard plastic materials can also contain extender oils, however, it was estimated that the content of extender oils and thereby the possible PAH content would more common in soft plastic materials, and products of hard plastic materials was therefore not included in this study.

2.5.1 Investigations of PAHs in products

At the moment the knowledge of PAHs in child articles on the Danish market is very limited. In Germany the BfR (Bundesinstitut für Risikobewertung) have made larger investigations on PAHs in both consumer products and in toys. The investigations found that a number of products contained PAHs. However, it has not been possible to obtain these reports – only summary from them. Apart from the German investigations the number of report on PAHs in toys and childcare articles is very scarce.

BAuA (2010) has summarised a number of investigations of PAH in toys and other consumer products as background information for a proposal of a

restriction of PAHs under the REACH Regulation. The investigations were made by TÛV Rheinland, Stiftung Warentest and ÔKO-TEST.

The results of the investigation done by different research teams and consumer groups have been aggregated within a number of categories (see also table 2.4):

- Electrical devices
- Grips and handles (grips/handles made of rubber or plastic e.g. of tools (hammer, screwdriver, knives, pliers, bicycles, gardening tools, buggies, stationary bicycles, walking frames, torches, handle coating)
- Contact areas of sports equipment and other articles
- Toys (balls, figures, toy cars, run bikes, coloured pencils, shuttlecocks, toy guns, electrical parts of toy train sets)
- Materials with close contact to the body (shoes, gloves, underwear, working clothes, flip-flops)
- Other products with skin contact (ski goggles, headphones, pulse monitors, eye-cups, desk pads, bracelets, steering wheel covers, computer mice, mouse pads, furniture handles, watch straps)
- Tyres and rolls (car tyres, tyre cover, transport wheel, rolls of transport aid)
- Other products

In table 2.4 are given two concentrations of sum (sum PAH), where the concentrations on selected PAHs are summed up; the sum of 16 EPA PAHs (EPA PAH sum) and 6 selected PAHs which also are included in the 16 EPA PAHs. The maximum levels of Benzo(a)pyrene, EPA PAHs and PAH-6 are found in tyres. This is also the group with the highest fraction of samples containing PAHs. The maximum levels for toys were 65.9 mg benzo(a)pyrene/kg, 1992 mg EPA PAHs/kg, and 447 mg PAH-6/kg. The fraction of toy samples below detection limit was 94.7%, 18.5%, and 87.8% for respectively Benzo(a)pyrene, EPA PAH sum and PAH-6.

Table 2.4. Overview of analytical data. Based on BAuA (2010).

Category	Substance	Max content mg/kg	Fraction of samples (%)		
			nd[1]	<1 mg/kg	>10 mg/kg
All categories (n=5278)	Benzo(a)pyrene	1200	91.9	95.3	2.8
	EPA PAH sum	25400	22	50	14.9
	PAH-6[2]	6930	83.9	90.7	5.2
Electrical devices (n=1705)	Benzo(a)pyrene	195	91.9	94.8	3
	EPA PAH sum	4516	16.2	46	17.2
	PAH-6	1915	87.8	92	5.3
Grips, handles (n=541)	Benzo(a)pyrene	98	90.4	92.8	5.6
	EPA PAH sum	3699	20.7	46.6	18.5
	PAH-6	2483	81.7	89.3	7.5
Contact areas of sports equipment and other articles (n=120)	Benzo(a)pyrene	129	87.5	90	5.8
	EPA PAH sum	1801	5.8	24	22.3
	PAH-6	995	73.1	83.3	9.3
Toys (n=340)	Benzo(a)pyrene	65.9	94.7	97.1	0.9
	EPA PAH sum	1992	18.5	50.6	9.7
	PAH-6	447	87.8	94.3	3.7
Materials with close contact to the body (n=535)	Benzo(a)pyrene	111	88.2	97.6	1.3
	EPA PAH sum	1503	18.1	37.8	19.7
	PAH-6	412	61.4	79.6	4.7
Other products with skin contact (n=460)	Benzo(a)pyrene	530	94.8	96.5	2.6
	EPA PAH sum	9300	23.3	60.4	8.1
	PAH-6	3380	90.8	94.1	4
Tyres, rolls (n=35)	Benzo(a)pyrene	1200	60	65.7	22.9
	EPA PAH sum	25400	2.9	20	42.9
	PAH-6	6930	45.7	60	34.4
Other products (n=1519)	Benzo(a)pyrene	380	93.2	96.1	1.9
	EPA PAH sum	9574	32.5	59.1	11.4
	PAH-6	1994	85.7	92.5	4

1. Not detected. The detection limit varies between the different laboratories but is assumed to be 0.2 mg/kg or lower.
2. PAH-6: Benzo(a)pyrene, benzo(a)anthracene, dibenzo(a,h)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, and chrysene.

