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CMR Substances in Toys – Market Surveillance and Risk Assessment

Survey of Chemical Substances in Consumer Products 141, 2015

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CMR Substances in Toys – Market Surveillance and Risk Assessment

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Foreword

This project on CMR substances in toys was carried out in the period from March 2014 to July 2015.

The report describes the results of phase 1 of the project which comprises a survey of the CMR substances found in toys. This project focuses on CMR substances which are not phthalates since phthalates in toys are covered by another on-going project on chemical substances in consumer products. The survey covers studies and analyses of toys carried out by government authorities, consumer organisations and the industry in Denmark and other countries in the EU. The survey includes substances with a harmonised CLP classification and substances with a notified self-classification. The CMR substances found in different toys are classified by types of toys, toy products and materials. The concentration of CMR substances (total contents and migration) in different toys is also presented where data has been available.

Phase 1 resulted in an overview and proposed which types of toys should be checked for their content of CMR substances and which substances should be analysed for. Based on recommendations from phase 1, the Chemical Inspection Service (CIS) under the Danish Environmental Protection Agency extracted 30 toy products which were analysed for their content of CMR substances in phase 2 of the project. By way of introduction, the toy products were screened for their content of chemical substances. Using the results from the screening process 24 CMR substances were selected for quantitative analysis of the content concentration in the toy products concerned. The quantitative analyses were supplemented by migration testing and analysis of two CMR substances. The two substances were selected due to their relatively high concentration level (although below the threshold value) in two different toy products.

Based on the analysis results found in phase 2, a total of ten CMR substances were selected for assessment in relation to exposure, health and hazard rating in phase 3 of the project.

The project was executed by Danish Technological Institute (phases 1–3) together with COWI A/S who undertook the quality assurance of the health assessment realised in phase 3 of the project.

The following participated in the project:

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The project had a follow-up group comprising Shima Dobel, Maiken Guldborg Rasmussen and Hanne Thygesen from the Danish Environmental Protection Agency.

The project is funded by the Danish Environmental Protection Agency.

Conclusion and Summary

Background
CMR substances constitute a very large group of different chemical compounds comprising organic, inorganic and organometallic compounds. CMR covers Carcinogenic (Carc), Mutagenic (Muta) and Reprotoxic (Repr) substances designated by one of the three categories 1A, 1B or 2 (cf. the CLP regulation) that with regard to e.g. carcinogenic effects state if the substance is "Carcinogenic to humans" (Carc 1A), "Considered to be carcinogenic to humans" (Carc 1B) or "Suspected to be carcinogenic to humans" (Carc 2).

This report provides a survey of CMR substances found in toys in Denmark and in Europe. The project focuses on CMR substances that are not phthalates as phthalates in toys are covered by another project on chemical substances in consumer products. For this project, the Chemical Inspection Service (CIS) under the Danish Environmental Protection Agency gathered 30 toy products of which 28 were analysed for their content of CMR substances. Based on the analysis results, a total of 10 CMR substances were selected for assessment in relation to exposure, health hazard and risk.

Objective
The objective of this project is:
- to identify the presence of CMR substances in toy products based on literature studies of existing investigations and knowledge
- to analyse the content and migration of CMR substances for a number of selected products
- to make a risk assessment of products with a significant content/migration of CMR substances.

Survey
Based on a review of toy products notified under the European Commission's RAPEX (Rapid alert system for non-food dangerous products) the survey emphasized that materials such as 'Dyed/painted item' (e.g. toy cars), 'Wood (painted/treated)' (e.g. puzzles) and 'Textiles' (e.g. dolls and soft toys) comprised 62% of the toy products that contain CMR substances.

A comparison of the above-mentioned with search results on CMR substances found in toys, e.g. from the Danish EPA's database, revealed that some substance groups such as metals (especially lead and chromium as well as nickel and organotin), VOCs (including formaldehyde and toluene) and azo dyes (in particular dyes based on 4-aminoazobenzene) were frequently found in toys.

By far (>60%), most of the toys containing CMR substances are produced in China. The results from the survey (chapter 2) suggest that the likelihood of finding toys that contain CMR substances is most eminent under the following conditions:
- Toys that come together with children's magazines that can be purchased at various newsagents and toys sold together with food (e.g., fast food or candy). It is estimated that these toys are very likely to contain CMR substances, in view of the price of the primary product and the resulting low cost price of the toy product.
- Merchandise (popular, not least because of intensive marketing) with particular focus on the place of production (e.g., China) – likewise an increased risk of counterfeit products.
- Toy from 'One Euro Shops', supermarket on-the-spot bargains and vending machines with toys.

Chemical analysis
On the basis of the above survey, the Chemical Inspection Service (CIS) selected 30 toy products of which 28 were selected for chemical analysis. Two products were rejected; one because it was a cosmetics product (make-up) and not a toy and the other because it was found that the product most likely was identical to one of the other products selected (same appearance and same producer, only another packaging). The chemical analyses of selected toy products were conducted according to the following procedure (carried out in chronological order):

- Screening analyses of 28 products
- Quantitative analyses of 24 selected CMR substances from the screening
- Migration analysis of two CMR substances selected from an overall worst-case risk assessment based on 100% migration

Initially, semi quantitative screenings were conducted by gas chromatography (GC/MS) and screening analyses using X-ray to determine the content of CMR substances or any indication of these in the 28 products. Some of the toys tested were composed of several different materials, e.g., textile, foam, plastic, wood etc. For those products, the screening analyses were conducted either on selected components or on mixed samples of several individual components (see chapter 4 for details on samples and sub-samples).

Based on the screening analyses, 24 substances were selected for quantitative analysis. The substances were selected in consideration of their self-classification or harmonised classification as CMR substances. The results of the quantitative analyses of specific substances by GC/MS showed that the content of CMR substances was relatively low (in general <1000 mg/kg) and that the existing limits of each CMR substance were not exceeded.

Therefore, it was decided to carry out a worst-case risk assessment assuming that the contents of the CMR substances found in the toys could migrate (100% migration). According to the risk assessments, the substances aniline and dimethyltin dichloride (DMTC) produced the highest health hazard, which resulted in a subsequent migration analysis of the two products (skipping rope (product no. 608) and toy figurines (product no. 597)) that contained these substances. No migration of aniline or DMTC was demonstrated to artificial saliva or artificial sweat, respectively, in spite of the relatively high content of the two substances in the samples (650 mg aniline/kg and 1200 mg DMTC/kg, respectively). That means that the substances do not migrate to the aqueous simulants due to the substances' physical and/or chemical linkage in the products.

Exposure and health assessment
Exposure scenarios were defined for 11 toy products (chapter 6), which, according to the chemical analysis, contain the CMR substances that were selected for health assessment. The migration analyses for artificial sweat and saliva showed no migration of aniline or DMTC within the duration of the test (60 min.) above the detection limit for the methods of analysis (0.05 mg/kg for aniline and 60 mg/kg for DMTC, respectively). The results of the migration analysis were used to develop detailed exposure scenarios for the two products by using the detection limit to calculate the worst-case parameters with regard to the substance amount. A 100% migration was applied for the other products.

Children aged 3–6 months, 1–3 years and 3–6 years, respectively, were chosen for the exposure scenarios, based on the expected target group and use (exposure route). Generally, the selected products were placed in two categories: dermal exposure or oral exposure. However, for two products (toy slime (product no. 598) and flexible ball with rattle (product no. 553)) it was not possible to say in advance, which route of exposure should be regarded as worst-case for the two products.

The chosen parameters for the exposure calculations were set up for products with dermal or oral exposure, respectively, as worst-case scenario and exposure calculations were carried out. For products where the dermal as well as oral exposures were calculated, the highest value was chosen as worst-case exposure for the risk assessment.

The health assessment (chapter 7) was carried out for the following 10 CMR substances:

- 2-Mercaptobenzothiazole (MBT) – CAS no. 149-30-4
- Aniline – CAS no. 62-53-3
- Butylated hydroxytoluene (BHT) – CAS no. 128-37-0
- Dimethyltin dichloride (DMTC) – CAS no. 753-73-1
- Ethylbenzene – CAS no. 100-41-4
- Formaldehyde– CAS no. 50-00-0
- Phenyl isocyanate – CAS no. 103-71-9
- Styrene – CAS no. 100-42-5
- o-Toluenesulfonamide (o-TSA) – CAS no. 88-19-7
- p-Toluenesulfonamide (p-TSA) – CAS no. 70-55-3

The 10 substances were mainly assessed in the light of the risk assessment reports from the EU, the American Environmental Protection Agency (US EPA) and international organisations (e.g., the OECD) as well as assessments from REACH registration dossiers. Each individual CMR substance was assessed according to:

- Identification, classification and physiochemical properties
- Absorption and distribution
- Local effects: Irritation and allergies (skin/eye/respiratory irritation, corrosiveness and sensitisation)
- Systemic effects: Acute or chronic effects
- Identification of critical effect and determination of safe dose (DNEL/DMEL)

For five of the 10 CMR substances, the critical effect was the reprotoxic effect of which ethylbenzene was not classified in this category (harmonised classification). For phenyl isocyanate it was not possible to identify a critical effect. The critical effect of o-TSA was assessed to be hepatotoxicity, while it for formaldehyde was assessed to be induction and generation of allergy by dermal exposure. An oral toxic effect of formaldehyde is also considered relevant and therefore a DNEL is established (Table 63). For the two remaining CMR substances (MBT and aniline), the critical effect was carcinogenic. However, it was only possible to determine a DMEL for aniline from the available data. Consequently, a DNEL/DMEL could be determined for only eight out of 10 CMR substances.

Risk assessment

In general, the risk assessment of the selected CMR substances (where such an assessment could be performed) shows that there is no health risk associated with any of the toys that were investigated. In the case of two of the substances, MBT and phenyl isocyanate, it was not possible to perform a risk assessment due to the absence of toxicology data. Several worst-case assumptions have been made in the overall risk assessment, e.g. in connection with the exposure scenarios for the CMR substances. Overall, this means that the actual risk associated with the investigated CMR substances is likely to be even lower than stated in the report. One CMR substance, o-TSA, presented a health risk under worst-case assumptions by dermal exposure in connection with the use of toy slime (product no. 598) containing o-TSA. However, in a more realistic exposure scenario of the product the subsequent risk assessment indicated that o-TSA did not constitute a health risk.

Conclusion

The overall conclusion of the report is that CMR substances exist in a wide range of toy products but in concentrations that are below the permitted limits of each CMR substance. Under worst-case assumptions, the health assessment of 10 CMR substances that appeared in the highest concentrations in 11 selected toys showed no risk for these substances that can be assessed.

Sammenfatning og konklusion

Baggrund
CMR-stoffer er en meget stor gruppe af forskellige kemiske forbindelser, der omfatter såvel organiske og uorganiske som organiske-metalliske forbindelser. CMR dækker Carcinogene (Carc), Mutagene (Muta) og Reprotoksike (Repr) stoffer og opgives med angivelse af én af tre kategorier 1A, 1B eller 2 (jf. CLP-forordningen), som fx med hensyn til carcinogene effekter angiver, om stoffet 'Kan fremkalde kræft' (Carc 1A), 'Anses for at være kræftfremkaldende' (Carc 1B) eller er 'Mistænkt for at være kræftfremkaldende' (Carc 2).

Denne rapport dækker en kortlægning af CMR-stoffer, der er fundet i legetøj i Danmark og Europa. Der fokuseres på CMR-stoffer, som ikke er ftalater, da ftalater i legetøj dækkes af et andet igangværende projekt om kemiske stoffer i forbrugerprodukter. På baggrund af kortlægningen blev 30 legetøjsprodukter indsamlet af Miljøstyrelsens Kemikalieinspektion, hvoraf 28 blev analyseret for indhold af CMR-stoffer. På baggrund af analyseresultaterne blev der udvalgt 10 CMR-stoffer, som blev vurderet i forhold til eksponering, sundhedsfare og risiko.

Formål
Formålet med projektet er:
- at kortlægge forekomsten af CMR-stoffer i legetøjsprodukter ud fra en litteraturgennemgang af eksisterende undersøgelser og eksisterende viden
- at analysere indholdet og migrationen af CMR-stoffer i et antal udvalgte produkter
- at foretage en risikovurdering for produkter med et væsentligt indhold/afgivelse af CMR-stoffer.

Kortlægning
Kortlægningen (kapitel 2) fremhævede på baggrund af en gennemgang af legetøjsprodukter notificeret under EU-kommissionens RAPEX (Rapid alert system for non-food dangerous products) database, at materialer som 'Indfarvet/malet emne' (fx legetøjsbiler) 'Træ (malet/behandlet)' (fx puslespil) og 'Tekstil' (fx dukker og tøjdyr) udgjorde 62 % af legetøjsprodukterne som indeholdt CMR-stoffer.

En sammenholdelse af ovennævnte med søgningsresultater på CMR-stoffer i legetøj, blandt andet fra Miljøstyrelsens database, viste, at nogle stofgrupper, såsom metaller (særligt bly, krom, nikkel og organotin), flygtige organiske forbindelser (VOC'er, herunder formaldehyd og toluen) samt azofarvestoffer (særligt farvestoffer baseret på 4-aminoazobenzen), var særligt hyppigt forekommende i legetøj.

Langt størstedelen (>60 %) af legetøj indeholdende CMR-stoffer produceres i Kina, og resultaterne fra kortlægningen (kapitel 2) peger på, at sandsynligheden for at finde legetøj indeholdende CMR-stoffer må anses for at være højest under følgende forhold:
- Legetøj, der gratis følger med børnemagasiner/blade, som kan købes i diverse kiosker, samt legetøj, som sælges sammen med mad (fx fastfood og slik). Sandsynligheden for indhold af CMR-stoffer i dette legetøj må anses for høj - primærproduktets pris taget i betragtning må kostprisen for legetøjsproduktet være lav.
- Licensartikler (populære ikke mindst pga. intensiv markedsføring) med særlig fokus på, hvor produktet er fremstillet (fx Kina) – ligeledes forhøjet risiko for kopiprodukter.

- Legetøj fra One Euro Shop-butikker, tilbudskasser i supermarkeder og betalingsautomater med legetøj.

Kemisk analyse
På baggrund af ovenstående kortlægning udtog Miljøstyrelsens Kemikalieinspektion 30 legetøjsprodukter, og 28 produkter blev derefter udvalgt til kemiske analyse. To produkter udgik; det ene, fordi det var et kosmetisk (makeup) produkt og ikke legetøj, og det andet, fordi det blev vurderet, at produktet sandsynligvis var identisk med et af de øvrige, udvalgte produkter (samme udseende og samme producent, blot en anden emballage). Fremgangsmåden for gennemførelse af de kemiske analyser af udvalgte legetøjsprodukter bestod af følgende trin (afviklet i kronologisk rækkefølge):

- Screeningsanalyser af 28 produkter
- Kvantitativ analyser af 24 udvalgte CMR-stoffer fra screeningen
- Migrationsanalyse af to CMR-stoffer valgt ud fra en overordnet worst case-risikovurdering baseret på 100 % migration.

Der blev indledningsvist gennemført semikvantitative screeninger ved GC/MS samt screeningsanalyser ved røntgen for indhold af CMR-stoffer eller indikationer på disse i de 28 produkter. For nogle produkter bestod legetøjet af flere forskellige materialer, fx tekstil, skum, plast og træ. For sådanne produkter blev screeningsanalyserne enten foretaget på udvalgte dele eller på blandede prøver af flere enkeltdele (se detaljer om prøver og delprøver i kapitel 4).

Baseret på screeningsanalyserne blev der udvalgt 24 stoffer til kvantitative analyser. Stofferne blev udvalgt på baggrund af stoffernes selvklassificering eller harmoniserede klassificering som CMR-stof. Resultaterne af de kvantitative analyser af specifikke stoffer ved GC/MS viste, at indholdet af CMR-stofferne var forholdsvis lavt (generelt <1000 mg/kg), og at der ikke var overskridelser af de gældende grænser for de enkelte CMR-stoffer.

Det blev derfor besluttet at foretage en worst case-risikovurdering, hvor det blev antaget, at indholdet af CMR-stoffer identificeret i legetøj kunne migrere (100 % migration). Risikovurderingerne viste, at stofferne anilin og dimethyltindichlor (DMTC) gav den højeste sundhedsrisiko, hvorfor der efterfølgende blev foretaget migrationsanalyse på de to produkter (sjippetov (produktnr. 608) og legetøjsfigur (produktnr. 597)), som indeholdt disse stoffer. Der blev ikke påvist migration af anillin eller DMTC til henholdsvis kunstigt spyt eller kunstig sved på trods af det relativt høje indhold af de to stoffer i prøverne (hhv. 650 mg anilin/kg og 1200 mg DMTC/kg). Stofferne migrerer således ikke til de vandige simulanter på grund af stoffernes fysiske og/eller kemiske binding i produkterne.

Eksponering og sundhedsvurdering
Der blev opstillet eksponeringsscenarier for 11 legetøjsprodukter (kapitel 6), som ifølge den kemiske analyse indeholdt de CMR-stoffer, som blev udvalgt til sundhedsvurdering. Migrationsanalysen til hhv. sved og spyt viste som nævnt ingen migration af anilin og DMTC inden for testens varighed (60 min) over detektionsgrænsen for analysemetoderne (hhv. 0,05 mg/kg for anilin og 60 mg/kg for DMTC). Resultaterne af migrationsanalysen blev anvendt til at udvikle detaljerede eksponeringsscenarier for de to produkter ved at bruge detektionsgrænsen til beregning af worst case-parametre med hensyn til stofmængden. For de øvrige produkter blev en migration på 100 % anvendt.

Som udgangspunkt for eksponeringsscenarierne blev der fokuseret på børn i alderen 3-6 måneder, 1-3 år eller 3-6 år baseret på produktets forventede målgruppe og anvendelse (eksponeringsvej). Overordnet faldt de udvalgte produkter i to kategorier: dermal eksponering eller oral eksponering. To produkter (legetøjsslim (produktnr. 598) og bøjelig bold med rangle (produktnr. 553)) blev imidlertid vurderet til at kunne give anledning til både en oral og en dermal eksponering, idet det

ikke på forhånd kunne vurderes, hvilken eksponeringsvej der kunne anses som worst case for disse to produkter.

Der blev opstillet relevante parametre til eksponeringsberegninger for produkter med hhv. dermal og oral eksponering som worst case, hvorefter der blev foretaget eksponeringsberegninger. For produkter, hvor der blev beregnet for både en dermal og oral eksponering, blev den største værdi valgt som worst case-eksponering til risikovurdering.

Sundhedsvurderingen (kapitel 7) blev foretaget for følgende 10 CMR-stoffer:
- 2-Mercaptobenzothiazol (MBT) – CAS-nr. 149-30-4
- Anilin – CAS-nr. 62-53-3
- Butyleret hydroxytoluen (BHT) – CAS-nr. 128-37-0
- Dimethyltindichlor (DMTC) – CAS-nr. 753-73-1
- Ethylbenzen – CAS-nr. 100-41-4
- Formaldehyd– CAS-nr. 50-00-0
- Phenylisocyanat – CAS-nr. 103-71-9
- Styren – CAS-nr. 100-42-5
- o-Toluensulfonamid (o-TSA) – CAS-nr. 88-19-7
- p-Toluensulfonamid (p-TSA) – CAS-nr. 70-55-3.

De 10 stoffer blev vurderet primært ud fra risikovurderingsrapporter fra EU, den amerikanske miljøstyrelse (US EPA) og internationale organisationer (fx OECD) samt vurderinger fra REACH registreringsdossier. Hvert enkelt CMR-stof blev vurderet i forhold til:
- Identifikation, klassificering og fysisk-kemiske egenskaber
- Optagelse og distribution
- Lokale effekter: Irritation og allergi (hud og øjne, respiratorisk irritation, korrosivitet og sensibilisering)
- Systemiske effekter: Akutte og kroniske effekter
- Identifikation af kritisk effekt og fastsættelse af sikker dosis (DNEL/DMEL).

For fem af de 10 CMR-stoffer var den kritiske effekt reprotoksisk effekt, hvoraf ethylbenzen ikke var klassificeret under denne kategori (harmoniseret klassificering). For phenylisocyanat kunne der ikke identificeres en kritisk effekt. Den kritiske effekt for o-TSA blev vurderet til at være levertoksicitet, mens den for formaldehyd anses for at være induktion og fremkaldelse af allergi ved dermal eksponering. En oral toksisk effekt af formaldehyd anses også for at være relevant, hvorfor en DNEL er fundet (se tabel 63) og vil blive medtaget i det følgende. For de to resterende CMR-stoffer (MBT og anilin) var den kritiske effekt carcinogen effekt, men ud fra de tilgængelige data var det kun muligt at bestemme en DMEL for anilin. Der kunne således fastsættes en DNEL/DMEL for otte af de 10 CMR-stoffer.

Risikovurdering
Overordnet set viser risikovurderingen (hvor vurderingen kunne gennemføres) af de udvalgte CMR-stoffer, at der for alle de undersøgte legetøjsprodukter ikke er nogen sundhedsmæssig risiko. For to af stofferne, MBT og phenylisocyanat, kunne der ikke foretages en risikovurdering på grund af manglende toksikologiske data. Der er foretaget flere worst case-antagelser i den samlede risikovurdering, blandt andet i forbindelse med opstillingen af eksponeringsscenarierne for CMR-stofferne. Overordnet set betyder det, at den reelle sundhedsmæssige risiko ved de undersøgte CMR-stoffer højst sandsynligt er endnu lavere end angivet i rapporten. Et CMR-stof o-TSA udgjorde under worst case-antagelser en sundhedsmæssig risiko ved dermal eksponering i forbindelse med brug af legetøjsslim (produktnr. 598) indeholdende o-TSA. Ved anvendelse af et mere realistisk eksponeringsscenarie for produktet indikerede den efterfølgende risikovurdering imidlertid, at o-TSA ikke udgjorde en sundhedsmæssig risiko.

Konklusion

Den overordnede konklusion på rapporten er, at der findes CMR-stoffer i et bredt udvalg af legetøjsprodukter, men i koncentrationer som for ligger under de tilladte grænser for de enkelte CMR-stoffer. Den sundhedsmæssige vurdering af 10 CMR-stoffer, som forekom i de højeste koncentrationer i 11 udvalgte legetøjsprodukter viste, at der under worst case-antagelser ikke var nogen risiko ved de stoffer, som kan vurderes.

1. Introduction

1.1 Background

The Danish Government and the Red-Green Alliance want to protect children and young people against hazardous and unnecessary chemical substances. For this purpose, they want to provide more information about and intensify the control with consumer products aimed at children, also unborn babies and young people under 14.

The Danish Executive Order on Toys (BEK no. 13 of 10 January 2011) bans CMR substances[1] in the accessible parts of toys, unless the concentration of the CMR substances is below the specific classification threshold (2). In cases, where substances have a lower, specific threshold limit that limit will prevail. As the classification of substances and the classification thresholds have not been defined to protect children when using the substances in the products, e.g. in toys, the classification threshold for some substances may be relatively high as for some substances effects can be observed below the classification thresholds.

CMR substances constitute a very large group of different chemical compounds comprising organic, inorganic and organometallic compounds. CMR covers carcinogenic (Carc), mutagenic (Muta) and reprotoxic (Repr) substances and are stated with one of the three categories 1A, 1B or 2 cf. the CLP regulation (2). If a mixture contains a substance in one of the three categories, then that will generally lead to a classification if the content exceeds a given concentration. The three categories state the following (the generic concentration limit for classification of a mixture is stated in brackets):

Carcinogenic CMR substances
- Carc 1A: Carcinogenic to humans (≥0.1%)
- Carc 1B: Considered to be carcinogenic to humans (≥0.1%)
- Carc 2: Suspected to be carcinogenic to humans (≥1.0%)

Mutagenic CMR substances
- Muta 1A: Can induce damage to genetic material (≥0.1%)
- Muta 1B: Considered to induce damage to genetic material (≥0.1%)
- Muta 2: Suspected to induce damage to genetic material (≥1.0%)

Reprotoxic CMR substances
- Repr 1A: Can damage fertility or the unborn child (≥0.3%)
- Repr 1B: Considered to have adverse effects on fertility or the unborn child (≥0.3%)
- Repr 2: Suspected to have adverse effects on fertility or the unborn child (≥3.0%)

The substances may for example be used as additives, in the production of plastic, rubber, textiles or in surface coatings for toys.

[1] The CMR category covers chemical substances with carcinogenic (C), mutagenic (M) and reprotoxic (R) effects on human health. Carcinogens are likely to cause cancer whereas mutagens may induce changes to the volume or structure of the genetic material (DNA/the genetic material). The latter may lead to genetic changes in an individual (which may evolve into cancer) or such substances can be inherited and thereby might lead to congenital damage in the offspring if the mutations are caused by the parents' reproductive cells (egg or sperm cells).

The substances can be used or be present in the form of:

- Softeners
- Flame retardants
- Solvents
- Antioxidants and UV stabilisers
- Foaming agents
- Dyes
- Monomers and conversion products
- Procurement of a Bill of Materials (list of raw materials) from suppliers
- Safety assessment of the chemicals used
- Declarations of Compliance from suppliers
- Declarations of non-use of certain chemicals
- Testing (verification) of raw materials and finished products

As many types of plastic, rubber and textile exist, the range of possible CMR substances is large. This is one of the aspects addressed by an on-going study undertaken by COWI A/S and Danish Technological Institute (3). The investigation counted between 50 and 60 CMR substances that are not phthalates but might be found in plastic.

Apart from the phthalates not covered by this project, it is the immediate assessment of Danish Technological Institute that the knowledge of other CMR substances in toys in studies that have been carried out is relatively limited. Not least because phthalates often constitute the highest concentration by content in the products, but also because phthalates are the most frequently found CMR substances in toys[2].

1.2 Objective

The objective of this project is to describe and identify the presence of CMR substances in toy products based on literature studies of existing investigations and knowledge (phase 1), to analyse the content and migration of CMR substances for a number of selected products (phase 2), and to make a risk assessment of products with a significant content of CMR substances (phase 3).

1.3 Focus for selecting toys and CMR substances

The toys selected for investigation in this project are mainly toys that are *intended* for oral use, toys *likely* to be used orally and toys with *long-term skin exposure*. The project will focus specifically on genotoxic carcinogens, which are substances classified as both carcinogenic (Carc) and hazardous to the genes (Muta). Focus is especially on genotoxic carcinogens since no lower threshold has been defined for when the substances result in effects.

The CMR substances in this project were selected in the light of substances with a harmonized CLP classification (2) such as Carc, Muta or Repr. Potential CMR substances with a self-classification such as Carc, Muta or Repr were also selected. The self-classified CMR substances are based on one or more notifications from industry that indicate a danger assessment of the substance. In addition to harmonized and self-classified CMR substances, substances classified by the US EPA as carcinogenic have in some cases been included. In this report, the substances comprised by one of the above classifications are collectively referred to as CMR substances.

While work was being carried out on this report many amendments were agreed on in the CLP regulation (4), and they have affected the classification of some of the substances that were selected for the exposure, health and risk assessment (chapters 6-8). In that connection, dimethyltin dichloride (DMTC), which previously was self-classified, received a harmonized classification as Repr.2. The harmonized classification of ethylbenzene has been updated, but pointing forward it is still not classified as Carc, Muta or Repr according to CLP. The harmonized classification of

[2] Expert opinion: Nils H. Nilsson, Danish Technological Institute

formaldehyde has also been updated and amended from Carc 2 to Carc 1B. This report states the future classifications, which are expected to enter into force by 1 April 2015 at the earliest (4). Reference is made to previous harmonized classifications or self-classifications in the report, where relevant.

2. Survey

For the selection of literature and sources of information, the following references were used as background material. 'Clarifying Note Concerning Potential Content of Chemical Substances in Toys' (5), which describes the types of CMR substances potentially found in plastic, rubber and textiles as well as in coated and dyed items; 'Prioritized hazardous substances in plastic materials' (6), which among others characterises the most widely used plastic materials and their contents of CMR substances, if any; and an on-going literature study published by the Danish Environmental Protection Agency (the Danish EPA) with the title 'Survey and health/environmental assessment of plastic types' (3) which reviews relevant undesired substances, including CMR substances, in plastics (this study relies on an overall list which is based on state-of-the-art knowledge, including the 151 substances included in the SVHC list[3] at the end of 2013).

The literature studies carried out for this report provide an overview of the primary literature (scientific literature) and of reports and analyses of toys produced by Danish and foreign government authorities and consumer organisations. This report also discusses experience and measures taken in relation to CMR substances in toys by the trade organisations for toys in Denmark and the rest of Europe.

Taking the CLP Regulation (2) issued by the European Chemicals Agency (ECHA) and the ECHA CLP inventory (7) as its point of departure, this report comprises substances that are covered by the decision to harmonise classification and substances that have no harmonised classification and that are subjected to 'self-classification'. A few instances include substances classified by the US Environmental Protection Agency (US EPA) as carcinogens.

The project has generated a list stating which CMR substances have been identified in different types of toys and, where possible, the material used for the toy. The contents of CMR substances are also stated, where possible, and the results of any emission tests or migration tests are also presented. As already mentioned, products containing phthalates are not included in the overview.

2.1 Scientific literature

In order to acquire an overview of the primary scientific articles on toys and CMR substances, a number of searches were conducted in the international database PubMed (8), under the US National Library of Medicines.

A specific combination search for title and abstract using the search string 'Child*' and 'Toy*'[4] resulted in 1926 references. Adding the search terms 'Consumer', 'Chemical*', 'Hazard*', 'Exposure' and 'Tox*' one by one to the search string produced 52, 50, 84, 215 and 67 results, respectively. A review of these search findings led to 15 references[5] (references overlap in several searches), which were relevant in terms of CMR substances in toys (references specifically for phthalates were disregarded). A search string comprising all the search words 'Child*', 'Toy*' and 'CMR' was unsuccessful. Out of these fifteen references, all of them, apart from two references, focused on metals (including antimony, arsenic, lead (particularly frequent), cadmium, chromium, organic tin

[3] The SVHC list covers "Substances of Very High Concern" – http://echa.europa.eu/da/candidate-list-table
[4] The asterisk (*) can be used in wild card searches comprising all phrases containing the word indicated (in this case "Toy")
[5] PubMed ID (PMID) with the references: 24560284, 23241693, 15466115, 23780492, 20873709, 24641994, 24345102, 19095292, 1782825, 24359710, 22443256, 19958743, 14606431, 19569352, 19191927

compounds and nickel) found in for example toy jewellery for children. Several references list China as the producing country (imported products). In addition to metals (primarily lead and cadmium) as CMR substances in toys, one of the references, a 2010 feature article in the international magazine Environmental Science & Technology, also points to azo dyes (e.g. benzidine) and brominated flame retardants, including decabromodiphenyl ether (deca-BDE, CAS no. 1163-19-5) (8). deca-BDE has been classified as probably carcinogenic to humans (Carc B) by the US EPA and has been self-classified as a mutagen (Muta 2) in ECHA's CLP database.

2.2 National and international databases

2.2.1 The Danish EPA database of chemical substances in consumer products

A search of products in the Danish EPA database (9) of chemical substances in consumer products with a marking of the field 'Screening' produced 4,471 results. These results were studied and reduced to 580 chemical substances associated with toy products. Toys with phthalates as the only CMR substance(s) were likewise excluded. Next, toys containing chemical substances that could not be categorised as CMR substances (as defined in chapter 1.3) and chemical substances without a CAS no. were removed. Products that did not declare the concentration of the chemical substance were also removed. The final list of 121 toy products with 53 CMR substances can be found in Appendix 1. Table 1 below lists the CMR substances in toys that were identified in the Danish EPA database of chemical substances in consumer products.

