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Survey of unwanted additives in PVC products imported over the internet

Environmental Project

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Contents

Preface

This report describes the results of a project about selected additives in PVC-based products, which may be purchased online by private customers from countries outside Denmark. The project examines examples of various types of consumer products to clarify which of several selected additives may be found in these consumer products purchased outside Denmark. The selection of additives investigated is delimited partly by the tender (heat stabilizers, softeners such as phthalates and SCCP as well as 32 substances used in PVC from the PLASI database) and in addition via prioritization of substances and analyses within the budget frame during the project.

The project was carried out from May until December 2019 for the Danish Environmental Protection Agency by Danish Technological Institute with DHI as sub-contractor on description and evaluation of the environmentally and health-related properties of the additives.

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Summary and conclusions

Project focus

Polyvinyl chloride (PVC) is globally considered as an important type of plastic having good properties for a wide range of consumer products. Many different additives can be added to this material, among others, softening agents, pigments, and stabilizing agents, which help to achieve the desired properties of the material. Yet, additives can have a negative impact on the environment and health and on the recycling of these materials. In the European Union (EU), restrictions have been introduced on several additives, but many products today are purchased on the internet in web shops outside the EU.

The main aim of this project was to find out if a Danish consumer is exposed to problematic substances when purchasing PVC-products in web shops outside Denmark. Thus, this project investigates the content of selected problematic additives in certain products purchased in web shops inside the EU (except Denmark) and outside the EU. Thereafter, the environmental and health-related characteristics and barriers of the identified substances were analyzed in relation to recycling. The contents of these problematic substances were compared with the contents of consumer products acquired in Denmark in control campaigns from the Chemical Inspection Service in 2018 on DIY retailer products and on children's toys. In addition, the project also assessed whether the analyzed products would have been legal if they were marketed in Denmark.

This project focuses on the following additives in PVC: heat stabilizers, softening agents such as phthalates and short-chain chlorinated paraffins (SCCPs). Furthermore, initial focus was also on 32 substances indicated as being used in PVC according to the PLASI database. These 32 substances were assessed and prioritized according to their CLP hazard classification and hazard profile according to the five impact areas prioritized as the five adverse effects in the "Political agreement on new joint chemicals initiatives 2018-21" of the Danish government.

Selection and purchase of consumer products

For the analyses, the products were selected according to various criteria; among others, that they are consumer goods that are common applications of PVC, that they are typically purchased by Danish consumers on foreign websites and that they are purchased from frequently used foreign web shops. Fulfilment of the criteria were based on data from the report Survey of PVC in Denmark 2018 (Survey of PVC in Denmark 2018) as well as data from the Association of Danish Internet Trade (FDIH). Furthermore, product types allowing comparison to products in the previous control campaigns by the Chemical Inspection Service possible (products purchased from DIY retailers and children's toy products) had to be included, and it was a precondition that the product types represented a broad variety of products.

First, the criteria were drawn up in a prioritization matrix of product types, which was later used to create a list of 95 specific products. This list was then used to choose and purchase 76 products out of which 74 were received and included in the analysis program. The purchased consumer products were categorized according to the following product types:

- Swimming equipment, e.g. beach toy animals, beach toys, swimming and paddle pools;
- Dolls and toy figures;
- Outdoor toys;
- Bags, suitcases, pencil cases;
- Products for pets, e.g. squeaky toys, equipment;
- Hobby products, e.g. beads, sheets, foil, tape;

- Home textiles, e.g. shower curtains, oil cloth;
- Rugs, mats, mattresses;
- Balls, e.g. yoga balls, footballs;
- Clothes with prints, e.g. men's clothes, women's clothes, children's clothes (not rainwear);
- Footwear (artificial leather and soles), e.g. sports shoes, sandals, shoes, boots;
- Rainwear, ponchos, rubber boots, umbrellas;
- Tarpaulins (incl. various protective wrappings for camping and outdoor equipment);
- Garden hoses;
- Garden/home articles;
- Gloves (protective/garden);
- Cycling equipment (saddle, pads, tape);
- Electronic items, e.g. gadgets, shavers and electric toothbrushes;
- Equipment for mobile phones, iPads, etc.
- Personal care items;
- Building materials;
- Sex toy.

The products included products made of hard PVC, incl. transparent, hard PVC, as well as products made of soft PVC. Furthermore, several products were purchased for comparison with products in the control campaigns from the Chemical Inspection Service in 2018 on DIY retailer products and children's toy products.

Analysis results

For products purchased for this project, the materials were initially analyzed for chlorine content as an indication of PVC. As a result, only 54 products were included in the following analyses. The remaining 20 products did not contain chlorine. The initial screening also detected several metals/chemical elements.

All PVC-containing products were subsequently analyzed for specific metals/chemical elements to show the extent to which heat stabilizers containing regulated substances (lead, cadmium, tin) and other specific substances (boron, antimony, phosphorus) have been applied, as indicators of selected substances from the PLASI database. For soft PVC products, a content analysis was carried out to find specific phthalates and short-chain chlorinated paraffins (SCCPs). At the same time, a general screening for other substances was also performed. The analysis results were compared with application limitations in Danish and European regulation.

Selected metals

Content of the metals lead (in total in nine products) and cadmium (in total in four products) was detected in concentrations that would prohibit marketing of these products on the Danish market. Four products were investigated for organotin compounds, but no violations of the existing Danish and European regulations were detected. Since no analyses were carried out for lead, cadmium and tin during the control campaigns from the Chemical Inspection Service in 2018 on DIY retailer products and on children's toys, it is not possible to make a comparison with products on the Danish market. The results of the product analyses for chemical elements do not show a systematic difference in the number of threshold value violations as to whether the product is purchased inside the EU (except Denmark) or outside the EU.

Phthalates and SCCPs

11 different phthalates were identified and quantified in the analyzed products, but the content of more than half of the identified phthalates is below 1%. The diversity of phthalates used as softening agents in the analyzed products of this project is limited to the phthalates DBP, DIBP, DEHP and DINP. The analyses showed alternative softening agents, among others, DEHT, which is a terephthalate and was found in most of the analyzed products. The analysis results do not show a systematic difference in the content of the different phthalates as to whether the product is purchased inside the EU (except Denmark) compared to outside the EU.

For electronics, the content of the regulated phthalates DBP and DEHP was detected in one product (phone charger, product no. 67).

In children's toys, the content of the regulated phthalates DBP, DEHP and DINP was detected in one out of five products (bath ducks, product no. 4). It would not be legal to market these products on the Danish market.

During the control campaign from the Chemical Inspection Service in 2018 on CMR substances in children's toys (purchased only in Denmark),[1] it was found that only 1 out of 64 products did not live up to the Danish legislation requirements. DEHT was also found in most of the products in this project. The number of examined toys in this project is too small to be able to compare the threshold value violations in toys sold on the Danish market with toys sold on foreign websites.

The analysis results of the Swedish inspection of e-trade[2] showed that 10 out of 32 children's toys contained substances above threshold values for both phthalates and SCCPs. However, the extent to which the products were made of PVC was not indicated, and, thus, it is not possible to make a direct comparison. Violations have been identified in children's toys purchased in web shops from Sweden, other EU countries and countries outside the EU.

In the control campaign from the Chemical Inspection Service in 2018 for control according to article 33. 2[3] in the REACH regulation, 52 different products were purchased from DIY retailers, and five different phthalates were identified in these products. These phthalates were DEHP, DIBP, DBP, DIDP[4] and didecan-2-ylphthalate[5]. Similarly, in this present project, the DEHT was found in most of the products. 25 of the products (48%) analyzed during the control campaign had contents of DEHP, DIBP and/or DBP with a concentration that exceeded 0.1%, which will be regulated starting July 2020. In comparison, this concentration was exceeded in this present project for 9 out of 16 products (56%). Four of these products were purchased on websites inside the EU (except Denmark), and five were purchased outside the EU. Thus, it cannot be concluded that there is a significant difference between purchases made inside and outside the EU regarding the violations of the upcoming regulation based on this study.

In total, five products were identified with a concentration of SCCPs exceeding the threshold value. Three of these products are categorized as products also available from Danish DIY retailers. SCCPs have been detected in one children's toy (product no.12), while no products with content of SCCPs exceeding the threshold value were detected during the control campaign from the Chemical Inspection Service in 2018. However, statistically it is not possible to conclude any difference between these two types of purchases and the violation of the SCCP threshold value. Three products with detected SCCP content were purchased on websites inside the EU (except Denmark), and two were purchased outside the EU. Thus, the analysis results indicate no systematic difference in the violation of SCCP threshold values as to whether the products have been purchased or produced inside the EU (except Denmark) versus outside the EU.

[1] Kontrol af CMR-stoffer i legetøj, 2018.

[2] Tillsyn av e-handel 2018, KEMI, Kemikalieinspektionen, Sverige, https://www.kemi.se/global/tillsyns-pm/2018/tillsyn-12-18-tillsyn-av-e-handel.pdf

[3] REACH: Kontrol af art. 33.2 informationspligten i byggemarkeder – 2018

[4] CAS No. 26761-40-0

[5] CAS No. 28029-89-2

Other substances

Products made of soft material have been studied to identify other types of substances that may have been added. In 41 products, 54 different substances were identified with CAS number. For these substances, any classification was identified according to the C&L Inventory of the European Chemicals Agency. All substances detected in concentrations above 1% do have a known softening property, and none of them have a harmonized classification. The remaining substances were all found in amounts below 1% (many considerably lower than 1%) and are not considered as intentionally added additives to PVC.

ICP analysis demonstrated that a large part of the analyzed PVC products contained phosphorus. The two soft PVC products 14 and 16 contained phosphorus-containing substances as identified by GC-MS screening. For product no.14, two substances were identified belonging to the organophosphite group described in the report Survey of PVC in Denmark 2018 as being considered co-stabilizers. In product no.16, ostizicer, which is a flame retardant, was identified.

Harmonized classification exists for three of the identified substances: BPA, isophorone and 2-[2-(2-butoxyethoxy)ethoxy] ethanol, while most of the substances have notified classifications. Selected substances were examined further in relation to their environmental and health effects.

Assessment of results according to Danish/European legislation

TABLE 1 shows a complete overview of products that would be illegal if they had been marketed on the Danish market. In total, 13 out of 54 examined products, corresponding to 24%, exceed the permitted threshold values for marketing on the Danish market, out of which six products exceed permitted threshold values for more than one regulation.

TABLE 1. Overview of products, where concentrations are compared with the application limitations in Danish and European legislations. TV = threshold value. %RSD is the percentage standard deviation for a duplicate determination.