BAuA (2010) does not in general go into details concerning the specific products. However, it has been possible to identify the following list of toys and childcare articles. In all the below mentioned categories there were found products with elevated or strongly elevated PAH levels in some of the investigated products (TÛV Rheinland, Stiftung Warentest and ÔKO-TEST). According to BAuA elevated PAH level is defined as >0.1 mg/kg Σ PAHs and strongly elevated level as >1 mg/kg Σ PAHs. The Σ PAHs is defined as the sum of 24 PAHs. It is not specified what 24 PAHs that are included in the sum.

Toys and childcare articles containing PAHs:

- Children footwear: Plastic clogs/sandals, rubber boots, sneakers
- Toy and products used in water: Inflatable water toys, Swimming aids, Children swimming pools
- Baby strollers and buggies
- Doll buggies
- Erasers
- Children's bicycles: horns, grips and seats
- Plastic toy figures
- Carnival masks
- Children's trainer bikes
- Children's mud pants
- Teething rings
- Children's tooth brushes

These results from the German investigations were used in the final selection of products (see chapter 2.7).

2.6 Regulation of PAHs in consumer products

This section presents European regulation of PAH in products and ecolabelling criteria.

2.6.1 EU regulation of chemical substances (REACH)

The European regulation of chemicals, REACH regulation (EC) No. 1907/2006 (EC, 2006) include certain PAHs in a specified use i.e. the content in extender oils used for production of tyres. The limit values for PAHs are:

- <1 mg benzo(a)pyrene/kg extender oil
- <10 mg Σ PAH/kg extender oil, where Σ PAH/kg = Benzo(a)pyrene, benzo(e)pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, dibenzo(ah)anthracene.

2.6.2 Toy safety directive

Regulation by EU on safety of toys is at the moment covered by directive 88/378/EEC.

A new directive 2009/48/EC will be in force in 2011, except the requirements set out in Part III of Annex II concerning chemical properties, which will be in force by the 20 July 2013.

Directive 88/378/EEC (EC, 1988) do not address PAH explicit; however, it states that "Toys must not contain dangerous substances or mixtures within the meaning of Directives 67/548/EEC and 88/379/EEC in amounts which may harm the health of children using them. At all events it is strictly forbidden to include, in a toy, dangerous substances or mixtures if they are intended to be used as such while the toy is being used".

The new toy safety directive 2009/48/EC (EC, 2009) do not address PAH explicit, however, CMR substances must only be used in not available part of toys or in concentrations below the classification limits. This means that

classified PAHs (see table 2.1) in the new toy directive must have a concentration limit on 0.1% w/w or less depending on the specific classification limit.

2.6.3 Ecolabelling

Besides the restriction in REACH and the new toy safety directive 2009/48/EC, criteria have also been laid down under the Nordic Environmental labelling scheme. So-called Ecolabelling criteria have been developed for two product groups relevant for exposure to PAHs. The product groups are:

- Toys (Nordic Ecolabelling, 2009)
- Vehicle tyres (Nordic Ecolabelling, 2010)

2.6.3.1 Toys

The Nordic Ecolabelling criteria for toys contains requirements to a number of materials e.g. ***plastic and rubber***, textiles, skins and leather, wood and wood based materials etc. For plastics and rubber one of the criteria focuses on additives. Criteria R5 is presented in the box below (Nordic Ecolabelling, 2009).

R5 Additives to plastic and rubber

The following additives must not be actively added to plastics/plastic parts and rubber:

substances classified in any of the following hazardous classification lists (actual risk phrases in brackets):
May cause cancer with symbol T (R45, R49)
May cause cancer with symbol Xn (R40)
May impair infertility with symbol T (R60, R61).
May impair infertility with symbol Xn (R62, R63)
May cause heritable genetic damage with symbol T (R46)
May cause heritable genetic damage with symbol Xn (R68).
In accordance with regulations in force in any Nordic country and/or with the EU classification system Directive 67/548/EEC (with adaptations and amendments).

substances based on lead, cadmium, mercury and their compounds and organotin compounds
phthalates
halogenated organic compounds
Bisphenol A

Tin organic compounds are defined as compounds in which tin is bound directly to the carbon atom.

Eco labelling is therefore a good tool for supporting the new toy directive as the producers of toys, that are approved to such a labelling, have taken an extended responsibility that the quality of the materials used in the production of toys follows the legislation. Thereby the eco labelling will contribute as an additionally insurance of the quality of the product by controlling the whole production chain in relation to the producer as well as the consumer.

The criteria concerning hazardous classification of additives may be relevant for PAHs in toys added as mixtures (e.g. extender oils). Extender oils containing e.g. more than 0.01 %w/w of benzo(a)pyrene has to be classified as hazardous and labelled by CARC2, R45. Eco labelled products must not contain oils that are classified due to their content of PAHs.