TABLE 1

LIST OF SPECIFIC CMR SUBSTANCES, BASED ON DATA FROM THE DANISH EPA'S CONSUMER PROJECTS*

CMR substance	CAS no.	CMR category	Found in toys
Naphthalene	91-20-3	Carc 2	12
Phenanthrene	85-01-8	Carc 2**	10
Isophorone (3,5,5-Trimethyl-2-	78-59-1	Carc 2	7
Toluene	108-88-3	Repr 2	7
BHT	128-37-0	Carc 1B/2, Muta 1B/2, Repr 2**	5
Anthracene	120-12-7	Carc 2**	4
Antimony	7440-36-0	Carc 2**	3
Cadmium	7440-43-9	Carc 1B, Muta 2, Repr 2	3
Dibenzo(a,h)anthracene	53-70-3	Carc 1B	3
Ethylbenzene #	100-41-4	Carc 2 ***	3
Chromium	7440-47-3	Carc 1B/2, Muta 2**	3
Phenol	108-95-2	Muta 2	3
Manganese	7439-96-5	Muta 1B, Repr 1B/2**	3
Copper	7440-50-8	Repr 2	3
N-nitroso-dimethylamin	62-75-9	Carc 1B	2
Chrysene	218-01-9	Carc 1B, Muta 2	2
Aniline	62-53-3	Carc 2, Muta 2	2
Cobalt	7440-48-4	Carc 1B/2, Repr 2**	2

CMR substance	CAS no.	CMR category	Found in toys
N-nitroso-dibutylamin	924-16-3	Carc 2**	2
Lead	7439-92-1	Carc 2, Repr 1A/B**	2
Nickel	7440-02-0	Carc 2	2
Indeno(1,2,3-cd)pyrene	193-39-5	Carc 2**	2
Methylparabene	99-76-3	Muta 2**	2
N,N-Dimethylformamide	68-12-2	Repr 1B	2
N,N-dimethylacetamide	127-19-5	Repr 1B	2
2-Ethoxyethanol	110-80-5	Repr 1B	2
p-Anisidine	104-94-9	Carc 1B**	1
Benzene	71-43-2	Carc 1A, Muta 1B	1
Benzo(e)pyren	192-97-2	Carc 1B	1
Benzo(a)anthracene	56-55-3	Carc 1B	1
Styrene #	100-42-5	Repr 2	1
N-nitroso-diphenylamine	86-30-6	Carc 2, Muta 2**	1
Bis(2-ethylhexyl)hexanedioate	103-23-1	Carc 2, Repr 2**	1
Dichloromethane	75-09-2	Carc 2	1
Formaldehyde #	50-00-0	Carc 1B, Muta 2	1
Furfural	98-01-1	Carc 2	1
Tetrahydrofuran	109-99-9	Carc 2	1
2H-1-Benzopyran-2-on	91-64-5	Carc 2**	1
Tetradecansyre	544-63-8	Carc 2**	1
Arsenic	7784-42-1	Carc A****	1
Camphor	76-22-2	Muta 2, Repr 1A**	1
2-methylpropanal	78-84-2	Muta 2**	1
1,2-Diethoxyethane	629-14-1	Repr 1A	1
2-Methoxyethanol	109-86-4	Repr 1B	1
Mercury	7439-97-6	Repr 1B	1
Formamide	75-12-7	Repr 1B	1
1-Methyl-2-pyrrolidinone	872-50-4	Repr 1B	1
Dimethylformamide	68-12-2	Repr 1B	1
1,1-Dimethoxypropane	4744-10-9	Repr 1B	1
2-Ethylhexansyre	149-57-5	Repr 2	1
2-Hexanone	591-78-6	Repr 2	1

CMR substance	CAS no.	CMR category	Found in toys
Carbon disulfide	75-15-0	Repr 2	1
Diisopropylether	108-20-3	Repr 2 **	1

* Based on reports from the Danish EPA on identification of chemical substances in consumer products (11–19); **Self-classified CLP classification; ***Not classified as CMR under the harmonised CLP classification of the substance, but notified as Carc 2 under previously self-classified CLP classification; **** US EPA category for carcinogens (A: Carcinogenic to humans; B: Probably carcinogenic to humans; C: Possibly carcinogenic to humans). #Classification stated in the table reflects the classification of the substance according to the future amendment of the CLP regulation (4).

2.2.2 RAPEX

The European Commission's RAPEX (rapid alert system for non-food dangerous products) database (20) relies on reports from national authorities. RAPEX was set up as an alert system that ensures fast information exchange between the member states and the European Commission about measures taken to prevent or restrict marketing or use of products that constitute a serious hazard to human health and consumer safety. RAPEX does not comprise foods, pharmaceutics or medical devices, which are covered by other systems. The database is updated weekly.

The following search criteria were used to extract data from RAPEX on toys on 3 April 2014:

Product category: 'Toy'
Product type: 'All' (covering 'Professional' and 'Consumer')
Years: 'All' (2005-2014)
Risk type: 'All' (covering 'Serious' and 'Other')
Risk: 'Chemical'

The searches produced 1,184 results (toy products), all within the 'Serious' risk type and the 'Consumer' product type. The results were reviewed and all toy products with phthalates as the only CMR substance(s) were eliminated – equivalent to about 85% of all the toy products. Next, toys with chemical substances that could not be characterised as CMR substances were removed – equivalent to about 2% of the results. The final list of 154 toy products (about 13% of the results) containing CMR substances can be found in Appendix 2, which comprises sample photos of the toy products reported and lists the concentrations of the contents.

Table 2 provides a list of the 24 CMR substances that were identified in the 154 toy products, distributed according to frequency relative to presence in toy. It appears that the most frequent (non-phthalate) CMR substances found in the RAPEX search were lead, chromium, formaldehyde, N-nitrosamines, 4-aminoazobenzene and benzene, totalling a frequency of 86%. Out of the 24 listed CMR substances, 16 substances are also found in Table 1 above, which is based on data from the Danish EPA. Out of the eight CMR substances not listed in Table 1, seven are azo dyes.

TABLE 2

LIST OF SPECIFIC CMR SUBSTANCES, BASED ON DATA (2005–2014) FROM RAPEX

CMR substance*	CAS no.	Substance group	CMR category	Found in toys
Lead	7439-92-1	Metal	Carc 2, Repr 1A, Repr 1B**	69
Chromium	7440-47-3	Metal	Carc 1B, Carc 2, Muta 2**	48
Formaldehyde #	50-00-0	VOC[6]	Carc 1B, Muta 2	19
N-nitrosamines	62-75-9; 55-18-5	Nitrosamines	Carc 1B (CAS no. 62-75-9) Carc 1A/B, Muta 2** (CAS no.	16
4-aminoazobenzene	60-09-3	Azo dye	Carc 1B	15
Benzene	71-43-2	VOC	Carc 1A, Muta 1B	13
Naphthalene	91-20-3	PAH (polycyclic	Carc 2	4
Toluene	108-88-3	VOC	Repr 2	4
Nickel	7440-02-0	Metal	Carc 2	3
4,4'-Bi-o-toluidine	119-93-7	Azo dye	Carc 1B	2
Ethylbenzene #	100-41-4	VOC	Carc 2 ***	2
Isophorone (3,5,5-Trimethyl-2-cyclohexen-1-on)	78-59-1	VOC	Carc 2	2
Benzidine	92-87-5	Azo dye	Carc 1B, Muta 2, Repr 2	1
Cadmium	7440-43-9	Metal	Carc 1B, Muta 2, Repr 2	1
Styrene #	100-42-5	VOC	Repr 2	1
4,4'-methylene bis(2-cloro	101-14-4	Azo dye	Carc 1B	1
4-methyl-m-phenylenediamine	95-80-7	Azo dye	Carc 1B	1
3,3'-dimethoxybenzidine	119-90-4	Azo dye	Carc 1B	1
Creosote	8001-58-9	PAH	Carc 1B	1
O-toluidine	95-53-4	Azo dye	Carc 1B	1
Aniline	62-53-3	VOC	Carc 2, Muta 2	1
Antimony	7440-36-0	Metal	Carc 2**	1
Arsenic	7784-42-1	Metal	Carc A****	1
Phenol	108-95-2	VOC	Muta 2	1

* Substances written in bold are also listed in Table 1, which is based on the Danish EPA database of chemical substances in consumer products; **Aelf-classified CLP classification; ;*** Not classified as CMR under the harmonised CLP classification of the substance, but notified as Carc 2 under previously self-classified CLP classification; **** US EPA category for carcinogens (A: Carcinogenic to humans; B: Probably carcinogenic to humans; C: Possibly carcinogenic to humans). #Classification stated in the table reflects the classification of the substance according to the future amendment of the CLP regulation (4).

[6] Volatile Organic Compound

Table 3 lists CMR substances classified by type of toy, product and material. The five most frequent types of toys comprise 63% of all products of which wooden toys alone make up about 18%.

TABLE 3
LIST OF CMR SUBSTANCES CLASSIFIED BY TYPE OF TOY, PRODUCT AND MATERIAL, BASED ON DATA (2005–2014) FROM RAPEX*

Type of toy	Product	Material**	CMR substance
Wooden toys (28)	Puzzles (11)	Wood (painted/treated) (11)	Formaldehyde (11) Lead (1)
	Games (5)	Wood (painted/treated) (5)	Formaldehyde (3) Lead, chromium (2)
	Musical toys (2)	Wood (painted/treated) (2)	Lead, chromium (1) O-toluidine (1)
	Jumping jack (2)	Wood (painted/treated) (2)	Lead, chromium (2)
	Alphabet board (1)	Wood (painted/treated) (1)	Lead, chromium (1)
	Blocks (1)	Wood (painted/treated) (1)	Formaldehyde (1)
	Abacus (1)	Wood (painted/treated) (1)	Lead (1)
	DIY bird house (1)	Wood (painted/treated) (1)	Formaldehyde (1)
	Train (1)	Wood (painted/treated) (1)	Lead, chromium (1)
	Magnetic holder (1)	Wood (painted/treated) (1)	Formaldehyde (1)
	Ring pyramid (1)	Wood (painted/treated) (1)	Lead (1)
	Pull-along animal (1)	Wood (painted/treated) (1)	Lead, chromium (1)
Games & activities (19)	Weapons (3)	Dyed/painted items (2) Plastic (1)	Lead (1) Chromium (1) Toluene (1)
	Musical toys (2)	Dyed/painted items (2)	Lead (2) Chromium (1)
	Yo-yo (2)	Plastic (2)	Ethylbenzene (2) Toluene (2)
	Balance toy (1)	Dyed/painted items (1)	Lead, chromium (1)
	Punching bag (1)	Dyed/painted items (1)	Lead, chromium (1)
	Ball (1)	Dyed/painted items (1)	Lead (1)
	Dart (1)	Foam (1)	Benzene (1)
	Fishing tackle (1)	Metal (1)	Lead (1)
	Blocks (1)	Dyed/painted items (1)	Lead, chromium (1)
	Balls (1)	Dyed/painted items (1)	Cadmium (1)
	Play mat (1)	Dyed/painted items (1)	Lead (1)
	Key ring (1)	Metal (1)	Nickel (1)
	Puzzle (1)	Metal (1)	Nickel (1)
	Pull-along animal (1)	Dyed/painted items (1)	Lead (1)
	Pull-along cart (1)	Plastic (1)	Lead (1)

Type of toy	Product	Material**	CMR substance
Vehicles (18)	Car (15)	Dyed/painted items (15)	Lead (15) Chromium (12)
	Train (2)	Solvent (1) Dyed/painted items (1)	Benzene (1) Lead, chromium (1)
	Tractor etc. (1)	Dyed/painted items (1)	Lead, chromium (1)
Balloons (16)	Balloons (15)	Rubber (15)	N-nitrosamines (15)
	Balloon paste (1)	Unknown (1)	Benzene (1)
Dolls etc. (16)	Doll (10)	Textiles*** (6) Dyed/painted items (2) Metal (1) Plastic (1)	4-aminoazobenzene (6) 3,3'-dimethoxybenzidine (1) Lead (3) Chromium (2) Phenol (1)
	Hand doll (6)	Textiles*** (6)	4-aminoazobenzene (4) 4-methyl-m-phenylendiamine (1) Benzidine (1)
Costumes (14)	Make-up (10)	Powder/paste (10)	Lead (9) Chromium (9) Antimony (1) Arsenic (1)
	Costumes (3)	Textiles*** (3)	4-aminoazobenzene (2) 4,4'-Bi-o-toluidine (1)
	Mask (1)	Dyed/painted items (1)	Lead (1)
Drawing & painting (12)	Colouring pens (11)	Solvent (11)	Benzene (10) Aniline (1)
	Chalk (1)	Dyed/painted items (1)	Lead, chromium (1)
Soft toys (10)	Teddy bear (2)	Textiles*** (1) Dyed/painted items (1)	Lead (2) Chromium (1)
	Dog (2)	Dyed/painted items (2)	Lead (2)
	Rabbit (2)	Textiles*** (1) Unknown (1)	4-aminoazobenzene (1) Formaldehyde (1)
	Book (1)	Textiles*** (1)	4,4'-methylene bis(2-chloro aniline) (1)
	Rocking horse (1)	Dyed/painted items (1)	Lead (1)
	Horse (1)	Dyed/painted items (1)	Lead, chromium (1)
	Animal bag (1)	Textiles*** (1)	4,4'-Bi-o-toluidine (1)

Type of toy	Product	Material**	CMR substance
Domestic (7)	Shovel (2)	Metal (1) Dyed/painted items (1)	Lead (1) Lead, chromium (1)
	Workbench (1)	Dyed/painted items (1)	Lead, chromium (1)
	Binoculars (1)	Plastic (1)	Naphthalene, toluene, styrene (1)
	Toy bag (1)	Dyed/painted items (1)	Lead, chromium (1)
	Cooking set (1)	Dyed/painted items (1)	Lead (1)
	Tea set (1)	Plastic (1)	Nickel (1)
Baby activity toys (5)	Soft toys (2)	Textiles*** (2)	4-aminoazobenzene (1) Lead, chromium (1)
	Activity mat (1)	Textiles*** (1)	4-aminoazobenzene (1)
	Rattle (1)	Wood (painted/treated) (1)	Lead, chromium (1)
	Writing board (1)	Textiles*** (1)	Formaldehyde (1)
Figurines (5)	Dinosaurs (3)	Dyed/painted items (2) Plastic (1)	Lead (2) Chromium (1) Creosote (1)
	Horse (1)	Rubber (1)	N-nitrosamines (1)
	Winnie the Pooh (1)	Rubber (1)	Phenol (1)
Swimming gear (3)	Swimming ring (2)	Plastic (2)	Isoforone (2) Phenol (1) Toluene (1)
	Swimming toys (1)	Dyed/painted items (1)	Lead, chromium (1)
Slimy toys (1)	Slimy toys (1)	Gel (1)	Phenol (1)

* The numbers in brackets indicate the number of products in that particular category (column). ** The material(s) listed constitute the most problematic material in the toy. ** Textiles include fabrics (primarily for the toy type categories 'Dolls etc.' and 'Costumes') and plush (primarily the toy type category 'Soft toys').

Table 4 shows the distribution of materials and their contents of CMR substances. The three most commonly used material types 'Dyed/painted item' (e.g. cars), 'Wood (painted/treated)' (e.g. puzzles) and 'Textiles' (e.g. dolls and soft toys) comprise a total of 62% of the toy products and the dominant CMR substances are lead, formaldehyde and 4-aminoazobenzene, respectively.

TABLE 4

LIST OF CMR SUBSTANCES DISTRIBUTED ON MATERIAL, BASED ON DATA (2005–2014) FROM RAPEX*

Material	CMR substance	Content concentration**	Emission/migration
Dyed/painted items (44) This material category primarily comprises dyed plastics	Lead (42)	Unknown* (2) 100-999 mg/kg (28) 1000-9999 mg/kg (10) 10000+ mg/kg (2)	
	Chromium (28)	Unknown* (2) 50-499 mg/kg (22) 500-999 mg/kg (2) 1000+ mg/kg (2)	
	Cadmium (1)	189-539 mg/kg (1)	

Material	CMR substance	Content concentration**	Emission/migration
Wood (painted/treated) (29) This material category primarily comprises treated wood	Formaldehyde (17)	Unknown* (4) 100-999 mg/kg (11) 1000-3000 mg/kg (2)	Emission (24 hours) (2) 206 mg/kg 234-688 mg/kg
	Lead (12)	Unknown* (2) 100-999 mg/kg (9) 1260 mg/kg (1)	
	Chromium (9)	Unknown* (1) 50-499 mg/kg (8)	
	O-toluidine (1)	170 mg/kg (1)	
Textiles (23) This material category includes fabrics (primary for the toy type categories 'Dolls etc.' and 'Costumes') and plush (primarily the toy type category 'Soft toys').	4-aminoazobenzene (15)	Unknown* (1) 50-499 mg/kg (10) 500-2000 mg/kg (4)	
	4,4'-Bi-o-toluidine (2)	48 mg/kg (1) 516 mg/kg (1)	
	Lead (2)	Unknown* (2)	
	4,4'-methylene bis(2-chloro aniline) (1)	116-186 mg/kg (1)	
	4-methyl-m-phenylendiamine (1)	55.2 mg/kg (1)	
	3,3'-dimethoxybenzidine (1)	Unknown* (1)	
	Benzidine (1)	41.9 mg/kg (1)	
	Formaldehyde (1)	90 mg/kg (1)	
	Chromium (1)	Unknown* (1)	
Rubber (17)	N-nitrosamines (16)	Unknown* (2) 0.050-0.099 mg/kg (5) 0.100-0.999 mg/kg (7) 1-3 mg/kg (2)	
	Phenol (1)	370 mg/kg (1)	
Solvent (12)	Benzene (11)	Unknown* (3) 5-49 mg/kg (7) 120-254 mg/kg (1)	
	Aniline (1)	Unknown* (1)	
Plastic (10)	Toluene (5)	Unknown* (5)	
	Ethylbenzene (2)	Unknown* (2)	
	Phenol (2)	100-999 mg/kg (2)	
	Isoforone (2)	Unknown* (1) 64 mg/kg (1)	
	Lead (1)	170 mg/kg (1)	
	Creosote (1)	Unknown* (1)	

Material	CMR substance	Content concentration**	Emission/migration
	Naphthalene (1)	Unknown* (1)	
	Nickel (1)		Migration (1) 0.40 mg/dm²
	Styrene (1)	Unknown* (1)	
Powder/paste (10)	Lead (9)	100-999 mg/kg (3) 1000-9999 mg/kg (5) 31795 mg/kg (1)	
	Chromium (9)	Unknown* (1) 50-499 mg/kg (7) 16424 mg/kg (1)	
	Antimony (1)	765 mg/kg (1)	
	Arsenic (1)	49 mg/kg (1)	
Metal (5)	Lead (3)	Unknown* (2) 1307 mg/kg (1)	
	Nickel (2)		Migration (2) 0.83 µg/cm²/week (1) 34.5 µg/cm²/week (1)
	Chromium (1)	Unknown* (1)	
Unknown (2)	Formaldehyde (1)	58 mg/kg (1)	
	Benzene (1)	37.6-45.6 mg/kg (1)	
Gel (1)	Phenol (1)	285 mg/kg	
Foam (1)	Benzene (1)	190 mg/kg (1)	

* The concentration is not stated as a specific value in RAPEX, but mostly covers concentrations that exceed the specific threshold for the substance, cf. relevant standards (e.g. EN 71) or legislation (e.g. REACH).

The diagrams below give an overview of the production places of the 154 toy products containing CMR substances (Figure 1) and the year of reporting (Figure 2). It can be seen that more than 77% of the reported toy products were produced in Asia, 67% of which in China.

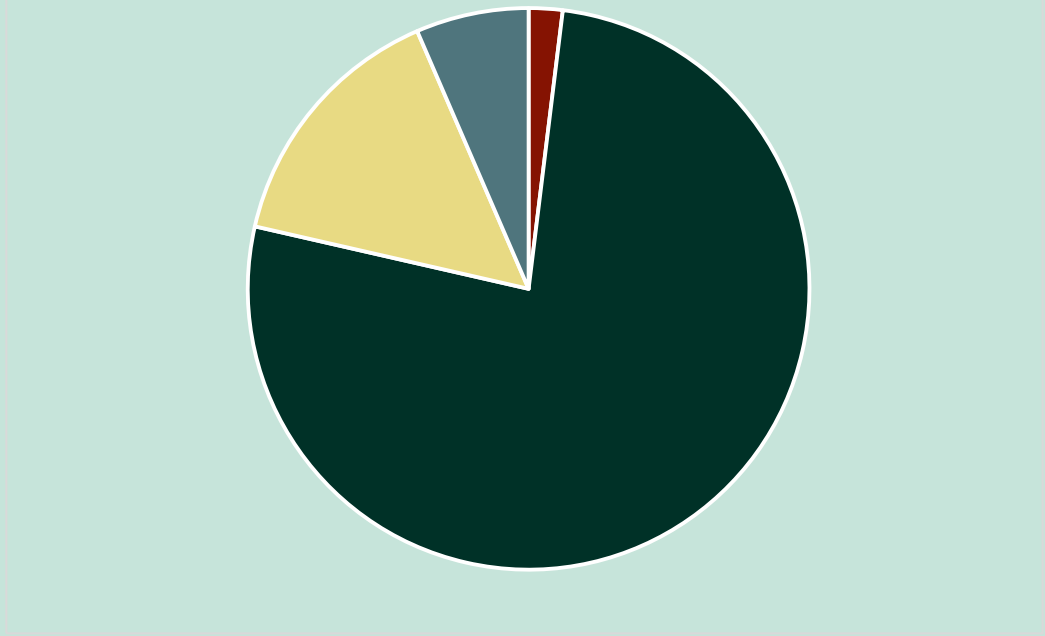


FIGURE 1
REGIONS THAT PRODUCED TOYS WITH CMR SUBSTANCES IN THE PERIOD 2005-2014

Figure 2 shows that the number of reported toy products peaked in 2008. In parallel with this there seems to be a trend in the declining number of reports on toys with CMR substances (phthalates not included).

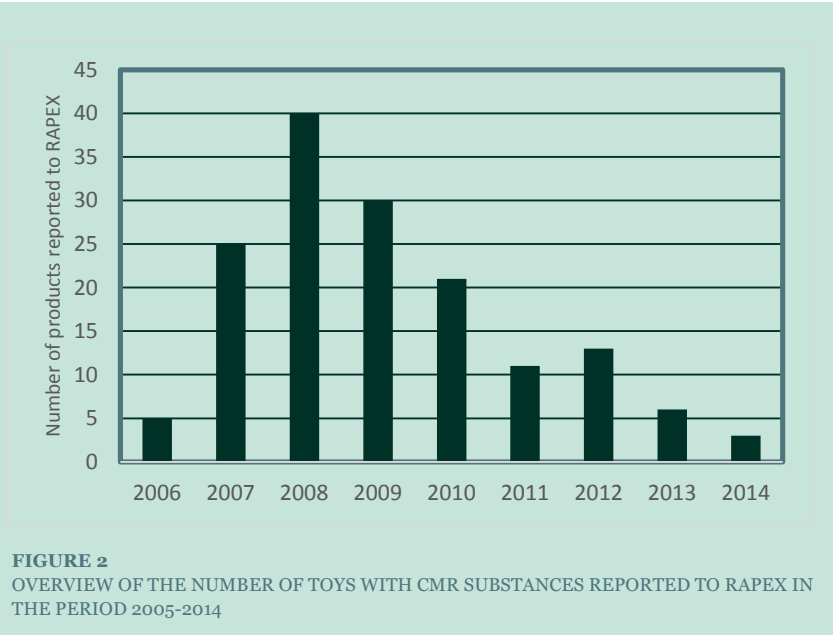


FIGURE 2
OVERVIEW OF THE NUMBER OF TOYS WITH CMR SUBSTANCES REPORTED TO RAPEX IN THE PERIOD 2005-2014

2.3 International public bodies and authorities

2.3.1 National Health and Nutrition Examination Survey (NHANES)

A search on the website of the US National Health and Nutrition Examination Survey (NHANES) (20) using the search term 'Toy' produced 58 results - none of these containing CMR substances (beyond phthalates).

2.3.2 Bundesinstitut für Risikobewertung (BfR)

A search on the website of the German Bundesinstitut für Risikobewertung (BfR) (22) using the search term 'Toys' produced 20 results (a search using the term 'Toy' only produced a single search result). Twelve of these results were relevant and in particular six BfR opinion papers (23-28) that focus on CMR substances in toys, including metals (antimony, arsenic, lead, cadmium, chromium and nickel), N-nitrosamines (e.g. in balloons and other rubber-based materials), polycyclic aromatic hydrocarbons (PAH) and phenol.

2.3.3 Umweltbundesamt (UBA)

In 2011, the German environmental protection agency, UBA, (29) published an extensive report in German on CMR substances and other problematic substances in consumer products. The UBA has produced a master list of CMR substances found in consumer products in 'toys', 'electric devices' and 'carpets and wallpaper' categories. This master list comprises a total of 275 CMR substances in category 1A and 1B and 153 CMR substances in category 2. The investigation also included information from for example the Danish EPA (12-15), BfR (25, 26), the Swedish and the Finnish EPAs, the European Food Safety Authority (EFSA), the European Commission Directorate-General for the Environment (DG ENV), RAPEX (20), toy producers (enquiries made to Mattel and Toys'R'Us, among others), test results from consumer organisations (ÖKO-TEST and Warentest) and their own data (for the full reference list see pages 214-217 of the UBA report). As regards their own data, the UBA report describes 35 toy products, e.g. plastic beach toys, bathing rings, teething rings, rubber balls and diving gear (snorkel and mask). Several of the investigated toy products contained CMR substances (e.g., azo dyes or VOCs, see table below) and were mainly (63%) produced in China.

Based on the above information sources from the period 1999–2009 and their own data from the period 2009–2010, UBA has composed a list of problematic substances (not just CMR substances) in toys. The list comprises 69 different substances. Twenty-six of these are not relevant either because they cannot be categorised as CMR substances (19 out of 26 substances) or because they are phthalates (seven substances: e.g. BBP, DBP, DEHP, DIBP, DINP, DIDP). The remaining 43 substances come within category 1A, 1B or 2 of the CMR substances, and of these 14 substances were not identified in the Danish EPA database (10) or through RAPEX notifications (20) (focusing on toy products in connection with the search). Table 5 below lists the 14 CMR substances identified by UBA but not through the Danish EPA database or RAPEX notifications. The fourteen substances are azo dyes, flame retardants, metals and VOCs, which is consistent with previous findings.

Appendices 3B (pp. 244–294) and 3C (pp. 295–315) of the UBA report (29) offer a detailed description of among others the emission (after one hour) of VOCs from selected pool toys (mostly plastic bathing toys) and the concentration content in different types of plastic toys. It is outside the framework of this part report to repeat all the results, especially since most of the data is from 2008 or older.

TABLE 5

UMWELTSBUNDESAMT: LIST OF 14 SPECIFIC CMR SUBSTANCES BY SUBSTANCE GROUP

Substance group	CMR substance	Category
Azo dye	4-Chlor-o-toluidine (CAS no. 95-69-2) p-Chloraniline (CAS no. 106-47-8)* 1-Phenylazo-2-naphthol (CAS no. 842-07-9)	Carc 1B, Muta 2 Carc 1B Carc 2, Muta 2
Flame retardant	Boron** (CAS no. 10043-35-3, 10043-35-3, 13840-56-7, 11113-50-1) Tris(2-chlorethyl)phosphate (TCEP) (CAS no. 115-96-8)	Repr 1B Carc 2, Repr 1B

Substance group	CMR substance	Category
Metal	Zinc** (CAS no. 13530-65-9, 11103-86-9) Organotin**	Carc 1A, Muta 2, Repr 2***
Monomes	Bisphenol A (BPA) (CAS no. 80-05-7)	Repr 2
VOC	2-Ethoxyethyl acetate (CAS no. 111-15-9) Nitrobenzol (CAS no. 98-95-3) Octamethylcyclotetrasiloxane (CAS no. 556-67-2) Perchlorethylene (CAS no. 127-18-4) Chloroform (CAS no. 67-66-3) Trichlorethylene (CAS no. 79-01-6)	Repr 1B Carc 2, Repr 1B Repr 2 Carc 2 Carc 2, Repr 2 Carc 1B, Muta 2

* Previously reported in the survey from the Danish EPA concerning hobby articles for children (17). ** The name of this substance covers several chemical compounds, some of which are listed as CMR substances (e.g. boric acid and zinc chromate). *** Self-classified CLP classification.

2.4 Consumer organisations

2.4.1 ANEC

The European consumer association ANEC (30) has been an active player in the field of chemical substances in toy products since 2001 and has for example advocated in connection with the revision of the European Toy Safety Directive (2009/48/EC) (31). A search using the term 'Toy' in ANEC's position papers (2001–2014) produced 19 results, five of which (32–36) concern CMR substances in toys. ANEC has generally focused on CMR substances in toys and has for example advocated in favour of using specific migration analyses and concentration levels (36).

2.4.2 The Danish consumer council TÆNK

A search conducted as a subscriber using the term 'Legetøj' (Danish for 'toy(s)') on the website of the Danish consumer council TÆNK (37) produced 20 results, two of which were associated with testing for CMR substances in children's toys aimed at <3 year olds (38) and >3 year olds (39), respectively. Appendix 3 provides a list of the products tested by TÆNK. Nineteen out of 35 tested products purchased in Denmark contained the CMR substances formaldehyde, nickel, unspecified organic tin compounds, PAHs and nonylphenol. Ten of these 19 toy products (about 53%) had been produced in China. Table 6 shows the distribution of the toys on types/materials and the identified CMR substance(s).

TABLE 6

TÆNK: LIST OF CMR SUBSTANCES CLASSIFIED BY TYPE OF TOY AND MATERIAL

CMR substance	CAS no.	CMR category	Type of toy*	Material
Formaldehyde	50-00-0	Carc 1B, Muta 2#	Wooden toys (2)	Wood
Nickel	7440-02-0	Carc 2	Wooden toys (3) Plastic toys (1)	Metal components Plastic
Organic tin compounds**	76-87-9 900-95-8	Carc 2 Repr 2	Wooden toys (5) Plastic toys (1)	Metal components Plastic

CMR substance	CAS no.	CMR category	Type of toy*	Material
PAH (polycyclic aromatic hydrocarbons)	-	Carc***	Wooden toys (5) Plastic toys (3) Soft toys (3) Doll (1)	Lacquer (paint) Velcro, plastic Rubber, plush Velcro
Nonylphenol	25154-52-3	Repr 2		

* The number in brackets indicates the number of products; ** The CAS no. for tin compounds with harmonised CLP classification is indicated; *** Some PAHs are classified as carcinogenic (refer e.g. to Tables 1 and 2). #Classification stated in the table reflects the classification of the substance according to the future amendment of the CLP regulation (4).

2.4.3 ÖKO-TEST

Searching the website of the German consumer organisation ÖKO-TEST (39) produced 23 results (articles) using the term 'Spielzeug' (German for 'Toy') in the 'Kinder/Familie' (Children/Family) category. Many of these articles discuss hazardous, chemical groups of substances (such as softeners and flame retardants), including CMR substances, in toy products. Available information on the website does not immediately indicate which specific products contain the given chemical substances. Furthermore, the level of information relative to chemicals is based on groups of substances rather than on specific chemical substances. ÖKO-TEST refers to RAPEX in several articles (40) as a source of information on hazardous chemicals in toys and other consumer products. According to ÖKO-TEST the price can be used as a general quality indicator, with a few exceptions. On its website, ÖKO-TEST specifically mentions toys with an increased risk of containing CMR substances and lists among others merchandise in the form of toys from manufacturers such as Disney, Hello Kitty, Star Wars, Spider Man, toys sold with children's magazines and toys from 'One Euro Shops ' and toys produced in China (40).

2.5 Trade organisations

With the purpose of determining whether the industry has taken specific measures to reduce the use of CMR substances in toys, a number of industrial organisations within the toy industry received an e-mail where they i.a. were asked the following: '*... has the toy industry taken active measures to reduce the use of CMR substances in toy products? If so, which measures has the industry taken to achieve this (e.g. random testing carried out by Intertek or other accredited companies, completion of solemn declaration forms or declarations of compliance (for example in relation to EU directive 2009/48/EC) from suppliers)?*'

Danish Technological Institute contacted the Joint Council of the Danish Toy Trade (Legetøjsbranchens Fællesråd), the Joint Council of Art & Hobby Materials (FFFH) in Denmark, Toy Industries of Europe (TIE) and Nordic toys. However, TIE did not react to our enquiry and the Joint Council of the Danish Toy Trade referred to the individual manufacturers.