Product			**Substance***			**Regulation**	**TV**
No.	PVC	Name	Name	mg/kg	%RSD		[mg/kg]
4	Soft	Bath ducks	DBP DEHP	17,000 103,000	3.2 2.1	REACH No 1907/2006, Annex XVII, entry 51	1000
			DINP	145,000	9.4	REACH no. 1907/2006, appendix XVII, entry 52	1000
12	Soft	Jump rope	Cd	210	0.9	Government order: BEK no. 858 of 05/09/2009	75
			SCCP	37,000	3.1	POP Regulation (EU) No 2019/1021	1500
21	Soft	Hobby cutting board	Pb	935	0.2	Government order: BEK no. 856 of 05/09/2009	100
			SCCP	4,900	16	POP Regulation (EU) No 2019/1021	1500
23	Soft	Wall sticker	Pb	4,000	3.0	Government order: BEK no. 856 of 05/09/2009	100
			Cd	450	2.3	Government order: BEK no. 858 of 05/09/2009	75
25	Soft	Tape	Pb	1,050	4.4	Government order: BEK no. 856 of 05/09/2009	100
			Cd	130	3.1	REACH No 1907/2006, Annex XVII, entry 23.	100

			SCCP	13,000	4.9	POPs Regulation (EU) No 2019/1021	1500
26	Soft	Tape	Pb	1,100	3.4	Government order: BEK no. 856 of 05/09/2009	100
			SCCP	12,000	2.2	POP Regulation (EU) No 2019/1021	1500
29	Soft	Car mat	Pb	2,600	4.0	Government order: BEK no. 856 of 05/09/2009	100
30	Soft	Car mat	Pb	2,600	4.6	Government order: BEK no. 856 of 05/09/2009	100
			SCCP	5,800	0.5	POP Regulation (EU) No 2019/1021	1500
36	Soft	Football	Cd	150	1.1	Government order: BEK no. 858 of 05/09/2009	75
52	Soft	Garden hose	Pb	850	0.02	Government order: BEK no. 856 of 05/09/2009	100
67	Soft	Phone charger	DBP DEHP	13,000 5,400	7.4 4.8	Government order: BEK no. 720 of 09/07/2019	1000
73	Hard	Pipe joint	Pb	9,000	4.7	Government order: BEK no. 856 of 05/09/2009	100
74	Hard	Pipe joint	Pb	9,700	3.6	Government order: BEK no. 856 of 05/09/2009	100

* Analytic uncertainty for methods: SCCP 35 %, metals 15%, phthalates 18 % (expanded 35 %). For details on methods, see Appendix 4.

In Appendix 3, name and country of origin of the web shop has been provided for each product. A comparison of country of origin of web shop for products with violations (see TABLE 1), were they purchased on the Danish market, indicates that the 13 products are distributed as follows: six products are purchased in the EU (except Denmark), four are purchased outside the EU, and three are unknown. As a result, this project does not show a significant difference in the number of legislation violations for products purchased within the EU (except Denmark) and outside the EU (as shown in TABLE 1).

Furthermore, 22 out of 41 examined products (54%) contain DIBP, DEHP and DBP in concentrations above 0.1% (1000 mg/kg). From July 2020, it will be prohibited selling products containing the mentioned phthalates in the EU according to REACH regulation no. 1907/2006, appendix XVII, entry 51 with a threshold value of 0.1%. This refers to the following products:

- Diver goggles (6)
- Jump rope (11+12)
- Biting toy animal for pets (17+18)
- Feeding mat (19+20)
- Hobby cutting board (21+22)
- Wall sticker (23)
- Tape (25+26)
- Car mat (29+30)
- Yoga ball (33+34).
- Football (36)
- Sandals (39)
- Flip-flops (42)
- Rainwear (43)
- Garden hose (52)
- Gloves (55)

The products are distributed as follows: nine products are purchased in the EU (except Denmark), eleven are purchased outside the EU and two have an unknown country of origin. Thus, it is not possible to conclude that there is a difference between purchases inside and outside the EU regarding the violations of the upcoming regulation.

Additive properties and impact on recycling potential

After product analyses, the project group together with the Danish Environmental Agency selected 21 substances for hazard assessment in the same way as substances from the PLASI database were assessed. In addition to the hazard profiles, the regulative status according to CLP classification, REACH regulation/measures and the regulation regarding the substance content in electronic equipment and children's toys were described.

Based on the above-mentioned and according to the identified concentrations in PVC products, a range of additives were identified, for which follow-up assessments were suggested regarding the substance properties and their future application in PVC.

The assessment of the identified additives did not indicate factual technical barriers for recycling. However, for a material such as PVC, which can be and often is added many additives, it is a great dilemma that the properties generated by adding additives cannot be controlled in the recycled material, unless there is full traceability and clean fractions. It was also evaluated that the use of regranulated PVC in products may be a challenge with no risk of exceeding threshold values for additives. The results of this project show that particularly cadmium and lead and some softening agents can constitute an impediment due to the high content and may limit the recycling potential of the regranulate.

Future tests for substances of concern in PVC

In this project, examples of the occurrence of several additives were found in a wide range of consumer products. To achieve a more structured knowledge of the tendencies in the application and occurrence of additives, it is suggested to delimit the project to achieve more focused knowledge and information. This can be done by limiting the focus on either looking for specific additives or the specific consumer products that are of interest to gain further knowledge. Both parts should be limited by setting specific criteria, e.g. health effects of additives or product types used, for example by vulnerable groups such as children. Irrespective of the focus, the additive function should be associated to the product types to develop a targeted analysis program.

Additive prioritization can be based on the existing knowledge of the environmental and health effects of additives, or be based on the lack of knowledge of the environmental and health effects of additives found in products combined with an assessed relevance, e.g. by being registered in REACH, which suggests a considerable occurrence of the additive.

10 out of the 32 substances from the PLASI database, which are used in PVC, were prioritized based on the knowledge of their inherent effects or the suspicion of inherent effects in relation to the five adverse effects. For these additives, it would be relevant to acquire more knowledge on their function, occurrence and application, e.g. from the PLASI database, and carry out a detailed assessment of the toxicological and ecotoxicological data for the additive; thus, prioritizing and focusing products and the analysis program. Similarly, a range of softening additives in products were identified and are suggested to be prioritized according to these factors: whether they are applied in a considerable tonnage in general (they are REACH registered); they are not regulated and the knowledge of the inherent effects is insufficient or uncertain. Also, for these additives, it would be relevant to acquire more knowledge on their function, occurrence and application, as well as assess the toxicological and ecotoxicological data for these additives in order to prioritize and focus products and the analysis program.

1. Introduction

1.1 Background

Globally, polyvinyl chloride (PVC) is the third-most produced type of plastic. With properties such as good mechanical strength, low water absorption, good chemical resistance and compatibility with a wide range of additives, it is used in a large number of consumer products such as toys, sports equipment, shoes, clothes, swimming equipment and electronics. However, a large part of the functional additives such as e.g. softeners, flame retardants, pigments, biocides and various stabilizers have proven to be problematic substances, which may be both harmful, and may prevent future recycling of the material, in violation of initiative 25 in the Danish plastics action plan dealing with common European requirements related to design with the purpose of recycling.[6] In addition, the Danish "Political agreement on new joint chemicals initiatives 2018-21" aims at an increased focus on the problematic substances in PVC.[7]

According to the recent "Survey of PVC in Denmark 2018", the environmental and health-related focus is particularly on heat stabilizers and softeners, as these particular additives are characteristic of PVC.[8] Previously, heat stabilizers were based on lead and cadmium. Today, this type of heat stabilizer is prohibited in Denmark, which is why heat stabilizers are now based on e.g. barium, zinc, calcium, magnesium, potassium or organotin. Most of these heat stabilizers are not classified, whereas some organotin stabilizers are also prohibited, and others have problematic health effects and are under evaluation in accordance with REACH. Concerning softeners, focus has been primarily on the environmentally harmful short-chain chlorinated paraffins (SCCP) and on the phthalate group, where several of the substances are endocrine disrupters and/or CMR substances.

EU restrictions have been imposed on many of the substances mentioned above, but today, more and more consumer products are purchased online from countries outside the EU. These products are not subject to EU-harmonized product law, and, therefore, the consumer cannot rely on the same kind of product safety as to the contents of problematic substances compared to products purchased in Denmark or the EU.

The work described in this report has mainly involved gaining more knowledge of the contents of problematic substances in PVC products purchased by private consumers from websites outside Denmark and the EU, respectively. In addition, the report describes the extent to which the problematic substances identified may hinder recycling of PVC products by end-of-life and, thereby, hinder implementation of a circular resource economy in Denmark.

1.2 Purpose

The purpose of the project has been to investigate the contents of selected problematic additives (softeners, heat stabilizers, flame retardants, etc.) in selected PVC-based products purchased online from foreign websites by private consumers. Based on the result of these investigations it was concluded whether the products would be illegal had they been marketed in Denmark. In addition, it was estimated whether there was a significant difference in the

[6] https://mfvm.dk/fileadmin/user_upload/MFVM/Publikationer/NY_Regeringens_plastikhandlingsplan_full_version_FINAL_0123-2019.pdf

[7] https://mfvm.dk/fileadmin/user_upload/MFVM/Nyheder/Faelles_Kemiaftale_2018-21.pdf

[8] Lassen et al.: Kortlægning af PVC i Danmark 2018, Miljøprojekt nr. 2049, 2018.

amount of problematic substances in PVC products on the Danish market, in the rest of the EU and on markets outside the EU, respectively, by comparing with data from products included in previous control campaigns from the Chemical Inspection Service.

1.3 Delimitation

In the tender, the project was limited to deal with three groups of additives for PVC:

1) Heat stabilizers
2) Softeners: Phthalates and short-chain chlorinated paraffins (SCCP)
3) Substances selected from the PLASI database

As an introductory part of the project, the preselected substances from the PLASI database were evaluated to further reduce the number of substances to include in the project. This reduction was carried out based on *i*) a screening of several environmental and health parameters as well as *ii*) an overall evaluation of the total value of the analysis results obtainable within the framework of the project. The overall evaluation resulted in a further delimitation of the project to not include analyses of substances from the PLASI database. This evaluation has been described in greater detail in chapter 2 of the report.

1.4 Report structure

Chapter 2 describes the evaluation of the 32 preselected substances from the PLASI database and the reason for deselecting these substances within the framework of this project. Furthermore, the chapter describes recommendations as to how further information on substances from the PLASI database can be gathered for a possible subsequent project.

Chapter 3 describes and substantiates the choice of products purchased and analyzed, while analyses and results are presented in chapter 4. Conclusions pertaining to possible differences between the contents of the additives domestically and abroad as well as relating to products purchased or produced within or outside the EU, are also part of this chapter.

Chapter 5 reviews environmental and health parameters for the heat stabilizers and the phthalates and SCCP softeners found in the analyzed products, and chapter 6 discusses how the identified substances focused on in this project might influence the recycling of the PVC products and materials.

Finally, chapter 7 contains a discussion and a conclusion pertaining to the implication of results found and their influence on PVC products, and recommendations will be provided as to knowledge relevant for future projects.

2. Selected additives from the PLASI database

2.1 Foundation for prioritizing substances from PLASI database

In addition to the focus on heat stabilizers and softeners, the Danish Environmental Protection Agency also wanted to prioritize 10 substances listed in the PLASI database to assess the possibilities of including these in the analysis program.