2.6.3.2 Vehicle tyres

The environmental labelling criteria for vehicle tyres contain requirements to content of PAHs in oils used in the tyres as well as limit values for PAHs in tyres. Criteria R6 considers a limit of the total content of measured PAHs according to IP 346[3] method (max 3%) and a limit for 8 PAHs included in the REACH Regulation and for Benzo(a)pyrene at 8 mg/kg and 1 mg/kg, respectively (Nordic Ecolabelling, 2010).

R6 PAHs in oil The total content of polycyclic aromatic compounds (PAH) in oil used in the tyre must not exceed 3% measured according to IP 346 method. Analysis of PAHs in the tyre must be performed according to procedures in Appendix 2. The limit values for the contents of a total of 8 PAHs (according to EU Directive 2005/69/EC) and benzo(a)pyrene (BaP) must not exceeded 8 ppm for the 8 PAHs and 1 ppm for BaP.

Application of the IP 346 method and the calibration conditions is described in foreword to annex 1 to 6 in the REACH regulation EC no. 1907/2006 referring to PAHs.

2.6.4 Proposed regulation by Germany

UBA (2010) has proposed REACH, Annex XVII to be changed/extended to cover PAHs in consumer products by adding a Fifth paragraph to the section on PAH: "5. Articles which could be used by consumers (including articles in contact with the oral mucosa, toys, and childcare articles) shall not be placed on the market, if they contain any of the PAHs listed in column 1 at levels above the limit of quantification (LOQ). Currently the LOQ is located at 0.2 mg/kg for any of the listed PAHs". The eight PAHs included in this proposal are:

- Benzo(a)pyrene
- Benzo(e)pyrene
- Benzo(b)fluoranthene
- Benzo(j)fluoranthene
- Benzo(k)fluoranthene
- Benzo(a)anthracene
- Chrysene
- Dibenzo(a,h)anthracene

2.7 Selection of products for test

There is no legal demand for product declaration for toys. Based on the presented knowledge on potential PAH content of additives, the following criteria have therefore been considered in the selection (not prioritised):

[3] Method IP 346 is a chemical screening assay for dermal carcinogenicity. The princip is that the principal carcinogens in oils are PAHs, and that the biologically active members of the class are extractable into dimethyl sulfoxide, DMSO. The end-point measured in IP 346 is the weight percent of extracted compounds which equal to the PAHs. The European Commission mandates that Method IP 346 be used as the basis for labelling certain petroleum refinery products for carcinogenicity.

- Products in which PAHs have been found in other investigations
- rubber like material[4]
- imported "cheap" products made from rubber-like material
- black products made from rubber-like material
- imported products (e.g. from Asia) made from rubber like material
- products with close contact to skin or designed to be mouthed
- common products
- products made of recycled materials

For more details on the considerations of the selection of the specific products, see section 3.1. Table 2.5 present the candidates of products for the screening survey of the PAH content in toys and childcare articles.

Table 2.5 Toys and childcare articles suggested for this screening test for PAH content

No.	Product category	Comments	Reference
1	Toothbrush for children	PAH content verified in selected products	BAuA, 2010
2	Plastic clogs for children	PAH content verified in selected products.	BAuA, 2010 Swedish Nature Conservation, 2010
3	Beach sandals	High levels of PAHs found in footwear	BAuA, 2010
4	Rubber bracelet	Skin contact	
5	Wheels/tyres from children's carts/doll buggies	PAH content verified in selected products	BAuA, 2010
6	Wheels/tyres from scooters	PAH content verified in selected products	BAuA, 2010
7	Tyres from bicycles	PAH content verified in selected products	BAuA, 2010
8	Grips from scooters	High levels of PAHs found in grips	BAuA, 2010
9	Grips from bicycles	High levels of PAHs found in grips	BAuA, 2010
10	Erasers	PAH content verified in selected products	BAuA, 2010
11	Plastic toy figures	PAH content verified in selected products	BAuA, 2010
12	Plastic dolls	Skin contact, common use	BAuA, 2010
13	Teething rings	Skin contact, PAH content verified in selected products	BAuA, 2010
14	Carnival masks	Skin contact, PAH content verified in selected products	BAuA, 2010
15	Swimming aids (e.g. goggles)	Skin contact, PAH content verified in selected products	BAuA, 2010
16	Baby bib of plastic	Skin contact	
17	Plastic balls, soft	PAH content verified in selected products	BAuA, 2010
18	Plastic balls, solid	PAH content verified in selected products	BAuA, 2010
19	Product made of recycled material	The specific product will depend on what is available	
20	Products of synthetic leather	Material: PVC. Extender oils are used to improve the texture,	

[4] Rubber-like material: natural rubber, synthetic rubber and mixtures of natural and synthetic rubber.

		common use	
21	Wheels from toy cars	Expected to contain extender oils, common use	
22	Balloons	Material: Latex. Extender oils are used to improve the texture, common use	

The products in table 2.6 were considered; however, according to the material composition they were found not to be relevant to include in the investigation.