FFFH replied that the Council is highly focused on CMR substances in materials for use in creative activities and for hobby use; for example play dough can be relevant for a toy manufacturer. FFFH has laid down a series of industry specific requirements to chemical substances in the products that the members produce, import or distribute. In selected areas, these criteria are more stringent than applicable legislation (41) and they are covered by the Council's own A-label (Figure 3), which for example serves to ensure that a product may not contain 0.1% (w/w) or more of substances classified as Carc, Muta or Repr in the categories 1, 2, 3 or 1A, 1B, 2. In order to be able to apply the A-label to their products, the FFFH members must produce a product data sheet, often in consultation with an external consultant, and safeguard compliance with the criteria.

FIGURE 3: A-LABEL OF THE FFFH

By way of introduction, TIE replied that in their opinion RAPEX is not a good indicator of the actions of well-reputed companies and how they control the safety of their toy products. According to TIE, their members have strived to avoid the presence of hazardous substances in toys (including CMR substances) in quantities that could constitute a health hazard to children. TIE members apply a combination of the following criteria in order to safeguard compliance with applicable requirements:

- Procurement of a Bill of Materials (list of raw materials) from suppliers
- Safety assessment of the chemicals used
- Declarations of Compliance from suppliers
- Declarations of non-use of certain chemicals
- Testing (verification) of raw materials and finished products

TIE finds that the revised European Toy Safety Directive, including the compulsory safety assessment of chemicals, has aided the companies to adapt their administration of chemical safety in toys.

2.6 Summary and conclusion

RAPEX notifications only concern toys where the concentration of chemical substances is problematic. Based on RAPEX (Table 4) the materials 'Dyed/painted item' (e.g. toy cars), 'Wood (painted/treated)' (e.g. puzzles) and 'Textiles' (e.g. dolls and soft toys) comprise 62% of the toy products containing CMR substances (refer to Appendix 2 for specific products). In terms of these materials and compared with the CMR substances found when searching the Danish EPA database (Table 1), RAPEX (Table 2), UBA's report (Table 5) and TÆNK (Table 6), metals (especially lead and chromium and nickel and organotin), VOCs (including formaldehyde and toluene) and azo dyes (in particular dyes based on 4-aminoazobenzene) were found frequently in toys.

By far (>60%), most of the toys containing CMR substances were produced in China. The results in this chapter 2 suggest that the likelihood of finding toys containing CMR substances must be most eminent under conditions as described by for example RAPEX, TÆNK and ÖKO-TEST (see sections 2.2.2, 2.4.2, 2.4.3). They are for instance:

- Toys that are free of charge and come together with children's magazines that can be purchased at various newsagents and toys sold together with food (e.g. fast food and candy). It is estimated that these toys are highly likely to contain CMR substances, in view of the price of the primary product and the resulting low cost price for the toy product.
- Merchandise (popular, not least because of intensive marketing) with particular focus on the place of production (e.g. China) – likewise an increased risk of counterfeit products.
- Toy from 'One Euro Shops', supermarket on-the-spot bargains and vending machines with toys.

3. Selecting products and substances for chemical analysis

This chapter is a brief explanation of how the rest of the work in connection with this report was carried out. The recommendation to the Chemical Inspection Service (CIS) of the Danish EPA concerning selection of products for examination of their content of CMR substances was founded on aspects such as the price of the product (focusing on low cost products), country of origin (focusing on China) and to some degree the product's expected useful life in the market (focusing on products characterised by a short life in the market). The survey led to the conclusion (see section 2.6) that these types of products are expected to be most likely to contain CMR substances.

The Chemical Inspection Service extracted 30 toy products from the general recommendation of which 28 products were selected for chemical analysis (see Table 7 below). Two products were rejected; one because it was a cosmetics product (make-up) and not a toy (no. 604) and the other because it was found that the product most likely was identical to one of the other products selected (same appearance and same producer, only another packaging) (no. 606).

TABLE 7

LIST OF THE 28 PRODUCTS SUBJECTED TO CHEMICAL ANALYSIS

CIS sample no.	Product	Material
549	Toy garden tools	Plastic
550	Chalk	Chalk
551	Cloth book	Textile
552	Teddy bear	Textile
553	Flexible ball with a rattle	Plastic
554	Wooden puzzle	Wood
555	Wooden puzzle	Wood
594	Bracelet	Plastic
595	Spider	Plastic
596	Soldiers	Plastic
597	Figurines	Plastic
598	Slime	Slime
599	Toy cars	Metal
600	Wig	Textile
601	Toy car (with soft tyres)	Metal

CIS sample no.	Product	Material
602	Toy cars	Plastic
603	Small bouncing balls	Plastic
604	Accessories for children's magazine	Cosmetics
605	Accessories for children's magazine	Plastic
606	Chalk	Chalk
607	Doll	Textile
608	Skipping rope	Wood
609	Dinosaur	Plastic
610	Toy ball	Plastic
611	Dice (soft material)	Plastic
612	Teddy bear	Textile
613	Sword	Plastic/textile
614	Bow and arrows	Plastic
615	Teddy bear	Textile
616	Tiara	Plastic

The chemical analyses of the selected toy products were conducted according to the following procedure (carried out in chronological order):

- Screening analysis of 28 products
- Quantitative analysis of 24 selected substances from the screening
- Migration analysis of two substances selected from an overall worst-case risk assessment based on 100% migration (see below)

Initially, semi quantitative screenings were conducted by gas chromatography (GC/MS) and screening analyses using X-ray to determine the content of CMR substances or any indication of these in the 28 products. Some of the toys tested were composed of several different materials, e.g. textile, foam, plastic, wood etc. For these products, the screening analyses were conducted either on selected components or on mixed samples of several individual components. See chapter 4 for details about samples and sub-samples.

Based on the results of the screening analyses, 24 substances were selected for quantitative analysis in consultation with the Danish EPA. These substances were selected considering their harmonized classification as CMR or because the substances were self-classified as CMR substances. Finally, one single substance (2-Mercapto-benzotiazol) was included according to the classification of the American authorities.

The results of the quantitative analyses demonstrated that the content of the substances was relatively low. Therefore, it was decided to carry out a worst-case risk assessment assuming that the contents of the substances found in the toys could migrate. In the cases where this method identified a risk, migration analyses were conducted of the substances.

According to the risk assessments, the substances aniline and dimethyltin dichloride (DMTC) produced the highest health hazard and this resulted in a subsequent migration analysis of the two products (skipping rope (608) and figurines (597)) which contained these substances.

The following chapter presents the results from the screening in addition to the quantitative analyses and the migration analyses.

4. Chemical analyses

This chapter presents a description of the method and the results of the screening analyses, quantitative analyses and migration analyses.

Based on the survey, a total of 28 toys were extracted for chemical analysis. Since some of these toys were composed of different materials, several sub-samples were extracted from some of these products for the analyses. Initially, screening analyses using gas chromatography (GC/MS) and X-ray (XRF) were conducted. The screening analyses by GC/MS were carried out to determine the content of volatile and semi-volatile organic compounds, respectively. The screening analyses using X-ray were used to determine the elements contained in the samples as they could provide an indication of the content of inorganic CMR substances and possible metalliferous organic compounds.

4.1 Screening analyses

Screening analyses were conducted of all 28 toys selected for chemical analysis (see chapter 3 for details of the selection of samples). The GC/MS screening analyses were carried out on 27 toys (a total of 33 sub-samples) and X-ray screening was carried out on 10 toys (11 sub-samples). Table 8 below provides a list of the toys and sub-samples subjected to screening analysis.

TABLE 8

SAMPLES AND SUB-SAMPLES SUBJECTED TO SCREENING ANALYSES BY GC/MS AND X-RAY

Sample no.	Product	Sample/Sub-sample for GC/MS	Sample/Sub-sample for X-ray
549	Toy garden tools	Composite sample of the different materials	Red plastic on shovel
550	Chalk	Composite sample of four colours	Yellow chalk
551A	Cloth book	Composite sample of outer textile and edging	-
551B	Cloth book	Composite sample of tie-string, elastics and mirror	-
551C	Cloth book	Composite sample of cloud, grass band, butterflies, snail shell and flower	-
552	Teddy bear	Light brown textile	-
553A	Flexible ball with a rattle	Yellow and blue plastic ring	Yellow ring
553B	Flexible ball with a rattle	Purple, green and pink plastic	-
554	Wooden puzzle	Composite sample of pieces with animals	Red barn
555	Wooden puzzle	Paper and glue	-
594	Plastic bracelet	Selected colours	-
595	Plastic spider	Composite sample of the colours	-

Sample no.	Product	Sample/Sub-sample for GC/MS	Sample/Sub-sample for X-ray
596	Plastic soldiers	Selected colours	-
597	Figurines	Composite sample of the plastic	Composite sample of yellow hair and yellow helmet
598	Toy glue	Sub-sample of the material	-
599	Toy cars	-	Red car
600	Toy wig	Sub-sample of the material	-
601	Toy car (with soft tyres)	Sub-sample of the soft tyres	Chassis
602A	Toy cars	Mixture of miscellaneous colours	Red car
602B	Toy cars	-	Yellow car
603A	Small bouncing balls	Sub-sample of the material, ball 1	-
603B	Small bouncing balls	Sub-sample of the material, ball 2	-
605	Toys for children's magazine	Sub-sample of the coloured plastic from rocket	-
607A	Textile doll	Composite sub-sample of hair and head	-
607B	Textile doll	Clothes	-
608A	Skipping rope	Scraping of green paint	-
608B	Skipping rope	Red ears from the figurine on the handle of the skipping rope	-
609	Dinosaur	Mixed sample of coloured plastic	-
610	Toy ball	Purple handle	-
611	Dice (soft plastic)	Sub-sample of the material	-
612	Teddy bear	Composite sample of dyed textile	-
613	Sword	Red textile on handle	Red scabbard
614	Bow and arrows	Yellow handle	-
615	Teddy bear	Composite sample of the textile	-
616	Tiara	Sub-sample of the material	Sub-sample of the material

-: Not analysed.

4.1.1 Screening analyses by GC/MS

Thirty-three sub-samples were screened for their content of volatile and semi-volatile organic compounds. The analyses cover an extensive number of volatile and semi-volatile organic compounds but the method is not equally ideal for all substances. For example volatile aldehydes, including formaldehyde, will not be found by using this method. Isocyanates, which may be present in the form of residual monomers, also require a specific analysis method. Since all substances were calculated against an internal standard, the results of the GC/MS screening must be considered semi-quantitative.

4.1.2 Analysis methods for screening analyses by GC/MS

Sub-samples of the selected materials (about 0.5–1.5 g, carefully weighed) were extracted by means of dichloromethane:acetone (1:1) with added deuterium-marked internal standards of naphthalene-d_8 and phenanthren-d_{10} using ultrasound for one hour followed by mechanical shaking for one

hour. The extract was analysed using capillary gas chromatography with mass spectrometry detection (GC/MS). The analyses were carried out by single analysis. The detected main components were identified by comparing the current mass spectrum with the mass spectrum in the NIST library[7].

The stated quantities were calculated using the response from the deuterium-marked internal standards of naphthalene-d_8 and phenanthren-d_{10} (semi-quantitative determination). The detection limits vary from 1 mg/kg to 50 mg/kg, depending on matrix and substance response. All substances demonstrated above the detection limit of the individual substances are reported. Table 9 lists the results for the 33 samples and sub-samples.

4.1.3 Results from screening analyses by GC/MS

TABLE 9

SAMPLE 549, PLASTIC SHOVEL, COMPOSITE SAMPLE OF MISCELLANEOUS COMPONENTS AND COLOURS
RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Chlorotrimethyltin	1066-45-1	22
2-Ethylhexanol	104-76-7	140
2-Ethyl-1-hexylacetate	103-09-3	24
2-Ethylhexylmercaptoacetate	7659-86-1	710
p-Toluenesulfonamide	70-55-3	30
2-Ethylhexylfumarat	141-02-6	8.0
Dioctadecyl thiodiacetate	4261-52-3	9.0
Bis(2-ethylhexyl)-terephthalate	6422-86-2	3200
Dilauryl-thiodipropionate (Advastab 800)	123-28-4	36
Sum of two unidentified substances		68

#Repr 2 (self-classified CLP classification).

TABLE 10

SAMPLE 550, CHALK, COMPOSITE SAMPLE OF FOUR COLOURS, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
1,4-Dichlorobenzene	106-46-7	2.0
Sum of o-, m-, p-Chloroaniline	95-51-2/108-42-9/106-47-8	2.0
Sum of 2,5- and 2,4-dichlorobenzamin	95-82-9/554-00-7	19
Aliphatic hydrocarbons, C_{15}–C_{30}	-	770

#Carc 2 (harmonised CLP classification); ## p-Chloranilin: Carc 1B (harmonised CLP classification), o-Chloranilin: Carc 1B, Muta 2, Repr 2 (self-classified CLP classification).

[7] National Institute of Standards and Technology (NIST), USA.

TABLE 11
SAMPLE 551, CLOTH BOOK, SUB-SAMPLE A: COMPOSITE SAMPLE OF OUTER TEXTILE AND EDGING, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Benzophenone	119-61-9	9.0
α,β-Di(5-methylbenzoxazol-2-yl)-ethen	1041-00-5	10
Squalene	111-02-4	6.0
1.1,4-Bis(aminomethyl)anthra-9,10-quinon	77862-13-6	13
2-(4-Acetylphenylamino)-1,4-naphthoquinon	88590-25-4	130
Diethyl 4-oxo-4H-quinolizin-1,3-dicarboxylate	54401-76-2	63
C.I. Disperse Blue 72	81-48-1	180
C.I. Disperse Red 60	17418-58-5	43

TABLE 12
SAMPLE 551, CLOTH BOOK, SUB-SAMPLE B: COMPOSITE SAMPLE OF TIE-STRING, ELASTICS AND MIRROR RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
2,4,7,9-Tetramethyl-5-decyn-4,7-diol	126-86-3	17
Dodecanoic acid	143-07-7	7
Benzyl benzoate	120-51-4	600
1,4-Butoxy-2,3-dicyanophenyl 4-(4-butylcyclohexyl)-benzoate	75941-90-1	19
1,4-Butoxy-2,3-dicyanophenyl 4-(4-butylcyclohexyl)-benzoate	75941-90-1	32
2-Mercaptobenzothiazole	149-30-4	57
Olein acid	112-80-1	54
Cryptopinone	472-39-9	25
Dehydroabietate	1740-19-8	79
Sum of two unidentified substances	-	120

Carc 1B (self-classified CLP classification).

TABLE 13
SAMPLE 551, CLOTH BOOK, SUB-SAMPLE C: COMPOSITE SAMPLE OF CLOUD, GRASS BAND, BUTTERFLIES, SNAIL SHELL AND FLOWER, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Benzophenone	119-61-9	6.2
Squalene	111-02-4	6.2
C.I. Disperse Red 60	17418-58-5	16
Sum of two unidentified substances	-	24

TABLE 14

SAMPLE 552, TEDDY BEAR, LIGHT BROWN TEXTILE, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Volatile and semi-volatile organic compounds	-	< 50

TABLE 15

SAMPLE 553, SUB-SAMPLE A: FLEXIBLE BALL WITH RATTLE, YELLOW AND BLUE COLOURS,
RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Nonanal	124-19-6	0.9
o-phthalic acid	88-99-3	3.1
Butylated hydroxytoluene (BHT)	128-37-0	19
Irganox 1076	2082-79-3	480
Aliphatic hydrocarbons, C_{15}–C_{34}	-	133000
Sum of two unidentified substances	-	130

#Carc 1B, Carc 2, Muta 1B, Muta 2, Repr 2 (self-classified CLP classification).

TABLE 16

SAMPLE 553, SUB-SAMPLE B: FLEXIBLE BALL, PURPLE, GREEN AND PINK
RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Butylated hydroxytoluene (BHT)	128-37-0	35
Irganox 1076	2082-79-3	360
Aliphatic hydrocarbons, C_{15}–C_{34}		101000
Sum of two unidentified substances		77

Carc 1B, Carc 2, Muta 1B, Muta 2, Repr 2 (self-classified CLP classification).

TABLE 17

SAMPLE 554, WOODEN PUZZLE, COMPOSITE SAMPLE OF PIECES WITH ANIMALS
RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Toluene	108-88-3	20
Hexanal	66-25-1	17
Hexan acid	142-62-1	27
1-Octanol	111-87-5	6
Octan acid	124-07-2	6
Nonanoic acid	112-05-0	37
Unidentified	-	8
Sum of hydrocarbons, $C_{21}H_{44}$ – $C_{34}H_{70}$	-	2200
β-Sitosterol	83-46-5	13

Repr 2 (harmonised CLP classification); ## Muta 2 (self-classified CLP classification).

TABLE 18
SAMPLE 555, WOODEN PUZZLE, PAPER AND GLUE, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
D-Limonene	5989-27-5	4
β-Eudesmin	17066-67-0	15
Benzophenone	119-61-9	64
Dibutyl phthalate (DBP)	84-74-2	140
β-Sitosterol	83-46-5	47
Unidentified additive	-	260
Aliphatic hydrocarbons, C_{20}–C_{34}	-	11200

TABLE 19
SAMPLE 594, PLASTIC BRACELET, SELECTED COLOURS, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Tetradecamethylcycloheptasiloxane	107-50-6	64
Hexadecamethylcyclooctasiloxane	556-68-3	230
Octadecamethylcyclononasiloxane	556-71-8	290
Eicosamethylcyclodecasiloxane	18772-36-6	350
Hexadacanoic acid	57-10-3	270
Siloxane	-	340
Octadecaneoic acid	57-11-4	410
Sum of siloxanes	-	6400

TABLE 20
SAMPLE 595, PLASTIC SPIDER, MISCELLANEOUS COLOURS, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Aliphatic hydrocarbons, C_{13}–C_{36}	-	213000

TABLE 21
SAMPLE 596, PLASTIC SOLDIERS, SELECTED COLOURS, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Diisobutyl phthalate (DIBP)	84-69-5	97
Dibutyl phthalate (DBP)	84-74-2	64
Eicosan	112-95-8	35
Sum of hydrocarbons, $C_{21}H_{44}$ – $C_{26}H_{54}$	-	320
Bis (2-ethylhexyl)phthalate (DEHP)	117-81-7	530
Unidentified substance	-	18

TABLE 22
SAMPLE 597, PLASTIC FROM FIGURINES
RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Methylmethacrylate	80-62-6	15
Chlorotrimethyltin	1066-45-1	95
p-Xylene	106-42-3	7
Cyclohexanone	108-94-1	180
Dimethyltin dichloride	753-73-1	130
C_9H_{12}-aromate	E.g. 620-14-4	13
Butylmethacrylate	97-88-1	8
2-Ethyl-1-hexanol	104-76-7	350
$C_{10}H_{16}$-aromate	-	24
2-Ethyl-1-hexylacetate	103-09-3	17
Sum of 2,4-, 3,4- and 3,5-dimethylbenzamin	95-68-1/95-64-7/ 108-69-0	17
2-Ethylhexyl thioglycolate	7659-86-1	1060
Dinonylester-1,2-Cyclohexandicarboxyl acid	NIST 339405*	25500

*This substance has no CAS no. in the NIST library. # Repr 2 (self-classified CLP classification); ## Repr 1B (self-classified CLP classification); ### Repr 2 (according to future harmonised CLP classification (4)); #### Muta 2 (self-classified CLP classification).

TABLE 23
SAMPLE 598, TOY SLIME, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
1,2-Propandiol	4254-14-2	3
Di-1,2-propylene glycol	110-98-5	5
o-Toluenesulfonamide	88-19-7	44
p-Toluenesulfonamide	70-55-3	84
o-Tolylsulfone	01/12/5097	3
Bisphenol A	80-05-7	2
Di-p-Tolylsulfone	599-66-6	5

Carc 1A, Carc 2 (self-classified CLP classification); ## Repr 2 (self-classified CLP classification); ### Repr 2 (harmonised CLP classification).

TABLE 24
SAMPLE 600, ORANGE WIG
RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Unidentified additive	-	23
hydrocarbons from plastic (PE or PP)	-	Found

TABLE 25
SAMPLE 601, SOFT TYRES FROM TOY CAR, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Aliphatic hydrocarbons, C_{16}	-	91
Aliphatic hydrocarbons, C_{16}–C_{18}	-	180
Aliphatic hydrocarbons, C_{18}	-	80
Unidentified	-	110
Bis(2-ethylhexyl)-terephthalate	6422-86-2	13300

TABLE 26
SAMPLE 602, PLASTIC CARS, VARIOUS COLOURS, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Butylcitrate	77-94-1	30
Unidentified, might be an aromatic bromine compound	-	4.0
Diglycidyl-bisphenol A	1675-54-3	14

TABLE 27
SAMPLE 603, RUBBER BALLS, SUB-SAMPLE A: BALL 1, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
2,2-Diethylhexanal	996-12-3	26
1,1,2,2-Tetrachloroethane	79-34-5	10
2,2,4,6,6-Pentamethylheptane	13475-82-6	7
Dihydroisophorone	873-94-9	28
Aliphatic hydrocarbons, C_{10}–C_{32}	-	120000

Carc 2 (self-classified CLP classification).

TABLE 28
SAMPLE 603, RUBBER BALLS, SUB-SAMPLE B: BALL 2, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
2,2-Diethylhexanal	996-12-3	74
1,1,2,2-Tetrachloroethane	79-34-5	25
2,2,4,6,6-Pentamethylheptane	13475-82-6	12
Dihydroisophorone	873-94-9	51
Aliphatic hydrocarbons, C_{10}–C_{32}	-	150000

Carc 2 (self-classified CLP classification).

TABLE 29
SAMPLE 605, COLOURED PLASTIC FROM TOYS FROM CHILDREN'S MAGAZINE, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Toluene	108-88-3	12
Chlorotrimethyltin	1066-45-1	11
Dimethyltin dichloride	753-73-1	38
a-Methylstyrene	98-83-9	15

Component	CAS no.	Contents [mg/kg]
2-Ethyl-1-hexanol	104-76-7	62
2-Ethyl-1-hexylacetate	103-09-3	11
Triacetin	102-76-1	17
2-Ethylhexyl thioglycolate	7659-86-1	130
o-Toluenesulfonamide	88-19-7	99
p-Toluenesulfonamide	70-55-3	310
1-Phenyl-1,3,3-trimethylindan	3910-35-8	43
2,3-Dimethyl-2,3-diphenylbutan	1889-67-4	24
Methylhexadecanoate	112-39-0	99
Hexadecanoic acid	57-10-3	41
Methyl stearate	112-61-8	51
2-Ethylhexyl methyl isophthalate	NIST 368502*	63
Methyl epoxystearate	2500-59-6	150
Terephthalate	6422-86-2	8400

* This substance has no CAS no. in the NIST library. # Repr 2 (harmonised CLP classification); ## Repr 2 (according to future harmonised CLP classification (4)); ### Repr 2 (self-classified CLP classification); #### Care 1A, Carc 2 2 (self-classified CLP classification).

TABLE 30
SAMPLE 607, TEXTILE DOLL, SUB-SAMPLE A: HAIR AND HEAD, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
3-Penten-2-ol	1569-50-2	9
3-Penten-2-on	625-33-2	7
1,1,2,2-Tetrachloroethane	79-34-5	5
Benzyl benzoate	120-51-4	19
Unidentified (might be sulphur-containing dye)	-	22
Unidentified (might be silane)	-	34

TABLE 31
SAMPLE 607, TEXTILE DOLL, SUB-SAMPLE B: CLOTHES, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Methylmethacrylate	80-62-6	79
Toluene	108-88-3	12
3-Penten-2-on	625-33-2	9
1,1,2,2-Tetrachloroethane	79-34-5	8
Neopentyl glycol	126-30-7	23
1,4-Butandiol	110-63-4	15
Dimethyl 2-methyl-5-methylenhexandioate	4513-62-6	8

Component	CAS no.	Contents [mg/kg]
Sum of 2,4- and 2,6-Toluene diisocyanate	584-84-9	330
5-Methyl-2-benzimidazolinon	5400-75-9	11
4,4'-Diphenylmethane diisocyanate (MDI)	101-68-8	40
Sum of two unidentified substances	-	110
Sum of three unidentified additives		150

Repr 2 (self-classified CLP classification); ## Repr 2 (harmonised CLP classification); ### Carc 2 (harmonised CLP classification).

TABLE 32
SAMPLE 608, SKIPPING ROPE WITH GREEN HANDLE, SUB-SAMPLE A: SCRAPING OF GREEN PAINT RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Phenyl isocyanate	103-71-9	160
Benzaldehyde	100-52-7	200
Aniline	62-53-3	180
Dipropylene glycol monomethyl ether	20324-32-7	390
Benzoyl alcohol	100-51-6	400
4,4-Dimethylcyclohexadienon	1073-14-9	49
Octahydro-4,7-methanoinden	6004-38-2	41
m-, o- or p-Chloroaniline	108-42-9/95-51-2/ 106-47-8	41
4-Chlorophenylisocyanate	104-12-1	210
Dipropylene glycol n-butylether	29911-28-2	1300
o-phthalic acid	88-99-3	110
Kodaflex (TXIB)	6846-50-0	580
3-Hydroxy-2,4,4-trimethylpentyl 2-methyl propanoate	74367-34-3	830
Dodecanol	112-53-8	280
4-Chlor-2-nitroaniline	89-63-4	59
N-(2-Chloro-1-benzofuran-3-yl)-acetamide	67382-11-0	470
2-Chlorobenzonitril	873-32-5	140
Costuslactone	553-21-9	25
Sum of three unidentified substances	-	12000

Carc 2 (self-classified CLP classification); ## Carc 2, Muta 2 (harmonised CLP classification); ### p-Chloranilin: Carc 1B (harmonised CLP classification), o-Chloranilin: Carc 1B, Muta 2, Repr 2 (self-classified CLP classification).

TABLE 33
SAMPLE 608, SKIPPING ROPE WITH GREEN HANDLE, SUB-SAMPLE B: RED EARS ON HANDLE RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]*
Cyclohexanone	108-94-1	Found
Benzaldehyde	100-52-7	Found
Benzoyl alcohol	100-51-6	Found
Octahydro-4,7-methanoinden	6004-38-2	Found
Butyldiglycol	112-34-5	Found
o-phthalic acid	88-99-3	Found
Kodaflex (TXIB)	6846-50-0	Found
3-Hydroxy-2,4,4-trimethylpentyl 2-methyl propanoate	74367-34-3	Found
Tetramethyl decyndiol	126-86-3	Found
Dodecanol	112-53-8	Found
1-[2-(Isobutyryloxy)-1-methylethyl]-2,2-dimethylpropyl 2-methylpropanoate	74381-40-1	Found
2-Isopropoxyethyl benzoate	95241-36-4	Found
Hexadecanoic acid (palimitic acid)	57-10-3	Found
γ-Stearolactone	502-26-1	Found
Diglycol dibenzoate	120-55-8	Found

* Concentrations are not stated in mg/kg since both ears of the figurine on the skipping rope were analysed with both wood and applied paint.

TABLE 34
SAMPLE 609, DINOSAUR, COLOURED PLASTIC, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
sec-Butylacetate	105-46-4	28
Toluene	108-88-3	15
Ethylbenzene	100-41-4	40
Sum of m- and p-xylene	108-38-3/106-42-3	30
Sum af o-xylene and styrene	95-47-6/100-42-5	35
1,1,2,2-Tetrachloroethane	79-34-5	8
Butylmethacrylate	97-88-1	7
D-Limonene	5989-27-5	19
n-Tridecane	629-50-5	7
hydrocarbon, $C_{14}H_{28}$	-	15
n-Tetradecane	629-59-4	24
p-Toluenesulfonamide	70-55-3	30
Bis(2-ethylhexyl)-phthalate	117-81-7	25

Component	CAS no.	Contents [mg/kg]
Bis(2-ethylhexyl)-terephthalate	6422-86-2	17
Unidentified additive	-	53

Repr 2 (harmonised CLP classification); ## Not classified as CMR under harmonised CLP classification (current, and future amendment (4)), but notified as Carc 2 under previous self-classified CLP classification; ### p-xylene: Repr 1B (self-classified CLP classification); #4: styrene: Repr 2 (harmonised CLP classification); #5: Repr 2 (self-classified CLP classification).

TABLE 35
SAMPLE 610, TOY BALL, PURPLE PLASTIC HANDLE, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
2,4-Dimethylheptan	2213-23-2	17
1,3-Dimethylheptan	2216-34-4	5
Sum of two unidentified additives	-	80

TABLE 36
SAMPLE 611, DICE IN SOFT PLASTIC, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
$C_{30}H_{52}O_2$ components*	-	176000

* No sign of any PAH content (polyaromatic hydrocarbons).

TABLE 37
SAMPLE 612, TEDDYB BEAR, COMPOSITE SAMPLE OF DYED TEXTILE, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
6-Methoxyquinolin-1-oxide	6563-13-9	4
Benzyl benzoate	120-51-4	6
5,6-Dichlor-2-benzothiazolamine	24072-75-1	26
9-Octadecenamide	301-02-0	4
C.I. Disperse Red 60/71/83	17418-58-5	48
Sum of four unidentified substances	-	200
Aliphatic hydrocarbons, C_{20}–C_{26}	-	410

TABLE 38
SAMPLE 613, SWORD, RED TEXTILE ON HANDLE, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
1,1,2,2-Tetrachloroethane	79-34-5	5
n-Dodecan	112-40-3	11
Decanoic acid	143-07-7	120
Octaethylene glycol monododecyl ether	3055-98-9	23
Isopropyl myristate	110-27-0	23
n-Hexadecanoic acid	57-10-3	130
Hepta-ethylene glycol	5617-32-3	76
Sum of four unidentified substances	-	1500

TABLE 39
SAMPLE 614, BOW AND ARROWS IN PLASTIC, YELLOW HANDLE, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Trichloroacetone	918-00-3	8
1,1,2,2-Tetrachloroethane	79-34-5	20
o-Toluenesulfonamide	88-19-7	38
p-Toluenesulfonamide	70-55-3	69
Bis(2-ethylhexyl)-phthalate	117-81-7	18
Bis(2-ethylhexyl)-terephthalate	6422-86-2	8
Unidentified additive	-	68

Carc 1A, Carc 2 (self-classified CLP classification); ## Repr 2 (self-classified CLP classification).

TABLE 40
SAMPLE 615, TEDDY BEAR, COMPOSITE SAMPLE OF TEXTILE, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
9-Octadecenamide	301-02-0	4
Decyl oleate	3687-46-5	19
Perhaps silane	-	39
Sum of four unidentified substances	-	68

TABLE 41
SAMPLE 616, SILVERY TIARA, RESULTS OF SCREENING BY GC/MS

Component	CAS no.	Contents [mg/kg]
Toluene	108-88-3	54
Ethylbenzene	-	6
m-, p-Xylene	-	13
o-Xylene	-	16
Sum of 2,4- and 2,6-Toluene diisocyanate	584-84-9/91-08-7	9
Sum of three unidentified substances	-	94
Unidentified additive	-	12

Repr 2 (harmonised CLP classification); ## Not classified as CMR under harmonised CLP classification (current and future amendment (4)), but notified as Carc 2 under previous self-classified CLP classification; ### p-xylene: Repr 1B (self-classified CLP classification); m- and o-Xylene: Repr 2 (self-classified CLP classification); #4: Carc 2 (harmonised CLP classification).

As mentioned in the introduction, GC/MS screening covers a wide range of volatile and semi-volatile organic compounds but the method is not suitable for all substances. For example volatile aldehydes, including formaldehyde, will not be found by using this method. Isocyanates also require a specific analysis method. For this reason quantitative analyses were conducted for these substances. The results from the GC/MS screening analysis were used to select the quantitative specific analyses for organic CMR substances. See chapter 4.2 for a discussion of the selected quantitative analyses.

The screening demonstrated a number of substances that were unidentifiable since they were not available in the NIST library. There will be no health assessments nor any environmental assessments of these substances and therefore they will not be discussed further in this report. For a list of sub-samples for quantitative analyses, see chapter 4.2, Quantitative analyses.

4.1.4 Screening analyses by X-ray

Ten pieces of toy generating a total of eleven sub-samples were extracted for X-ray (XRF) screening analysis. Screening by X-ray will reveal all elements with an atomic number higher than 8. Consequently, the X-ray analysis can determine whether the samples contain heavy metals and indicate whether critical inorganic compounds or organic metalliferous compounds are present.

4.1.5 Analysis methods for screening analyses by X-ray

The samples were analysed for their content of elements using wavelength dispersive (WD) X-ray analysis; Philips PW2400/UNIQUANT ver. 5.49.