The PLASI database originates from the PLASI project ”High volume plastic additives survey”, which is a collaboration between the European Chemicals Agency and the industry. The project was completed in 2018 and the result of the project is a database of more than 400 substances used as additives for plastic. The database includes, among other things, the substances’ technical function and their theoretical potential for release from the plastic matrix. All substances in the database are registered under REACH in the tonnage band above 100 t/a. In addition to several heat stabilizers and softeners for PVC, the database contains 32 other additives used in PVC.

These 32 additional additives to PVC are listed in Appendix 1. To identify the ten most critical of the substances for possible involvement in the subsequent analysis program, a screening of the 32 substances’ environmental and health hazardous effects was performed. As criteria for prioritizing the substances, the Danish Environmental Protection Agency wanted to take as its starting point ”The five adverse effects in focus” described in “Political agreement on new joint chemicals initiatives 2018-21”. These include:

- carcinogenic, mutagenic or repro-toxic effects
- brain-damaging effects or substances affecting brain development
- endocrine-disrupting effects
- allergenic effects
- environmentally hazardous effects.

The prioritization regarding these effects was made by seeking information about the chemical hazard information profile of the substances. This was done based on the substances’ CLP classification partly in Appendix VI to the CLP regulation (EC no 1272/2008, where the EU-harmonized classification is stated) and partly by examining the classifications specified in the REACH regulation. Based on the classification, it can be immediately seen whether the substances are considered carcinogenic, mutagenic, repro-toxic or allergenic, or whether the substances are environmentally hazardous. In terms of brain-damaging effect, this will appear from a STOT RE 1 or a STOT RE 2 classification, indicating the central nervous system as the target organ.

However, the classification does not say anything about any endocrine-disrupting effects, which is why this property was examined by checking the following relevant lists, where information on suspected endocrine-disrupting substances can be found: CIRCABC[9] , the Candidate List of substances of very high concern[10], CoRAP from ECHA (the European Chemicals Agency)[11], the EU's Priority list[12] as well as from the screening in the Toxcast database[13]. The Toxcast database is a large database, that covers *in vitro* data on a wide range of substances, including assays relevant to endocrine-disrupting effects, such as estrogen and androgenic activity, etc.

In addition, the status and priorities on the European Chemicals Agency's website for the individual substances were reviewed to investigate whether the substances were particularly suspected of any of the above harmful effects, including PBT and vPvB properties.

Appendix 1 provides an overview of the 32 investigated substances selected from the PLASI database, where classification or suspicion of/indication of the prioritized harmful effects described above is stated.

2.2 Results of the hazard screening of PLASI substances

Based on this review, the substances were – based on their overall effects – prioritized as respectively:

- High priority (+++)
- Second priority (++)
- Low priority (+)
- Not prioritized ( )

The prioritization of the individual substances is listed separately in the *Priority* column in Appendix 1. For prioritization of the individual substances, account was taken as to whether the substance possessed more than one of the hazardous effects, and in which effect category the substance was classified (e.g. the priority of a substance that is classified as Repr 1B is higher than a substance which is classified as Repr 2). For the endocrine-disrupting effects, account was taken as to whether there were indications of endocrine-disrupting effects in several databases (Appendix 2). In addition, the assessment also included further studies/initiatives if they had been initiated in REACH based on suspicion of one of the selected harmful effects.

From this, the ten highest-priority substances could be designated. As indicated below, five substances rated high priority (+++), and five substances rated second priority (++):

[9] List of biocidally active substances in the process of exclusion or substitution. https://circabc.europa.eu/faces/jsp/extension/wai/navigation/container.jsp

[10] https://echa.europa.eu/da/candidate-list-table

[11] https://echa.europa.eu/da/information-on-chemicals/evaluation/community-rolling-action-plan/corap-table

[12] https://ec.europa.eu/environment/chemicals/endocrine/strategy/substances_en.htm#priority_list

[13] https://www.epa.gov/chemical-research/toxcast-dashboard

2.2.1 Highest priority (+++) substances

Disodium tetraborate (CAS No. 1330-43-4; 1303-96-4;12179-04-3)

Function: Antistatic, flame retardant, other stabilizer

The substance is classified as repro-toxic in category 1B, and as a SVHC substance and a Candidate List substance it is currently in the process of being included on the approval list (substance no. 11 among the selected substances from the PLASI database, Appendix 1).

Ethanol, 2,2'-iminobis-, N-C12-18-alkyl derivates (CAS No. 71786-60-2).

Function: Antistatic

The substance is classified as corrosive and as repro-toxic in category 2. In addition, it is classified for its chronic effects on the aquatic environment. The reproductively harmful effects must be further investigated on the basis of indications of further harmful effects in connection with the substance evaluation under REACH (substance no. 21 among the selected substances from the PLASI database, Appendix 1).

Phenol, isopropylated, phosphate (CAS No. 68937-41-7)

Function: Flame retardant, softener

There are indications suggesting that the substance may have endocrine-disrupting effects. The substance is classified as repro-toxic in category 2 and for chronic effects on the aquatic environment. In connection with the review of the REACH registration, the endocrine-disrupting and repro-toxic effects must be further investigated on the basis of indications in the existing dossier (substance no. 27 among the selected substances from the PLASI database, Appendix 1).

Alkanes, C14-17, chloro (CAS No. 85535-85-9).

Function: Flame retardant, softener

The substance is classified for chronic effects on the aquatic environment and for being able to pass into breast milk. It has been suspected to be a PBT/vPvB substance in connection with the substance evaluation under REACH (substance no. 29 among the selected substances from the PLASI database, Appendix 1).

Reaction mass of tris(2-chloropropyl) phosphate and tris(2-chloro-1-methylethyl) phosphate and Phosphoric acid, bis(2-chloro-1-methylethyl) 2-chloropropyl ester and Phosphoric acid, 2-chloro-1-methylethyl bis(2-chloropropyl) ester (EC no 911-815-4)

Function: Flame retardant, softener

The substance is classified as having acute adverse health effects by oral ingestion, category 4. The Danish Environmental Protection Agency is currently conducting a substance evaluation, where endocrine-disrupting, repro-toxic and carcinogenic effects are suspected (CoRAP list). The substance is also suspected to be a PBT/vPvB substance (substance no. 31 among the selected substances from the PLASI database Appendix 1).

2.2.2 Second priority (++) substances

6,6'-di-tert-butyl-4,4'-butylidenedi-m-cresol (CAS No. 85-60-9).

Function: Antioxidant, other stabilizer

In the REACH registration, the substance is listed with no hazard classification. However, there are indications of endocrine-disrupting effects of the substance, and in connection with the substance evaluation under REACH, the substance is suspected of repro-toxic/endocrine-disrupting effects as well as of PBT/vPvB properties (substance no. 1 among the selected substances from the PLASI database, Appendix 1).

2-(2H-benzotriazole-2-yl)-p-cresol (CAS No. -22-4)

Function: UV-/light stabilizer, other stabilizer

The substance is classified for chronic effects on the aquatic environment, as well as skin allergenic effects. There are also indications of endocrine-disrupting effects (substance no. 16 among the selected substances from the PLASI database, Appendix 1).

Ethanol, 2,2'-iminobis-, N-(C13-15-branched and linear alkyl) derivates (CAS No. 97925-95-6)

Function: Antioxidant, antistatic

The substance is classified as repro-toxic in category 2 and a classification proposal for a harmonized classification in category 1B is being processed by the European Chemicals Agency (substance no. 20 among the selected substances from the PLASI database, Appendix 1).

Azodicarbonamide (CAS No. 123-77-3)

Function: Flame retardant, foaming agent

The substance is classified as an allergen by inhalation and is in the process of being included as a SVHC substance (substance no. 25 among the selected substances from the PLASI database, Appendix 1).

1,1'-(isopropylidene)bis[3,5-dibromo-4-(2,3-dibromo-2-methylpropoxy)benzene] (CAS No. 97416-84-7)

Function: Flame retardant

In the REACH registration, the substance is listed with no hazard classification. However, the substance is suspected to be endocrine-disrupting and in connection with the substance evaluation under REACH, the substance is suspected of endocrine-disrupting effects as well as of PBT/vPvB properties (substance no. 30 among the selected substances from the PLASI database, Appendix 1).

2.3 Considerations about including the PLASI substances in the analysis program

Following the above prioritization, it was assessed to which extent it was relevant to include the substances in the subsequent analysis program.

Initially, considerations were made about the selected substances from the PLASI database, which vary greatly in terms of structure and chemical properties. The substances were assessed on the basis of which method of chemical analysis was expected to be most suitable. Although a number of the substances can be analyzed using the same method principle, method optimization will be needed for the individual substances. For a number of compounds, it is also a challenge or impossible to obtain a reference substance to perform identification and quantitative analysis.

The inorganic PLASI substances can be analyzed for chemical substances such as e.g. boron, but it is not possible to identify the substance, e.g. disodium tetraborate, as there may be other sources of e.g. boron in the material. The contents of the chemical elements can therefore only be used as an indication of the addition of an inorganic stabilizer.

At the same time, there is a lack of information on the relationship between the substances and the product type, which means that there is a risk of selecting products that are analyzed for irrelevant substances. In order to create an effective analysis program, it will be important to include as much information as possible about e.g. the substances' function and use in various product types, e.g. to focus the resources on products where the specifics substances can presumably be found, because their function is relevant in this particular product type.

For the majority of the 32 substances from the PLASI database, there are currently no commercial laboratories that can offer to analyze the substances without a prior method phasing-in and validation. This is because the substances are not regulated and therefore there is no demand for the analyses. Thus, the costs are relatively high for the analyses and for less focused analysis campaigns, while greater effect can be achieved by designing an analysis program for delimited product types, where the individual substance is expected to have a relevant function.

Therefore, the conclusion was that analysis of even the highest priority substances from the PLASI database with problematic environmental and health effects would require several methods, which should be phased-in and validated. Thus, it was only possible to analyze a few products within the project's budget and time frame. Combined with the fact that greater efficiency could be expected from an analysis program with products targeted the individual substances' function rather than the products in this project, which focuses on as broad and varied product types as possible, it was decided not to include selected substances from the PLASI database in the analysis program. This instead provided an opportunity to include the purchase of several products in the project.

In the following section, substances with the highest and second priority are reviewed with regard to chemical properties and discussion of methods of analysis for use in any future projects.

2.3.1 Highest priority (+++) substances

Disodium tetraborate (CAS No. 1330-43-4; 1303-96-4; 12179-04-3)

Commercially, disodium tetraborate is better known as borax and is often used as a disinfectant. In polymer chemistry, borax has several functions, where it can stabilize a polymer by inducing hydrogen bonds to the polymer chain through the oxygen atoms present in the molecule. At the same time, borax has a large electron system, which enables it to eliminate radical compounds, and, therefore, it can act as a flame retardant. Borax is an inorganic substance, and analysis of the substance will depend on quantification of boron and subsequent conversion to borax. Therefore, other boron components will also contribute to the calculated content and give a false positive. Therefore, it will be worst-case content. It is not possible to determine the proportion of borax unless it is a crystal structure (determination using EDX), and it will, therefore, be necessary to quantify organoboron substances separately, calculate the boron content and subtract it from the borax calculation.