Table 2.6. Products excluded from the study

No.	Product	Comments
1	"Slime"	Slime is made from guar gum and borax (sodium borate)
2	"Magic sand"	"Magic sand" is made from sand and trimethylsilanol
3	"soft floor puzzles"	Is made of foam plastic polymer (MST report nr 70 2006)

3 Test results

3.1 Procedure for selection and purchase of the specific products

A range of different stores was selected in order to cover the range of different categories of toys and childcare articles (see table 2.5). However, as this is a screening investigation not covering the whole market, stores representing a significant share of the market was prioritised. Products were purchased from supermarkets, sport goods shops, toy shops, discount shops, clothes shops and book shops.

Baby shops were considered but as they primarily sell expensive products from northern Europe they were given up upon. In general there are a lot of Nordic produced baby products.

For the selected products, maximum 3-4 shops were visited for purchase. If the selected product type were not available from the stores visited, the product type was given up upon. Table 3.1 provides a description of the different types of products which were purchased. Table 3.2 describes the products which were not available from the store visits and were therefore not purchased. The specific purchased products are described in details in the appendix A.

Focus were given towards the cheapest products, based on the hypothesis that these are highest risk products with respect to the production process being based on low quality extender oils. To the extent that country origin of the product could be identified, the aim was to choose products from Asia based on the hypothesis that cheap products from production countries outside EU may have a higher risk of containing PAHs due to a weaker regulation and possible also lower quality of the production materials. As carbon black is included in this investigation, products with black colour were chosen. In cases where this was not possible, products in different colours were purchased. The focus was put on products with high skin contact. Branded goods were given low priority. Products made of rubber and soft plastic materials were chosen (see table 3.1), whereas hard plastic materials were avoided (see table 3.2), as it was expected that extender oils are more common in soft plastic materials. Products of foam plastics were also avoided as these were not expected to contain extender oils. Many grips and handles on toys and childcare articles are made of foam plastics.

Table 3.1 Toys and childcare articles purchased for this screening test for PAH content.

No.	Articles	Land of origin
1	Toothbrush for children	China
2	plastic clogs for children	China
3	Bathing shoe	Italy
4	bracelet for children, synthetic leather	China
5	Bicycle 3-5 years, Tyre	Indonesia
6	Scooters, grip	China
7	Bicycle 3-5 years, grip	Indonesia
8	Eraser	??
9	Rubber duck	China
10	squeeze ball with liquid inside	China
11	Plastic doll	China
12	Cooling teething ring	China
13	Goggles for children	China
14	Baby bib, plastic	Italy
15	rubber ball, solid	??
16	Toy bag in synthetic leather	China
17	Toy car with rubber wheels	China, Hong Kong
18	Balloons	??
19	Squeeze-bulb horn	??
20	Pen with rubber handle	??

Table 3.2. Products given up upon

No.	Product	Comments
1	Products made of recycled material	Searched for on the internet. However, very few products have been found and it was difficult to judge the "softness" of the material on the screen
2	Carnival masks of latex	Toy shops: only masks of foam plastic or vinyl have been found. Role-playing shops: latex products were of a too good quality (Danish produced) and primarily for adults.
3	Wheels/tyres from children's carts/doll buggies	Apart from Brio, there was only found products with handles of plastic foam and hard wheels
4	Wheels/tyres from scooters	It was not possible to find products with soft wheels, only hard wheels or wheels was made of foam plastic

3.2 Method of analysis, screening

The products were analysed according to a German standard for analysis of PAHs in consumer products (ZEK 01-2-08). The method is published by "Central Experience Exchange Committee (ZEK)" together with the German accreditation body "German Accreditation Body for GS Mark issuing Bodies (ZLS)". The method was used in this investigation with some modifications, as there in this project only have been done a screening for PAHs. Further the detection limits has been improved compared to the German standard.

3.2.1 Sample preparation

A representative partial sample was taken from the material. The sample was cut in small pieces approx. 2-3 mm. For products which were larger or more

inhomogeneous, samples were taken from surfaces where the skin contact was expected to be high (e.g. collar of a baby bib).

3.2.2 Extraction method

The samples each of approximately 0.5 g was placed in a 25 ml extraction bottle and spiked with 5 ^{13}C- or deuterium labelled PAHs (2-methyl-Naphatalene, phenanthrene, anthracene, fluoranthene and pyrene) 2-methyl-Naphatalene, phenanthrene and fluoranthene was used for QA/QC, and for a few samples where there were interferences anthracene or pyrene were used. The samples were extracted with 10 ml of toluene by ultra sonification in a 60ºC water bath for one hour. 2 ml of the extract was filtered through a paper filter and washed with pentane. The combined solvents were evaporated to 1 ml and analysed directly on GC-MS. For a few products it was nessesary to dilute the extract as the consistency of the extract was too thick. In those cases the detection limit was elevated (is indicated under the results).