All elements found to be above the detection limit were reported quantitatively. The detection limits and the estimated uncertainty of the analyses, which varies for the samples, can be found in Table 42 below, which lists the results of the analyses.

4.1.6 Results from the screening analyses by X-ray

TABLE 42
ANALYSIS RESULTS - SCREENING ANALYSES BY X-RAY IN W/W%

Unit: w/w% Component	549	550	553	554	597	599	601	602 red	602, yellow	613	616
Magnesium (Mg)	0.005	0.12	0.01	0.24	<0.01	<0.01	0.004	0.05	0.08	0.003	0.02
Aluminium (Al)	0.013	0.19	<0.01	0.030	0.21	3.2	5.9	0.67	0.72	0.005	1.0
Silicon	0.017	0.50	<0.01	0.041	<0.01	0.03	8.4	0.96	1.1	0.010	0.03
Phosphorous (P)	0.003	0.003	<0.01	0.011	0.01	0.01	0.024	0.12	0.14	0.002	<0.01
Sulphur (S)	0.084	17	0.56	0.087	0.08	<0.01	1.9	0.18	0.22	0.036	<0.01
Chlorine (Cl)	0.009	0.013	0.02	0.390	9.3	<0.01	1.0	0.68	3.7	0.015	0.06
Calcium (Ca)	0.008	22	1.2	18	0.29	<0.01	0.076	0.09	0.06	0,080	<0.01
Titanium (Ti)	0.023	0.016	0.06	0.003	1.4	1.2	3.1	13	31	0.043	<0.01
Iron (Fe)	<0.001	0.18	<0.01	0.019	<0.01	<0.01	0.11	0.03	0.03	0.004	<0.01
Copper (Cu)	<0.001	0.001	<0.01	<0.001	<0.01	<0.01	0.087	0.02	<0.01	0.002	<0.01
Zink (Zn)	0.003	<0.001	0.02	0.002	<0.01	6.1	77	84	62	0.002	<0.01
Zirconium (Zr)	0.001	<0.001	<0.01	0.002	<0.01	<0.01	<0.001	0.05	0.09	0.001	<0.01
Molybdenum (Mo)	<0.001	0.003	<0.01	0.002	<0.01	<0.01	0.011	0.02	0.02	<0.001	<0.01
Tin (Sn)	<0.001	0.001	<0.01	0.001	0.11	<0.01	0.003	<0.01	<0.01	<0.001	<0.01
Detection limit	0.001-0.002	0.001-0.002	0.01	0.001-0.002	0.01	0.01	0.001-0.002	0.02	0.01	0.001-0.002	0.01
%RSD	10	10	20-60	10	20-60	20-60	10	20-60	20-60	10	20-60

Samples 553, 597, 599, 601, 602 red and 602 yellow and 616 either do not have a plane surface or are inhomogeneous and hence the detection limits and the uncertainty of these analyses are elevated for these samples. In view of the high findings for tin in sample 597 (plastic) from the figurines subjected to X-ray analysis, the sample was also examined for its content of the organotin compound dimethyltin dichloride, which was also found by GC/MS. The X-ray screening analyses did not give rise to additional investigations.

4.2 Quantitative analyses

Based on the semi-quantitative results from the screening analyses, quantitative analyses were conducted for 24 specific CMR substances. These substances were selected in view of their concentration levels (with the highest content concentrations >100 mg/kg). In addition, CMR substances were selected that immediately appeared in a slightly lower concentration. These substances have previously been investigated by the Danish EPA (e.g. styrene).

Considering the screening results, the substances stated in Table 43 were selected for quantitative analysis.

In addition, the following substances that could not be determined through the GC/MS screening analysis were selected for relevant products:

- Selected isocyanates: 2,4- and 2,6-Toluene diisocyanate (2,4- and 2,6-TDI) and 4,4'-Diphenylmethane diisocyanate (MDI)
- Formaldehyde
- Amines derived from the azo dyes

The specific sections discussing the analyses of the substances substantiate the choice of products analysed for these substances.

The table below lists the quantitative analyses on the selected products.

TABLE 43
SAMPLES AND SUB-SAMPLES FOR QUANTITATIVE IDENTIFICATION OF SPECIFIC CMR SUBSTANCES

CMR Substance	Samples
Aniline	608A: Skipping rope, green paint on handles
Butylated hydroxytoluene (BHT)	553A: Flexible ball in soft plastic with rattle, yellow and blue colours 553B: Flexible ball in soft plastic with rattle, yellow and blue colours 611: Dice in soft plastic
Dimethyltin dichloride	597: Figurines, composite sample of the plastic
Dihydrisophorone	603B: Small bouncing balls in plastic, ball 2
Ethylbenzene	609: Dinosaur in plastic
2-Mercaptobenzothiazole	551B: Play book made of textile, composite sample of tie-string, elastics and mirror
Methylmetacrylate	607B: Textile doll, clothes
Phenyl isocyanate	608A: Skipping rope, green paint on handles
Styrene	609: Dinosaur in plastic
Toluene	616: “Silver” tiara
o-Toluenesulfonamide	598: Toy slime 605: Toy from children's magazine, coloured plastic

CMR Substance	Samples
	614: Bow and arrow in plastic, yellow handle
p-Toluenesulfonamide	598: Toy slime 605: Toy from children's magazine, coloured plastic 614: Bow and arrows in plastic, yellow handle
Selected isocyanates: 2,4- and 2,6-Toluene diisocyanate (2,4- og 2,6-TDI) plus 4,4'-Diphenylmethane diisocyanate (MDI)	607B: Textile doll, clothes
Formaldehyde	554: Wooden puzzle, animal pieces 555: Wooden puzzle, paper and glue 598: Toy slime
Azo dyes (derived amines)	600: Orange play wig 607A: Textile doll, hair 607B: Textile doll, head 607C: Textile doll, clothes 608A: Skipping rope, green paint on handles

4.2.1 Analysis method for quantitative analyses by GC/MS

Quantitative analyses were conducted for 13 individual substances using GC/MS analysis (see the list stating CAS no. and detection limit in Table 44). Sub-samples of the selected materials (sub-samples as for the screenings) were weighed carefully (app. 0.5–1.5 g) and extracted by means of a dichloromethane:acetone solvent (1:1) with added deuterium-marked internal standards of naphthalene-d_8 and phenanthren-d_{10} using ultrasound for one hour followed by mechanical shaking for one hour. The extract was analysed using capillary gas chromatography with mass spectrometry detection (GC/MS). The quantification was carried out against external standards of all substances. Two independent control samples were produced as calibration standards. True double determination was conducted and the average double determinations are reported.
The detection limits can be found in Table 44.
The uncertainty of the analysis is 10-25% RSD, depending on the substance and the matrix.

4.2.2 Analysis results for the quantitative analyses by GC/MS

The analysis results can be found in Table 44.

The results of the quantitative analyses of specific substances using GC/MS show that the thresholds applicable to the individual substances reported above have not been exceeded. According to the toy directive (1) it is not acceptable if CMR substances are present in concentrations above the classification limit in the easily accessible parts of the toy.

4.2.3 Formaldehyde

Three samples were selected for specific analysis of formaldehyde since formaldehyde is undetectable using GC/MS screening analysis. The two samples of wooden puzzles were selected as glued wooden products may contain formaldehyde. In addition, the toy slime sample was selected as the product may have been preserved by using formaldehyde or formaldehyde liberators.

4.2.4 Analysis method for free formaldehyde by HPLC

Sub-samples were carefully weighed, extracted in an ultrasound bath for 60 minutes at 40°C and derived using DNPH reagent. The formaldehyde derivative was analysed using high-performance liquid chromatography (HPLC) with UV detection. True double determination was conducted and the results and averages are reported. Analytical uncertainty: 15% RSD

4.2.5 Analysis results for free formaldehyde by HPLC

The analysis results can be found in Table 44.
One of the wooden puzzles, sample 554, features with its 190 mg/kg the highest concentration of formaldehyde. However, the formaldehyde content is for all three samples below 1000 mg/kg and therefore under the classification limit of 0.1% (1).

4.2.6 Isocyanates

A single sample was selected for quantitative determination of isocyanates since these were found in the sample in connection with the screening analyses. The samples were analysed for their content of the isocyanates 2,4- and 2,6-toluene diisocyanate (2,4- and 2,6-TDI) and for 4,4'-Diphenylmethane diisocyanate (MDI).

4.2.7 Analysis method for isocyanates by HPLC

Sub-samples were weighed and extracted using dichloromethane with internal standard added and followed by derivatisation. The analysis was conducted using HPLC with fluorescence detector for 2,4- and 2,6-toluene diisocyanate (2,4- and 2,6-TDI), CAS nos. 584-84-9 and 91-08-7 and 4,4'-Diphenylmethan diisocyanate, (MDI), CAS no. 101-68-8. True triple determinations were conducted. The results of these and the averaged are reported. Analytical uncertainty: 15% RSD

4.2.8 Analysis results for isocyanates by HPLC

The analysis results can be found in Table 44. A relatively low content of 2,4- and 2,6-TDI was found in the three sub-samples and no MDI was detected. The GC/MS screening analyses showed a 330 mg/kg concentration content of isocyanates 2,4- and 2,6-TDI in the clothes and a 40 mg/kg concentration content of MDI. The specific analyses for TDI and MDI were unable to repeat these findings. Consequently, it is clear from the results of the specific analyses that GC/MS screening analysis cannot be used to determine the presence of these isocyanates.

4.2.9 Aromatic amines derived from azo dyes

Since the aromatic amines derived from the azo dyes require analysis using a specific method, five samples were selected from the textiles since by experience textiles are highly likely to contain these substances.

4.2.10 Analysis method for aromatic amines derived from azo dyes

The analyses were conducted in accordance with EN 14362-1:2012 (textiles) using GC/MS analysis. A portion of about 0.5 g of the sub-samples of the selected materials was carefully weighed. The analyses were conducted as true double determination. The quantification was conducted as a comparison with external standards of all aromatic amines derived from the azo dyes in accordance with REACH, Annex XVII. Two independent control samples were produced as calibration standards. The analyses were carried out in accordance with an accredited method.

Specific analysis for 4-aminoazobenzen was not conducted since aniline and 4-phenylendiamine were not found in significant quantities.

4.2.11 Analysis results for azo dyes

The analysis results can be found in Table 44.

Aromatic amines derived from the azo dyes were not found in any of the five samples in quantities that exceed the detection limit of 2–5 mg/kg. This means that all five samples comply with the threshold value of 30 mg/kg for the sum of derived amines, as laid down in REACH, Annex XVII.

The analysis comprises a wide range of aromatic amines. A full list of all substances investigated can be found in Appendix 4.

4.2.12 Analysis results for the quantitative analyses

The table below provides an overview of the results of the quantitative analyses of all analysed samples.

TABLE 44
RESULTS FOR QUANTITATIVE DETERMINATIONS

Substance	CAS no.	Sample	Result [mg/kg]	Detection limit [mg/kg]
Aniline	62-53-3	608	650 *	30
Butylated hydroxytoluene (BHT)	128-37-0	553A 553B 611	25 44 230	5
Dimethyltin dichloride	753-73-1	597	1200	550
Dihydroisophorone	873-94-9	603B	69	5
Ethylbenzene	100-41-4	609	26	5
2-Mercaptobenzothiazole	149-30-4	551B	310	120
Methylmetacrylate	80-62-6	607B	120	10
Phenyl isocyanate	103-71-9	608	280*	30
Styrene	100-42-5	609	23	5
Toluene	108-88-3	616	76	5
o-Toluenesulfonamide	88-19-7	598 605 614	81 210 44	30
p-Toluenesulfonamide	70-55-3	598 605 614	160 790 120	30
Formaldehyde	50-00-0	554 555 598	190 44 6.4	0.5
Sum of 2,4- and 2,6-Toluene diisocyanate (2,4- and 2,6-TDI),	584-84-9/ 91-08-7	607B	0.22**	0.01
4,4'-Diphenylmethane diisocyanate (MDI)	101-68-8	607B	< 0.01**	0.01

Substance	CAS no.	Sample	Result [mg/kg]	Detection limit [mg/kg]
Azo dyes (derived amines)	-	600 607A 607B 607C 608A	< 5 < 5 < 5 < 5 < 5	2 – 5***

<: Means less than the detection limit stated. * The sub-sample is paint from the wooden handle of the skipping rope. The sample is not homogeneous since the amount of wood scraped off with the paint varies. ** The sum of 2,4-andg 2,6-TDI in the three types of textile (from the blouse and two types of textile from the skirt) determined through triple determination of each type of textile; *** The detection limit is stated for each amine; #Self-classified CLP classification; ## Not classified as CMR under the harmonised CLP classification, but notified as Carc 2 under previous self-classified CLP classification; ### US EPA category for carcinogens (A: Carcinogenic to humans, B: Probably carcinogenic to humans, C: Possibly carcinogenic to humans); #### The classification stated in the table reflects the classification of the substance according to the future amendment in the CLP regulation (4).

4.3 Migration testing

Based on the results of the quantitative analyses compared with the worst-case risk assessments, which assumed a 100% migration of the substances found, two samples were selected for migration testing, for artificial saliva and artificial sweat, respectively.
The following samples were selected:

TABLE 45
SAMPLES SELECTED FOR MIGRATION TESTING

Sample no.	Product	Sub-sample for migration test	Migration fluid	Substance
597	Figurines	Composite sample of the plastic	Artificial saliva	Dimethyltin dichloride
608A	Skipping rope	Green paint scrapped off handles	Artificial sweat	Aniline

Artificial saliva was selected for migration testing of the figurines because children may very likely be sucking these since the toys are intended for children from only 2 years of age, according to their labelling (2+). Selecting artificial sweat for migration testing of the skipping rope handles was the immediate choice since the handles will be in contact with the palms of the person using the skipping rope.

4.3.1 Method for migration testing

Migration fluid of artificial saliva was produced by means of deionised water, calcium chloride, magnesium chloride, potassium carbonate, potassium chloride, potassium phosphate, sodium chloride and hydrochloric acid for adjustment of pH to 6.8 in accordance with the JRC report, 20001 EUR 19826 EN. The artificial saliva was heated to 37°C in an attempt to copy the body temperature. The sample quantity to migration fluid ratio was 2.5 g to 50 ml simulant.

Migration fluid of artificial sweat was produced in accordance with ISO 105-E04 as for ÖKO-TEST, where the simulant consists of 1-histidine-monohydrochloride-1-hydrate, sodium chloride, sodium dihydrogene-phosphate and sodium hydroxide for adjustment of pH to 5.5. The artificial sweat was heated to 37°C in an attempt to copy the body temperature. The sample quantity to migration fluid ratio was 2.5 g to 50 ml simulant.

A sub-sample with a known weight was extracted from the two samples. The sub-samples were placed in a known quantity of the heated simulant in a temperature controlled heating cupboard at 37°C and in static contact with the simulant for a period of 60 minutes.

After 60 minutes of migration to the artificial saliva or artificial sweat at 37°C, the sub-samples were removed from the migration fluid. The migration fluid was immediately extracted using dichloromethane and stored under cold conditions until it was analysed for specific substances.

The migration tests were conducted as true double determinations.

4.3.2 Analysis method for dimethyltin dichloride in migration fluid

A known sub-sample of the migration was weighed. Extraction was conducted using dichloromethane and the sub-sample was subsequently analysed using GC/MS analysis. Internal standards of deuterated naphthalene and phenanthrene were used. Dimethyltin dichloride was quantified against calibration standards.

4.3.3 Analysis results for dimethyltin dichloride in migration fluid

Dimethyltin dichloride was not found in quantities exceeding the detection limit of 60 mg/kg.

4.3.4 Analysis method for aniline in migration fluid

A known sub-sample of the migration was weighed. Extraction was conducted using dichloromethane and subsequent analysis through GC/MS was carried out. Internal standards of deuterated naphthalene and phenanthrene were used. Aniline was quantified against calibration standards.

4.3.5 Analysis results for aniline in migration fluid

Aniline was not found in quantities exceeding the detection limit of 0.05 mg/kg.

4.4 Summary of the chemical analyses

4.4.1 Summary of the screening analyses

Many different types of toy were selected, and consequently the results of the GC/MS screening analyses for the volatile and semi-volatile organic compounds vary as could be expected.
For some of the samples only very few volatile or semi-volatile organic compounds were found whereas up to 15 different components were found in other samples. 24 CMR substances were found using screening analysis in concentrations that were interesting for the selection of samples for the quantitative analyses. Of these, only 10 CMR substances had a harmonised classification.

The GC/MS screening found a number of substances that were unidentifiable as they do not appear in the NIST library. Therefore, no health assessments will be carried out of these substances and they will not be discussed further in this report.

X-ray analysis detected only one single potentially critical result, i.e., a high content of tin in sample 597 from toy figurines (plastic). In the same sample, the GC/MS screening analysis detected some dimethyltin dichloride. The content was confirmed by the quantitative analysis.

4.4.2 Summary of the quantitative analyses

Formaldehyde was found in all three samples selected for the analysis. One of the wooden puzzles, sample 554, contains with 190 mg/kg the highest concentration of formaldehyde. However, the formaldehyde content is for all three samples below 1000 mg/kg.

A relatively low content of 2,4- and 2,6-TDI was found in the three sub-samples of clothes and no MDI was detected. The GC/MS screening analyses showed a 330 mg/kg concentration content of isocyanates 2,4- and 2,6-TDI in the clothes and a 40 mg/kg concentration content of MDI. The specific analyses for TDI and MDI were unable to repeat these findings. Consequently, it is clear from the results of the specific analyses that GC/MS screening analysis cannot be used to determine the presence of these isocyanates.

Aromatic amines derived from the azo dyes were not found in any of the five samples in quantities that exceed the detection limit of 2–5 mg/kg. This means that all five samples comply with the threshold value of 30 mg/kg for the sum of derived amines, as laid down in REACH, Annex XVII.

The results of the quantitative analyses of specific substances using GC/MS show that the current limit of each CMR substance in toys has not been exceeded.

4.4.3 Summary of the migration testing

Migration testing found no liberation of aniline or dimethyltin dichloride for artificial saliva or artificial sweat, despite the very high content of both substances in the samples. This means that the substances do not migrate to the water-based simulant due to the physical and/or chemical binding of the substances in the products.

4.4.4 Summary of chemical analyses compared to the results of the survey

The chemical analyses identified many of the same CMR substances that according to the survey typically are used in toys, e.g., substances such as toluene, BHT, styrene and formaldehyde. There is also good accordance between the type of toy, material and the identified CMR substances in the survey and the chemical analyses, respectively, carried out in this project. According to the survey, formaldehyde is typically found in wooden toys and ethylbenzene, toluene and styrene are e.g. typically found in plastic materials, which the chemical analyses of this project also demonstrated. A lot of information was not found in connection with the survey concerning concentration intervals for the individual CMR substances in toys, but for formaldehyde a concentration interval of 100-999 mg/kg was stated for painted/treated wood (Table 4). That concentration interval is in good accordance with the 190 mg/kg formaldehyde that was found in a wooden puzzle (sample 554).

5. Selecting CMR substances for exposure, health and risk assessment

Based on the quantitative analysis results (see section 4.2) a total of ten CMR substances were selected for exposure, health and risk assessment. Generally, the selection focused on the CMR substances featuring the highest content concentrations (>100 mg/kg) of the toy products concerned and on the CMR substances, which are classified as mutagenic (Muta) and carcinogenic (Carc).

The 10 selected CMR substances and their classification appear in Table 46.

TABLE 46: SELECTED SUBSTANCES FOR EXPOSURE, HEALTH AND RISK ASSESSMENT

Substance	CAS no.	CMR category	Detailed explanation of CMR category
2-Mercapto-benzothiazole (MBT)	149-30-4	Carc C *	US EPA classification. Not CMR substance according to the harmonised classification. Previous self-classifications state 3 notified out of 1258 Carc 1B.
Aniline	62-53-3	Carc 2, Muta 2	Harmonised classification
Butylated hydroxytoluene (BHT)	128-37-0	Carc 1B/2, Muta 1B/2, Repr 2	Self-classification: 1/10 notified out of 3625 9/3 notified out of 3625 10 notified out of 3625
Dimethyltin dichloride (DMTC)	753-73-1	Repr 2	Harmonised classification
Ethylbenzene	100-41-4	Carc 2	Not CMR substance according to the harmonised classification. Previous self-classifications state 18 notified out of 3941 Carc 2
Formaldehyde	50-00-0	Carc 1B, Muta 2	Harmonised classification
Phenyl Isocyanate	103-71-9	Carc 2	Self-classification 1 notified out of 269

Substance	CAS no.	CMR category	Detailed explanation of CMR category
Styrene	100-42-5	Repr 2	Harmonised classification
o-Toluensulfonamide (o-TSA)	88-19-7	Carc 1A/2	Self-classification 1/25 notified out of 42
p-Toluensulfonamide (p-TSA)	70-55-3	Repr 2	Self-classification 3 notified out of 204

*US EPA category for carcinogens (A: Carcinogenic to humans; B: Probably carcinogenic to humans; C: Possibly carcinogenic to humans).

6. Exposure scenarios

6.1 Background

As described in the summary, this project has focused on the expected content of CMR substances in different types of toys such as:

- Toys sold to children together with magazines, for example in kiosks, and toys sold together with food (for example fast food and sweets)
- Products produced under licence (popular brands, especially due to extensive marketing) with a particular focus on where the product is manufactured (also an increased risk of copy products)
- Toy from 'One Euro Shops', supermarket on-the-spot bargains and vending machines with toys
- Toys produced in China

This project focused on these types of toys, as they are highly likely to contain CMR substances, since the price of the product is expected to be low, and the product is often sold for a brief period only (limited possibility of control).

The degree to which the consumer will be exposed to the CMR substances in the toys (dermally and orally) will depend on a variety of parameters, such as:

- The route of exposure (how a person is exposed to the CMR substances)
- The duration of exposure
- The frequency of exposure
- The amount of product used/ingested
- The amount of CMR substances in the product
- The amount of CMR substance to which a person is actually exposed when using the product
- Individual and age-specific parameters such as body weight and skin area
- Absorption of the substance

Most exposure scenarios are covered by the REACH regulation: *"Guidance on Information Requirements and Chemical Safety Assessment. Chapter R.15 - Consumer exposure estimation",* version 2.1 dated October 2012 (42). Recommendations for relevant parameters can be found in the regulation as well as other sources, such as "Existing Default Values and Recommendations for Exposure Assessment" (46) and relevant publications from the Dutch research institute, RIVM[8] (43-45). Initially, an assessment has been made on the basis of worst-case scenarios. If worst-case scenarios show a high risk, more refined scenarios will subsequently be assessed according to selected parameters. The parameters are described in more detail in Table 47.

[8] Rijks Instituut voor Volksgezondheid & Milieu (RIVM), The National Institute for Public Health and the Environment, the Netherlands

TABLE 47
DESCRIPTION OF PARAMETERS THAT AFFECT EXPOSURE

Parameter	Description
Route of exposure	The route of exposure may be oral, dermal or through inhalation, depending on how the product is used. A toy designed for very young children presents a risk that part of the substance will migrate out of the product and be swallowed if the child sucks on the product.
Duration	The duration is determined on the basis of the expected use of the product and has in impact on the exposure. The duration will be relevant if a substance, for example, migrates out of a product at a known speed. This increases the exposure if the product is used over an extended period of time.
Frequency	The frequency is determined according to expected use, i.e. it is estimated how many times a product is used per day or per year.
The amount of product used/ingested	The amount of product to be taken into consideration in terms of exposure is determined on the basis of the above-mentioned parameters. Examples are the overall size of the product or rather the part of the product that enters the mouth.
The amount of substance in the product	The concentration of the substance in a product will determine the extent of the exposure. This can often be determined by chemical analysis.
The amount of substance to which a person is actually exposed	A person using the product is often not exposed to 100% of the substance contained in the product. Depending on the properties of the substance, it may migrate out of a toy into sweat or saliva at a certain rate. This means that the actual amount to which a person is exposed will depend on the duration of use.
Body weight	The risk associated with exposure to a specific amount of substance often depends on the person exposed. In children, whose total body weight is less than that of an adult, a given amount of substance will result in a higher exposure per kg, which means that the toxicological limit values are more easily exceeded in children.
Absorption of the substance	Generally, the body does not absorb 100% of a substance to which a person is exposed orally, dermally or through inhalation. Substances are absorbed in the system at different rates depending on their properties. A lower rate of absorption results in a lower degree of exposure to the substance.

Eleven products were selected for exposure assessment. An initial worst-case scenario assessment of exposure and risk was undertaken on the basis of the quantitative analyses. This assessment was based on the assumption that the entire content of the substances identified in the quantitative analyses could migrate. This worst-case scenario assessment was performed to determine whether it was necessary to carry out migration analyses, as the migration of the substance is not expected to exceed the content. According to this worst-case risk assessment, the two substances aniline and dimethyltin dichloride (DMTC) presented the greatest risk, and a migration analysis was therefore performed on the two products containing these substances (skipping rope (no. 608) and toy figurine (no. 597)).

Children aged 3–6 months, 1–3 years or 3–6 years were chosen for the exposure scenarios for the eleven products, based on the age of the children expected to use the products in question (see Table 48). The route of exposure, which, according to the worst-case scenario, is expected to lead to the greatest exposure for each individual product, was also assessed based on expected use and age group. It is estimated that many of the selected products come into contact with skin during use, and that several of the products are used by an age group in which a small amount of oral ingestion of the product may occur if children suck or chew on them during use. The selected products fall

into two categories based on exposure route: dermal exposure and oral exposure. The categories can be seen from Table 48.

Some products can be presumed to result in both oral and dermal exposure, for example toy slime (no. 598), where the product may come into contact with the skin during use, but where oral exposure e.g. as hand-to-mouth transfer is also regarded as a realistic route of exposure. As far as the dice (no. 611) are concerned, oral exposure is not regarded as relevant, as the size of the dice would present a risk of suffocation if used by children who put things in their mouth while playing. In the case of this product, parents are therefore presumed to pay attention during play to prevent the product from being placed in the mouth, which means that exposure to the substances is by dermal contact only. The both book (no. 551) can be opened up and used in bed to prevent the child from falling out. The worst-case exposure is therefore deemed to be dermal exposure in connection with skin contact during sleep.

TABLE 48
OUTLINE OF PRODUCTS USED IN EXPOSURE ASSESSMENT. CHOICE OF AGE GROUP, IDENTIFICATION OF EXPECTED WORST-CASE ROUTE OF EXPOSURE AND QUANTITATIVE ANALYSIS RESULTS FOR SELECTED CMR SUBSTANCES.

Type of toy	Age group	Substance and concentration	Identification of expected worst-case exposure route
Wooden puzzle (554)	1-3-year-old child	Formaldehyde 190 mg/kg	Oral
Wooden puzzle (555)	1-3-year-old child	Formaldehyde 44 mg/kg	Oral
Toy figurine (597)	1-3-year-old child	Dimethyltin dichloride 1200 mg/kg	Oral
Toys for children's magazine (605)	1-3-year-old child	o-Toluenesulfonamide 210 mg/kg p-Toluenesulfonamide 790 mg/kg	Oral
Dinosaur (609)	1-3-year-old child	Ethylbenzene 26 mg/kg Styrene 23 mg/kg	Oral
Flexible ball with rattle (553)	3–6-months-old child	BHT 25 mg/kg (sample A) and 44 mg/kg (sample B)	Dermal and oral
Toy slime (598)	1-3-year-old child	o-Toluenesulfonamide 81 mg/kg Formaldehyde 6.4 mg/kg	Dermal and oral
Cloth book (551B)	3–6-months-old child	2-Mercapto-benzothiazole 310 mg/kg	Dermal
Skipping rope (608)	3-6-year-old child	Aniline 650 mg/kg Phenyl isocyanate 280 mg/kg	Dermal
Dice (soft plastic) (611)	1-3-year-old child	BHT 230 mg/kg	Dermal
Bow and arrow (614)	3-6-year-old child	o-Toluenesulfonamide 44 mg/kg p-Toluenesulfonamide 120 mg/kg	Dermal

6.2 Calculation formulas

The amount of CMR substances in toys to which children are exposed is calculated according to the following formulas, depending on whether the exposure is dermal or oral. Dermal exposure and oral exposure are moreover calculated differently, depending on whether anything is known about the migration of the substances in the products in question.

Formulas are shown for the following scenarios:

- Dermal exposure to substances that migrate out of a product
- Oral exposure to an ingested substance

6.2.1 Dermal exposure to substances that migrate out of a product

In the case of products that are not applied directly to the skin, exposure only occurs if the substances migrate out of the product. According to the REACH regulation on consumer exposure (42), the dermal exposure to a substance migrating out of a product is determined using the formula below (formulas R.15-7 and R.15-8). The skin area exposed to the substance is calculated using the following equation:

$$D_{der} = \frac{Q_{prod} \times Fc_{prod} \times Fc_{migr} \times F_{contact} \times T_{contact} \times n \times 1000}{BW}$$

in which

D_{der}	The dermal dosage, i.e. the amount of substance potentially absorbed per kg body weight	mg/kg BW/day
Q_{prod}	The amount of product used	g
Fc_{prod}	The weight fraction of the substance in the product	NA
Fc_{migr}	The rate of migration of the substance from the product to the skin per unit of time	g/g/day
$F_{contact}$	The fraction of the skin's contact area, to take into account that the skin is only partially in contact with the product (standard = 1)	cm^2/cm^2
$T_{contact}$	Duration of contact between product and skin	days
n	Number of occurrences per day	/day
BW	Body weight	kg

6.2.2 Oral exposure to an ingested substance

In children using toy products, a small amount of the product may be ingested such as slime, which ends up on the fingers and is then transferred to the mouth, or toy products for young children who chew or suck on the products for extended periods. Oral exposure is mainly assumed to take place in children under three (45). According to the REACH regulation on consumer exposure (42), the oral intake of a substance can be determined using the following formula (formula R.15-11):

$$D_{oral} = \frac{Q_{prod\ indtag} \times Fc_{prod} \times n \times 1000}{BW}$$

in which

D_{oral}	Ingestion per day per kg body weight	mg/kg BW/day
$Q_{prod\ intake}$	The amount of product ingested	g
Fc_{prod}	The weight fraction of the substance in the product	NA

n	Number of occurrences per day	/day
BW	Body weight	kg

According to the REACH regulation, ingestion by children who suck or chew on the product is estimated using the following formula:

$$Q_{prod\ indtag} = CA \cdot TL \cdot \rho$$

in which

CA	Contact area (standard 10 cm^2)	cm^2
TL	The thickness of the layer in contact with the body during mouthing (standard 0.001–0.01 cm)	cm
ρ	Density of product	g/cm^3

Assuming a density of 1 g/cm^3 in this calculation, a worst-case scenario involving contact with 0.01 cm of the product would result in ingestion of 0.1 g of the product. In comparison, the new toy safety directive indicates in connection with the determination of migration limits for metals that the maximum amount ingested by a child from scratched toys is 8 mg in the case of solid toys (i.e. not liquid or fragile), which also is stated in RIVMs recommendation on assessment of chemicals in toys (45). 0.1 g is considered as worst-case scenario.

In this calculation, it is moreover assumed that the child ingests 100% of the content in the layer, which is in contact with the mouth (100% migration).

6.3 Elaboration on relevant exposure parameters

This section discusses different relevant exposure parameters that have been chosen to calculate the exposure associated with the selected toys. The data for the exposure parameters is based on the recommendations in the report "Existing Default Values and Recommendations for Exposure Assessment" prepared by the Nordic Exposure Group for Health and published by the Nordic Council of Ministers (46). The report discusses the standard values used in exposure calculations in, for example, REACH (EU), and outside the EU, with a view to harmonising the use of standard values in exposure assessments. The data on the body weight of children available in the report is much more detailed than in the REACH regulation. The present report in therefore based on these recommendations and not on the standard values indicated in the REACH regulation.

6.3.1 Parameters for dermal exposure to substances that migrate out of a product

All the selected toys are regarded as solid products where the amount of CMR substance to which a child is exposed will depend on the amount of CMR substance that migrates out of the product and comes into direct contact with the mouth or skin during play. For two of the products, these quantities were identified during the migration analyses, while no specific knowledge about migration is available for the remaining products.