Ethanol, 2,2'-iminobis-, N-C12-18-alkyl derivates (CAS No. 71786-60-2)

The substance is an UVCB substance,[14] as it is a variable alkyl chain and, therefore, not a well-defined molecule. It is a tertiary amine, which is not UV active and has an estimated pK_a value of 8.8. It will, therefore, be an analysis to be performed by LC/MS or alternatively by GC-MS with control of pH and with positive control by extraction. Due to the relatively low molecular weight and solubility of the polymer, the substance is considered to have a relatively high risk of exposure, as it must be expected to have some mobility in the polymer matrix.

Phenol, isopropylated, phosphate (CAS No. 68937-41-7)

The substance is an UVCB substance consisting of four well-defined compounds. These are phosphate components with three side chains, being either benzene rings or benzene rings with an isopropyl group in the para position. These are organophosphorus flame retardants, the version of which without the isopropyl group is triphenyl phosphate (TPP, CAS no. 115-86-6) and isopropyl versions are not the non-chlorinated versions of TCPP (CAS no. 13674-84-5). There is no immediate reason for the component to be listed as an UVCB substance, as the individual components are well-defined. The components can be analyzed by GC-MS.

Alkanes, C14-17, chloro (CAS No. 85535-85-9)

Chlorinated alkanes, C14-C17 are UVCB substances. This is due to both varying alkane chain length, but also varying degrees of chlorination. It is stated by Euro Chlor/Halogens[15] that European producers are very careful not to carry out full chlorination of alkanes, as it lowers the biodegradability considerably, but also that the industry is aware that there is not the same attention among Asian producers. At the same time, it is stated that chloroalkanes are used as a primary protection against electric fire, as they are used as flame retardants in cable sheaths. The components can be analyzed by GC-MS.

Reaction mass of tris(2-chloropropyl) phosphate and tris(2-chloro-1-methylethyl) phosphate and Phosphoric acid, bis(2-chloro-1-methylethyl) 2-chloropropyl ester and Phosphoric acid, 2-chloro-1-methylethyl bis(2-chloropropyl) ester (EC no. 911-815-4)

These are organophosphate flame retardants. It is TCPP (CAS No. 13674-84-5) in different versions, where a methyl group in the molecule is moved around. Similar properties are expected from the reaction mass as in TCPP, as there is overall great molecular similarity. An unknown amount is also contained, which is not trisubstituted phosphate, but also di- and monosubstituted. The properties of these are not known as they have not been studied individually. Mono- and disubstituted must be expected due to lack of reactivity, as greater fire-retardant efficacy of trisubstituted phosphate compounds is expected. The substances are expected to be able to be analyzed by GC-MS.

2.3.2 Second priority (++) substances

6,6'-di-tert-butyl-4,4'-butylidenedi-m-cresol (CAS No. 85-60-9)

The substance is a stabilizer and probably also has an effect as a softener. The substance is similar to BHT, but is larger molecularly, which makes migration in the polymer matrix less likely. The substance is possibly too heavy for GC-MS analysis, but can be quantified by HPLC/UV.

[14] UVCB: *Unknown or variable composition, complex reaction products or biological materials*. The substance consists of many different components, and some of these may not be known; the composition may vary or be hard to predict, and therefore UVBCs are often not fully identifiable.

[15] https://www.eurochlor.org/about-us/halogens-cluster/

2-(2H-benzotriazole-2-yl)-p-cresol (CAS No. 2440-22-4)

This is an UV stabilizer to extend the life of the polymer. The component has triazole functionality, which means that the substance can be positively charged in its binding to the polymer chain. Therefore, the substance should probably be analyzed by HPLC-UV.

Ethanol, 2,2'-iminobis-, N-(C13-15-branched and linear alkyl) derivates (CAS No. 97925-95-6)

The substance is an UVCB substance and the same substance as the one previously described under CAS No. 71786-60-2, however, this is limited to chain lengths between C13 and C15. According to the REACH dossier, there are four specific components C13 and C15 in the linear version as well as C12 and C14 with a methyl group on the chain. The substance should probably be analyzed as described for the substance Ethanol, 2,2'-iminobis-, N-C12-18-alkyl derivates, CAS No. 71786-60-2.

Azodicarbonamide (CAS No. 123-77-3)

The substance is well-defined. It is an unstable, reactive molecule and is not expected to have a direct fire-retardant effect as described in the PLASI database. It is probably part of a fire-retardant system. It is known from other laboratories that analysis of the component is problematic and that it degrades during the analysis, which makes quantification difficult.

1,1'-(isopropylidene)bis[3,5-dibromo-4-(2,3-dibromo-2-methylpropoxy)benzene] (CAS No. 97416-84-7)

The substance is a brominated flame retardant. The substance melts at approx. 90°C, and low migration in the polymer matrix is expected due to size and melting point. The substance will have to be analyzed with liquid chromatography (HPLC/UV or LC/MS).

3. Selection of PVC products

This chapter describes the procedure of selecting PVC products for purchase and subsequent analysis, and the specifically selected product types and products that were a part of the process and subsequently passed on to initial analyses, described in the following chapter.

3.1 Strategy and method

The main purpose of the product selection was to select products that most likely contain PVC and are representative in relation to Danish consumers' purchases of various products on foreign websites.

The selection of PVC products was initiated by determining the *product types* to be included in the product list and assessing the extent to which they should be represented. Based on this, a gross list consisting of approx. 80 specific products was made, from which a number of *products* could subsequently be prioritized for purchase and analysis (see **FIGURE 1**). The methodological approach to the selection of products for procurement was based on data and assessments to ensure compliance with the criteria set out below. For each criterion, the method is briefly described:

1) *The products consist entirely or partly of PVC and are representative of typical applications for PVC.*
   For this, data and knowledge from the Danish report *Survey of PVC in Denmark 2018*[8] were used, as well as existing knowledge about the use of plastic materials for plastic products. As not all websites provide relevant or correct product information, e.g. whether the product contains PVC, more products have been purchased than expected to be able to analyze.
2) *The products are representative of consumer products typically purchased from foreign websites (within/outside the EU).*
   The data from the Association of Danish Internet Trading (FDIH) in the form of extracts from the FDIH yearly run 2018 (Årskørsel FDIH, 2018) were used to recommend a gross list consisting of products that represent the Danish consumers' purchases on foreign websites in relation to both product groups and quantitative distribution among the froups. The data extract consisted of 84 product groups and the number of personal purchases in these product groups made on the internet by Danish consumers.
3) *The products purchased from a representative group of websites, i.e. a part of the products must be purchased from those foreign websites, which are most frequently used for internet purchases by Danish consumers.*
   The data on the 20 most popular web shops were obtained from the FDIH yearly run 2018 (Årskørsel FDIH, 2018) and used to prioritize foreign websites from inside and outside the EU, respectively.
4) *The list contains product types that are also included in the control campaigns from the Chemical Inspection Service in 2018 on DIY retailer products [16] and children's toys[17] to ensure that data for some products in this project can be compared to the results of the two mentioned projects from 2018.*
   It was specifically ensured that the gross list included toy products and products that can be purchased from DIY retailers, and the following product selection involved considerations about the possibilities to compare the results of this project with the results of the two mentioned projects of 2018.
5) *A wide range of products / product types*
   After the methodical approach to the establishment of a priority matrix and a gross list

[16] REACH: Kontrol af art. 33.2 informationspligten i byggemarkeder – 2018.

[17] Kontrol af CMR-stoffer i legetøj, 2018.

based on the above-mentioned criteria, the Environmental Protection Agency further chose to include more product types to increase the broadness of products included in the survey.

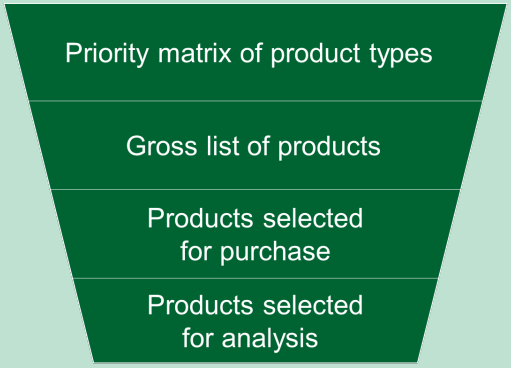

FIGURE 1. Illustration of the methodical approach to product selection.

3.2 Prioritization of product types

The introductory prioritization of product types, to be included in the gross list based on the above-mentioned criteria, was performed by comparing the data for which application fields are relevant from the Danish report *Survey of PVC in Denmark 2018*[8] with the data from the FDIH yearly run (Årskørsel FDIH, 2018) (point 1 and 2 in the criteria list). These background data describe, from two distinct approaches, important parameters for the selection of products, but cannot be directly combined to provide a concrete answer to which products must be analyzed. Instead, an assessment of the likelihood that a specific product type consists entirely or partially of PVC, and that the Danish consumer purchases this product type on foreign web shops, was performed. Below, the background of the used data is described, and the assessment of the likelihood of the product consisting of PVC and that it can be purchased via a foreign web shop has been summarized in **TABLE 2**.

In relation to the creation of the FDIH yearly run 2018 (Årskørsel FDIH, 2018), 14,544 respondents were asked the following question "*Which product or service did you recently purchase on the internet?*". These replies were reviewed in the FDIH yearly run 2018 (Årskørselen) with an aim, among others, to show the distribution of purchases within ten main product categories (further divided into subcategories), and the data on whether the purchases have been made on a Danish website. In this project, these data from the FDIH yearly run 2018 (Årskørsel FDIH, 2018) were further processed in the following way:

- All categories consisting of non-physical products (e.g. streaming, online services, travels, gift cards, etc.) were removed to only include data for the number of purchases within each product group and purchases made in foreign web shops.[18]
- It was concluded that groceries as a category was of no primary relevance for this project and were, thus, excluded. The category of groceries covers purchases of groceries, takeaway, food subscriptions, etc. which are not PVC and which mainly constitute Danish purchases (89%). However, this category could include (and generally relevant for all categories) packaging of PVC, but since "packaging" as a product type is not the focus area of this project, it was excluded from the product type prioritization.

[18] The survey gave responses on whether the purchase was made in "Denmark", "Different foreign countries" or "Do not know". In average, the answer "Do not know" was 11%, and according to communication with PDIH it was assumed that these are primarily non-Danish websites. The percentage of foreign purchases is assumed to be 100% minus the percentage of Danish purchases.

It is important to mention that the product range within different categories vary considerably in the FDIH yearly run 2018 (Årskørsel FDIH, 2018), which highly affects the significance of the absolute number of purchases in each category. Furthermore, the overview of the total number of purchases in one category does not say anything concrete about the individual products in the category, or if these are often specific products in the category that are purchased on foreign websites. For prioritization of product types, the statistics are used only as help to decide, which products should be prioritized.