3.2.2.1 Analysis on GC-MS

5 deuterium labelled PAHs were added to the extract as injection standards. The samples were analysed on GC-MS in SIM mode. An external standard for verification of the PAHs was analysed together with the samples.

The samples were screened for 17 PAHs, including the 8 PAHs regulated under the REACH Regulation and the 16 EPA PAHs, in order to make sure that the screening cover the PAH parameter group relatively broadly. Some of the PAHs are reported as sum, as these are difficult to separate chromatographically.

The following PAHs were included in the analysis:
Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo(a)anthracene, Chrysene/ Triphenylene (sum), Benzo(b+j+k)fluoranthenes (sum), Benzo(e)pyrene, Benzo(a)pyrene, Indeno(1.2.3-cd)pyrene, Benzo(ghi)perylene, Dibenzo(ah)-anthracene.

3.2.3 Quality assurance (QA/QC)

As this is a screening project the quality assurance and documentation as well as the analytical quality was more limited as the exact concentrations were not documented. The Danish EPA standard demand for documentation of analysis was therefore not followed strictly. In order to make sure that there were no false positive or negative results and that the analysis was performed with a known and documented detection limits the following parts of QA/QC was included in the analysis.

- Recovery standards for control of the analytical quality
- Injections standards to control the performance of the GC-MS
- Control against an external standard on high and low concentrations levels of PAHs in order to verify the found PAHs and estimate the range on the concentration level (semi quantitative)
- Blind samples

The detection limits was based on 5 times the signal-to-noise ratio on the GC-MS. The detection limits are given in table 3.3.

Table 3.3. Detection limits of the specific PAHs

PAH	Detection limits mg/kg
Naphthalene	0.003
Acenaphthylene	0.01
Acenaphthene	0.01
Fluorene	0.005
Phenanthrene	0.005
Anthracene	0.005
Fluoranthene	0.002
Pyrene	0.002
Benzo(a)anthracene	0.005
Chrysene/Triphenylene	0.01
Benzo(b+j+k)fluoranthenes	0.01
Benzo(e)pyrene	0.005
Benzo(a)pyrene	0.01
Indeno(1.2.3-cd)pyrene	0.025
Benzo(ghi)perylene	0.01
Dibenzo(ah)anthracene	0.01

3.3 Analytical results

3.3.1 Comments on the analytical method

In the proposal it was suggested to concentrate the extracts quite a lot in order to obtain a low detection limit as possible. However, for the soft rubber products it appeared that the consistency of the extracts became too thick, and it was therefore decided to increase the final solvent volume for all the samples. This increased the detection limits (see table 3.3).

3.3.2 Analytical results from the investigation

20 samples were analysed. The results are shown in table 3.4 and 3.5. As this is a screening investigation a concentration range is given for the single PAHs as well as the sum of PAH concentrations (see below table 3.4). The sum of PAHs was calculated from all PAHs (total PAH sum) as well as from the 8 REACH PAHs (REACH PAH sum). Further, the sum of PAHs was calculated from the 16 EPA PAHs (EPA PAH sum) as well as the 6 EU PAHs (6-PAH sum) (see below table 2.4) that were included in the German investigations in order to be able to compare the results from this investigation with the German investigations. In the following evaluation the results for EPA PAH sum is compared with the German investigations. However, for all products the sum of all PAHs (total PAH sum) are within in the same concentration range as EPA PAH sum.

Table 3.4 PAHs in toys and childcare articles (mg/kg). The levels are semi quantitative determined