The publication by the Nordic Exposure Group for Health (46) contains recommended standard values for some types of toys, but generally uses standard values for products that are less solid or liquid. The latter is irrelevant for the assessment of the selected products.

The report on identification and health assessment of preservatives in toys ("Kortlægning og sundhedsmæssig vurdering af konserveringsmidler i legetøj") from 2014 uses a product amount of 350 g to determine the dermal exposure from slime toys (47). That value was chosen because slime

is considered comparable to play dough, for which the Nordic Exposure Group for Health has recommended the mentioned product quantity of 350 g (46).

As far as the other solid products are concerned, the expected contact area (see Table 49) is used to calculate the product quantity, and it is presumed that substance in the outermost layer (0.1 cm) will migrate out. The contact area has been determined on the basis of the estimated surface of each product which is likely to come into contact with the skin during use. In the case of skipping rope, this involves the palms of both hands, corresponding to 50% of the surface of the hands. Standard skin areas for children as shown in (46) have been used to calculate the contact areas. This means that the product quantity is calculated as the product of the contact area, the thickness of the contact layer and the density of the material.

The analysis results shown in Table 48 have been used in the calculations, except for aniline in skipping rope (no. 608). The result of the migration analysis shows that the amount of aniline migrating from the skipping rope does not exceed the detection limit (0.05 mg/kg) for the 60 minute migration period. Here the project uses a worst-case migration from the skipping rope based on the detection limit (0.05 mg/kg) to calculate a refined Fc_{prod}.

The concentration of the substance that one person potentially is exposed to per application (occurrence) is assumed to be the content of the substance in the product (found by analysis) stated in the unit g substance/g product as it is assumed that 100% of the substance migrates during the occurrence. Tcontact is set to 1 occurrence and therefore the product FCprod x FCmigr x Tcontact has a total unit g substance/g product as stated in Table 49.

TABLE 49
OUTLINE OF THE EXPOSURE PARAMETERS USED FOR DERMAL EXPOSURE

Type of toy	Contact area	Contact area** (cm^2)	Qprod (g)	Fcprod x Fcmigr (-)	Fcontact x n	BW* (kg)
Cloth book (551B)	25% of the head of a 3-6-months-old child	173	17.3	Analysis result	3 times per day 100 times per year	6.7
Flexible ball with rattle (553)	25% of the head of a 3-6-months-old child	173	17.3	Analysis result	3 times per day 100 times per year	6.7
Toy slime (598)	-	-	350	Analysis result	45 min per day 100 times per year	11.6
Skipping rope (608)	50% of the hands of a 3-6-months-old child	185	18.5	Analysis result or detection limit	30 min per day 100 times per year	17.5
Dice (soft plastic) (611)	All sides of the dice	40	4	Analysis result	30 min per day 100 times per year	11.6

Type of toy	Contact area	Contact area** (cm²)	Qprod (g)	Fcprod x Fcmigr (-)	Fcontact x n	BW* (kg)
Bow and arrow (614)	50% of the hands of a 3-6-months-old child	185	18.5	Analysis result	60 min per day 100 times per year	17.5

* BW indicates the body weight for children aged 3-6 months (6.7 kg), 1–3 years (11.6 kg) and 3–<6 years (17.5 kg), based on (46); ** The contact area is calculated on the basis of the amount of surface area of children's body parts recommended in (46). ***This is the product of the analysis result stated in the weight fraction and the migration is set to 100% within the contact time per occurrence.

6.3.2 Parameters used for oral exposure to ingested substances

The product nos. 551, 555, 597, 605 and 609 are all regarded as solid products with the same expected worst-case route of exposure (oral). Children aged 1-3 years are assumed to ingest 0.1 g of the product based on a standard contact area of 10 cm², a layer of 0.1 cm in contact with the skin and a density of 1 g/cm (see section 6.2.2 (42).

The report "Kortlægning og sundhedsmæssig vurdering af konserveringsmidler i legetøj" from 2014 uses 1 g of product for oral ingestion for slime toys (47). This value was chosen because slime is considered comparable to play dough, for which the Nordic Exposure Group for Health has recommended the mentioned product quantity of 1 g (46).

The analysis results shown in Table 48 have been used in the calculations, except for DMTC in the toy figurine (no. 597). The result of the migration analysis shows that the amount of DMTC migrating from the toy figurine does not exceed the detection limit (60 mg/kg) for a 60-minute migration period. This corresponds to <5% of the content. A factor of Fc_{prod} is therefore used to assess the worst-case exposure from the toy figurine, adjusted to make allowance for the fact that very little of the DMTC content actually migrates out of the product and is absorbed. The calculation uses a worst-case migration time of 30 minutes. This value is based on data from RIVM, taking into account the average time during which children aged 0–3 years suck or chew on the products during use (43). It is assumed that the migration that takes place during this interval will not exceed 2.5% of the total content of DMTC.

TABLE 50
OUTLINE OF THE EXPOSURE PARAMETERS USED FOR ORAL EXPOSURE

Type of toy	Qprod intake (g)	N	BW (kg)
Flexible ball with rattle (553)	0.1	100 times a year	6.7
Wooden puzzle (554)	0.1	100 times a year	11.6
Wooden puzzle (555)	0.1	100 times a year	11.6
Toy figurine (597)	0.1	100 times a year	11.6
Toy slime (598)	1	100 times a year	11.6
Toys for children's magazine (605)	0.1	100 times a year	11.6
Dinosaur (609)	0.1	100 times a year	11.6

* BW indicates the body weight for children aged 3–6 months (6.7 kg) and 1–3 years (11.6 kg), respectively, based on (46).

6.4 Exposure calculations

6.4.1 Example of calculation of dermal exposure

The calculation for toy slime (no. 598) is used as an example. The following is a calculation of exposure to o-Toluenesulfonamide (o-TSA) based on the assumption that the case involves dermal exposure to a substance migrating out of a product and using the following input to the formula:

Q_{prod}	= 350 g
Fc_{prod}	= 0.000081 g/g
Fc_{migr} x $F_{contact}$ x $T_{contact}$[9]	= 1
n	= 0.274 /day
BW	= 11.6 kg

This results in the following calculation:

$$D_{der} = \frac{Q_{prod} \times Fc_{prod} \times Fc_{migr} \times F_{contact} \times T_{contact} \times n \times 1000}{BW}$$

$$= \frac{350\ g \cdot 0{,}000081\ g/g \cdot 1 \cdot 0{,}274\ dag^{-1} \cdot 1000}{11{,}6\ kg}$$

$$= 0{,}67 \text{ mg/kg lgv/dag}$$

6.4.2 Example of calculation of oral exposure

The calculation for toys for children's magazine (no. 605) is used as an example. The following is a calculation of exposure to o-TSA based on the assumption that the case involves oral exposure to a substance that is ingested, using the following input to the formula:

$Q_{prod\ intake}$ = 10 cm² x 0.01 cm x 1 g/cm	= 0.1 g
Fc_{prod} = 210 mg/kg	= 0.00021 g/g
n	= 0.274 /day
BW	= 11.6 kg

$$D_{oral} = \frac{Q_{prod\ intake} \times Fc_{prod} \times n \times 1000}{BW} = \frac{0.1g \cdot 0.00021g/g \cdot 0.274\ day^{-1} \cdot 1000}{11.6\ kg}$$

$$= 0.0005 \text{ mg/kg BW/day}$$

6.5 Results: Exposure calculations

The results of the exposure calculations are listed in dermal exposure (Table 51) and oral exposure (Table 52) for each selected substance.

TABLE 51
RESULT OF EXPOSURE CALCULATION FOR DERMAL INTAKE

Chemical substance	Product	Q_{prod} (g)	Fc_{prod} x Fc_{migr} x $T_{contact}$ (g/g)*	n (day^{-1})	BW (kg)	D_{Der} (mg/kg/day)
2-Mercapto-benzothiazole (MBT)	Cloth book (551B)	17.3	0.00031	0.27	6.7	0.219

[9] The value of Fc_{migr} x $F_{contact}$ x $T_{contact}$ = 1 indicates that each occurrence exposes the individual to the total amount of the substance present in the part of the product that comes into contact with the skin (100% migration), presuming full skin contact ($F_{contact}$ = 1).

Chemical substance	Product	Q_{prod} (g)	Fc_{prod} x Fc_{migr} x $T_{contact}$ (g/g)*	n (day^{-1})	BW (kg)	D_{Der} (mg/kg/day)
Aniline	Skipping rope(608)	18.5	0.00065	0.27	17.5	0.188
Aniline	Skipping rope (608) - migration	18.5	2.5×10-8**	0.27	17.5	7.2×10-6
Butylated hydroxytoluene (BHT)	Flexible ball with rattle (553A)	17.3	0.000025	0.27	6.7	0.018
Butylated hydroxytoluene (BHT)	Flexible ball with rattle (553B)	17.3	0.000044	0.27	6.7	0.031
Butylated hydroxytoluene (BHT)	Dice (soft plastic) (611)	4	0.00023	0.27	11.6	0.022
Formaldehyde	Toy slime (598)	350	6.4x10-6	0.27	11.6	0.053
Phenyl Isocyanate	Skipping rope (608)	18.5	0.00028	0.27	17.5	0.081
o-Toluensulfon-amide (o-TSA)	Toy slime (598)	350	0.000081	0.274	11.6	0.67
o-Toluensulfon-amide (o-TSA)	Bow and arrows (614)	18.5	0.000044	0.274	17.5	0.013
p-Toluensulfon-amide (p-TSA)	Bow and arrows (614)	18.5	0.00012	0.27	17.5	0.035

*This is the result of the analysis result stated in weight fraction and migration fixed at 100% within the contact time per occurrence; ** The value is calculated on the basis of the detection limit for the migration analysis which was not exceeded in the migration test that was carried out.

TABLE 52
RESULT OF EXPOSURE CALCULATION FOR ORAL INTAKE

Chemical substance	Product	Q_{prod} (g)	Fc_{prod} (-)	n (day^{-1})	BW (kg)	D_{Oral} (mg/kg/day)
Butylated hydroxytoluene (BHT)	Flexible ball with rattle (553A)	0.1	0.000025	0.27	6.7	0.0001
Butylated hydroxytoluene (BHT)	Flexible ball with rattle (553B)	0.1	0.000044	0.27	6.7	0.00018

Chemical substance	Product	Q_{prod} (g)	Fc_{prod} (-)	n (day^{-1})	BW (kg)	D_{Oral} (mg/kg/day)
Dimethyltin dichloride (DMTC)	Figurine (597)	0.1	0.0012	0.27	11.6	0.00283
Dimethyltin dichloride (DMTC)	Figurine (597) – migration	0.1	0.00003*	0.27	11.6	7.1×10-5
Ethylbenzene	Dinosaur (609)	0.1	0.000026	0.27	11.6	6.1×10-5
Formaldehyde	Wooden puzzle (554)	0.1	0.00019	0.27	11.6	0.00045
Formaldehyde	Wooden puzzle (555)	0.1	0.000044	0.27	11.6	0.0001
Formaldehyde	Toy slime (598)	1	6.4x10-6	0.27	11.6	0.00015
Styrene	Dinosaur (609)	0.1	0.000023	0.27	11.6	5.4×10-5
o-Toluensulfon-amide (o-TSA)	Accessories for children's magazine (605)	0.1	0.00021	0.27	11.6	0.0005
o-Toluensulfon-amide (o-TSA)	Toy slime (598)	1	0.000081	0.27	11.6	0.0019
p-Toluensulfon-amide (p-TSA)	Accessories for children's magazine (605)	0.1	0.00079	0.27	11.6	0.0019

6.6 Summary and conclusion

Exposure scenarios were defined for 11 toy products, which, according to the chemical analysis, contain the CMR substances that were selected for health assessment (see also Chapter 5). The initial assessment of the exposure and risk indicated that the analysis results for aniline and DMTC showed the highest risk associated with use, and migration analyses were therefore performed on the two products containing these substances (one substance in each product). The migration analyses for artificial sweat and saliva, respectively, showed no migration of the two substances for the duration of the test (60 min.) above the detection limit for the methods of analysis (0.05 mg/kg for aniline and 60 mg/kg for DMTC, respectively). The results of the migration analysis were used to develop detailed exposure scenarios for the two products using the detection limit to calculate the worst-case parameters with regard to the amount of the substance. A migration rate of 100% was assumed for the other products.

Children aged 3–6 months, 1–3 years and 3–6 years, respectively, were chosen for the exposure scenarios for the eleven products, based on the expected target group and use (route of exposure) (see Table 48). It is estimated that many of the selected products come into contact with skin during use, and that some of the products are used by an age group in which a small amount the product may be ingested if the children suck or chew on the products during use. Generally, the selected products fall into two categories; dermal exposure and oral exposure (the categories can be seen from Table 48). Two products are estimated to give rise to both oral and dermal exposure (toy slime no. 598 and flexible ball with rattle no. 553), and it is impossible to say in advance which route should be regarded as the worst-case scenario for these two products. As far as the dice (no. 611) are concerned, oral exposure is not regarded as relevant, as the size of the dice would present a risk of suffocation if used by children who put things in their mouth while playing. The cloth book (no. 551B) can be unfolded and used to prevent the child from falling out of bed, so the main exposure is expected to be by skin contact during sleep.

The chosen parameters for the exposure calculations have been divided into dermal exposure as the worst-case scenario in Table 4 and products with oral exposure as the worst-case scenario in Table 50.

The results of the exposure calculations are summarised in Table 51 and 52. In the case of products where both dermal and oral exposures have been calculated, both calculations are shown in the table, but the highest value has been selected as the worst-case exposure for use in the risk assessment.

It should be noted that the calculations are based on a number of worst-case assumptions about the use of the products and the migration of the substances in the products. These worst-case assumptions have been made because the calculations are used to demonstrate whether even a worst-case scenario would present a risk. If this is not the case, it will be reasonable to assume that there is no risk.

7. Health assessment

Chapter 7 provides an overview of the health hazards generally known for the selected CMR substances. The information is primarily based on risk assessment reports from the EU, the American Environmental Protection Agency (US EPA) and international organisations (e.g. the OECD) as well as assessments from the REACH registration dossier, which is used when no information is available from public sources (in accordance with (48)). In such cases, we have mainly used studies based on an established OECD test guideline, preferably carried out in accordance with GLP (Good Laboratory Practice) standards. Special attention has been paid to CMR defects and the routes of exposure, as outlined for the different substances in the previous chapter. Each individual CMR substance will be assessed according to:

- Identification, classification and physiochemical properties
- Absorption and distribution
- Local effects: Irritation and allergies (skin/eye/respiratory irritation, corrosiveness and sensitisation
- Systemic effects: Acute and chronic effects
- Identification of critical effect and determination of safe dose (DNEL/DMEL[10])

The assessments are based on the CLP classification and health hazard classes, and hazard statements are included for the analysed CMR substances beginning with the CMR categories and followed by the remaining human toxicological hazard classes with the corresponding hazard statements H300-H373. For self-classified substances, the tables show the aggregated hazard classes and statements that have been notified for the substances in question. In the case of identical classifications in relevant categories (e.g., Acute Tox. 2 and Acute Tox. 3), the most conservative (worst-case) classification is mentioned. 2-Mercapto-benzothiazole has not been categorised as a CMR, see the harmonised CLP classification of the substance, but has been included as the US EPA suspects it of being potentially carcinogenic.

In general, the classification is based on 100% absorption of the substance. Irritation and allergy as well as acute and chronic effects will be assessed in the light of the CLP classification of the substance and depending on the type of classification (self-classification or harmonised classification). A safe chronic dosage (DN(M)EL) will be established for the relevant routes of exposure (dermal and oral), but if a critical effect or (DN(M)EL) cannot be established, the substance will not be taken into consideration in the subsequent risk assessment in Chapter 8.

7.1 2-Mercapto-benzothiazole (MBT)

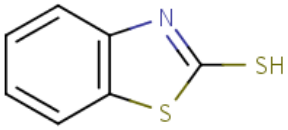
In 2008, an extensive EU risk assessment report was published on N-Cyclohexylbenzothiazole-2-sulphenamide (CBS) (49), including a health assessment of its most dominant breakdown product, 2-Mercapto-benzothiazole (MBT). CBS and other benzothiazole sulphonamides are formed by oxidation of a mixture of MBT and cyclohexylamines or similar amines (49). This report, including any individual studies, which may already have been reported, constitutes the main basis for the following health assessment.

[10] DNEL: Derived No Effect Level – DMEL: Derived Minimal Effect Level

7.1.1 Identification, classification and physiochemical properties

The physiochemical properties of the substance and its classification in the ECHA inventory (CLP) can be found in the table below.

TABLE 53
IDENTIFICATION, CLASSIFICATION AND PHYSIOCHEMICAL PROPERTIES

Chemical name	2-Mercaptobenzothiazole
Synonyms	2-Mercaptobenzothiazole 2-Benzothiazolethiol Mercaptobenzothiazol 2-Mercaptobenzthiazole 2-Mercaptobenzothiazole 2-Mercptobenzothiazole 2-Merkaptobenzotiazol 2-Merkaptobenzthiazol Mercaptobenzothiazole Mercaptobenzothiazole (VAN)
CAS no.	149-30-4
EC no.	205-736-8
Chemical structure	
Classification Harmonised CLP classification* (Regulation 1272, 2008) US EPA**	Skin Sens. 1, H317 – May cause an allergic skin reaction Carc C – Possible human carcinogen
Physical condition	Solid
Molar weight	167.26 g/mol
Melting point	181°C
Boiling point	260°C
Vapour pressure	4.64E^{-4} mm Hg
Octanol/water distribution (log Pow)	2.42
Water solubility	0.120 g/L

*Harmonised classification: http://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/cl-inventory/view-notification-summary/77605
**Categorised as carcinogenic by the US EPA: http://npic.orst.edu/chemicals_evaluated.pdf.

7.1.2 Absorption and distribution

Experiments with radioactively labelled MBT in rats show that approximately 33% of the substance is absorbed during dermal exposure. Once absorbed, MBT was distributed throughout the body, and 13–33% of the radioactively labelled substance was excreted in the urine 3–6 hours after exposure, while a small fraction (approx. 1%) was excreted in the faeces. The absorption and distribution through oral exposure followed a similar pattern in rats; in this case MBT was rapidly and almost completely (100%) absorbed in the gastrointestinal tract (49).

MBT is broken down in the cytochrome P450 (CYP450) enzyme system (see for example (50)), where the substance is oxidised and either becomes conjugated to glutathione (GSH) or undergoes further enzymatic hydrolysis, whereupon it is excreted (primarily) in the urine (49).

In humans and mammals, the CYP450 enzymes are present in the vast majority of organs and tissues, where they play an important role in the synthesis and conversion of hormones, cholesterol and vitamin D. CYP450 enzymes also play a special role in the metabolisation of xenobiotic substances. This function is primarily performed by the liver.

7.1.3 Local effects: Irritation and allergy

Animal experiments have shown MBT to cause allergic skin reactions, and the harmonised CLP classification of MBT is Skin Sens. 1. Clinical observations also show that MBT is a common (present in a large number of rubber-based products) and important contact allergen (49). For MBT and its related parent compound, CBS, contact allergy is the most relevant toxicological effect parameter (49).

7.1.4 Systemic effects: Acute and chronic effects

Animal experiments on rats (with repeated or long-term oral exposure) have reported reduced body weight, inflammation in the stomach (ulcer) and histopathological changes in the kidneys. In a long-term study over a two-year exposure period, reduced survival rates were also observed in male and female rats at doses of 375 and 750 mg/kg BW/day, respectively (49). A more short-term inhalation study (15 days) on rats with two hours of daily exposure to 300–400 mg MBT/m^3 also showed reduced body weight compared with the control rats (49). A sub-chronic NOAEL for systemic effects of MBT in rats of 375 mg/kg BW/day has been determined. Experiments with mice have resulted in the same value (49). Several animal experiments with MBT did not show any reprotoxic effects (49).

No mutagenic effects of MBT have been demonstrated in standard gene mutation tests in bacteria (Ames) and in mammalian cell lines. MBT was capable of inducing structural chromosome effects in CHO cells upon metabolic activation (S-9), but only in the presence of S-9. Marginal effects have also been demonstrated in connection with the exchange of genetic material between chromosomes (SCE), but the general conclusion is nevertheless that MBT is not mutagenic (49).

A comprehensive two-year study on both mice and rats (both genders) analysed the carcinogenic effect of MBT. The experimental animals were given corn oil containing up to 375-750 mg MBT/kg BW/day five times a week. There was an increase in the occurrence of several types of tumours in rats exposed to MBT, but not all types of tumours were associated with the maximum dose. In general there was evidence of a carcinogenic effect of MBT in male rats and to some extent in female rats but no evidence of carcinogenic activity in male mice. The conclusion was that MBT cannot be regarded as carcinogenic at a dose of 350-750 mg/kg BW/day in mice and rats (49).

7.1.5 Identification of critical effect and determination of a safe dose

The critical effect for MBT could be a carcinogenic effect, but no useful information has been identified that makes it possible to calculate a DMEL for the substance. However, a newer American report from NIOHS (National Institute for Occupational Safety and Health) on the basis of several national and international sources points out that MBT is not regarded as carcinogenic through dermal exposure (52). On the other hand, there is stronger evidence that MBT can have a sensitising effect in connection with dermal exposure, which also is supported by the harmonised classification of the substance, but it has not been possible to determine a NOAEL for that critical effect (53). Therefore a critical effect of MBT cannot be risk assessed in the following chapter.

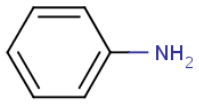
7.2 Aniline

7.2.1 Identification, classification and physiochemical properties

Before REACH was implemented in 2007, a number of other regulations and directives governed the use of chemical substances in Europe, including the Existing Substances Regulation (ESR) (54). The ESR regulation covered the chemical substances available on the European market before 1982 and ensured that the Commission together with the member countries regularly drafted a priority list of chemical substances that required immediate attention due to their potential effect(s) on human health and the environment. During the period 1994–2007, four such priority lists were published covering a total of 141 chemical substances. Aniline is listed as one of these 141 chemical substances.

The physiochemical properties of the substance and its classification in the ECHA inventory (CLP) can be found in the table below.

TABLE 54
IDENTIFICATION, CLASSIFICATION AND PHYSIOCHEMICAL PROPERTIES

Chemical name	Aniline
Synonyms	Benzenamine Phenylamine Aminophen Aminobenzene
CAS no.	62-53-3
EC no.	200-539-3
Chemical structure	
Classification Harmonised CLP classification* (Regulation 1272, 2008)	Carc. 2, H351 – Suspected of causing cancer Muta. 2, H341 – Suspected of causing genetic defects Acute Tox. 3, H301, H311, H331 – Toxic if swallowed, in contact with skin or if inhaled Skin Sens. 1, H317 – May cause an allergic skin reaction Eye Dam. 1, H318 – Causes serious eye damage STOT RE 1, H372 – Causes damage to organs (the spleen) through prolonged or repeated exposure
Physical condition	Liquid
Molar weight	93.13 g/mol
Melting point	-6.3 °C
Boiling point	184.1 °C
Vapour pressure	0.49 mm Hg
Octanol/water distribution (log	0.9
Water solubility	36 g/L

*Harmonised classification: http://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/cl-inventory/view-notification-summary/115877.

7.2.2 Absorption and distribution

Aniline is highly water-soluble and easily absorbed orally, by inhalation or through dermal exposure. A comprehensive EU risk assessment report (55) concludes that the substance is relatively easily absorbed dermally, which is the main route of exposure in this study. Several reports based on studies of the dermal intake in humans estimate a dermal absorption of the substance of up to 38% (55). Aniline is generally broken down by the CYP450 enzyme system (phase 1) and is subsequently (phase 2) bio-transformed into acetanilide by the enzyme N-acetyltransferase, and after metabolic transformation of the aniline, the metabolites are excreted, mainly via the urine. Genetically, Europeans can be divided into two main groups: 'slow acetylators' and 'fast acetylators'. These groups reflect the ability of the sub-populations to break down aniline. In the slow acetylators group, a slow enzymatic transformation (acetylation) of the aniline takes place, and the conversion to acetanilide is suppressed. This results in the production of other metabolites (phenylhydroxylamine, nitrobenzene and aminophenol), which leads to the formation of methaemoglobin, which is an oxidised version of a haemoglobin that is unable to bind oxygen (55). Most of the methaemoglobin is again converted to haemoglobin in the red blood cells by the enzyme methaemoglobin-reductase. Increased amounts of methaemoglobin in the blood (methaemoglobinemia) may give a blueish colour to the skin (cyanosis).

Studies of rats with radioactively labelled aniline show that the substance is primarily distributed to the red blood cells, followed by the blood plasma, spleen, kidneys, lungs, heart, brain and fatty tissue. Repeated exposure results in accumulation in the spleen (55).

7.2.3 Local effects: Irritation and allergy

In the harmonised classification under CLP, aniline is classified as a substance that may cause allergic skin reactions (Skin Sens. 1) and severe eye damage (Eye Dam. 1).

Data from animal experiments indicate that aniline cause mild to moderate sensitisation following skin exposure (allergic skin reaction). Allergic skin reactions to aniline have also been reported in humans, primarily in patients suffering from atopic dermatitis, often in connection with cross-reactions to similar substances. Respiratory sensitisation has not been observed but cannot be excluded (55).

Unpublished animal experiments on rabbits show that aniline can cause a brief (a few days) rash on the skin (erythema) following application of concentrated aniline (no information is available regarding the purity of the substance or the exposure time). On the other hand, exposure of the eyes to concentrated aniline may cause serious long-term damage (pannus – cloudiness of the cornea). However, aniline is not corrosive to skin and eyes (55).

7.2.4 Systemic effects: Acute and chronic effects

Acute aniline poisoning has been documented in several cases. In adults (average body weight of 70 kg), an oral intake exceeding 800 mg/kg BW or inhalation of air with concentrations exceeding 25 µg/m^3 can be fatal. Aniline poisoning is primarily characterised by the symptom 'cyanosis', which is a blue/purple colouring of the skin as a result of low oxygen saturation in the blood. Accompanying (milder) symptoms include headache, dizziness, nausea, vomiting, chest and stomach pain/cramps, fatigue, irregular breathing and an increased heart rate (55).

Upon repeated exposure, the main toxicological effect of aniline is haemotoxicity (in lay terms: poisoning of the red blood cells). Experiments on rats show that this effect is independent of the route of exposure. Experience from humans who have repeatedly been exposed to aniline indicates that haemotoxicity can be observed at oral doses in excess of 0.4 mg/kg BW/day (55).

In vitro studies of mammalian cell lines have shown that aniline has genotoxic effects. These effects include mutagenicity, chromosomal deviations and the exchange of genetic material between

chromosomes (SCE - Sister Chromatid Exchanges). The mutagenicity of aniline is also supported by several studies that demonstrate damage to the DNA and binding (adducts) of aniline to DNA (55). Based on these and other studies, aniline has been classified as Muta 2 (Suspected of causing genetic damage).

Since the 19th century, aniline has been suspected of being carcinogenic. Health and safety data, for example, show increased occurrence of bladder cancer among workers who have been exposed during work in the chemical industry, but it was not possible to identify aniline as the main cause in any particular case. Several animal experiments nevertheless support the suspicion. In a comprehensive and long-term (2 years) experiment on rats exposed to an oral dose of aniline (7.22 and 72 mg/kg BW/day), increased occurrence of cancer of the spleen was observed, especially in male rats (55). Based on these findings and supported by a range of empirical data from literature (reported in (55)), there is a basis for suspecting aniline of being carcinogenic in humans without having a threshold value for this effect.

7.2.5 Identification of critical effect and determination of a safe dose

The carcinogenic effect is regarded as the critical effect. This is supported by the Danish EPA, which has previously reached the same conclusion in connection with dermal exposure to aniline in tattoo inks (56).

In the above-mentioned report from the Danish EPA, a DMEL was determined for dermal exposure to aniline (56), as estimated in the EU risk assessment report on aniline (55). Here, T25[11] for rats was estimated at 46 mg/kg BW/day (55) and using a safety factor (AS) of 10, HT25 (Human T25) was estimated at 4.6 mg/kg BW/day for oral exposure (56). Based on an HT25 value of 4.6 mg/kg BW/day and using an HtLF (high to low dose risk extrapolation) factor of 250,000 (standard for 10^{-6} risk of death when T25 is used as a potency estimator), a DMEL dermal for carcinogenic effects can be estimated at 2×10^{-5} mg/kg BW/day, corresponding to 20 ng/kg BW/day or 0.00002 mg/kg BW/day (56).

7.3 Butylated hydroxytoluene (BHT)

In 2002, the UNEP (United Nations Environment Programme) prepared an extensive report as part of the OECD's SIDS (Screening Information Dataset) series on BHT (58) and the toxicological effects of the substance on humans and the environment. This report, including any individual studies, which may already have been reported, constitutes the main basis for the following health assessment.

7.3.1 Identification, classification and physiochemical properties

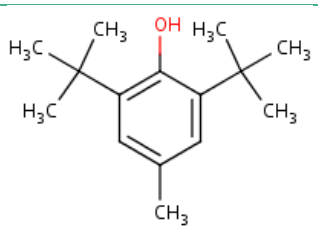
The physiochemical properties of the substance and its classification in the ECHA inventory (CLP) can be found in the Table 55.

7.3.2 Absorption and distribution

A study on the absorption of BHT and an analysis of its metabolites in humans (oral exposure) showed that BHT is primarily excreted via the urine as a carboxylised metabolite (BHT-COOH) and secondarily as N-benzoylglycine (benzoylamino-acetic acid). Experiments have shown that similar toxicokinetics apply to absorption and metabolisation in rats (59). This metabolisation indicates that BHT is converted via the CYP450 enzyme system, where the substance is oxidised and, in some cases, conjugated to glutathione (GSH) or undergoes further enzymatic hydrolysis before being excreted via the urine (59). BHT is thought to become distributed throughout the body but has preference for distribution and bio-accumulation in fatty tissue and, for example, breast milk (58, 59) on account of the somewhat highly non-polar (lipophilic) characteristics of the substance (see the log Pow in the table below).

[11] T25 is defined as the chronic doses that will induce tumours in 25% of a population after correction for spontaneous occurrence of tumours within the standard lifespan of the species in question. The T25 concept is defined by Dybing et al. (57).

TABLE 55
IDENTIFICATION, CLASSIFICATION AND PHYSIOCHEMICAL PROPERTIES

Chemical name	Butylated hydroxytoluene
Synonyms	1-Hydroxy-4-methyl-2.6-di-tert-butylbenzene 2,6-Bis(1,1-dimethylethyl)-4-methylphenol 2,6-Di-t-butyl-4-methylphenol 2,6-Di-t-butyl-p-cresol 2,6-Di-terc.butyl-p-kresol 2,6-Di-tert-butyl-1-hydroxy-4-methylbenzene 2,6-Di-tert-butyl-4-cresol 2,6-Di-tert-butyl-4-hydroxytoluene 2,6-Di-tert-butyl-4-methylhydroxybenzene 2,6-Di-tert-butyl-4-methylphenol 2,6-Di-tert-butyl-p-cresol 2,6-Di-tert-butyl-p-methylphenol 3,5-Di-tert-butyl-4-hydroxytoluene 4-Hydroxy-3,5-di-tert-butyltoluene 4-Methyl-2,6-di-terc. Butylfenol
CAS no.	128-37-0
EC no.	204-881-4
Chemical structure	
Classification Self-classified CLP classification* (Regulation 1272, 2008)	Carc 1B, H350 – May cause cancer (1/3625) Carc 2, H351 – Suspected of causing cancer (10/3625) Muta 1B, H340 – Regarded as being able to cause genetic defects (9/3625) Muta 2, H341 – Suspected of causing genetic defects (3/3625) Repr 2, H361 – Suspected of damaging fertility or the unborn child Acute Tox. 3, H301 – Toxic if swallowed Acute Tox. 4, H312 – Harmful in contact with skin Skin Irrit. 2, H315 – Causes skin irritation Skin Sens. 1, H317 – May cause an allergic skin reaction Eye Irrit. 2, H319 – Causes serious eye irritation Resp. Sens. 1, H334 – May cause allergy or asthma symptoms or breathing difficulties if inhaled STOT RE 3, H335 – May cause respiratory irritation STOT SE 1, H370 – Causes damage to organs
Physical condition	Solid
Molar weight	220.35 g/mol
Melting point	71°C
Boiling point	265°C
Vapour pressure	<0.01 mm Hg (20°C)
Octanol/water distribution (log Pow)	5.1
Water solubility	0.6 mg/L

*The number of notifications that have indicated a CMR category appear in the brackets: http://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/cl-inventory/view-notification-summary/24787.