The survey of the number of purchases was compared against which product groups most likely contained PVC. These numbers are, however, only indirectly visible in the form of the distribution of the total PVC content divided across product types. For example, it is stated in *Survey of PVC in Denmark 2018* that hard PVC is mainly used in the building and construction industries.[8] The statistics describes the share of the total amount of PVC supply that is used within the specific category, and 46% of the total supply is used in “Pipe, drainage, fittings”. However, this number does not provide any information on the likelihood whether a random pipe on the market is made of PVC (and, thus, is relevant for this project), because this likelihood also depends on if the pipe more often is produced by other materials. So, even though the percentage of the total supply of PVC for one product type is high, it does not mean that it is a PVC-based product that is often on the market. Contrary, there may be scopes of application where a product type uses e.g. 5% of the total PVC supply (tonnage-wise), but if this product always contains PVC it is highly relevant to include it in this project. However, the applied product categories in the two sets of materials do not always match. Hence, the comparison of the two different statistics; the FDIH yearly run 2018 (Årskørsel FDIH, 2018) and usage of PVC supply for both hard and soft PVC from *Survey of PVC in Denmark 2018* could only be carried out qualitatively.

A priority matrix on the relevant product types was created based on the information in the FDIH yearly run 2018 (Årskørsel FDIH, 2018) and the knowledge on which products could be typically produced from PVC. For each product type, the likelihood for the following two points was rated on a scale from 1-3, where 1 is low and 3 is very high likelihood:

- PVC material:
  Likelihood that a product is entirely or partially produced out of PVC. The assessment is based on the data on the usage from PVC supply[8] as well as the existing knowledge about the production of plastic products.
- Purchases on foreign websites:
  Likelihood that a specific PVC product type can be purchased on foreign websites. The assessment is based on the data from the FDIH yearly run 2018 (Årskørsel FDIH, 2018) for relevant product categories.

Furthermore, all categories from FDIH with more than 40 foreign purchases were included on the list of product types in the priority matrix with an exception of categories such as ”Jewelry”, ”Cosmetic products and equipment” and ”Nutritional supplements and health products”, since it is assumed that the likelihood is very low (or 0) to be able to find PVC products in this type of products typically purchased on foreign websites, when the packaging is excluded.

TABLE 2. Priority matrix: List of product types with likelihood assessment that a concrete product of this product type consists entirely or partially of PVC (referred to as *PVC material*), and that the product type is purchased by the Danish consumer on foreign websites (referred to as *Foreign internet purchases*). 3 indicates the highest likelihood, and 1 indicates the lowest likelihood. *Choice* indicates with + those product types that based on the matrix total value are selected for the gross list, while a T indicates product types that are additional choices.

Product type [a]	PVC application scope [b]	Possible FDIH category [c]	PVC material	Foreign web purchases	Total	Choice
Swimming equipment, e.g. beach toy animals, beach toys, swimming and paddle pools •	Swimming and paddle pools, etc.	Toys and family games Sports and leisure equipment	3	2	5	+
Dolls and toy figures	Toys incl. dolls and doll parts	Toys and family games	2	1	3	T
Outdoor toys	Toys incl. dolls and doll parts	Toys and family games	2	1	3	T
Bags, suitcases, pencil cases	Bags and suitcases	Bags and equipment, e.g. beach toy animals, beach toys, swimming and paddle pools;	2	2	4	+
Products for pets, e.g. squeaky toys, equipment	Toys incl. dolls and doll parts	Products for pets	3	3	6	+
Office supplies, e.g. binders, plastic pockets, folders	Office supplies	Office supplies	2	1	3	
Hobby articles, e.g. beads, pegboards, foils, tape	Pegboards, ark, film	Hobby articles	2	3	5	+
	Other products made of plastic foils	Hobby articles	1	3	4	+
	Coated paper and cardboard	Hobby articles	1	3	4	+
	Textile fabric with PVC surface	Hobby articles	3	3	6	+
Photos, posters, home decor	Coated paper and cardboard	Photo processing/products Home decorations/art	1	2	3	
Kitchen equipment	Plates, sheets, film	Kitchen equipment	1	1	2	
Home textiles, e.g. shower curtains, oil cloth	Office supplies, table linen, curtains	Home textiles	3	2	5	+

	Textile fabric with PVC surface					
Baby articles, e.g. bibs, sheets	Textile fabric with PVC surface	Baby articles	2	1	3	
Rugs, mats, mattresses	Textile fabric with PVC surface	Sports and fitness equipment Camping and outdoor equipment	2	2	4	+
Balls, e.g. yoga balls, footballs	Textile fabric with PVC surface	Sports and fitness equipment	2	2	4	+
Clothes with print, e.g. men's, women's and, children's clothes (not rainwear)	Clothes	Clothing, footwear and jewelry Sports and hobby equipment	1	3	4	+
Jewelry	Other products from hard PVC	Jewelry	1	2	3	
Footwear (artificial leather and soles), e.g. sports footwear, sandals, shoes, boots	Boots and vaders, shoes and soles	Shoes/footwear Sports clothing and footwear	1	3	4	+
Rainwear, ponchos, rubber boots, umbrellas	Clothes	Clothing, footwear and jewelry	2	3	5	+
	Textile fabric with PVC surface	Camping and outdoor equipment	2	2	4	+
Tarpaulins (incl. different protective packaging for camping and outdoor equipment)	Tarpaulins	Camping and outdoor equipment Garden machines Building materials Car, boat and bicycle equipment	3	1	4	+
Garden/home articles	Other products from hard PVC	Home, garden and plants	1	2	3	T
Garden hoses	Soft pipes and hoses	Garden machines	3	1	4	+
Gloves (protective/garden)	Clothes	Home, garden and plants	1	2	3	T
Car interior/equipment	Cars and other vehicles	Car and motorcycle	1	2	3	T
Cycling equipment (saddles, pads, tape)	Textile fabric with PVC surface Plates, sheets, film	Bicycle and cycling equipment	2	1	3	T

Electronic items, e.g. gadgets, shavers and electric toothbrushes	Cables and wires Wires and other electronic components	Electronics Household electronics	2	3	5	+
Computer hardware	Other products from hard PVC Wires and other electronic components	Computer hardware	0-1	3	3-4	
CD, DVD, Blu-ray, PC-games, console games	Other products from hard PVC	CD, DVD, Blu-ray, PC-games, console games	0-1	3	3-4	
Equipment for mobile phones, tablets, etc.	Equipment for mobile phones, tablets, etc.	Mobile phones and mobile phone equipment	3	3	6	+

a indicates product type as defined in this project

b indicates product category to which the product type is assessed to belong to in Survey of PVC in Denmark 2018

c indicates category to which the product type is assed to belong to in the FDIH yearly run 2018 (Årskørsel FDIH, 2018).

The priority matrix above contains in total 27 product types, from which product types for the gross list were prioritized. According to the assessed likelihoods, 18 product types were selected (indicated with an **+** in the column *Choice*), with the total score of 4 or above to be represented on the gross list. Furthermore, it was discussed whether some product types should be included with more products compared to others in the gross list in order to represent a larger share of these product types purchased by consumers on the internet on foreign websites. However, this was declined by the Environmental Protection Agency to be able to ensure a more extensive range of products.

Six additional product types (all with the total score of 3) were included as "possible product types for the gross list" to give greater priority to the product broadness and represent the consumer products purchased on foreign websites as broadly as possible. The selected product types are indicated with a **T** in the column *Choice* in **TABLE 2**. These additional choices also ensured that the criteria 4) to include toys and DIY retailer products for comparison with previous projects (section 3.1, page 24) was fulfilled. As almost half of the hard PVC supply is used for "Pipes, drainage, fittings",[8] this product type was also included from the priority matrix even despite the assessment that they are not often purchased on foreign websites.

3.3 Creation of gross list of PVC products

The gross list had to consist of at least 40 different products, where each product had to be purchased in a version from both a European and a non-European website, i.e. in total 80 specific products on the gross list. Products on the gross list were chosen within the selected product types and with an assumption that buyers do not usually purchase very large products (due to, among others, shipping costs), and also usually not very expensive products due to guarantee and return policies.

In addition to a representative selection of product types, it was also attempted to choose products from a representative group of websites according to criteria 3) (section 3.1, page 24). The 20 most visited web shops indicated in the FDIH yearly run 2018 (Årskørsel FDIH, 2018) were used as the point of departure in this project as only these foreign websites were relevant, and, thus, included in this project (i.e. shops without a Danish company registration number and/or VAT number). Further, websites, which were selling food products and/or non-physical products only, were not included. Many general web shops abroad do not send products to Denmark, or very high shipping costs or fees are applied to purchases, which is the reason why it was highly unlikely that the common consumer would make purchases on these websites. **TABLE 3** shows a list of primary web shops included in the work with products in the gross list provided that the selected product types from the priority matrix above allowed it.

TABLE 3. List of the most visited web shops (according to the FDIH yearly run 2018 (Årskørsel FDIH, 2018), which were included in the creation of the gross list of PVC products. Furthermore, all other web shops from which products from the product list were purchased can be found in Appendix 3.

Website	Product types	Website country of origin
Amazon.com, Amazon.co.uk, etc.	All	USA, UK, etc.
Wish.com	All	USA
eBay	All	USA
Cdon.com	All	Sweden
Aliexpress.com	All	China
Asos	Shoes, clothes & jewelry Sportswear and shoes	UK

The products on the gross list were found by internet searches in Danish and English. With regard to purchase countries (i.e. the country from which the product is purchased from), it was also necessary to have a broad representation of different countries. This was complicated because internet-based market places such as wish.com, eBay and Amazon are the most widely visited foreign web shops by Danish consumers for internet purchases. These market places facilitate the sales of products from many sellers worldwide, and the production, purchase or shipping country of origin is often not indicated, and even if it is, there is always some uncertainty about the correctness of this information. In some cases, this information is available in relation to the purchase completion and receipt of the product (e.g. order confirmation or indication of ”Made in [country]” on the product). However, on many websites it was complicated or even impossible to find (trustworthy) information about the purchase country, country of origin or which country the product has been shipped from. Available information was used to select products in the widest possible range, and products with this information were chosen for the gross list rather than corresponding products without this information in order to comply with the prioritization of products from different countries, as well as, for example, a specific inclusion of products out of hard PVC[19] from North America. According to the above-mentioned, Danish Technological Institute created a gross list consisting of 83 different products, where the description of 80 products indicated that the product consisted entirely or partially of PVC, while the remaining three products had no indication of PVC content. For these products, an estimated likelihood for content of PVC was indicated.

[19] For possible content of tin stabilizers according to the project *Recommendations for analysis program for testing of which organotin compounds are used in PVC*, Danish Technological Institute, 2018, created for the Environmental Protection Agency.

Based on the above-mentioned gross list, the Danish Environmental Protection Agency requested inclusion of a few additional products within building materials / products, cosmetics / personal care items and sex toys, as well as several products made of hard PVC. To increase the number of products made of hard PVC, the Danish Environmental Protection Agency chose to replace some products made of soft PVC with products made of hard PVC, where possible, within the same product type, from a list of examples retrieved from *PVC Informationsrådet* (PVC Information Council, an interest group financed by Danish PVC-processing companies and The European Council of Vinyl Manufacturers). These changes in the gross list resulted in the fact that the list featured more products, represented a broader range of products, and included more hard products than the previous original version of the gross list. As a result, the final gross list of products for purchase consisted of 95 products.