PAH	Toothbrush	plastic clogs	Bathing shoe	bracelet	Bicycle, Tyre	Scooters, grip	Bicycle, grip	Eraser	Rubber duck	squeeze ball
Naphthalene	0.5-1.0	<0.2	0.2-0.5	<0.2	0.5-1.0	<0.2	<0.2	<0.2	0.2-0.5	0.2-0.5
acenaphthylene	<0.2	<0.2	<0.2	DL	1-5	<0.2	<0.2	DL	<0.2	0.2-0.5
Acenaphthene	0.2-0.5	DL	0.2-0.5	DL	1-5	n.a.	<0.2	<0.2	n.a.	n.a.
Fluorene	<0.2	DL	0.2-0.5	<0.2	5-10	0.5-1.0	DL	DL	<0.2	0.5-1.0
Phenanthrene	<0.2	0.2-0.5	1-5	0.2-0.5	10-25	0.5-1.0	<0.2	<0.2	<0.2	0.2-0.5
Anthracene	<0.2	<0.2	DL	<0.2	5-10	<0.2	<0.2	DL	<0.2	DL*
Fluoranthene	<0.2	<0.2	0.2-0.5	<0.2	10-25	0.2	<0.2	<0.2	<0.2	0.2-0.5
Pyrene	DL	0.5-1.0	<0.2	<0.2	25-50	0.2	DL	<0.2	<0.2	<0.2
Benzo(a)anthracene	DL	DL	DL	DL	10-25	DL	DL	DL	DL	DL*
Chrysene/ Triphenylene	<0.2	<0.2	DL	DL	25-50	<0.2	DL	DL	DL	DL*
Benzo(b+j+k) fluoranthenes	DL	<0.2	DL	DL	10-25	DL	DL	DL	DL	DL*
Benzo(e)pyrene	<0.2	<0.2	DL	DL	5-10	0.5-1.0	<0.2	DL	n.a.	DL*
Benzo(a)pyrene	DL	DL	DL	<0.2	1-5	<0,2	DL	DL	DL	DL*
Indeno(1.2.3-cd) pyrene	DL	DL	DL	DL	1-5	DL	DL	DL	DL	<0.2
Benzo(ghi)perylene	DL	<0.2	DL	DL	5-10	<0,2	DL	DL	DL	DL*
Dibenzo(ah) anthracene	DL	DL	DL	DL	1-5	DL	n.a.	<0.2	DL	DL*
total PAHs sum	1-10	1-10	1-10	<1	100-1000	1-10	<1	<1	<1	1-10
EPA PAHs sum	1-10	1-10	1-10	<1	100-1000	1-10	<1	<1	<1	1-10
6-PAH sum	<1	<1	<1	<1	10-100	<1	0	<1	<1	<1
REACH PAH sum	<1	<1	<1	<1	10-100	1-10	<1	<1	<1	<1
No of PAH above DL	10	13	7	7	19	12	7	6	7	7

DL: The concentration is under the detection limits (see table 3.3). DL*: Detection limit elevated (factor of two)
n.a.: Not analysed due to chromatographic difficulties (e.g. interference)
Concentration ranges for single PAHs: DL-0.2; 0.2-0.5; 0.5-1; 1-5; 5-10; 10-25; 25-50 mg/kg
For PAH sum: <1; 1-10; 10-100; 100-1000 mg/kg

Table 3.5 PAHs in toys and childcare articles (mg/kg). The levels are semi quantitative determined

PAH	Plastic doll	teething ring	Goggles	Baby bib	rubber ball, solid	Toy bag	Toy car, Wheels	Balloons	Squeeze-bulb horn	Pen
Naphthalene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.2-0.5	0.2-0.5	<0.2	<0.2
acenaphthylene	<0.2	<0.2	DL	DL	<0,2	DL	DL	DL*	<0.2	DL
Acenaphthene	1-5	DL*	DL	DL	n.a.	DL	0.5-1.0	DL*	n.a.	<0.2
Fluorene	<0.2	DL*	<0.2	DL	0.2-0.5	<0.2	0.2-0.5	<0.2	<0.2	<0.2
Phenanthrene	<0.2	<0.2	<0.2	<0.2	0.2-0.5	<0.2	0.2-0.5	<0.2	<0.2	0.2-0.5
Anthracene	<0.2	DL*	DL	DL	<0.2	<0.2	<0.2	DL*	<0.2	<0.2
Fluoranthene	<0.2	DL*	DL	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Pyrene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Benzo(a)anthracene	DL	DL*	DL	n.a.	DL	DL	DL	<0.2	DL	n.a.
Chrysene/Triphenylene	<0.2	DL*	DL	DL	DL	<0.2	DL	<0.2	DL	DL
Benzo(b+j+k)fluoranthenes	n.a.	DL*	n.a.	DL	<0.2	DL	n.a.	<0.2	<0.2	DL
Benzo(e)pyrene	n.a.	n.a.	n.a.	DL	<0.2	<0.2	DL	n.a.	DL	<0.2
Benzo(a)pyrene	DL	n.a.	DL	<0.2	DL	<0.2	DL	DL*	DL	DL
Indeno(1.2.3-cd)pyrene	DL	DL*	DL	DL	DL	DL	<0.2	DL*	DL	DL
Benzo(ghi)perylene	DL	DL*	DL	<0.2	DL	DL	<0.2	DL*	<0.2	DL
Dibenzo(ah)anthracene	DL	DL*	DL	DL	DL	DL	<0.2	<0.2	DL	DL
total PAHs sum	1-10	<1	<1	<1	1-10	<1	1-10	<1	<1	<1
EPA PAHs sum	1-10	<1	<1	<1	1-10	<1	1-10	<1	<1	<1
6-PAH sum	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
REACH PAH sum	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
No of PAH above DL	10	4	4	6	11	10	10	12	11	8

Explanation to the table, see under table 3.4

As this is a screening project the results are given in concentration ranges (see below 3.4). However, the estimates within the concentration ranges are fairly precise due to the analytical method.