BHT undergoes extensive biotransformation in the liver such as enterohepatic recirculation[12] (59). Such recirculation of a given substance generally has the potential to increase the time a substance is present in the body and any pharmacological or toxicological effect it may have (60). The biotransformation of BHT results, among other things, in the production of a number of metabolites that are reactive and therefore have the potential to initiate cell damage (in the form of oxidative stress) (59).

The above-mentioned studies of the absorption of BHT in humans and rats involved oral exposure. UNEP (58) reports that the dermal absorption of BHT through intact skin is minimal. Various parameters determine the extent to which a substance is absorbed through the skin. Only low-molecular substances (MW <500 g/mol), for example, can be absorbed through the skin. In addition, dermal absorption is greatest for substances with a log Pow between +1 and +2, but as it has not been possible to find data on the dermal absorption of BHT, a worst-case absorption of 100% has been presumed for both routes of exposure.

7.3.3 Local effects: Irritation and allergy

BHT has been used extensively as an antioxidant in both foodstuffs and consumer goods for many years. Despite this long-term and extensive use, only few cases of allergic reactions have been reported in individuals who have been exposed dermally or orally. Annual experiments with guinea pigs support the theory that BHT is not sensitising. Several experiments on rabbits also show that BHT only has the potential to cause light irritation of skin and eyes (58).

7.3.4 Systemic effects: Acute and chronic effects

In acute experiments on rats, the dermal and oral LD50 values[13] were found to be >2000 mg/kg BW and >2930 mg/kg BW, which shows that the acute toxicity of BHT is low in relation to these routes of exposure (58).

Long-term exposure (90 days) of rats shows that the liver and thyroid gland are target organs and that a dose >25 mg/kg BW/day results in a hyperactive thyroid, enlarged liver and the induction of several liver enzymes, among other things. Based on these results, a NOAEL of 25 mg/kg BW/day has been defined for chronic exposure (58).

Experiments on mice and rats show that BHT has a reprotoxic effect in the form of a reduction in the size of the litters at a dose of 100 mg/kg BW/day. Based on these studies, a NOAEL of 25 mg/kg BW/day has been established. No teratogenic effects of BHT were identified in the offspring (58). As mentioned in section 7.3.2, BHT bioaccumulates. In this regard, the REACH consortium behind the registration of BHT points to an experiment on rats that showed reduced growth in suckling young rats in which BHT was found in high concentrations in the mother's milk (58).

No mutagenic or carcinogenic effects of BHT have been established (58), and the substance is also not listed in the IRIS database of the US EPA, where other carcinogenic effects are listed for other substances (51). This is also supported by an earlier report by the American National Cancer Institute (NCI), according to which a comprehensive study on mice and rats was unable to detect a carcinogenic effect from BHT (61).

7.3.5 Identification of critical effect and determination of safe dose

Based on the above-mentioned studies of oral exposure in rats, the critical effect is related to the reprotoxicity at a NOAEL of 25 mg/kg BW/day (58).
A safety factor (AS) of 2 is used to determine the oral and dermal DNEL for BHT. This covers the difference in the duration of the exposure (from sub-chronic to chronic), a factor for interspecies

[12] A biological process in which pharmaceutical substances and xenobiotics circulate from the liver to the gallbladder followed by absorption in the small intestine and recirculation back to the liver.
[13] LD_{50}: Lethal dose (LD) which results in 50% mortality.

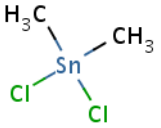
variation (allometric scaling) of 4 (rats) and a factor 2.5 for the remaining differences between species, as indicated in Chapter R.8 of the ECHA's "Guidance on information requirements and chemical safety assessment" (62). A standard safety factor of 10 has also been used for differences within the individual species. A combined safety factor of 200 has therefore been used, which produces a DNEL for BHT of 0.125 mg/kg BW/day.

7.4 Dimethyltin dichloride (DMTC)

7.4.1 Identification, classification and physiochemical properties

The physiochemical properties of the substance and its classification in the ECHA inventory (CLP) can be found in Table 56.

TABLE 56
IDENTIFICATION, CLASSIFICATION AND PHYSIOCHEMICAL PROPERTIES

Chemical name	Dimethyltin dichloride
Synonyms	Dichlorid dimethylcinicity Dichlorodimethylstannane Dichlorodimethyltin Dimethyldichlorostannane Dimethyldichlorotin Dimethyltin dichloride Dimethyltindichloride Stannane, dichlorodimethyl-
CAS no.	753-73-1
EC no.	212-039-2
Chemical structure	
Classification Harmonised CLP classification* (Regulation 1272, 2008)	Repr. 2, H361d – Suspected of damaging the unborn child Acute Tox. 2, H330 – Fatal if inhaled Acute Tox. 3, H301, H311, – Toxic if swallowed and toxic in contact with skin STOT RE 1, H372 – Causes damage to organs (nervous system, immune system) through prolonged or repeated exposure – Skin Corr. 1B, H314 – Causes severe skin burns and eye damage
Physical condition	Solid
Molar weight	219.69 g/mol
Melting point	106.5 °C
Boiling point	189 °C
Vapour pressure	-
Octanol/water distribution (log	-1.06
Water solubility	20 g/L

*Harmonised classification cf. 6th amendment of CLP (4).

7.4.2 Absorption and distribution

In an unpublished study from the REACH registration of DMTC, absorption of the substance was studied in rats following intravenous and oral exposure to 10 mg/kg. The concentration of DMTC in the blood dropped significantly (by a factor 10) within the first 12 hours following both types of dosage, while the remaining DMTC could be traced for up to 268 hours (approx. 11 days) following exposure, and is presumed to be absorbed in the red blood cells. Most of the substance was excreted in the urine within 24 hours: approximately 40% following oral exposure, whereas 100% was excreted following intravenous exposure (63). Dermal absorption of DMTC through the skin (human model) is estimated at 20% of the applied dose (63).

Another experiment on rats has shown that DMTC following oral exposure via drinking water is absorbed in the gastrointestinal tract and that the substance can be transferred from the placenta to the blood and brain of the foetus and thus cause prenatal neurotoxic effects on the offspring (see below) (64).

A summary report from the US EPA based on several studies with different animal models indicates that DMTC metabolises via the CYP450 enzyme system (65).

Due to the high degree of water solubility (see Table 56), an oral absorption fraction of one is used.

7.4.3 Local effects: Irritation and allergy

Several animal experiments with dermal exposure show that DMTC may cause severe skin burns (65), and the substance will be classified as Skin Corr. 1B in the new harmonised CLP classification. There are also reasons to believe that DMTC may cause burns to the airways if the substance is inhaled.

No studies exist that give reasons to believe that DMTC may cause allergies (63, 64).

7.4.4 Systemic effects: Acute and chronic effects

DMTC is classified as fatal if inhaled (Acute Tox. 2) and toxic if swallowed or in contact with skin (Acute Tox. 3) based on several experiments on rats (64).

The toxicity of DMTC to humans has for example been described in connection with an occurrence where six industrial workers at a chemical factory unintentionally inhaled an unknown concentration of methyltin. The immediate symptoms were headache, tinnitus, deafness, loss of memory, disorientation, aggression, psychoses and other serious forms of neuropsychiatric behaviour. One of the industrial workers died after the occurrence, while two of the surviving workers presented neurological damage more than six years later. The remaining three workers were able to resume their work at the factory but suffered from memory loss for six months following the occurrence (63).

Several experiments on rats with repeated or long-term oral exposure to DMTC have demonstrated that the substance causes damage to offspring in the form of effects on the central nervous system (63, 64). On that basis, DMTC has been classified as Repr. 2 and STOT RE 1.

No mutagenic or carcinogenic effects of DMTC have been established (63, 64), and the substance is also not listed in the IRIS database of the US EPA, where other carcinogenic effects are listed for other substances (51).

7.4.5 Identification of critical effect and determination of a safe dose

According to several chronic studies of oral exposure in rats, the critical effect is related to reprotoxicity. Several NOAEL values are shown for this effect parameter in the interval 0.4–0.6 mg/kg BW/day (63, 64).

Based on the above, the lowest NOAEL value of 0.4 mg/kg BW/day is used. A standard safety factor (AS) of 2 is used to determine the DNEL. This covers the difference in the duration of exposure (from sub-chronic to chronic), a factor for interspecies variation (allometric scaling) of 4 (rats) and a factor 2.5 for the remaining differences between species, as indicated in Chapter R.8 of ECHA's "Guidance on information requirements and chemical safety assessment" (62). A standard safety factor of 10 has also been used for differences within the individual species. A combined safety factor of 200 has therefore been used, which produces a DNEL oral for DMTC of 0.002 mg/kg BW/day.

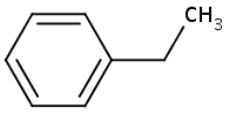
7.5 Ethylbenzene

7.5.1 Identification, classification and physiochemical properties

Ethylbenzene is, like aniline (see section 7.2), one of the 141 selected substances listed under the ESR regulation which were selected for an EU risk assessment. This risk assessment only covers the environment and not the health aspects of the substance (66).

The physiochemical properties of the substance and its classification in the ECHA inventory (CLP) can be found in Table 57.

TABLE 57
IDENTIFICATION, CLASSIFICATION AND PHYSIOCHEMICAL PROPERTIES

Chemical name	Ethylbenzene
Synonyms	Aethylbenzol Benzene, ethyl- EB Ethyl benzene Ethylbenzeen Ethylbenzene Ethylbenzol Etilbenzene Etylobenzen Phenylethane
CAS no.	100-41-4
EC no.	202-849-4
Chemical structure	
Classification Harmonised CLP classification* (Regulation 1272, 2008)	Asp. Tox. 1, H304 – May be fatal if swallowed and enters airways – Acute Tox. 4, H332 – Harmful if inhaled – STOT RE 2, H373 – May cause damage to organs (hearing) through prolonged or repeated exposure
Physical condition	Liquid
Molar weight	106.17 g/mol
Melting point	-95°C
Boiling point	136.1°C

Chemical name	Ethylbenzene
Vapour pressure	9.6 mm Hg
Octanol/water distribution (log Pow)	3.13
Water solubility	169 mg/L

*Harmonised classification cf. 6th amendment of CLP (4). Not classified as CMR under the harmonised CLP classification, but notified as Carc 2 under the previous CLP self-classification.

7.5.2 Absorption and distribution

Structurally, ethylbenzene is related to other aromatic compounds (e.g. aniline, phenyl isocyanate and styrene), and the general biotransformation of this type of substance takes place via the CYP450 enzyme system (as described in section 7.1.2). Many of the biological activities of the aromatic compounds are identical. Ethylbenzene, benzene and toluene, for example, are easily absorbed following exposure through inhalation and distributed to fatty tissue, liver, kidneys, bone marrow and nerve tissue (67). As mentioned above (see sections 7.1.2, 7.2.2. and 7.3.2) aromatic compounds are excreted relatively fast in the urine.

The relative water solubility of ethylbenzene is not high, but as it has been impossible to find data relating to oral intake, a worst-case intake of 100% is assumed.

7.5.3 Local effects: Irritation and allergy

Unpublished data made available in connection with the REACH registration of ethylbenzene shows that the substance may cause moderate irritation of the skin and mild irritation of the eyes (67). Several self-classified CLP notifications also classify the substance as Skin Irrit. 2 and Eye Irrit. 2, but this classification has not been implemented in the harmonised classification (see table above). There are no indications that ethylbenzene may cause allergies (67).

7.5.4 Systemic effects: Acute and chronic effects

In acute mortality experiments, the dermal and oral LD50 values were found to be 20,000 mg/kg BW in rabbits, and 3,500 mg/kg BW in rats, respectively, which shows that ethylbenzene is characterised by low acute toxicity for these routes of exposure (67).

The sensory irritation potential of a number of airborne chemical substances, including ethylbenzene, have also been studied. The relative strength was evaluated by determining the RD50 (the concentration associated with a 50% reduction in respiratory rate), and the RD50 for ethylbenzene was found to be 1432 ppm (67).

Several sub-chronic (28, 90 and 182 days) studies on rats with repeated oral exposure show that ethylbenzene has a toxic effect on the liver, and a NOAEL of 75–136 mg/kg BW/day has been established. A sub-chronic (28 days) inhalation study on rats established a NOAEL of 800 ppm.

In a first-generation reproduction study on rats exposed to ethylbenzene through inhalation, no effects were demonstrated for 1,000 ppm (NOAEL for the parent generation (Fo)), but an effect was nevertheless demonstrated in suckling young rats (F1) in the form of reduced weight at 500–1,000 ppm. However, there was no evidence that ethylbenzene had a direct teratogenic effect on the offspring at vapour concentrations of up to 2,000 ppm. A weak effect of ethylbenzene on development was, however, visible in the form of the reduced weight of the foetuses and a higher variation in the skeletal development at 1,000–2,000 ppm. Based on these results, a NOAEL for teratogenic effects of 2,000 ppm was established and a NOAEL for developmental effects of 500 ppm (67).

The National Toxicology Program (NTP) of the American authorities has previously reported that ethylbenzene may be carcinogenic based on long-term (2 years) oral exposure experiments on mice

and rats (68). This data was re-assessed in a subsequent study, and the conclusion was that the observed forms of cancer that had been reported by NTP were age-related and not relevant for human health (69). This is also supported by the fact that ethylbenzene is listed in the IRIS database of the US EPA (51) as "not classified as carcinogenic to humans".

Based on unpublished (67) and published studies (68), ethylbenzene is not regarded as being mutagenic.

7.5.5 Identification of critical effect and determination of safe dose

Following implementation of the harmonised CLP classification (1/12/2014), ethylbenzene is not classified as a CMR substance. It also appears from the self-classified notifications of the substance that the CMR category Carc 2 has only been used in one of the 33 notifications. A reprotoxic effect of ethylbenzene has, however, been identified with an established NOAEL of 500 ppm. This value has been estimated on the basis of inhalation, but oral exposure is the relevant route in this context. A conservative 'route-route' extrapolation between routes of exposure, from inhalation to oral exposure, is therefore used to estimate the oral NOAEL. In the above-mentioned experiment (67), the air concentration of 500 ppm ethylbenzene can be converted directly to 500 mg/m^3. According to ECHA's "Guidance on information requirements and chemical safety assessment" (62), a rat's daily respiratory volume is 1.15 m^3/kg BW/day, which means that 575 mg/kg BW/day is inhaled. The NOAEL oral is extrapolated from this value by multiplying with a factor 2 (which takes into account the difference in absorption between inhalation and the oral route of exposure) (62). This produces a NOAEL oral for the reprotoxic effect of 1150 mg/kg BW/day.

Based on the above, a standard safety factor (AS) 2 is used to determine the DNEL. This covers the difference in the duration of the exposure (from sub-chronic to chronic), a factor for interspecies variation (allometric scaling) of 4 (rats) and a factor 2.5 for the remaining differences between species, as indicated in Chapter R.8 of ECHA's "Guidance on information requirements and chemical safety assessment" (62). A standard safety factor of 10 has also been used for differences within the individual species. A combined safety factor of 200 has therefore been used, which produces a DNEL oral for ethylbenzene of 5.75 mg/kg BW/day.

7.6 Formaldehyde

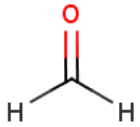
Formaldehyde is listed on the Danish EPA list of unwanted substances (LOUS), and in this context the authorities have begun collecting and structuring existing data on the use, regulation and environmental and health effects of the substance as well as alternative substances (70). Further information about formaldehyde has been found in IARC monographs (71, 72), OECD SIDS (73) and by going through toxicology data from WHO (74) and the Danish EPA (47).

7.6.1 Identification, classification and physiochemical properties

The physiochemical properties of the substance and its classification in the ECHA inventory (CLP) are shown in Table 58.

TABLE 58
IDENTIFICATION, CLASSIFICATION AND PHYSIOCHEMICAL PROPERTIES

Chemical name	Formaldehyde
Synonyms	Formalin Methanal Methylaldehyde Methylenoxide
CAS no.	50-00-0
EC no.	200-001-8

Chemical name	Formaldehyde
Chemical structure	
Classification Harmonised CLP classification* (Regulation 1272, 2008)	Carc. 1B, H350 – May cause cancer Muta. 2, H341 – Suspected of causing genetic defects Acute Tox. 3*, H301, H311, H331 – Toxic if swallowed, if in contact with skin or if inhaled Skin Corr. 1B, H314 – Causes severe skin burns and eye damage Skin Sens. 1, H317 – May cause an allergic skin reaction
Physical condition	Gas
Molar weight	30.03 g/mol
Melting point	-92°C
Boiling point	-19.1°C
Vapour pressure	3886 mm Hg
Octanol/water distribution (log	0.35
Water solubility	550 g/L

*Harmonised classification cf. 6th amendment of CLP (4).

7.6.2 Absorption and distribution

There is only very little data available about dermal absorption of formaldehyde. Although the substance is capable of penetrating the skin, dermal absorption is considered to be relatively low. According to an assessment by the EU's Scientific Committee for Consumer Safety (SCCS) a rat experiment demonstrated a relatively modest 5% dermal absorption during 48 hours of exposure to a cream (75). In addition, a newer opinion from SCCS states that animal studies with formaldehyde show that the substance penetrates the skin (0.5-9% depending on the type) (76).

Due to the solubility in water of formaldehyde, the substance is absorbed quickly through the airways and the gastrointestinal tract. Since formaldehyde quickly metabolises in the body through various enzyme reactions, the concentration of formaldehyde in the blood of rats, monkeys and humans does not increase following exposure to high concentrations of formaldehyde (only 15, 6 and 2 ppm, respectively) (73). Tests show that about 40% of the formaldehyde inhaled disappears with the exhaled air within 70 hours after exposure while 17% is excreted in urine and 5% in faeces. The remaining 35-39% remained in the body.

7.6.3 Local effects: Irritation and allergy

Formaldehyde causes irritation of the eyes, skin and mucous membranes and has the classification Skin Corr. 1B, H314 (concentrations above 25%). Moderate irritation of the eyes, nose and throat is seen at 2-3 ppm (73).

As can be seen from the harmonised classification, formaldehyde is also considered an allergen (Skin Sens. 1, H317, concentrations above 0.2%). Contact with the substance can produce an eczema that affects the immune system and causes rashes, blisters and squamous, dry skin that itches or burns (73). An induction threshold for the development of allergy to formaldehyde has not been determined but it is believed to <5% in an aqueous solution. Generation of allergic reactions in

already sensitised individuals has been observed as low as for an 0.05% concentration of formaldehyde (76).

7.6.4 Systemic effects: Acute and chronic effects

Formaldehyde has a harmonised classification as Acute Tox. 3 (H301, H311, H331 – Toxic if swallowed, in contact with skin and inhaled). The substance has a high acute toxicity and LD50 values of 600-800 mg/kg LVG have been reported for oral ingestion in rats (73). The SCCS, however, points to LD50 values of 100-200 mg/kg BW (75).

For rabbits a study conducted a while ago stated a dermal LD_{50} value of 270 mg/kg BW, whereas an inhaled LC_{50} value[14] (four hours) of 578 mg/m^3 (480 ppm) is stated for rats (73).

When inhaled, formaldehyde causes irritation of the eyes, nose and throat. Exposure to higher concentrations of formaldehyde vapours (>120 mg/m^3) caused high saliva generation, acute dyspnoea, vomiting, muscular spasms, cramps and eventually death (73).

Repeated exposure to formaldehyde causes only toxic effects in tissue in direct contact with the substance when inhaled, orally ingested or through dermal exposure. The effects depend on the level of concentration and are characterised by local cell disintegration and subsequent reestablishment of the damage (70). Damage to the subjects is typically seen in the nose after inhalation, in the stomach after oral ingestion or on the skin after skin contact (73). According to the OECD (73), the lowest NOAEL values observed for repeated exposure to formaldehyde are 1-2 ppm (equivalent to 1-2.5 mg/m^3) for exposure through inhalation. The effect for oral ingestion in rats was found at 260 mg/l through drinking water, equivalent to 15 mg/kg BW/day. For dermal exposure systemic toxicity is not found for formaldehyde in concentrations up to 1% (which was the highest concentration tested). The oral study lasted two years, during which period rats were administered doses of formaldehyde in concentrations of 20, 260 and 1900 mg/l through their drinking water. The rats given the highest dose had a reduced food intake and reduced progression of their body weight. Consequently, NOAEL was set at 15 mg/kg BW/day, which was confirmed by similar results in two other studies (a 2-year study and a 28-day study).

According to a number of studies, formaldehyde is slightly genotoxic and has induced genetic mutations and chromosomal deviations in mammalian cells. However, the genotoxic effects seem to be limited to cells in direct contact with the substance. It is therefore the conclusion of both the OECD and the ECHA Committee for Risk Assessment (RAC) that formaldehyde is a substance that causes local mutagenic effects (73, 77). The substance is classified as Muta. 2 (H341 - Suspected of causing genetic defects).

According to several studies, formaldehyde is carcinogenic to humans through inhalation and causes tumours in the upper airways (73). Formaldehyde was upgraded to a higher class from Carc. 2 (H351 – Suspected of causing cancer) to Carc. 1B (H350 – May cause cancer) in 2014. Inhalation of concentration at or above 10 ppm (12 mg/m^3) causes an increase in the presence of tumours in the noses of rats. In contrast, there is no increase in the presence of tumours in other organs following inhalation, and there is found to be no correlation between the generation of tumours and exposure to formaldehyde through other routes of exposure (73). Limited evidence is found to exist for a causal relationship between formaldehyde exposure and tumours in the nose in epidemiological studies of working environments (73). Experimental results and mechanistic data support that there is a dose-response relationship for induction of nose tumours for formaldehyde (77). OECD (73) concludes that formaldehyde is not expected to be a potential carcinogen to humans at low exposures. Overall, there is no convincing documentation that substantiates

[14] LC_{50}: Lethal concentration (LC) which results in 50% mortality.

carcinogenic effects for places that are not in direct contact with substances or via routes other than exposure through inhalation (77).

Long-term experiments involving chronic oral dosages of formaldehyde to rats do not indicate that the substance may be congenital or cause reproductive damage (73). Concentrations of formaldehyde which cause an acute toxic effect on the place of exposure do not lead to a significantly systemic dose and therefore do not cause systemic toxicity. Formaldehyde react spontaneously with cellular nucleofiles and is quickly metabolised by various enzymes (73).

7.6.5 Identification of critical effect and determination of a safe dose

Formaldehyde can produce cancer but is expected only to manifest itself through inhalation, and likewise no T25 or other relevant parameters to determine a DMEL have been established. Exposure to formaldehyde through the toy products in this project are expected only to take place either through dermal contact or oral ingestion. The formaldehyde in the products can evaporate thereby enabling inhalation of the substance. However, this level is expected to be very low (47) - and the carcinogenic potential is consequently not estimated to be relevant to the risk assessment discussed in the next chapter. For the mutagenic effect no relevant threshold value was established to assess the risk. The critical effect of exposure to formaldehyde on the skin is considered to be induction and generation of allergy, although clear threshold values for induction have not been determined. However, an effect for oral toxicity can be established on the basis of the above-mentioned 2-year study on rats (73), where rats orally exposed to formaldehyde through drinking water showed a reduced intake of food and reduced development in body weight.

With a starting point in the stated NOAEL of 15 mg/kg BW/day for rats in the mentioned study, a standard safety factor (AS) for interspecies variation (allometric scaling) on 4 (rats) was used to determine the DNEL together with a factor 2.5 for the remaining difference between species as stated in ECHA "Guidance on information requirements and chemical safety assessment – Chapter R.8" (62). Likewise, a standard safety factor of 10 was used for differences within the species. Therefore, a total safety factor of 100 was used, which gives a DNEL for formaldehyde of 0.15 mg/kg BW(day).

7.6.5.1 Allergy

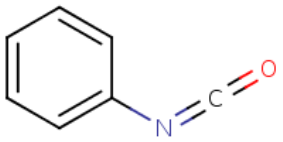
Positive response to patch tests on humans already appears from a 1% formaldehyde concentration, while the cause of allergic reactions in already sensitized individuals has been observed at much lower concentrations (limit values of 0.003% for aqueous solutions and 0.006% for products have been suggested (76)). Regarding an overall allergy risk assessment the concentration of formaldehyde in toy products will be compared with 1% for the development of allergy and 0.006% for the cause of allergy, respectively.

7.7 Phenyl Isocyanate

7.7.1 Identification, classification and physiochemical properties

The physiochemical properties of the substance and its classification in the ECHA inventory (CLP) can be found in Table 59.

TABLE 59
IDENTIFICATION, CLASSIFICATION AND PHYSIOCHEMICAL PROPERTIES

Chemical name	Phenyl isocyanate
Synonyms	Benzene, isocyanato- Carbanil Phenyl isocyanate Isocyanatobenzene Isocyanic acid, phenyl ester Carbanil Phenyl carbonimide Phenylcarbimide
CAS no.	103-71-9
EC no.	203-137-6
Chemical structure	
Classification Self-classified CLP classification* (Regulation 1272, 2008)	Carc 2, H351 – Suspected of causing cancer (1/269) Acute Tox. 4, H302 – Harmful if swallowed Skin Corr. 1B, H314 – Causes severe skin burns and eye damage Skin Sens. 1, H317 – May cause an allergic skin reaction Eye Dam. 1, H318 – Causes serious eye damage Acute Tox. 1, H330 – Fatal if inhaled Resp. Sens. 1, H334 – May cause allergy or asthma symptoms or breathing difficulties if inhaled STOT SE 3, H335 – May cause respiratory irritation
Physical condition	Liquid
Molar weight	119.12 g/mol
Melting point	-30 °C
Boiling point	163 °C
Vapour pressure	2.57 mm Hg
Octanol/water distribution (log	2.59
Water solubility	617 g/L

*The number of notifications that have stated a CMR category appear in the brackets: http://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/cl-inventory/view-notification-summary/104564.

7.7.2 Absorption and distribution

Structurally phenyl isocyanate is related to other aromatic compounds (e.g. aniline, ethylbenzene and styrene) and generally the biotransformation of this type of substances takes place via the CYP 450 enzyme system (as described in section 7.1.2). Many of the biological activities are identical for the aromatic compounds, as an example ethylbenzene, benzene and toluene are easily absorbed after exposure through inhalation and distributed to the fatty tissue, liver, kidneys, bone marrow and nerve tissue (67). As mentioned above (s sections 7.1.2, 7.2.2. and 7.3.2) aromatic compounds are excreted relatively fast in the urine.

The project has been unable to find information that describes the absorption and distribution of phenyl isocyanate in more detail. However, the substance is characterised by high water solubility

(the highest among the substances assessed) and the absorption is consequently estimated to be 100%.

7.7.3 Local effects: Irritation and allergy

Only a few overview reports or no risk assessment reports have been published on phenyl isocyanate. In 2008, the British working environment authorities produced a list of primary literature available at the time (78). This survey found no published studies that demonstrated that phenyl isocyanate should cause irritation or sensitization of the airways. Generally, there were found no other studies that described other aspects of the toxicity of the substance (78).

The REACH consortium behind the registration of phenyl isocyanate lists several unpublished rabbit experiments. The main conclusion of these experiments is that the substances causes irritation and a burning sensation in the skin and that it can cause irritation in the eyes (79). A working environment study involving 310 workers tested for their reaction to phenyl isocyanate on dermal exposure was also described. None of these exhibited any allergic reactions but three workers experienced irritation of the skin (79).

7.7.4 Systemic effects: Acute and chronic effects

An unpublished acute rat experiment with oral exposure established an LD50 of 887 mg/kg BW. Observation of the rats showed that the toxic effect affected the nervous system resulting in such symptoms as irregular breathing and uncoordinated movements. In addition to this the rats showed signs of cyanosis (see sections 7.2.2 and 7.2.4 on aniline). Acute dermal exposure experiments with rats and rabbits found an LD50 of >5000 mg/kg BW (79).

A sub-chronic reproduction experiment with mice involving repeated oral exposure did not demonstrate any teratogenic effects of phenyl isocyanate (79).

Based on the scarce available data there is likewise no evidence to suggest that phenyl isocyanate is mutagenic nor carcinogenic (79). This is further supported by the circumstance that the substance is not listed as carcinogenic in the IRIS database (51) and by a federal US working group (80).

7.7.5 Identification of critical effect and determination of safe dose

It can be seen from the notified self-classifications of phenyl isocyanate that CMR category Carc 2 is listed for only one of the 14 notifications - and there is no evidence that a CMR effect should be the critical effect of that substance. Based on the above it is not possible to identify an immediate critical effect for phenyl isocyanate. However, the risk assessment suggests that the critical effect most likely will be induction and a resultant allergic reaction. A threshold value for the induction remains to be determined, however, and for this reason the risk assessment in the next chapter will not comprise toys containing phenyl isocyanate.

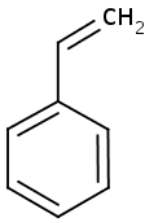
7.8 Styrene

7.8.1 Identification, classification and physiochemical properties

Like aniline (see section 7.2) and ethylbenzene (see section 7.5), styrene is one of the 141 substances selected for listing under the ESR regulation which were selected for an EU risk assessment. This risk assessment comprises only environmental factors and not health aspects associated with the substance (81).

The physiochemical properties of the substance and its classification in the ECHA inventory (CLP) can be found in Table 60.

TABLE 60
IDENTIFICATION, CLASSIFICATION AND PHYSIOCHEMICAL PROPERTIES

Chemical name	Styrene
Synonyms	Styreen Styrene Styrene Styrene monomers Styrol Styrole Styrolene
CAS no.	100-42-5
EC no.	202-851-5
Chemical structure	
Classification Harmonised CLP classification* (Regulation 1272, 2008)	Repr. 2, H361d – Suspected of damaging the unborn child Acute Tox. 4*, H332 – Harmful if inhaled STOT RE 1, H372 – Causes damage to organs (hearing) through prolonged or repeated exposure Skin Irrit. 2, H315 – Causes skin irritation Eye Irrit. 2, H319 – Causes serious eye irritation
Physical condition	Liquid
Molar weight	104.151 g/mol
Melting point	-31°C
Boiling point	145°C
Vapour pressure	6.4 mm Hg
Octanol/water distribution (log	2.95
Water solubility	310 mg/L

*Harmonised classification cf. 6th amendment of CLP (4).

7.8.2 Absorption and distribution

Humans easily absorb styrene vapours through inhalation and the absorbed fraction of the substance is about 100% in concentration levels of 10-200 ppm. Conversely, absorption of styrene (as a liquid or a gas) through skin contact is significantly lower - estimated at about 2-5% of the dose used. When it comes to oral intake of styrene there is no information available but based on the physiochemical properties and compared with data from animal experiments, the absorbed fraction is assumed to be about 100% (as for inhalation) (82).

Styrene and metabolites of the substance are distributed throughout the body, with the highest concentration in the fatty tissue. Normally, the concentration of styrene is also higher in the brain compared with the concentration in the blood. Mouse experiments have also shown that the substance can affect the foetus via the placenta.

In humans, styrene disintegrates relatively fast and is excreted in the urine. Styrene metabolises by means of the CYP450 enzyme system where the substance is oxidised to styrene-7,8-oxide (SO) and is either conjugated to glutathione (GSH) or undergoes further enzymatic hydrolysis and then it is excreted as N-benzoylglycine (benzoylamino-acetic acid). Most of the styrene (95%) is converted to SO. For more detailed description of the metabolism of styrene see the report "Survey of styrene" published by the Danish EPA (83).

7.8.3 Local effects: Irritation and allergy

Styrene is classified under CLP as a substance that can cause irritation of the skin (Skin Irrit. 2) and severe irritation of the eyes (Eye Irrit. 2). Available data about skin irritation following exposure to styrene in liquid form is a limited quality; however, it does indicate that repeated exposure is required to cause an effect. Conversely, liquid styrene and styrene vapour can cause irritation of the eyes. The NOAEC value (No Observed Adverse Effect Concentration) is set at 100 and 216 ppm for seven hours and one hour of exposure, respectively (82). Styrene can also cause respiratory irritation but at higher levels of concentration than those causing irritation of the eyes.