3.4 Selection of products for purchase

Danish Technological Institute made a recommendation for the selection of 52 products, which was the starting point for the number of products for selection. This recommendation was based on choosing a weighted number of products (0, 1 or 2 set[20]) depending on the consumers' purchase patterns for different product[21], including the selected product types: building materials / products, cosmetics / personal care products and sex toys. Thus, the recommendation consisted of in total of 2 x 26 products (from web shops both from the EU and outside the EU)[22]. 20 out of these products were selected as products made of hard PVC[23], and five of these were selected because they were made of hard and transparent PVC. In addition, 16 products were directly comparable to the products from the control campaign from the Chemical Inspection Service in 2018 on DIY retailer products, and eight products were directly comparable to products from the control campaign from the Chemical Inspection Service in 2018 on children's toys.

Based on the recommendation and on considerations on how to best spend resources released by not including analysis of substances from the PLASI database, the Danish Environmental Protection Agency decided to follow the recommendation and further choose 24 adtional products to increase the broadness products and product types. Products were selected in pairs from each product type, so that one product in each pair was purchased in EU-based non-Danish web shop, but the other from a web shop outside the EU. Thus, the selected products for purchase consisted of 2 x 38 products. Among these, 22 products were expected to be made of hard PVC, out of which five products were made from hard, transparent PVC, while 54 of the purchased products were made of soft PVC. 20 of the selected products could be directly compared to products from the Chemical Inspection Service campaign in 2018 on DIY retailer products, and 12 products could be directly compared to products from the control campaign by the Chemical Inspection Service in 2018 on children's toys.

When purchasing the products, the country of origin of the web shop, which was one of the criteria for the purchased products, was registered. The country of production is, by contrast, typically not indicated for the products in the web shop, but was registered to the extent possible

[20] A set means that the same product is purchased from web shops both inside and outside the EU, for example, one oil cloth inside the EU and another one outside the EU, or one oil cloth and one swimming pool inside the EU and each product type also outside the EU.

[21] According to data from FDIH yearly run 2018 (Årskørsel FDIH, 2018.)

[22] Assuming that all selected products are still available for purchase at the time of purchase, and that the received products corresponded to the expected, e.g. that they actually consistent of PVC.

[23] The products in the prioritized product types consisted most often of soft PVC rather than hard PVC. The Danish Environmental Protection Agency wished to achieve a more evenly distributed representation not products out of soft and hard PVC, which is why all products out of hard PVC on the gross list were included in the recommendation.

upon receipt, see Appendix 3. Hence, it was identified that most of the purchased products are made in Asia irrespective of the country of origin of the web shop.[24]

Upon ordering the products, some of the specifically selected products were no longer available and were, thus, replaced by a corresponding product. Two products were not received within a time frame that allowed including these in further work, i.e. the final product list consisted of 74 products and is included in Appendix 3. In the product list, products purchased with an expectation to be able to be compared with products in the control campaigns by the Chemical Inspection Service of 2018 on DIY retailer products and children's toy, are indicated.

[24] 49 of the products are listed as made in China, or include text in Chinese; 20 of the products have unknown country of production, three products are listed as made in another country outside the EU, and two products are listed as made inside the EU (both types are sold on websites in the EU). Two products never emerged and are thus not included in the analysis.

4. Analysis of PVC products

4.1 Strategy for analysis

To ensure that the purchased products are entirely or partially made of PVC according to the product description, each product underwent initial EDXRF screening to identify chlorine. In some cases, it was possible to detect that products contrary to expectation did not contain PVC. These products were, thus, excluded from further analysis. In addition to chlorine, the screening detected a range of other chemical elements that could indicate the usage of stabilizers.

Heat stabilizers are a group of problematic additives in PVC, which are in the focus in this project. The used stabilizers cannot be directly detected, but their presence can be investigated by testing for specific metals that may be added to the PVC material either as liquid metals or metal systems.[8]

The screening results indicated the content of lead in some products. Since there are both national and EU regulations for lead- and cadmium-based stabilizers, it was decided to perform quantitative content analyses for these two metals. Also, there are regulations on specific organotin compounds. Thus, tin was included in the quantitative content analyses. Further information on these regulations is included in **TABLE 14**.

The chemical element phosphorus, which was detected in the screening in most of the products, is equally interesting because phosphorous-containing additives are added to PVC as co-stabilizers for metals.

The two chemical elements: boron and antimony were included in the analysis because these two chemical elements are included in some of the 32 substances selected from the PLASI database (see section 2.2). The substance disodium tetraborate, which contains boron, was one of the highest prioritized substances as to harmful effects. Also, antimony was included in the inorganic compound diantimony trioxide, which is suspected to be carcinogenic. Common for both compounds is that the substance was indirectly detected under the analysis of the specific chemical element.

The quantitative content analysis of the specific metals and chemical elements: tin, boron, antimony, and phosphorus were performed with ICP.

Tin was detected in a wide range of products. For four of these products, the quantitative analysis with ICP showed the content of tin, which exceeds the threshold value of 0.1% (1000 mg/kg). Thus, an additional analysis was performed to identify the type of organotin compound used in these four products.

Phthalates and short-chain chlorinated paraffins (SCCP), which may be included as softeners in PVC, are another group of additives of focus in this project. Many phthalates are repro-toxic and belong to the group of endocrine-disrupting substances, and SCCPs are harmful to the environment. Thus, the PVC-containing products, as identified by EDXRF screening, having a soft and flexible structure were selected for analyses for phthalates and SCCP.

Other additives can be identified in soft PVC upon screening of data acquired during analysis for phthalates. Based on the decision to exclude substances from the PLASI database from quantitative content analysis, it was possible to include these types of screenings in the analysis program to get additional information on which substances have been added to the purchased PVC products.

The overview of the existing legislation regarding the above-mentioned additives has been included in **TABLE 14**.

4.2 Identification of PVC products

The products purchased for the project were selected based on the product description, which indicated an entire or partial content of PVC. To confirm if the product materials consist of PVC, all products were screened with EDXRF.

PVC can contain up to 57% chlorine. The high chlorine content is used in relation to material identification with EDXRF screening. This method is described in Appendix 5. The method is a non-destructive chemical element analysis method, which qualitatively detects chemical elements in the material surface.

4.2.1 Results of screening of products for PVC

In 54 of the 76 purchased products (Appendix 3) chlorine was detected (see **TABLE 4** and **TABLE 5**), and it was, thus, concluded that the analyzed material consists of PVC. A product can consist of several types of materials, and the analyzed partial sample of a product is described in Appendix 3. The identified PVC-containing products are divided across 13 products of hard PVC and 41 products of soft PVC (see hard PVC in **TABLE 4** and soft PVC in **TABLE 5**).

Besides chlorine, a range of other chemical elements were detected in PVC-based products as indicated in **TABLE 4** and **TABLE 5**. Some of these chemical elements are especially interesting for this project, since focus is on, among others, the application of stabilizers in PVC. Stabilizers can be based on lead and cadmium, even though the usage of these is forbidden in Denmark. The results show that lead has been identified in three products. Furthermore, heat stabilizers can be based on, for example zinc, calcium, magnesium, and potassium, which have been found in several products.

Phosphorous is also an interesting chemical element as it is included in substances such as phosphites that may be added to PVC as co-stabilizers for metal stabilizers.[8] Phosphorous can also be included in other substances, for example phosphorous-based flame retardants.

The detection limit for each chemical element is product-dependent, and, thus, it cannot be excluded that some chemical elements in a product are not detected during screening with EDXRF.

TABLE 4. Screening results with EDXRF for products of hard PVC, x = detected.

Product		Chemical element															
No.	Name	Cl	Na	Ca	Ti	S	Al	Y	K	Si	Mg	Zn	P	Fe	Cu	Pb	Mn
7	Toy figure	x	x	x	x	x											
8	Toy figure	x	x	x		x	x			x							

Product		Chemical element															
No.	Name	Cl	Na	Ca	Ti	S	Al	Y	K	Si	Mg	Zn	P	Fe	Cu	Pb	Mn
9	Toy figure	x	x	x	x	x	x		x	x	x						
10	Toy figure	x	x	x	x	x	x		x	x		x					
53	Self-irrigation	x	x			x	x						x				
54	Self-irrigation	x	x			x	x						x				
59	Lamp	x	x		x	x				x							
60	Lamp	x	x		x	x											
65	iPad cover	x			x	x			x								
71	Pipe	x				x											
72	Pipe	x				x											
73	Pipe joint	x		x	x	x	x									x	
74	Pipe joint	x	x	x	x	x	x									x	

TABLE 5. Screening results with EDXRF for products of soft PVC, x = detected.

Product		Chemical element															
No.	Name	Cl	Na	Ca	Ti	S	Al	Y	K	Si	Mg	Zn	P	Fe	Cu	Pb	Mn
2	Bathing ring	x	x	x	x												
3	Bath duck	x	x	x	x	x											
4	Bath ducks	x	x	x	x	x	x	x	x								
5	Diving goggles	x	x	x		x											
6	Diving goggles	x	x	x		x			x								
11	Jump rope	x	x			x	x					x					
12	Jump rope	x	x			x	x										
13	Bag	x	x	x	x	x	x										
14	Bag	x	x	x	x	x	x						x				
15	Pencil case	x	x			x	x						x				
16	Pencil case	x	x			x	x						x				
17	Chew toys for pets	x	x	x	x	x	x						x				
18	Chew toys for pets	x	x	x		x	x										
19	Feeding mat	x	x	x		x					x	x		x			
20	Feeding mat	x		x	x	x	x			x	x	x		x			x
21	Hobby cutting board	x	x	x	x	x											
22	Hobby cutting board	x		x	x	x				x		x		x			
23	Wall sticker	x	x	x	x	x										x	
25	Tape	x	x	x	x	x	x			x				x			
26	Tape	x	x	x	x	x	x			x	x			x			
29	Car mat	x		x	x	x	x			x	x			x			
30	Car mat	x		x		x				x				x			
31	Yoga mat	x		x		x						x			x		
32	Yoga mat	x		x		x	x		x		x	x			x		
33	Yoga ball	x		x	x	x											
34	Yoga ball	x		x		x											
35	Football	x	x	x	x	x	x						x				

Product		Chemical element															
No.	Name	Cl	Na	Ca	Ti	S	Al	Y	K	Si	Mg	Zn	P	Fe	Cu	Pb	Mn
36	Football	x	x		x	x											
39	Sandal	x	x	x		x	x			x							
41	Flip-flops	x	x	x	x	x	x			x							
42	Flip-flops	x	x	x	x	x											
43	Rainwear	x	x	x	x	x	x			x	x		x				
44	Rainwear	x		x		x	x				x						
48	Cover for garden furniture	x			x	x											
50	Tarpaulin	x	x	x	x	x				x			x				
51	Garden hose	x					x										
52	Garden hose	x	x														
55	Gloves	x	x	x	x	x	x			x			x				
56	Gloves	x		x	x	x	x			x			x				
67	Phone charger	x		x	x	x	x			x	x			x			
75	Sex toy, arm	x	x	x		x	x			x		x					

4.3 Analysis of selected chemical elements with ICP

In total, 54 products with confirmed PVC content were analyzed with ICP to detect contents of the following chemical elements: lead (Pb), cadmium (Cd), tin (Sn), phosphorous (P), antimony (Sb) and boron (B). The applied methods are described in Appendix 4.