In general, PAHs were detected in all samples analysed. For the 20 samples 11 samples had concentrations in the range 0-1 mg/kg based on the EPA PAH sum. In these samples there was found 4 to 12 PAHs above the detection limits. 8 samples had a concentration range 1-10 mg/kg (7-13 PAHs were found above DL) and 1 sample 100-1000 mg/kg (19 PAH above DL). The latter was analysed twice on GC-MS in order to verify the results. If the data is evaluated as sum of the 8 REACH PAHs 18 samples were in the concentration range 0-1 mg/kg, one sample in the range 1-10 mg/kg and one in the range of 10-100 mg/kg. For Benzo(a)pyrene 5 samples had values above detection limit.

In general mainly the small molecular size PAHs were found in this study; i.e. the PAHs are arranged according to increasing molecular size vertical downwards in table 3.4 and 3.5. This could indicate that the extender oils used for many of products are relatively light mineral oils which mainly contain the small to medium molecular size PAHs. The tyre from the bicycle, however, shows a different pattern as it was dominated of the medium molecular size PAHs indication that a heavier mineral oil was used as extender oil. As a general rule the toxicity of PAHs increase with increasing molecular size.

For products with expected high skin contact; plastic clogs, scooters grips, squeeze ball and bathing shoes had PAH levels 1-10 mg/kg. Toothbrush, plastic doll and toy car wheels also had PAH levels 1-10 mg/kg, but these are considered to have less skin contact or for shorter period.

The two specific baby articles (baby bib and teething ring) both had levels below 1 mg/kg.

Concerning country of origin most of products were from China. Two products came from Italy, (bathing shoe and baby bib). For the bathing shoe the total sum of PAHs ranged 1-10 mg/kg whereas the baby bib was below 1 mg/kg. This shows that also European products can contain PAHs. One product came from Indonesia (bicycle, grip and tyre). The tyres had the highest amounts of PAHs among the products. The grip from the same bicycle had levels below 1 mg/kg for the sum of PAHs.

3.3.3 Comparison to other investigations

As mentioned earlier, several German investigations on PAHs in toys performed by the Bundesinstitut für Risikobewertung (BfR) has assessed a number of toys and childcare articles with respect to PAH concentrations in different product types. In about 70% of the 104 examined toy samples, PAHs were below detectable levels or contained less than 1 mg/kg PAHs. Between 1-10 mg/kg PAHs were detected in 19% and between 10-100 mg/kg PAHs in 7% of the samples. Furthermore, highest values between 100-1000 mg/kg PAHs were detected in 3% of the samples. A recent investigation of 40 toys found PAH content of < 0.2 mg/kg in 39 samples (BfR 2009a).

In comparison to the German investigations this screening study found 55% of the toy and childcare articles to contain less than 1 mg/kg PAHs. 1-10

mg/kg was detected in 40% of the samples and 100-1000 mg/kg was detected in 5 % of the samples (1 sample). Data is summarised in table 3.6.

Table 3.6 Number of samples found with PAH content in the present study and in BfR study

	Present study		BfR study	
No. of samples	20		140	
Concentration of PAHs	number	% of total	number	% of total
<1 mg/kg	11	55 %	98	70 %
1-10 mg/kg	8	40 %	27	19 %
10-100 mg/kg	0	0 %	10	7 %
100-1000 mg/kg	1	5 %	4	3 %

A reason for the higher percentage of samples with a PAH content in the range of 1-10 mg/kg is probably due to the significant lower detection limits in the present study compared to the German studies. The detection limits in the German studies is 0.2 mg/kg and in this study they are approximately 10-100 times lower (see table 3.3). This means that number PAHs that are detected and thereby contributing to the sum are much higher in this study. PAHs below detections limit are set to zero both in the German studies and in this study. Taking this into account it seems to appear that the result for this investigation follows the pattern of the German investigations. However, in the present study there has not been found as high maximum concentrations as in the German studies (table 2.4, 3.4 and 3.5).

The single sample in the present investigation with high concentrations of PAHs (bicycle tyre) was approximately 10 times lower than the highest concentration found in the German investigations for tyres.

3.3.4 Comparison of the results to regulations

Only in one case significant high amounts of PAHs was found; i.e. in the tyre of the children bicycle. The bicycle was intended for children, age 3-5 years, however, according to the toy directive 2009/48/EC the bicycle is not regulated under the directive as the height of the seat was more than 435 mm. If the results are compared to the limits in the REACH regulation assuming a content of extender oils of 40%, will the accepted concentration in the tyre be 0.4 mg/kg Benzo(a)pyrene and the sum of the eight PAHs 4 mg/kg. The analysed bicycle tyre has concentrations which are a factor of 17 times above the regulation for the sum of REACH PAHs and 9 times above the regulation for benzo(a)pyrene. If the content of extender oils are lower in the tyre the factor above the regulation limits will be even higher.

If the results are compared to the limit of 0.2 mg/kg in products which is proposed from the German authorities (see section 2.6.4) two products will exceed the suggested limit. The bicycle tyre will exceed the suggested limit for all 8 PAHs and scooter grip will exceed for one PAH, benzo(e)pyrene.