Extensive information about humans and about animal experiments does not give rise to classify styrene as an allergen (82).

7.8.4 Systemic effects: Acute and chronic effects

There is information about acute toxicity in humans following inhalation, which indicates effects from styrene on the central nervous system (CNS) at concentration levels of 200-400 ppm (over a period of 30-90 minutes). There is no immediate information about other acute effects of styrene on humans, and available animal experiments with mice are not considered useful since the acute effect of styrene on mice is different from that on humans (82). As regards the risk assessment the concentration where acute effects on the CNS are not observed is set at 100 ppm for seven hours of exposure (82).

There is extensive information from studies of the toxicity of styrene on humans from long-term (chronic) or repeated exposure. According to studies of the effects of styrene in the working environment the most frequent symptoms are irritation of the eyes and nose. However, disruption of the CNS (e.g. headache and lethargy) is considered the effect of most relevance to the health (82) - there is also considerable documentation of the neurotoxic effect of styrene in animal models. The effect of styrene on vision and in particular on hearing (ototoxicity) is considered the most relevant effect in relation to repeated exposure through inhalation. A previous study publish by the Danish EPA also indicates that long-term exposure to styrene through inhalation in the working environment can lead to partial loss of hearing (83). The ECHA Committee for Risk Assessment (RAC) concluded in 2012, upon request from the Danish EPA, that styrene should be classified as STOT SE1 (Causes damage to organs (hearing) through prolonged or repeated exposure).

In connection with that risk assessment of styrene, the substance was also classified as Repr. 2 (Suspected of damaging the unborn child) (84). Reprotoxic effects in the form of developmental defects (delayed development) have been demonstrated in a thoroughly documented second generation rat experiment. Based on this study the NOAEC is estimated to be 120 mg/kg/day (82). Extensive data is also available on the reprotoxic effects in humans from exposure in the working environment (e.g. miscarriage, disruptions of the menstrual cycle, fertility, semen quality, birth weight and mental development of the child); it is, however, impossible with certainty to draw any conclusion based on these studies (82).

As for chronic effects, there is no evidence of any mutagenic effects. Previously, the International Agency for Research on Cancer (IARC) believed that styrene might be carcinogenic to humans; according to the current conclusion, however, there is no evidence of any carcinogenic effect on

humans (82). This is further supported by the fact that styrene is not listed as a carcinogen in the IRIS database (51).

7.8.5 Identification of critical effect and determination of a safe dose

The critical effect of styrene is the reprotoxic effect of the substance with an estimated NOAEC of 120 mg/kg/day (extrapolated from a NOAEC of 650 mg/m³ (82)).

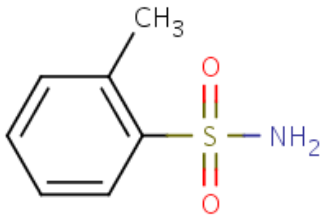
The NOAEC value is based on inhalatory exposure from a well-documented second generation rat study. As mentioned in section 7.8.2 intake and absorption of styrene through inhalation are equivalent to oral exposure, which means there is no safety factor (AS) in this context. On the contrary, the analysis uses a safety factor of 2 for individual differences in exposure duration (from sub-chronic to chronic), a factor for interspecies variation (allometric scaling) of 4 (rats) and a factor of 2.5 for the remaining differences between species, as indicated in Chapter R.8 of ECHA's "Guidance on information requirements and chemical safety assessment" (62). Likewise, a standard safety factor of 10 was applied to differences within the species. Therefore, a combined safety factor of 200 was used, which produced an oral DNEL of 0.6 mg/kg BW/day.

7.9 o-Toluenesulfonamide (o-TSA)

7.9.1 Identification, classification and physiochemical properties

The physiochemical properties of the substance and its classification in the ECHA inventory (CLP) can be found in Table 61.

TABLE 61
IDENTIFICATION, CLASSIFICATION AND PHYSIOCHEMICAL PROPERTIES

Chemical name	o-Toluenesulfonamide
Synonyms	2-Methylbenzenesulfonamide 2-Tolylsulfonamide Benzenesulfonamide, 2-methyl- o-Methylbenzenesulfonamide o-Toluenesulfonamide ortho-Toluenesulfonamide ortho-Toluol-sulfonamid Toluene-2-sulfonamide
CAS no.	88-19-7
EC no.	201-808-8
Chemical structure	
Classification Self-classified CLP classification* (Regulation 1272, 2008)	Carc 1A, H350 – May cause cancer (1/42) Carc 2, H351 – Suspected of causing cancer (25/42) Acute Tox. 4, H302, H312, H332 – Toxic if swallowed, in contact with skin and inhaled Skin Irrit. 2, H315 – Causes skin irritation Eye Irrit. 2, H319 – Causes serious eye irritation STOT SE 3, H335 – May cause respiratory irritation
Physical condition	Solid
Molar weight	171.22 g/mol

Chemical name	o-Toluenesulfonamide
Melting point	156.3°C
Boiling point	>270 °C
Vapour pressure	6.0E-5 mm Hg
Octanol/water distribution (log	0.84
Water solubility	1.62 g/L

*The number of notifications that have stated a CMR category appear in the brackets: http://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/cl-inventory/view-notification-summary/49782.

7.9.2 Absorption and distribution

It has not been possible to find relevant information about absorption and distribution of o-TSA in the literature. The relatively high water solubility and low log P_{ow} value do, however, give rise to assume that the substance is easily absorbed and distributed in most of the body. As described in the unpublished studies, according to the REACH consortium (85) that registered o-TSA, humans absorb the substance relatively easily and most of it (80%) is excreted through the urine within 48 hours. Studies with radioactively labelled o-TSA in rats shows that the primary disintegration products are toluene-2-sulphonamide and 2-sulphamoylbenzyl alcohol followed by a conjugation of these metabolites to glucuronic acid, and saccharin is also excreted (85). This supports the notion that o-TSA is disintegrated by the CYP450 enzyme system previously referred to.

The above data is primarily based on oral exposure with an assumed 100% absorption. However, the REACH consortium for o-TSA points out that toxicokinetic studies indicate that the intake from dermal exposure would be about 20% as a maximum.

7.9.3 Local effects: Irritation and allergy

A previous report produced by the Danish EPA (86) specified a series of toxic effects of o-TSA on human health. No immediate effects were found for skin, eyes and airways as indicated under the notified self-classification of o-TSA. Unpublished data stated in connection with the REACH registration of o-TSA shows that the substance may induce a weak irritation of the skin and eyes – although not to a degree that gives rise to classify the substance as a skin or eye irritant. Based on an unpublished "read-across" study with p-Toluenesulfonamide (p-TSA - which is discussed in section 7.10), the same REACH registration dossier for o-TSA found that neither o-TSA nor p-TSA has the potential to cause contact allergy (85).

7.9.4 Systemic effects: Acute and chronic effects

The above report produced by the Danish EPA (86) gave an overview of a small number of studies of acute and chronic effects of o-TSA. Among these a rat experiment shows that o-TSA is teratogenic (86).

Some weak mutagenic activity is indicated but there is limited evidence to suggest that o-TSA should be carcinogenic (86). The health assessment of the REACH registration of o-TSA reaches the same conclusion based on various *in vitro* genotoxic experiments (unpublished data) based on mammalian cell lines covering mutagenicity and chromosomal deviations among others (85). The substance is not listed as a carcinogenic substance in the IRIS database either (51).

An unpublished, sub-chronic rat experiment involving repeated exposure to o-TSA over a period of six weeks and focusing on the reproductive effect showed that adult rats were significantly more sensitive to the substance than their offspring (85). There was found no effect of o-TSA on reproduction relevant parameters (e.g. gestation period, size of litter and gender ratio) and there was found no teratogenic effects on the offspring. On the contrary, o-TSA led to, based on histopathological examinations, liver damage in both genders of adult rats and the experiment

established a NOAEL value of 20 mg/kg BW/day. For the offspring, NOAEL was estimated to be 100 mg/kg BW/day (85). By way of comparison, an unpublished sub chronic test with rabbits exposed orally to the structurally very similar substance (see chapter 7.10) p-TSA shows that a NOAEL for teratogenic effects on the embryo/foetal development can be determined to 113 mg/kg BW/day (87).

7.9.5 Identification of critical effect and determination of safe dose

The critical effect of o-TSA was identified as the teratogenic (reprotoxic) effect in a report published by the Danish EPA. The report emphasises, however, that the study, which produced the data, is incomplete and hence a NOAEL or a NOAEC value cannot be established (86). The above sub-chronic rat experiment identified a NOAEL for the offspring; however, the study does not consider the NOAEL referred to as being directly associated with the reprotoxic effect (85). The same study also proves that liver damage appears in connection with substantially lower concentrations, which from the available results demonstrates that this effect parameter is the critical effect of o-TSA. The same study also demonstrates that liver damages appear at much lower concentrations which from the available results demonstrates that this effect parameter is the critical effect of o-TSA. The NOAEL for liver damages is 20 mg/kg BW/day (85) and that value will be used to determine a DNEL for liver damages.

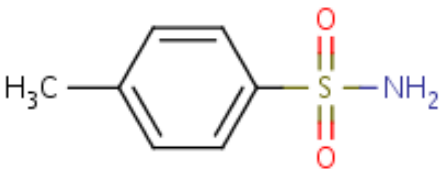
A safety factor (AS) of 2 is used for differences in exposure duration (from sub-chronic to chronic), a factor for interspecies variation (allometric scaling) of 4 (rats) and a factor of 2.5 for the remaining differences between species, as indicated in Chapter R.8 of ECHA's "Guidance on information requirements and chemical safety assessment" (62). A standard safety factor of 10 is used for individual differences within the species. Therefore, a combined safety factor of 200 has been used, which produces an oral and a dermal DNEL of 0.5 mg/kg BW/day.

7.10 p-Toluenesulfonamide (p-TSA)

7.10.1 Identification, classification and physiochemical properties

The physiochemical properties of the substance and its classification in the ECHA inventory (CLP) can be found in Table 62.

TABLE 62
IDENTIFICATION, CLASSIFICATION AND PHYSIOCHEMICAL PROPERTIES

Chemical name	p-Toluenesulfonamide
Synonyms	4-Methylbenzenesulfonamide 4-Toluenesulfanamide 4-Toluenesulfonic acid, amide Benzenesulfonamide, 4-methyl- p-Methylbenzenesulfonamide p-Toluenesulfamide p-Toluenesulfonamide
CAS no.	70-55-3
EC no.	200-741-1
Chemical structure	

Chemical name	p-Toluenesulfonamide
Classification Self-classified CLP classification* (Regulation 1272, 2008)	Repr 2, H361 – Suspected of damaging fertility or the unborn child (3/204) Skin Irrit. 2, H315 – Causes skin irritation Eye Irrit. 2, H319 – Causes serious eye irritation Acute Tox. 2, H330 – Fatal if inhaled STOT SE 3, H335 – May cause respiratory irritation
Physical condition	Solid
Molar weight	171.22 g/mol
Melting point	138.5 °C
Boiling point	221°C at 10 mmHg (www.inchem.org/documents/sids/sids/70553.pdf)
Vapour pressure	9.6E-5 mm Hg
Octanol/water distribution (log	0.82
Water solubility	3.16 g/L

*The number of notifications that have stated a CMR category appear in the brackets: http://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/cl-inventory/view-notification-summary/73930.

It is clear from the Tables 61 and 62 above that the structural similarity between o-TSA (section 7.9) and p-TSA is good. Only the position of the methyl group (CH_3) separates the two substances structurally. It was also evident from the previous section on o-TSA that toxicological information for p-TSA in some cases was used if data was missing for o-TSA (so-called "read-across" – as an example see section 7.9.3). The toxicological similarity of the substances was also supported by the many identical factors of the respective CPL classifications. o-TSA and p-TSA both had a self-classified CLP classification although both substances have been noted independently as acute toxic when inhaled (o-TSA as Acute Tox. 4 and p-TSA as Acute Tox 2) and as Skin Irrit. 2 (causes skin irritation), Eye Irrit. 2 (causes severe eye irritation) and STOT SE 3 (can cause irritation of the airways). Reference will also be made to information on o-TSA below to the extent the data on p-TSA is insufficient.

7.10.2 Absorption and distribution

It has not been possible to find relevant information about absorption and distribution of o-TSA in the literature. A rat experiment conducted some years ago involving oral exposure to radioactively labelled p-TSA (87) shows that most (66-89%) of the substance is quickly excreted in the urine. The predominant metabolite in the urine was 4-sulphamoyl benzoic acid, which supports (as for o-TSA) that p-TSA is disintegrated by the CYP450 enzyme system.

The relatively high water solubility and low log P_{ow} value do, however, as for o-TSA give rise to assume that the substance is easily absorbed and distributed in most of the body. Based on the above data 100% absorption is assumed. As already mentioned in section 7.9.2, toxicokinetic studies of o-TSA indicate that the absorption from dermal exposure will be about 20% as a maximum.

7.10.3 Local effects: Irritation and allergy

Unpublished data stated in connection with the REACH registration of p-TSA shows that the substance may induce weak irritation of the skin and eyes – although not to a degree that gives rise to classify the substance as a skin or eye irritant (87).

As already mentioned in section 7.9.3 an unpublished study of p-TSA gives rise to the assessment that neither o-TSA nor p-TSA have the potential to cause allergy from skin contact (85, 87).

7.10.4 Systemic effects: Acute and chronic effects

According to unpublished data acute oral exposure led to an LD50 for p-TSA of 2330 mg/kg BW in rats – and an experiment involving acute dermal exposure of rabbits to a TSA mixture (o/p-TSA) showed no mortality at 7500 mg/kg BW (87).

An unpublished rat experiment (90 days oral exposure) with p-TSA led to reduced body weight (21% lower than the control animals) and an estimated NOAEL of 214 and 248 mg/kg BW/day for male and female rats, respectively (87).

An unpublished second generation reproduction experiment with rats orally exposed to p-TSA led to toxic effects in the F0 and F1 parent generation for a test concentration of 3,000 ppm and a development-related toxicity (reduced body weight in gestating females) of 10,000 ppm (the highest test concentration). Reproduction and mating-related parameters were not affected at the highest test concentration. A NOAEL for development-related toxicity was estimated at 165 -237 mg/kg GW/day for male rates and 232-499 mg/kg GW/day for female rats (87).

An unpublished, sub-chronic study assessed the effect on prenatal development in rabbits orally exposed to p-TSA (87). Based on these results it was concluded that exposure of gestating rabbits to a high dose (11,000 ppm) of p-TSA during organ formation in the foetus could be compared to abnormal development of the spine and chest in the foetuses. Some of the exposed gestating rabbits were subjected to stress, however, in connection with the initial stages of the experiment, and for this reason these effects need not only be associated with p-TSA. No effects were found in the foetuses for lower doses of 1,000 and 3,000 ppm, respectively. This resulted in a NOAEL for teratogenic effects in the embryo/foetus development of 113 mg/kg BW/day (87).

Based on several *in vitro* genotoxic experiments, the health assessment of the REACH registration of p-TSA finds no evidence of mutagenicity or chromosomal deviations (87). The substance is not listed as a carcinogenic substance in the IRIS database either (51). This is concurrent with the results for o-TSA, which is not considered to exhibit mutagenic or carcinogenic effects either.

7.10.5 Identification of critical effect and determination of safe dose

In the light of the above, the critical effect is the teratogenic (reprotoxic) effect on the embryo/foetus development, for a NOAEL of 13 mg/kg BW/day. This NOAEL will be used to determine a reprotoxicity DNEL, which is concurrent with the CMR category (Repr 2), which is noted for p-TSA (self-classification).

A safety factor (AS) of 2 is used for individual differences in exposure duration (from sub-chronic to chronic), a factor for interspecies variation (allometric scaling) of 2.4 (rabbits) and a factor of 2.5 for the remaining differences between species, as indicated in Chapter R.8 of ECHA's "Guidance on information requirements and chemical safety assessment" (62) and a standard safety factor of 10 for individual differences within the species. Therefore, a combined safety factor of 120 has been used, which produces an oral and a dermal DNEL of 0.94 mg/kg BW/day.

7.11 Summary and conclusion

Table 63 provides an overview of the health assessments of the CMR substances examined – focussing on the established DN(M)EL and the primary references used for the substances concerned.

For five of the 10 CMR substances, the critical effect was the reprotoxic effect of which ethylbenzene was not classified in this category (harmonised classification). For phenyl isocyanate it was not possible to identify a critical effect. The critical effect of o-TSA was assessed to be hepatotoxicity, while it for formaldehyde was assessed to be induction and generation of allergy by dermal exposure. An oral toxic effect of formaldehyde is also considered relevant and therefore a DNEL is

established (Table 63). For the two remaining CMR substances (MBT and aniline), the critical effect was carcinogenic. However, it was only possible to determine a DMEL for aniline from the available data. Consequently, a DNEL/DMEL could be determined for only eight out of 10 CMR substances.

TABLE 63
OUTLINE OF THE HEALTH ASSESSMENT FOR CMR SUBSTANCES

CMR substance	CAS no.	Critical effect	Safe dose DN(M)EL	Reference
2-Mercapto-benzothiazole	149-30-4	Carcinogenic	The critical effect is a carcinogenic effect. However, there is no information available that can be used to calculate a DMEL for the substance.	49-53
Aniline	62-53-3	Carcinogenic	DMEL dermal: 0.000020 mg/kg BW/day	54-55
Butylated hydroxytoluene (BHT)	128-37-0	Reprotoxic	DNEL oral: 0.125 mg/kg BW/day DNEL dermal: 0.125 mg/kg BW/day	51, 58-61
Dimethyltin dichloride (DMTC)	753-73-1	Reprotoxic	DNEL oral: 0.002 mg/kg BW/day	51, 63-65
Ethylbenzene	100-41-4	Reprotoxic	DNEL oral: 5.75 mg/kg BW/day	51, 66-69
Formaldehyde	50-00-0	Acute toxic (oral)*	DNEL dermal: 0.15 mg/kg BW/day DNEL oral: 0.15 mg/kg BW/day	70-77
Phenyl isocyanate	103-71-9	-	Not possible to identify the critical effect. See section 7.7. for further details.	51, 67, 78-80
Styrene	100-42-5	Reprotoxic	DNEL oral: 0.6 mg/kg BW/day	51, 81-84
o-Toluene-	88-19-7	Hepatotoxic	DNEL oral:	51, 85-87

CMR substance	CAS no.	Critical effect	Safe dose DN(M)EL	Reference
sulfonamide (o-TSA)			0.1 mg/kg BW/day DNEL dermal: 0.1 mg/kg BW/day	
p-Toluene-sulfonamide (p-TSA)	70-55-3	Reprotoxic	DNEL oral: 0.94 mg/kg BW/day DNEL dermal: 0.94 mg/kg BW/day	51, 85, 87

* The critical effect is regarded to be development and cause of allergy, but assessment of oral toxicity is included in the following with application of the stated DNEL.

8. Risk assessment

8.1 Background

Exposure calculations for 10 CMR substances (chapter 6) were performed on the basis of the analysis results followed by a health assessment (chapter 7). This chapter contains a risk assessment of whether the use of the substances in the toys in question can be regarded as safe. The method used to calculate the risk of using the identified CMR substances in the selected toys is described below.

8.2 Risk calculation method

The risk was calculated using the risk assessment method recommended in the REACH regulation (88). In each individual case, the following formula, which calculates the Risk Characterisation Ratio (RCR) using the DN(M)EL for dermal (Dder) and oral (Doral) exposure, was used to assess whether a health risk exists.

$$RCR = \frac{D_{der}}{DN(M)EL}$$

or

$$RCR = \frac{D_{oral}}{DN(M)EL}$$

In the present project, the RCR calculation for the individual substances was performed on the basis of their worst-case route(s) of exposure identified in Chapter 6 (see Table 48).

8.3 Risk assessment

The health risk associated with exposure to a given concentration of a given substance over a given period of time is assessed on the basis of worst-case calculations for dermal (D_{der}) and oral (D_{oral}) exposure, respectively (see Tables 51-52). The result is then compared with the DN(M)EL value determined in chapter 7 under the health assessment (see Table 63). The risk of an effect is thus assessed on the basis of an RCR value, which is calculated as indicated in section 8.2.

An RCR value above 1 indicates that the substance in question is associated with a risk under the estimated worst-case assumptions. If the value is close to 1, the relevant exposure scenario is refined and the risk assessed on the basis of a more realistic scenario. It is also possible to include one of the parameters used in the risk assessment of the substance if relevant to determine a refined DN(M)EL value.

Table 64 shows the risk of the studied CMR substances. It was not possible to assess a worst-case risk for MBT and phenyl isocyanate, as a safe dose (DN(M)EL) for these substances could not be established (see sections 7.1.5 and 7.7.5).

TABLE 64

DESCRIPTION OF RISKS ASSOCIATED WITH DERMAL AND ORAL EXPOSURE TO CMR SUBSTANCES

CMR substance	Critical effect	RCR der	RCR oral	D_{der}	D_{oral}	DN(M)EL der	DN(M)EL oral
Aniline	Carcinogenic	0.360	-	7.2E-6* (608)	-	2.0E-5	-
BHT	Reprotoxic	0.248	0.001	0.031** (553B)	1.8E-4 (553B)	0.125	0.125
DMTC	Reprotoxic	-	0.036	-	7.1E-5* (597)	-	0.002
Ethylbenzene	Reprotoxic	-	1.1E-5	-	6.1E-5 (609)	-	5.75
Formaldehyde	Acute toxic (oral)	0.353	0.003	0.053	4.5E-4	0.15	0.15
o-TSA	Hepatotoxic	6.70	0.004	0.67** (598)	0.0019** (598)	0.5	0.5
p-TSA	Reprotoxic	0.037	0.002	0.035 (614)	0.0019 (605)	0.94	0.94
Styrene	Reprotoxic	-	9.0E-5	-	5.4E-5 (609)	-	0.6

* Calculation based on migration data. ** The substance is present in several products, but is shown here for the product with the highest level of Dder or Doral.

8.3.1 Allergy risk for formaldehyde

The formaldehyde concentrations in the analysed samples correspond to 0.019% (sample no. 554), 0.0044% (sample no. 555) and 0.00064% (sample no. 598). The formaldehyde content can be added as formaldehyde or originate from formaldehyde liberators that are used as preservatives (47), but the exact source is not known. As described in section 7.6, no clear concentration limit for sensitization or cause of an allergic reaction for formaldehyde has been determined. If a comparison is made with the suggested limit values for elicitation (causing allergic reactions in already sensitized individuals) of 0.006% for formaldehyde in products, the concentration in two out of three analysed products is below the limit value. The concentration in one single product (sample no. 554) is above 0.006%. However, patch tests were carried out with a liquid product, whereas the toy product is a solid product and therefore the migration out of the product is expected to be considerably lower. A direct comparison of the concentration would be an overestimate of the risk and not migration studies were carried out on formaldehyde that can clarify the risk further. Therefore, it is not possible to determine if the amount of formaldehyde represents a health-related risk in the product in question (sample no. 554). A report on preservatives in toys that was published by the Danish Environmental Protection Agency in 2014 found concentrations of formaldehyde in slime and play dough, respectively. The report concludes that the content might constitute a risk of allergy, but points out that especially products that remain on the skin for a longer period of time (47) are in question. However, the report also emphasizes that migration from the products is expected to be decisive for exposure (47). A report from 2008 on chemical substances in artificial nails and nail hardeners also demonstrates a content of formaldehyde in that type of products and points at a possible allergy risk (89).

8.3.2 Summation of RCR values for BHT, o-TSA and p-TSA

BHT, o-TSA and p-TSA are all found in more than one of the analysed products, and a risk assessment assuming exposure from several products was therefore calculated (see Table 65) using the following formula.

$$RCR = \frac{Exposure\ (D_{total})}{DN(M)EL} = \frac{D_{oral}}{DN(M)EL} + \frac{D_{der}}{DN(M)EL}$$

Where a product has been assessed for both a dermal and an oral route of exposure, the route that produces the highest exposure has been used in the summation of RCR. As a general rule (worst-case), the scenario does not take into account whether the product is used by the same age group.

TABLE 65

SUMMATION OF RCR VALUES FOR BHT, O-TSA AND P-TSA IN THE PRODUCTS INCLUDED IN THE RISK ASSESSMENT

Substance	RCR_{der}	RCR_{oral}	Σ RCR
BHT (553B)	0.248		**0.424**
BHT (611)	0.176		
o-TSA (598)	6.70		
o-TSA (605)		0.026	**6.731**
o-TSA (614)	0.005		
p-TSA (605)		0.002	**0.039**
p-TSA (614)	0.037		

8.3.3 Discussion of the risk assessment

The dermal and oral exposure levels for MBT and phenyl isocyanate are comparable to those of the other CMR substances. However, due to the lack of toxicology data, it is not possible to perform a risk assessment for these substances.

As shown in Tables 64 and 65, only one of the assessed CMR substances, o-TSA, presents a health risk (RCE = 1.34) in a worst-case exposure scenario and without considering special aspects relating to toxicology (e.g. the specific absorption relating to a specific route of exposure). The remaining CMR substances are divided into two groups: a group with very low RCR values below 0.01 and a group with RCR values in the range >0.01 to <0.4. Even in a risk assessment of the combined exposure to selected substances (BHT, o-TSA and p-TSA) from several products, only o-TSA has an RCR value above 1.

In general, there is therefore no need to refine the worst-case exposure scenarios for most of the CMR substances. However, a more realistic risk assessment is required for dermal exposure to o-TSA. It is possible to adjust selected parameters to calculate a more realistic exposure. In this context, general parameters such as the exposure frequency (which has been estimated at 100 times/year) and the applied product amount (Qprod) is estimated less conservatively.

The mentioned parameters were set high in the dermal exposure scenario for o-TSA, which gives an unrealistic conservative risk assessment of the substance. Table 66 gives an outline of the differences and states a more realistic D_{Der} for the product. It comprises a reduced product amount and exposure frequency where Qprod and n, respectively, are reduced by a factor 3.5 and 4. In that way, D_{Der} becomes 14 (3.5 x 4) times lower than calculated under worst-case assumptions. On the basis of the refined D_{Der} a more realistic RCR for o-TSA can be calculated to be 0.48 (0.048/0.1). The summed up RCR value for o-TSA also becomes substantially reduced (0.48 + 0.0004 + 0.026 = 0.506). In addition, toxiokinetic studies indicate that the absorption of o-TSA by dermal exposure max. will amount to app. 20% (85). With a starting point in the refined exposure assessment it can

also be anticipated that o-TSA does not represent a health risk, neither isolated or in connection with exposure from several products containing the substance.

TABLE 66
OUTLINE OF WORST-CASE AND REFINED EXPOSURE ASSESSMENT OF TOY SLIME (SAMPLE NO. 598).

Exposure scenario	Q_{prod} (g)	n (day^{-1})	D_{Der} (mg/kg/day)
Worst-case	350	0.274	0.67
Refined	100	0.069*	0.048

*The worst-case exposure frequency was set to 100 times/year – in the refined assessment the exposure Frequency is expected to be 25 times/year.

8.4 Summary and conclusion

In general, the risk assessment of the selected CMR substances, where such an assessment could be performed, shows that there is no health risk associated with any of the studied toys. In the case of two of the substances, MBT and phenyl isocyanate, it was not possible to perform a risk assessment due to the absence of toxicology data. Several worst-case assumptions were made in the overall risk assessment, for example in connection with the exposure scenarios for the CMR substances. Overall, this means that the actual risk associated with the studied CMR substances is likely to be even lower than shown in the report. One CMR substance, o-TSA, presented a health risk under worst-case assumptions for dermal exposure in connection with the use of toy slime (product no. 598), which contains o-TSA. However, when allowing for a dermal intake of 20% o-TSA the risk assessment did not show that o-TSA constituted a health risk.