4.3.1 Results from analysis of selected chemical elements

The analysis results show that in total 16 products contained lead and in total 11 products contained cadmium (see TABLE 6 and TABLE 7). Initially, the analysis was performed as single determinations, and only when there was a possibility that measurements would exceed the threshold value, duplicate determinations were performed. The results of determinations of selected chemical elements are shown in TABLE 6 (hard PVC) and TABLE 7 (soft PVC).

Tin was detected in a large part of the analyzed products. The analysis results show that in total 23 out of 54 products contain tin. The results show that in four products (product no. 53, 54, 71 and 72) the tin contents exceed the threshold value of 0.1% (1000 mg/kg) for selected

organotin compounds (see TABLE 14). Common for all four products is the fact that the material is a hard, transparent PVC that to a high degree is expected to contain tin compounds.[25] These four products were analyzed further to identify the used organotin compound (see section 4.3.2).

Phosphorous was identified in 15 products in concentrations up to 0.04% (400 mg/kg). The concentration of the specific phosphorous compound that may be found in the product is, however, considerably higher as only the weight percentage of phosphorus has been taken into consideration. For example, triphenylphosphine (CAS No. 101-02-0), which was identified in product no. 14 (see section 4.5.1) has a higher molecular weight than phosphorous and will, thus, have a weight percentage in the product that is 10 times higher compared to phosphorous. Depending on which specific phosphorous compound was used in the PVC material in

[25] Recommendations for analysis program regarding investigation of which organotin compounds are used in PVC, Danish Technological Institute, 2018, job for the Danish Environmental Protection Agency.

the specific product, the expected content of the specific phosphorous compound in the analyzed products will be approx. 0.4% (400 mg/kg). During screening, phosphorous-based substances were identified in both product 14 and 16. These two products are also among the products with the highest content of phosphorous.

Boron was not detected in any of the products. However, antimony was found in 17 products at concentration levels ranging from 0.0002% (2 mg/kg) to 0.9% (9000 mg/kg). In cases where antimony trioxide has been added to products, this would correspond to a content of this compound of up to approx. 1.1% (11,000 mg/kg).

The Danish Environmental Protection Agency assessed the analysis results in relation to the product type and according to the legislation that would be applicable if the product had been marketed in Denmark or the EU. This assessment disclosed violations of threshold values marked with 1-5 next to the respective analysis result in TABLE 6 and TABLE 7. Markings 1-5 have been described in detail after TABLE 7. Further information on the legislation is given in TABLE 14.

The analysis results indicate that the content of lead exceeded the threshold value in nine products, and the content of cadmium was above the threshold value in four products. The overview of these products is shown in TABLE 13, where the concentration of ingredient substances is compared to the application restrictions stated both in Danish and EU legislation. Since no analysis was performed for lead and cadmium in the control campaigns by the Chemical Inspection Service in 2018 for children's toys and DIY retailer products, it is not possible to compare these findings with the Danish market.

The analysis results indicate no systematic difference in the number of violations of threshold values as to whether the product is purchased inside the EU (except Denmark) or outside the EU.

TABLE 6. Results for detection of selected chemical elements in products of hard PVC. **"-"** indicates value below the detection limit (0.1% = 1000 mg/kg).

Unit: mg/kg		Chemical element, detection limit					
Product		Pb	Cd	Sn	P	Sb	B
No.	Name	2	2	2	100	2	400
7	Toy figure	-	-	89	140	-	-
8	Toy figure	-	-	2	-	-	-
9	Toy figure	-	-	-	-	-	-
10	Toy figure	-	-	-	-	-	-
53	Self-irrigation	6	-	3300[5)]	180	-	-
54	Self-irrigation	-	-	3300[5)]	-	-	-
59	Lamp	-	-	-	-	-	-
60	Lamp	-	-	-	-	-	-
65	iPad cover	-	-	-	-	120	-
71	Pipe	-	-	3000[5)]	-	-	-
72	Pipe	-	-	3800[5)]	-	-	-
73	Pipe joint	9000[3)]	-	3	-	-	-
74	Pipe joint	9700[3)]	-	-	-	-	-

TABLE 7. Results for detection of selected chemical elements in soft PVC products (0.1% = 1000 mg/kg). "-" indicates value below the detection limit.

Unit: mg/kg		Chemical element, detection limit					
Product		Pb	Cd	Sn	P	Sb	B
No.	Name	2	2	2	100	2	400
2	Bathing ring	-	-	-	107	-	-
3	Bath duck	-	-	-	-	-	-
4	Bath ducks	-	-	-	-	-	-
5	Diving goggles	-	-	510	-	-	-
6	Diving goggles	-	-	640	-	-	-
11	Jump rope	-	-	3	-	-	-
12	Jump rope	-	210[1)]	-	-	-	-
13	Bag	-	-	-	110	19	-
14	Bag	-	21	-	370	210	-
15	Pencil case	-	-	4	130	-	-
16	Pencil case	-	-	-	250	-	-
17	Chew toys	-	-	-	-	-	-
18	Chew toys	-	-	-	-	-	-
19	Feeding mat	-	-	-	-	-	-
20	Feeding mat	9	-	-	-	-	-
21	Hobby cutting board	935[3)]	26	280	110	200	-
22	Hobby cutting board	52	35	79	-	520	-
23	Wall sticker	4000[3)]	450[1)]	2	160	-	-
25	Tape	1050[3)]	130[2)]	-	-	-	-
26	Tape	1100[3)]	-	-	-	-	-
29	Car mat	2600[3)]	5	47	120	1800	-
30	Car mat	2600[3)]	-	-	-	-	-
31	Yoga mat	-	-	27	-	14	-
32	Yoga mat	-	-	-	-	17	-
33	Yoga ball	-	-	-	-	-	-
34	Yoga ball	-	-	7	-	-	-
35	Football	-	-	-	-	-	-
36	Football	-	150[1)]	-	160	-	-
39	Sandal	-	-	-	-	-	-
41	Flip-flops	-	-	770	-	-	-
42	Flip-flops	22	36	300	-	-	-
43	Rainwear	-	-	25	-	-	-
44	Rainwear	2	-	-	280	28	-
48	Cover for garden furniture	-	-	-	160	160	-
50	Tarpaulin	110[4)]	-	3	180	9400	-
51	Garden hose	-	-	-	-	2	-
52	Garden hose	850[3)]	29	87	-	48	-
55	Gloves	-	-	-	-	5	-
56	Gloves	-	-	-	-	62	-

Unit: mg/kg		Chemical element, detection limit					
Product		Pb	Cd	Sn	P	Sb	B
No.	Name	2	2	2	100	2	400
67	Phone charger	230[2)]	2	6	-	480	-
75	Sex toys, arm	-	-	-	140	-	-

Explanation of markings 1-5 added next to results TABLE 6 and TABLE 7 (see details about legislation in TABLE 14 and products in Appendix 3):

1) Assuming that the cadmium compound has been added as plastic stabilizer, and as the product is not subject to exceptions described in Appendix 1, entry 3 in government order on cadmium, BEK no. 858 of 05/09/2009, thus this applies with threshold value of 0.0075% (75 mg/kg), which is exceeded.
2) The product is subject to exceptions described in Appendix 1, entry 3 in government order on cadmium, BEK no. 858 of 05/09/2009, where REACH No 1907/2006, Annex XVII, entry 23, applies. The threshold value of 0.01% (100 mg/kg) is exceeded.
3) The product is not subject to REACH No1907/2006, Annex XVII, entry 63, since under normal or reasonably foreseeable circumstances of usage it is not placed in children's mouth, and, thus, is regulated by the government order on lead, government order BEK no. 856 of 05/09/2009 with threshold value of 0.01% (100 mg/kg), which is exceeded.
4) The product is not subject to REACH No 1907/2006, Annex XVII, entry 63, since under normal or reasonably foreseeable circumstances of usage it is not placed in children's mouth, and, thus, is regulated by the government order on lead, government order BEK no. 856 of 05/09/2009 with threshold value of 0.01% (100 mg/kg), but since RSD%=14[26], there is no violation of the threshold value.
5) The product is subject to REACH No 1907/2006, Annex XVII, entry 20. The threshold value of 1000 mg/kg (0.1%) for selected organotin compounds is exceeded. The type of organotin compound must be determined before it is decided if the legislation has been violated.

4.3.2 Identification of tin compounds

Tin content has been detected in four products exceeding 0.1% (1000 mg/kg). Additional analyses were performed for these products to identify tin compounds used in these products. Organotin compounds can be identified based on the original form in the organic tin-ion compound. The applied analysis method is described in Appendix 4. In total, seven different tin-ion compounds have been analyzed as shown in TABLE 8.

One of these tin-ion compounds have been identified in one product only. In this case, it is dibutyltin, which is regulated according to REACH.[27] The content, that is detected to 0.16 mg/kg of dibutyltin, corresponds to a tin content that is much lower than the threshold value of 0.1% (1000 mg/kg), and, hence, the product does not violate the restrictions in REACH. For further information on legislation, see TABLE 14.

The low content of dibutyltin indicates that other tin compounds than those analyzed for, have been added to product 71, since the content of tin measured with ICP is 0.3% (3000 mg/kg, see TABLE 6).

[26] RSD% is this percentage of the relative standard deviation for the analysis of duplicate determination of the concrete product. The analysis error is 15%.

[27] Regulation (EC) No 1907/2006, Annex XVII, entry 20.

TABLE 8. Results of detection of organotin ions. "-" indicates value below the detection limit.

Unit: mg/kg		Organotinion, detection limit						
Product		Mono-butyltin	Di-butyltin	Tri-butyltin	Tetra-butyltin	Tri-phe-nyltin	Mono-oc-tyltin	Di-octyltin
No.	Name	0.1	0.1	0.05	0.1	0.05	0.1	0.1
53	Self-irrigation	-	-	-	-	-	-	-
54	Self-irrigation	-	-	-	-	-	-	-
71	Pipes	-	0.16	-	-	-	-	-
72	Pipes	-	-	-	-	-	-	-

4.4 Analysis of softeners

Products of soft PVC material were analyzed for contents of two types of regulated softeners: phthalates and short-chain chlorinated paraffins (SCCP). Phthalates are regulated both on a national and EU level depending on the product type and the specific phthalate variant. SCCPs are EU-regulated. For further details on legislation, see TABLE 14. For information on the method, see Appendix 4.

4.4.1 Results for content of phthalates

Quantitative analysis results show that phthalates are found in almost all soft products in different concentrations (see TABLE 9), and in some products terephthalates were found. Upon GC-MS-screening, also other softeners were identified (see 4.5.1).