4 Conclusions

The aim of the present study was to investigate, at screening level, the presence of PAHs in toys and childcare articles in Denmark.

Extender oils and carbon black are considered to be the two main sources to PAHs in rubber and plastic materials.

It has not been possible to correlate different kind of extender oils and their PAH content with the different rubber- and plastic materials and further to correlate this information to the different toys and childcare articles. The literature survey showed that data are not available on the contents of the PAHs in the different extender oils, the use of extender oils and black carbon in rubber and plastic materials as well as the use in toys and childcare products.

The current regulations do not oblige producers to supply information about the quality, types and amounts of materials and additives used in the products they put on the market.

In qualitative terms, however, there seems to be a tendency for bias towards the low molecular weight PAHs being present in the selected survey products. This indicates the use of extender oils of the light mineral oil type as further described below. In general, the toxicity for PAHs increases with increasing molecular size.

For selection of relevant products for the investigation, the limited knowledge on the use of extender oils was used together with the results of German investigations on PAH in toys and other consumer products. In the selection and purchasing, products which potentially might have a high content of PAHs were chosen.

20 toys and childcare articles were analysed. The results showed that PAHs were found in all analysed samples. It can therefore be concluded that it is common for toy and childcare articles in the Danish market to contain PAHs.

In comparison to the German investigations the present study found a higher number of samples with detectable PAHs. This is probably due to lower detection limits compared to the German investigations.

55% of the samples contained <1 mg/kg; 40% contained 1-10 mg/kg and 5% (one sample) contained 100-1000 mg/kg of the EPA PAH sum. For the REACH PAH sum 90% of the samples were below 1 mg/kg, 5% in the range 1-10 mg/kg and 10-100 mg/kg, respectively. Benzo(a)pyrene were below detection limit in 75% of the samples.

Considering country of origin most products were produced in China. Two products were produced within EU. One of the product have concentration level between 10-100 mg/kg whereas the other were <1 mg/kg. This means that products produced Europe also have detectable amounts of PAHs.

Two baby articles were included in the study; both at concentration levels <1 mg/kg. For products with expected high skin contact four products have levels of 1-10 mg/kg, the rest were below 1 mg/kg.

If the found concentrations were compared to the limits for PAHs within REACH only one product (tyre from a bicycle) exceeded this limit even under the assumption that the tyre contains relatively high amount of extender oil (40%). The bicycle tyre is not regulated under the limits for car tyres in REACH.

At the present there are no specific regulation limits on PAHs in toys and childcare articles at the present but the EU toy directive (88/378/EC) regulates in general the content of chemicals in toys. The German authorities have suggested a limit of 0.2 mg/kg article of the 8 REACH PAHs. If the suggested limits are compared to the results in the present study exceed the bicycle tyre the limits for all 8 PAHs, whereas the scooter grip exceed for one PAH, benzo(e)pyrene.

Based on the investigation it must be concluded that even though this project have focussed on products where it would be more likely to find PAHs, PAHs are common in toys and childcare articles in Denmark, but for most products in relatively low concentration levels compared to the German studies.

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Appendix A

Product details

No.	product	Description of product	Country of origin	comment
1	Toothbrush brush for children	Toothbrush for children with rubber handle	China	
2	plastic clogs for children	black plastic clogs	China	
3	Bathing shoe	Material: clear soft rubber	Italy	cheap beach sandals are not available at time of the year
4	bracelet for children, synthetic leather	Material: Vinyl	China	The round rubber bracelet was not possible to find. Are maybe not trendy anymore.
5	Bicycle 3-5 years, Tyre	Ordinary tyres for bicycle	Indonesia	handle and tyre from the bicycle was used
6	Scooters, grip	Black grips, black hard plastic wheels	China	
7	Bicycle 3-5 years, grip	Black rubber handle	Indonesia	handle and tyre from the bicycle was used
8	Eraser	multicoloured, phthalate free	??	
9	Rubber duck	flexible rubber	China	
10	Rubber ball with liquid inside	very flexible rubber, has to be squeezed to be funny, high skin contact	China	
11	Plastic doll	Baby doll with body of fabric and head, arms and legs of soft plastic	China	
12	Cooling teething ring	Soft plastic with cooling liquid inside	China	
13	Goggles for children	Goggles with rubber edge	China	
14	Baby bib, plastic	Flexible cast plastic	Italy	The product is not common outside baby shops. Only few products found and none from Asia
15	rubber ball, solid	Material: Transparent rubber	??	
16	Toy bag in synthetic leather	Material: vinyl, another type than the bracelet	China	
17	Toy car with rubber wheels	Metal toy car with soft wheels	China	Many toy cars have hard plastic wheels
18	Balloons	Balloons with flags, material latex	??	
19	Squeeze-bulb horn	Squeeze-bulb horn of metal with handle of black rubber	??	
20	Pen with rubber handle	Handle of rubber	??	