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Appendix 1: The Danish EPA database of chemical substances in consumer products: Toy products with CMR substances*

Substance	Product	Content conc.	Unit	Analysis	CAS no.	CMR category
1,1-Dimethoxypropan	Slimy toys	5	%m/m	Total content	4744-10-9	Repr 1B
1,2-Diethoxyethan	Wooden toys	3.4	ug/g	Migration	629-14-1	Repr 1A
1-Methyl-2-pyrrolidinon	Wooden toys	28-59	ug/g	Migration	872-50-4	Repr 1B
2-Ethoxyethanol	Wooden toys	2.1-17	ug/g	Migration	110-80-5	Repr 1B
2-Ethoxyethanol	Colouring pens	7.4-19	mg/kg	Total content	110-80-5	Repr 1B
2-Ethylhexan	Wooden toys	3.2	ug/g	Migration	149-57-5	Repr 2
2H-1-Benzopyran-2-on	Flower w. padding	33	mg/kg	Total content	91-64-5	Carc 2**
2-Hexanon	Slimy toys	2.7-8	%m/m	Total content	591-78-6	Repr 2
2-Methoxyethanol	Wooden toys	0.9	ug/g	Migration	109-86-4	Repr 1B
2-methylpropenal	Balloons	0.17-0.85	area %	Total content	78-84-2	Muta 2**
Isophorone	Slimy toys	0-0.3	ug/g	Total content	78-59-1	Carc 2
Isophorone	Slimy toys	0-1.4	ug/g	Total content	78-59-1	Carc 2
Isophorone	Slimy toys	1.2-5.7	%m/m	Total content	78-59-1	Carc 2
Isophorone	Wooden toys	4.7-21	ug/g	Migration	78-59-1	Carc 2
Isophorone	Toy bag	1	ug/g	Emission	78-59-1	Carc 2
Isophorone	Toy bag	150	ug/g	Emission	78-59-1	Carc 2
Isophorone	Eraser	1	ug/g	Emission	78-59-1	Carc 2
Aniline	Balloons	3.36	area %	Total content	62-53-3	Carc 2, Muta 2
Aniline	Colouring pens	0.11-0.22	mg/kg	Total content	62-53-3	Carc 2, Muta 2
p-Anisidine	Colouring pens	0.12	mg/g	Total content	104-94-9	Carc 1B**
Anthracene	Ball	<0.2	mg/kg	Total content	120-12-7	Carc 2**
Anthracene	Doll	<0.2	mg/kg	Total content	120-12-7	Carc 2**
Anthracene	Rubber figurine	<0.2	mg/kg	Total content	120-12-7	Carc 2**
Anthracene	Car	<0.2	mg/kg	Total content	120-12-7	Carc 2**
Antimony	Balloons	< 6	mg/kg	Emission	7440-36-0	Carc 2**
Antimony	Slimy toys	0.23-3.8	ug/g	Total content	7440-36-0	Carc 2**
Antimony	Glitter glue	0.22	mg/kg	Total content	7440-36-0	Carc 2**
Arsenic	Balloons	< 2.5	ug/g	Migration	7440-38-2	Carc A***
Benzene	Balloons	2.44	area %	Total content	71-43-2	Carc 1A, Muta 1B
Benzo(a)anthracene	Balloons	<0.2	mg/kg	Total content	56-55-3	Carc 1B
Benzo(e)pyrene	Ball	<0.2	mg/kg	Total content	192-97-2	Carc 1B
BHT	Balloons	0.2-10.95	area %	Total content	128-37-0	Carc 1B/2, Muta 1B/2, Repr 2**
BHT	Flower w. padding	60	mg/kg	Total content	128-37-0	Carc 1B/2, Muta 1B/2, Repr 2**
BHT	Eraser	160	mg/kg	Total content	128-37-0	Carc 1B/2, Muta 1B/2, Repr 2**
BHT	Toy bag	1	ug/g	Emission	128-37-0	Carc 1B/2, Muta 1B/2, Repr 2**
BHT	Eraser	3-70	ug/g	Emission	128-37-0	Carc 1B/2, Muta 1B/2, Repr 2**
Bis(2-ethylhexyl) hexanedioate	Colouring pens	0.32-0.35	mg/kg	Total content	103-23-1	Carc 2, Repr 2**
Lead	Balloons	< 9	mg/kg	Emission	7439-92-1	Carc 2, Repro 1A/B**
Lead	Slimy toys	0.12-0.9	ug/g	Total content	7439-92-1	Carc 2, Repro 1A/B**
Cadmium	Balloons	< 5	mg/kg	Emission	7440-43-9	Carc 1B, Muta 2,

Substance	Product	Content conc.	Unit	Analysis	CAS no.	CMR category
						Repr 2
Cadmium	Pearl plate	<1	mg/kg	Total content	7440-43-9	Carc 1B, Muta 2, Repr 2
Cadmium	Tube pearls	<2	mg/kg	Total content	7440-43-9	Carc 1B, Muta 2, Repr 2
Camphor	Teddy bear	8-630	ug/g	Migration (16 timer)	76-22-2	Muta 2, Repr 1A**
Carbon disulphide	Balloons	3.29-20.98	area %	Total content	75-15-0	Repr 2
Chrysene	Balloons	<0.2	mg/kg	Total content	218-01-9	Carc 1B, Muta 2
Chrysene	Doll	<0.2	mg/kg	Total content	218-01-9	Carc 1B, Muta 2
Dibenzo(a,h)anthracene	Balloons	<0.2	mg/kg	Total content	53-70-3	Carc 1B
Dibenzo(a,h)anthracene	Car	<0.2	mg/kg	Total content	53-70-3	Carc 1B
Dibenzo(a,h)anthracene	Eraser	<0.2	mg/kg	Total content	53-70-3	Carc 1B
Dichloromethane	Slimy toys	3	%m/m	Total content	75-09-2	Carc 2
Diisopropyl ether	Wooden toys	6.8-17	ug/g	Migration	108-20-3	Repr 2**
Dimethylformamide	Balloons	0.53-3.52	areal %	Total content	68-12-2	Repr 1B
Ethyl benzene	Pearl plate	11.5-935	mg/kg	Total content	100-41-4	Carc 1A, Carc 2, Muta 1B**
Ethyl benzene	Tube pearls	<10	mg/kg	Total content	100-41-4	Carc 1A, Carc 2, Muta 1B**
Ethyl benzene	Slimy toys	0.8-100	mg/kg	Total content	100-41-4	Carc 1A, Carc 2, Muta 1B**
Formaldehyde	Glitter glue	0.06-63	mg/kg	Total content	50-00-0	Carc 2
Formamide	Wooden toys	18-69	ug/g	Migration	75-12-7	Repr 1B
Furfural	Wooden toys	0.5-4.6	ug/g	Migration	98-01-1	Carc 2
Indeno(1,2,3-cd)pyrene	Ball	<0.2	mg/kg	Total content	193-39-5	Carc 2**
Indeno(1,2,3-cd)pyrene	Car	<0.2	mg/kg	Total content	193-39-5	Carc 2**
Copper	Pearl plate	<2	mg/kg	Total content	7440-50-8	Repr 2**
Copper	Slimy toys	0.56-8.7	ug/g	Total content	7440-50-8	Repr 2**
Copper	Glitter glue	0.015-0.12	mg/kg	Total content	7440-50-8	Repr 2**
Cobalt	Pearl plate	<1	mg/kg	Total content	7440-48-4	Carc 1B/2, Repr 2**
Cobalt	Slimy toys	0.29	ug/g	Total content	7440-48-4	Carc 1B/2, Repr 2**
Chromium	Balloons	< 2.5	mg/kg	Emission	7440-47-3	Carc 1B/2, Muta 2**
Chromium	Pearl plate	<1	mg/kg	Total content	7440-47-3	Carc 1B/2, Muta 2**
Chromium	Tube pearls	29-45.5	mg/kg	Total content	7440-47-3	Carc 1B/2, Muta 2**
Chromium	Slimy toys	0.1-0.94	ug/g	Total content	7440-47-3	Carc 1B/2, Muta 2**
Mercury	Balloons	< 2.5	mg/kg	Emission	7439-97-6	Repr 1B
Manganese	Pearl plate	<2	mg/kg	Total content	7439-96-5	Muta 1B, Repr 1B/2**
Manganese	Tube pearls	64.5	mg/kg	Total content	7439-96-5	Muta 1B, Repr 1B/2**
Manganese	Slimy toys	0.13-2	ug/g	Total content	7439-96-5	Muta 1B, Repr 1B/2**
Methyl parabene	Slimy toys	0-1.8	ug/g	Total content	99-76-3	Muta 2**
Methyl parabene	Slimy toys	0-3.9	ug/g	Total content	99-76-3	Muta 2**
N,N-dimethylacetamide	Balloons	0.91	area %	Total content	127-19-5	Repr 1B
N,N-dimethylacetamide	Colouring pens	0.22-0.40	mg/kg	Total content	127-19-5	Repr 1B
N,N-dimethylformamide	Balloons	0.13-2.95	area %	Total content	68-12-2	Repr 1B
N,N-dimethylformamide	Slimy toys	0.4	%m/m	Total content	68-12-2	Repr 1B
Naphthalene	Slimy toys	0-0.02	ug/g	Total content	91-20-3	Carc 2
Naphthalene	Slimy toys	0-0.02	ug/g	Total content	91-20-3	Carc 2

Substance	Product	Content conc.	Unit	Analysis	CAS no.	CMR category
Naphthalene	Bracelet	<0.2	mg/kg	Total content	91-20-3	Carc 2
Naphthalene	Balloons	0,2-0,5	mg/kg	Total content	91-20-3	Carc 2
Naphthalene	Teething ring	<0,2	mg/kg	Total content	91-20-3	Carc 2
Naphthalene	Ball	<0,2-0,5	mg/kg	Total content	91-20-3	Carc 2
Naphthalene	Dall	<0,2	mg/kg	Total content	91-20-3	Carc 2
Naphthalene	Rubber figure	0,2-0,5	mg/kg	Total content	91-20-3	Carc 2
Naphthalene	Ballpoint pen	<0,2	mg/kg	Total content	91-20-3	Carc 2
Naphthalene	Car	0,2-0,5	mg/kg	Total content	91-20-3	Carc 2
Naphthalene	Swimming gear	<0,2	mg/kg	Total content	91-20-3	Carc 2
Naphthalene	Eraser	<0,2	mg/kg	Total content	91-20-3	Carc 2
Nickel	Balloons	< 2	mg/kg	Emission	7440-02-0	Carc 2
Nickel	Slimy toys	0,72-2,6	ug/g	Total content	7440-02-0	Carc 2
N-nitrosodibutylamine	Balloons	0,54	areal %	Total content	924-16-3	Carc 2**
N-nitrosodibutylamine	Balloons	0,006-0,08	mg/kg	Emission	924-16-3	Carc 2**
N-nitrosodimethylamine	Balloons	0,02-0,03	mg/kg	Emission	62-75-9	Carc 1B
N-nitrosodimethylamine	Balloons	0,64-0,83	areal %	Total content	62-75-9	Carc 1B
N-nitrosodiphenylamine	Balloons	0,006-0,009	mg/kg	Emission	86-30-6	Carc 2, Muta 2**
Phenanthrene	Bracelet	0,2-0,5	mg/kg	Total content	85-01-8	Carc 2**
Phenanthrene	Balloons	<0,2	mg/kg	Total content	85-01-8	Carc 2**
Phenanthrene	Teething ring	<0,2	mg/kg	Total content	85-01-8	Carc 2**
Phenanthrene	Ball	0,2-0,5	mg/kg	Total content	85-01-8	Carc 2**
Phenanthrene	Dall	<0,2	mg/kg	Total content	85-01-8	Carc 2**
Phenanthrene	Rubber figure	<0,2	mg/kg	Total content	85-01-8	Carc 2**
Phenanthrene	Ballpoint pen	0,2-0,5	mg/kg	Total content	85-01-8	Carc 2**
Phenanthrene	Car	0,2-0,5	mg/kg	Total content	85-01-8	Carc 2**
Phenanthrene	Swimming gear	<0,2	mg/kg	Total content	85-01-8	Carc 2**
Phenanthrene	Eraser	<0,2	mg/kg	Total content	85-01-8	Carc 2**
Phenol	Balloons	0,62	areal %	Total content	108-95-2	Muta 2
Phenol	Glitter glue	0,054	mg/kg	Total content	108-95-2	Muta 2
Phenol	Toy bag	1	ug/g	Emission	108-95-2	Muta 2
Styrene	Slimy toys	2-5,1	%m/m	Total content	100-42-5	Carc 2, Muta 2, Repr 1B**
Myristic acid	Eraser	140	mg/kg	Total content	544-63-8	Carc 2**
Tetrahydrofuran	Slimy toys	0,4-3,4	%m/m	Total content	109-99-9	Carc 2
Toluene	Rubber figure	500	mg/kg	Total content	108-88-3	Repr 2
Toluene	Pearl plate	8,8-72	mg/kg	Total content	108-88-3	Repr 2
Toluene	Tube pearls	<10	mg/kg	Total content	108-88-3	Repr 2
Toluene	Slimy toys	1-66	%m/m	Total content	108-88-3	Repr 2
Toluene	Slimy toys	0-1,8	ug/g	Total content	108-88-3	Repr 2
Toluene	Slimy toys	0-1,9	ug/g	Total content	108-88-3	Repr 2
Toluene	Wooden toys	1,0-5,3	ug/g	Migration	108-88-3	Repr 2

*Based on the reports from the Danish EPA on survey of chemical substances in consumer products (10-18), **Self-classified CLP classification, ***Not classified as CMR under harmonized CLP classification, but notified as Carc 2 under previous self-classified CLP classification; ****US EPA category for carcinogens (A: Carcinogenic to humans, B: Probably Carcinogenic to humans, C: Possibly carcinogenic to humans).

Appendix 2: RAPEX: Toy products containing CMR substances*

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Activity mat	Baby activity toys	Textile	China		4-aminoazobenzene	101 mg/kg
Alphabet board	Wooden toys	Wood (painted/treated)	China		Lead, chromium	1260 mg/kg (Pb), 185 mg/ kg (Cr)
Workbench	Domestic	Dyed/painted item	China		Lead, chromium	1471 mg/kg (Pb), 166 mg/ kg (Cr)
Beach toys	Swimming gear	Dyed/painted item	Hong Kong		Lead, chromium	3140 mg/kg (Pb), 660 mg/ kg (Cr)
Balance toys	Games & activities	Dyed/painted item	The Netherlands		Lead, chromium	2840-3040 mg/kg (Pb), 340-350 mg/ kg (Cr)

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Balloons	Balloons	Rubber	Spain		N-nitrosamines	0.0526 mg/kg
Balloons	Balloons	Rubber	Poland	 	N-nitrosamines	0.07-0.13 mg/kg
Balloons	Balloons	Rubber	China	 	N-nitrosamines	0.071 mg/kg
Balloons	Balloons	Rubber	Spain		N-nitrosamines	0.083 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Balloons	Balloons	Rubber	China		N-nitrosamines	0.091 mg/kg
Balloons	Balloons	Rubber	Germany		N-nitrosamines	0.112 mg/kg
Balloons	Balloons	Rubber	Mexico		N-nitrosamines	0.14-0.18 mg/kg
Balloons	Balloons	Rubber	Unknown	 	N-nitrosamines	0.163 mg/kg
Balloons	Balloons	Rubber	Mexico		N-nitrosamines	0.219 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Balloons	Balloons	Rubber	Mexico		N-nitrosamines	0.255 mg/kg
Balloons	Balloons	Rubber	Italy	  	N-nitrosamines	0.472 mg/kg
Balloons	Balloons	Rubber	Malaysia		N-nitrosamines	0.846 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Balloons	Balloons	Rubber	Spain		N-nitrosamines	1.3 mg/kg
Balloons	Balloons	Rubber	Spain		N-nitrosamines	2.66 mg/kg
Balloons	Balloons	Rubber	Taiwan		N-nitrosamines	Unknown
Teddy bear	Soft toys	Dyed/painted item	China	 	Lead, chromium	Above specific limit value

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Teddy bear	Soft toys	Textile	China		Lead	Above specific limit value
Book	Soft toys	Textile	Hong Kong		4,4'-methylen bis(2-chloroaniline)	116-186 mg/kg
Punching bag	Games & activities	Dyed/painted item	China		Lead, chromium	447 mg/kg (pb), 109 mg/ kg (Cr)
Ball	Games & activities	Dyed/painted item	China		Lead	98 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Dart	Games & activities	Foam	China		Benzene	190 mg/kg
Dinosaur	Figurine	Dyed/painted item	China	 	Lead, chromium	1792 mg/kg (Pb), 406.7 mg/kg (Cr)
Dinosaur	Figurine	Dyed/painted item	China		Lead	333 mg/kg
Dinosaur	Figurine	Plastic	China		Creosote	Unknown
Doll	Dolls etc.	Textile	Unknown	 	4-aminoazobenzene	1076 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Doll	Dolls etc.	Textile	China		4-aminoazobenzene	126 mg/kg
Doll	Dolls etc.	Dyed/painted item	China		Lead, chromium	128-338 mg/kg (Pb), 65 mg/ kg (Cr)
Doll	Dolls etc.	Textile	Unknown	 	4-aminoazobenzene	140-1400 mg/ kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Doll	Dolls etc.	Textile	Hong Kong		4-aminoazobenzene	156 mg/kg
Doll	Dolls etc.	Dyed/painted item	China		Lead	370 mg/kg
Doll	Dolls etc.	Textile	China		4-aminoazobenzene	770 mg/kg
Doll	Dolls etc.	Plastic	Hong Kong		Phenol	980 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Doll	Dolls etc.	Metal	China		Lead, chromium	Above specific limit value
Doll	Dolls etc.	Textile	China		4-aminoazobenzene, 3,3'-dimethoxybenzidine	Unknown
Chalk	Drawing & painting	Dyed/painted item	China		Lead, chromium	Unknown
Fishing tackle	Games & activities	Metal	Sweden		Lead	Unknown

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Workable balloon paste	Balloons	Unknown	Germany		Benzene	37.6-45.6 mg/ kg
Rocking horse	Soft toys	Dyed/painted item	China	 	Lead	100 mg/kg
Horse	Soft toys	Dyed/painted item	China		Lead, chromium	120-750 mg/ kg (Pb), 99 mg/ kg (Cr)
Horse	Figure	Rubber	China		N-nitrosamines	Unknown
Dog	Soft toys	Dyed/painted item	China		Lead	105 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Dog	Soft toys	Dyed/painted item	China		Lead	190 mg/kg
Hand doll	Dolls etc.	Textile	China		4-aminoazobenzene	315 mg/kg
Hand doll	Dolls etc.	Textile	China		4-aminoazobenzene	372 mg/kg
Hand doll	Dolls etc.	Textile	China	 	Benzidine	41.9 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Hand doll	Dolls etc.	Textile	China	 	4-methyl-m-phenylenediamine	55.2 mg/kg
Hand doll	Dolls etc.	Textile	China	   	4-aminoazobenzene	581 mg/kg
Hand doll	Dolls etc.	Textile	China		4-aminoazobenzene	96 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Rabbit	Soft toys	Textile	China		4-aminoazobenzene	332 mg/kg
Rabbit	Soft toys	Unknown	China		Formaldehyde	58 mg/kg
Binoculars	Domestic	Plastic	China		Naphthalene, toluene, styrene	Unknown
Bricks	Games & activities	Dyed/painted item	Russia		Lead, chromium	633-1263 mg/kg (Pb), 143-254 mg/ kg (Cr)
Bricks	Wooden toys	Wood (painted/treated)	Unknown		Formaldehyde	Emission (24 t) 233.8-687.9 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Make-up	Costumes	Powder/paste	China		Lead, chromium	1181.5 mg/kg (Pb), 260.3 mg/kg (Cr)
Make-up	Costumes	Powder/paste	China		Lead, chromium	1457 mg/kg (Pb), 288.3 mg/kg (Cr)
Make-up	Costumes	Powder/paste	China		Lead, chromium	1620 mg/kg (Pb), 172 mg/ kg (Cr)
Make-up	Costumes	Powder/paste	China		Lead, chromium	1647 mg/kg (Pb), 333 mg/ kg (Cr)
Make-up	Costumes	Powder/paste	China		Lead, chromium	260 mg/kg (Pb), 80 mg/ kg (Cr)

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Make-up	Costumes	Powder/paste	China		Lead, chromium, arsenic, antimony	31795 mg/kg (Pb), 16427 mg/kg (Cr), 49 mg/kg (As), 765 mg/kg (Sb)
Make-up	Costumes	Powder/paste	China		Lead, chromium	3450 mg/kg (Pb), 128 mg/kg (Cr)
Make-up	Costumes	Powder/paste	China		Lead	480.3-506.9 mg/kg
Make-up	Costumes	Powder/paste	China		Lead, chromium	872.6 mg/kg (Pb), 287 mg/kg (Cr)
Make-up	Costumes	Powder/paste	China		Chromium	Unknown

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Costume	Costumes	Textile	China		4-aminoazobenzene	1701 mg/kg
Costume	Costumes	Textile	The Philippines		4,4'-Bi-o-toluidin (3,3'-dimethylbenzidine)	516 mg/kg
Costume	Costumes	Textile	China		4-aminoazobenzene	89 mg/kg
Balls	Games & activities	Dyed/painted item	China		Cadmium	189-539 mg/ kg (Cd)
Abacus	Wooden toys	Wood (painted/treated)	China		Lead	140 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
DIY bird house	Wooden toys	Wood (painted/treated)	China		Formaldehyde	580 mg/kg
Activity mat	Games & activities	Dyed/painted item	Hong Kong		Lead	250 mg/kg
Toy bag	Domestic	Dyed/painted item	China		Lead, chromium	845 mg/kg (Pb), 120 mg/kg (Cr)
Car	Vehicles	Dyed/painted item	China		Lead, chromium	1156.4 mg/kg (Pb), 265.3 mg /kg (Cr)
Car	Vehicles	Dyed/painted item	China	 	Lead, chromium	11830 mg/kg (Pb), 1970 mg/ kg (Cr)

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Car	Vehicles	Dyed/painted item	China		Lead, chromium	15400 mg/kg (Pb), 3480 mg/kg (Cr)
Car	Vehicles	Dyed/painted item	China	 	Lead, chromium	181-8841 mg/kg (Pb), 239-338 mg/kg (Cr)
Car	Vehicles	Dyed/painted item	China	 	Lead, chromium	1820-3647 mg/kg (Pb), 317-343 mg/kg (cr)
Car	Vehicles	Dyed/painted item	China		Lead	204.4 mg/kg

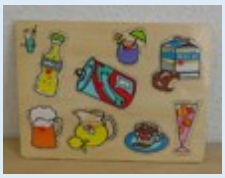
Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Car	Vehicles	Dyed/painted item	China	 	Lead	2540 mg/kg
Car	Vehicles	Dyed/painted item	China		Lead, chromium	3714 mg/kg (Pb), 825 mg/kg (Cr)
Car	Vehicles	Dyed/painted item	China	 	Lead, chromium	375-433 mg/kg (Pb), 97.9 mg/kg (Cr)
Car	Vehicles	Dyed/painted item	China	 	Lead, chromium	405 mg/kg (Pb), 79.7 mg/kg (Cr)
Car	Vehicles	Dyed/painted item	China	 	Lead	4074-5450 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Car	Vehicles	Dyed/painted item	China		Lead, chromium	499-1270 mg/kg (Pb), 95-280 mg/kg (Cr)
Car	Vehicles	Dyed/painted item	China		Lead, chromium	761.6 mg/kg (Pb), 158.2 mg/kg (Cr)
Car	Vehicles	Dyed/painted item	China		Lead, chromium	904 mg/kg (Pb), 191 mg/kg (Cr)
Car	Vehicles	Dyed/painted item	China		Lead, chromium	964.6 mg/kg (Pb), 242.9 mg/kg (Cr)
Train	Wooden toys	Wood (painted/treated)	Hong Kong		Lead, chromium	515 mg/kg (Pb), 110 mg/kg (Cr)

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Train	Vehicles	Dyed/painted item	China	 	Lead, chromium	534 mg/kg (Pb), 146 mg/kg (Cr)
Train	Vehicles	Solvent	China	 	Benzene	Unknown
Weapons	Games & activities	Dyed/painted item	China		Lead	225 mg/kg
Weapons	Games & activities	Dyed/painted item	China	 	Chromium	65-93 mg/kg
Weapons	Games & activities	Plastic	China		Toluene	Unknown

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Cooking set	Domestic	Dyed/painted item	China		Lead	374 mg/kg
Magnetic holder	Wooden toys	Wood (painted/treated)	China		Formaldehyde	910 mg/kg
Mask	Costumes	Dyed/painted item	China		Lead	137-146 mg/kg
Musical toys	Games & activities	Dyed/painted item	China		Lead	130-160 mg/kg
Musical toys	Wooden toys	Wood (painted/treated)	India		O-toluidine	170 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Musical toys	Games & activities	Dyed/painted item	China		Lead, chromium	1817-1844 mg/kg (Pb), 205-460 mg/kg (Cr)
Musical toys	Wooden toys	Wood (painted/treated)	Italy		Lead, chromium	Unknown
Key ring	Games & activities	Metal	China		Nickel	Migration: 0.83 µg/ cm²/week
Winnie the Pooh	Figurine	Rubber	China		Phenol	370 mg/kg
Puzzle	Wooden toys	Wood (painted/treated)	China	 	Formaldehyde	1133-1243 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Puzzle	Wooden toys	Wood (painted/treated)	The Netherlands	 	Formaldehyde	158-204 mg/kg
Puzzle	Wooden toys	Wood (painted/treated)	Unknown	 	Formaldehyde	180-230 mg/kg
Puzzle	Wooden toys	Wood (painted/treated)	The Czech Republic		Formaldehyde	202.6 mg/kg
Puzzle	Wooden toys	Wood (painted/treated)	Unknown		Formaldehyde	253 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Puzzle	Wooden toys	Wood (painted/treated)	The Netherlands		Formaldehyde	3000 mg/kg
Puzzle	Wooden toys	Wood (painted/treated)	The Czech Republic		Formaldehyde	511 mg/kg
Puzzle	Wooden toys	Wood (painted/treated)	China		Formaldehyde	704 mg/kg
Puzzle	Wooden toys	Wood (painted/treated)	China		Formaldehyde	Emission (24 t) 206 mg/kg
Puzzle	Games & activities	Metal	China	 	Nickel	Migration: 34.5 µg/cm²/ week

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Puzzle	Wooden toys	Wood (painted/treated)	China		Lead, formaldehyde	Above specific limit value
Puzzle	Wooden toys	Wood (painted/treated)	The Netherlands	 	Formaldehyde	Above specific limit value
Rattle	Baby activity toys	Wood (painted/treated)	Thailand		Lead, chromium	310-850 mg/kg (Pb), 120 mg/ kg (Cr)
Ring pyramid	Wooden toys	Wood (painted/treated)	Thailand		Lead	290 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Slimy toys	Slimy toys	Liquid/gel	China	 	Phenol	285 mg/kg
Shovel	Domestic	Metal	Germany		Lead	1307 mg/kg
Shovel	Domestic	Dyed/painted item	China		Lead, chromium	969-1540 mg/kg (Pb), 227-350 mg/kg (Cr)
Game	Wooden toys	Wood (painted/treated)	China		Formaldehyde	794.59 mg/kg
Game	Wooden toys	Wood (painted/treated)	Thailand		Lead, chromium	93-871 mg/kg (Pb), 22-184 mg/kg (Cr)

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Game	Wooden toys	Wood (painted/treated)	Thailand		Lead, chromium	93-871 mg/kg (Pb), 22-184 mg/kg (Cr)
Game	Wooden toys	Wood (painted/treated)	China		Formaldehyde	Above specific limit value
Game	Wooden toys	Wood (painted/treated)	China	 	Formaldehyde	Above specific limit value
Jumping jack	Wooden toys	Wood (painted/treated)	Russia		Lead, chromium	410-2000 mg/kg (Pb), 72-400 mg/kg (Cr)
Jumping jack	Wooden toys	Wood (painted/treated)	Russia		Lead, chromium	630 mg/kg (Pb), 130 mg/kg (Cr)

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Bathing ring	Swimming gear	Plastic	China	No picture	Isophorone, phenol	64 mg/kg, 129 mg/kg
Bathing ring	Swimming gear	Plastic	Unknown		Isophorone, toluene	Unknown
Animal bag	Soft toys	Textile	China		4,4'-Bi-o-toluidin (3,3'-dimethylbenzidine)	48 mg/kg
Writing board	Baby activity toys	Textile	Russia		Formaldehyde	90 mg/kg
Tea set	Domestic	Plastic	China		Nickel	Migration: 0.40 mg/dm2

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Tractor etc.	Vehicles	Dyed/painted item	Hong Kong		Lead, chromium	460 mg/kg (Pb), 90 mg/ kg (Cr)
Pull-along animal	Wooden toys	Wood (painted/treated)	Russia		Lead, chromium	570-2400 mg/kg (Pb), 120-340 mg/ kg (Cr)
Pull-along animal	Games & activities	Dyed/painted item	China	 	Lead	983 mg/kg
Pull-along cart	Games & activities	Plastic	China		Lead	170 mg/kg
Colouring pens	Drawing & painting	Solvent	Unknown	 	Benzene	10-92 mg/kg

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Colouring pens	Drawing & painting	Solvent	China	No picture	Benzene	12.4-75.6 mg/ kg
Colouring pens	Drawing & painting	Solvent	Unknown		Benzene	120-254 mg/kg
Colouring pens	Drawing & painting	Solvent	China		Benzene	19-308 mg/kg
Colouring pens	Drawing & painting	Solvent	China		Benzene	26-110 mg/kg
Colouring pens	Drawing & painting	Solvent	China		Benzene	29-31 mg/kg

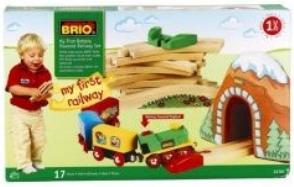
Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Colouring pens	Drawing & painting	Solvent	China		Benzene	38-70 mg/kg
Colouring pens	Drawing & painting	Solvent	China		Benzene	5-30.3 mg/kg
Colouring pens	Drawing & painting	Solvent	Unknown		Benzene	Above specific limit value
Colouring pens	Drawing & painting	Solvent	Ukraine		Aniline	Unknown
Colouring pens	Drawing & painting	Solvent	China		Benzene	Unknown

Product	Type of toy	Material	Producing country	Picture of product	Chemical(s)	Content conc.
Soft toys	Baby activity toys	Textile	China		4-aminoazobenzene	67 mg/kg
Soft toys	Baby activity toys	Textile	China	No picture	Lead, chromium	Above specific limit value
Yoyo	Games & activities	Plastic	China		Toluene, ethyl benzene	Unknown
Yoyo	Games & activities	Plastic	China		Toluene, ethyl benzene	Unknown

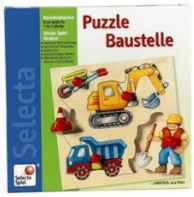
*CMR substances in toys arranged according to product type.

Appendix 3: TÆNK: Test of toys containing dangerous chemical substances*

Product	Age group	Price	Toy type	Critical discoveries	Produced in	Tested
Brio Safari figure-8 railway 	>3 years	279	Wood	Liberation of nickel from the metal hub caps. The orange wood is not resistant to sweat. The lacquer on the locomotive contains organic tin compounds, and the black lacquer on the locomotive contains PAH and octylphenol-ethoxylate.	China	2011
Papo Prince Phillip and Prince Phillip's horse 	>3 years	73	Plastic	Rider contains PAH.	China	2011
Chuggington Workshop Shed 	>3 years	150	Wood	Organic tin compounds in the lacquer.	China	2011
Bob the Builder Sprinter 	>3 years	230	Plastic	Liberation of nickel from the metal exhaust.	China	2011
Selecta Mein erster Ponyhof 	>3 years	360	Wood	Liberation of nickel from the metal lock and organic tin compounds in white lacquer on the handle. The lacquer also contains nonylphenol-ethoxylate.	Germany	2011

Product	Age group	Price	Toy type	Critical discoveries	Produced in	Tested
Zapf Creation Baby born 	>3 years	399	Doll	Nonylphenol in body parts of plastic and nonylphenol ethoxylate in hat and clothes.	China	2011
Brio My first railway with battery-driven engine 	<3 years	325	Wood	Flame retardant TCEP in the tunnel, nickel liberated from the hub caps, highest concentration of PAH and also a content of organotin compounds in the black chassis of the cars.	China	2010
Plan Toys Pull-along toys, Snake 	<3 years		Wood	The snake's rubber tongue can be pulled off with risk of swallowing. PAH in the snake and formaldehyde liberation from the cord.	Thailand	2010
Top-Toy ApS Food´n´fun Make your own sandwich 	<3 years	129	Plastic	Content of carcinogenic and allergy causing dyes in Velcro and PAH in Velcro and plastic parts.	Unknown	2010
Corolle Calin Yang 	<3 years	300	Doll	PAH in Velcro and nonylphenol in head.	China	2010

Product	Age group	Price	Toy type	Critical discoveries	Produced in	Tested
Diddl Mimihopps 	<3 years	149	Soft toys	Passed the safety test, but the felt carrot came loose. PAH in rubber band and nonylphenol ethoxylate in hair.	Unknown	2010
Goki Puzzle Baby animals 	<3 years	49	Wood	PAH in the lacquer.	Unknown	2010
Haba Discovery Bricks 	<3 years	179	Wood	Organic tin compounds and traces of DINP, but in part of the toy where skin contact is rather unlikely.	Germany	2010
Ikea Gosig Golden 	<3 years	59	Soft toys	PAH in plush.	Indonesia	2010
Ikea Mula Hammer log 	<3 years	49	Wood	PAH in the lacquer.	China	2010

Product	Age group	Price	Toy type	Critical discoveries	Produced in	Tested
Learning Curve Bob the Builder & Wendy 	<3 years	69	Plastic	PAH in lacquer and plastic and organic tin compounds.	China	2010
Selecta Knop Puzzle Construction Site 	>3 years	159	Wood	Liberation of formaldehyde from plywood.	Germany	2010
Steiff Edgar Teddy bear 	>3 years	229	Soft toys	PAH in Velcro.	Unknown	2010
Zapf Creation My little baby born 	>3 years	158	Doll	Nonylphenol in arms and legs.	China	2010

*The table has been modified according to the test results of TÆNK published at taenk.dk (38, 39) and shows 19 out of 35 tested products that contain dangerous chemical substances, including CMR substances. They comprise (the bracket states possible CAS no. and CMR category): Formaldehyde (CAS no. 50-00-0, Carc 2), Nickel (Carc 1A), Organic tin compounds (Carc, Repr), PAH / Polycyclic Aromatic Hydrocarbons (Carc), Nonylphenol (CAS no. 25154-52-3, Repr 2).

Appendix 4: Outline of aromatic amines derived from azo dyes covered by the analysis

Child car seat	
Dye	CAS no.
4-aminobiphenyl	92-67-1
Benzidine	92-87-5
4-chloro-o-toluidine	95-69-2
2-naphthylamine	91-59-8
o-aminoazotoluene	97-56-3
5-nitro-o-toluidine	99-55-8
4-chloroaniline	106-47-8
4-methoxy-m-phenylenediamine	615-05-4
4,4'-Diaminodiphenylmethane	101-77-9
3,3'- Dichlorobenzidine	91-94-1
3,3'- Dimethoxybenzidine	119-90-4
3,3'- Dimethylbenzidine	119-93-7
4,4'-Methylenedi-o-toluidine	838-88-0
p-Cresidine	120-71-8
4,4'-Methylen-bis-(2-chloraniline)	101-14-4
4,4'-Oxydianiline	101-80-4
4,4-Thiodianiline	139-65-1
o-Toluidine	95-53-4
4-Methyl-m-phenylenediamine	95-80-7
2,4,5-Trimethylaniline	137-17-7
o-Anisidine	90-04-0
2,4-Xylidine / 2,6-Xylidine	95-68-1/87-62-7

CMR Substances in Toys – Control and Risk Assessment

This report comprises a survey of CMR substances found in toys in Denmark and Europe. Focus is on CMR substances that are not phthalates, as phthalates in toys are covered by another on-going project on chemical substances in consumer products. In the light of the survey, the Chemical Inspection Service at the Danish EPA collected 30 toy products that were analysed for content of CMR substances. The toy products were screened for content of chemical substances, and 24 CMR substances were selected for quantitative analysis of the content concentration in the toys in question. The quantitative analyses were supplemented with migration tests and analyses of two CMR substances that had been chosen due to their relatively high concentration (however, below limit value) in two different toy products. In the light of the analysis results, 10 CMR substances were chosen that in the last phase of the project were assessed in relation to exposure, health and risk.

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