The classification and regulation of the detected phthalates is shown in TABLE 14.

11 different phthalates were identified, which are quantified in the analyzed products. The content for more than half of the identified phthalates is at residual concentration (below 1%), which means that the specific phthalate is not expected to have a softening effect on the material. In addition, these were found in very few products. The remaining four phthalates (DBP, DIBP, DEHP and DINP) were found in most products with very varying content and often combined with other phthalates.

DEHT, which is a terephthalate, was also found in most products, often in combination with one or several phthalates. DEHT is the primary softener in 11 products, of which two are children's toys (product 2 and 16).

Analysis results do not show any systematic difference between the content of the different phthalates in relation to whether the product is purchased or produced in EU compared to outside the EU. Despite the diversity of products, there is not much variation in phthalates used as softeners, i.e. added in amounts exceeding 1%, see TABLE 9.

The Danish Environmental Protection Agency has assessed the analysis results in relation to the product type and according to the legislation that would be applicable if the product had been marketed in Denmark or the EU. This assessment disclosed violations of threshold values in existing and future legislation, which are marked with 1-4 next to the respective analysis result in TABLE 9. Markings 1-4 have been described in detail after the table. Further information on the legislation can be found in TABLE 14.

Regulated phthalates (DBP and DEHP) were detected in one electronic article (product 67).

Five of the purchased products were categorized as children's toys (product 2, 3, 4, 15 and 16 in TABLE 9), and one of the products (product 4) contains regulated phthalates (DBP, DEHP and DINP) above the threshold value of 0.1% (1000 mg/kg).

During the Chemical Inspection Service control campaign in 2018 for control of CMR substances in toys (purchased only in Denmark), only one product out of 64 did not comply with Danish legislation. As in this project, DEHT was detected in most products investigated in the control campaign by the Chemical Inspection Service in 2018 (purchased only in Denmark). The number of analyzed children's toys is too low to be able to compare threshold value violations for the Danish children's toy market with toys from foreign websites.

Results from a Swedish Chemicals Agency e-commerce survey[28] showed that 10 out of 32 children's toys contained substances above threshold values, i.e. they contained phthalates and / or SCCPs. However, it was not indicated whether the products were made of PVC, and, thus, a direct comparison is not possible. Violations were also found in children's toys purchased from web shops in Sweden, in other EU -countries and countries outside the EU.

In this project, 16 products categorized as DIY retailer products (products 25-34, 43-44, 48, 50-52, 55-56) were purchased, see TABLE 9. Results showed that the added softeners are DBP, DIBP, DEHP, DINP, and DEHT. Nine of these products contain phthalates (DBP, DIBP and DEHP) that will be regulated in July 2020, see TABLE 14. Five of these products have been purchased on websites inside the EU (except Denmark), and four outside the EU.

In the Chemical Inspection Service control campaign in 2018 for the control of REACH-regulation art. 33.2[29], 52 different products were purchased from DIY retailers. Similar to the control campaign for children's toy products, the analysis results showed that most of the products contained DEHT or other non-regulated softeners. During the campaign, five different phthalates were identified in products: DBP, DIBP, DEHP, DIDP[30], and didecan-2-yl phthalate.[31] 25 of the products (48%) analyzed during the campaign contained DBP, DIBP and/or DEHP in concentrations that in total exceed 0.1%, which will be regulated in July 2020. By comparison, 9 out of 16 products in total exceeded 0.1% in this project (56%). Five of these products were purchased on websites in the EU (except Denmark), and four outside the EU.

Thus, it is not possible to conclude that there is a significant difference between purchases made inside or outside the EU as regards the violations of the future regulations.

[28] Tillsyn av e-handel 2018, KEMI, Swedish Chemicals Agency, Sweden

[29] REACH: Kontrol af art. 33.2 informationspligten i byggemarkeder – 2018

[30] CAS No. 26761-40-0

[31] CAS No. 28029-89-2

TABLE 9. Results for detection of phthalates and terephthalates in soft PVC products (10,000 mg/kg = 1%). "-" indicates value below the detection limit.

Unit: mg/kg		Softener, abbreviation, CAS No, detection limit											
		Diisobutyl phthalate	Dibutyl phthalate	Butylbenzyl phthalate	Bis (2-ethylhexyl) phthalate	Di-isononyl phthalate	Dimethyl phthalate	Diethyl phthalate	Dihexyl phthalate	Hexyl-2-ethylhexyl phthalate	Dinonyl phthalate	Dioctyl-iso phthalate	Di-(2-ethylhexyl)-terephthalate
		DIBP	DBP	BBP	DEHP	DINP	DMP	DEP	DHxP	HEHP	DNP	DOIP	DEHT
Product		84-69-5	84-74-2	85-68-7	117-81-7	28553-12-0	131-11-3	84-66-2	84-75-3	75673-16-4	84-76-4	137-89-3	6422-86-2
No.	Name	5	5	5	5	20	5	5	5	5	5	5	5
2	Bathing ring	-	-	-	-	-	-	-	-	-	-	-	288,000
3	Bath duck	-	-	-	-	-	-	-	-	-	-	-	-
4	Bath ducks	-	17,000[1)]	-	103,000[1)]	145,000[2)]	-	-	-	-	-	-	350
5	Diving goggles	80	30	-	-	-	-	-	-	-	-	-	422,000
6	Diving goggles	-	100	-	276,000[3)]	-	-	-	-	-	-	-	20
11	Jump rope	30	-	-	84,000[3)]	-	-	-	-	-	-	-	20
12	Jump rope	-	-	-	171,000[3)]	-	-	-	-	-	-	-	3,600
13	Bag	-	-	-	800	306,000	-	-	-	-	-	-	2,700
14	Bag	-	-	-	50	294,000	-	-	-	-	-	-	3,000
15	Pencil case	-	-	-	-	-	-	-	-	-	-	-	-
16	Pencil case	-	-	-	-	-	10	-	-	-	-	-	190,000
17	Chew toys for pets	10	60	-	167,000[3)]	29,000	-	-	-	-	-	-	40,000
18	Chew toys for pets	40	-	-	275,000[3)]	-	-	-	-	-	-	-	1,600
19	Feeding mat	-	-	-	136,000[3)]	-	-	-	-	-	-	-	11,000
20	Feeding mat	40	20	-	61,000[3)]	-	-	-	-	-	-	-	77,000
21	Hobby cutting board	2,100[3)]	3,200[3)]	-	17,800[3)]	16,000	-	-	-	-	-	-	25,000

Unit: mg/kg		Softener, abbreviation, CAS No, detection limit											
		Diisobutyl phthalate	**Dibutyl phthalate**	**Butylbenzyl phthalate**	**Bis (2-ethylhexyl) phthalate**	**Di-isononyl phthalate**	**Dimethyl phthalate**	**Diethyl phthalate**	**Dihexyl phthalate**	**Hexyl-2-ethylhexyl phthalate**	**Dinonyl phthalate**	**Dioctyl-iso phthalate**	**Di-(2-ethylhexyl)-terephthalate**
		DIBP	DBP	BBP	DEHP	DINP	DMP	DEP	DHxP	HEHP	DNP	DOIP	DEHT
Product		84-69-5	84-74-2	85-68-7	117-81-7	28553-12-0	131-11-3	84-66-2	84-75-3	75673-16-4	84-76-4	137-89-3	6422-86-2
No.	Name	5	5	5	5	20	5	5	5	5	5	5	5
22	Hobby cutting board	50	3,200[3)]	-	13,000[3)]	14,000	-	-	-	-	-	-	96,000
23	Wall sticker	-	-	-	118,000[3)]	-	-	-	-	-	-	-	3,800
25	Tape	14,000[3)]	68,000[3)]	-	-	-	-	-	-	-	-	-	-
26	Tape	120	72,000[3)]	-	-	-	-	-	-	-	-	-	520
29	Car mat	30	140	50	87,000[3)]	36,000	-	-	10	90	1200	1300	11000
30	Car mat	10	-	-	128,000[3)]	-	-	-	-	-	-	-	-
31	Yoga mat	5	-	-	-	-	-	-	-	-	-	-	290,000
32	Yoga mat	50	-	-	6	-	-	-	-	-	-	-	291,000
33	Yoga ball	418,000[3)]	-	-	-	-	-	-	-	-	-	-	1,100
34	Yoga ball	445,000[3)]	-	-	-	-	-	-	-	-	-	-	3,500
35	Football	90	-	-	7	-	-	-	-	-	-	-	178,000
36	Football	340	30	-	215,000[3)]	14,000	20	-	-	-	-	-	240
39	Sandal	178,000[3)]	38,000[3)]	-	-	-	-	-	-	-	-	-	60,000
41	Flip-flops	10	20	-	-	-	-	-	-	-	-	-	-
42	Flip-flops	3,900[3)]	297,000[3)]	-	32,000[3)]	1,200	50	40	-	-	-	-	2,200
43	Rainwear	30	870	-	177,000[3)]	7,700	-	-	-	-	-	-	1,300
44	Rainwear	-	20	-	-	-	-	-	-	-	-	-	183,000

Unit: mg/kg		Softener, abbreviation, CAS No, detection limit											
		Diisobutyl phthalate	Dibutyl phthalate	Butylbenzyl phthalate	Bis (2-ethylhexyl) phthalate	Di-isononyl phthalate	Dimethyl phthalate	Diethyl phthalate	Dihexyl phthalate	Hexyl-2-ethylhexyl phthalate	Dinonyl phthalate	Dioctyl-iso phthalate	Di-(2-ethylhexyl)-terephthalate
		DIBP	DBP	BBP	DEHP	DINP	DMP	DEP	DHxP	HEHP	DNP	DOIP	DEHT
Product		84-69-5	84-74-2	85-68-7	117-81-7	28553-12-0	131-11-3	84-66-2	84-75-3	75673-16-4	84-76-4	137-89-3	6422-86-2
No.	Name	5	5	5	5	20	5	5	5	5	5	5	5
48	Cover for garden furniture	-	-	-	47,000	-	-	-	-	-	-	-	40
50	Tarpaulin	-	-	-	-	218,000	-	-	-	-	-	-	-
51	Garden hose	-	-	-	-	-	30	-	-	-	-	-	229,000
52	Garden hose	2,800[3)]	52,000[3)]	-	61,000[3)]	22,700	3,800	20	-	-	-	-	5,100
55	Gloves	-	90	-	375,000[3)]	-	30	-	-	-	-	-	4,500
56	Gloves	-	20	-	-	74,000	50	-	-	-	-	-	90
67	Phone charger	230	13,000[4)]	-	5,400[4)]	-	-	-	-	-	-	40	82,000
75	Sex toy, arm	-	10	-	-	-	-	20	-	-	-	-	-

Explanation of markings included next to results in TABLE 9 (see information on legislation in TABLE 14 and products in Appendix 3):

1) The product is regulated by REACH No 1907/2006, Annex XVII, entry 51 with threshold value of 1000 mg/kg (0.1%), which is exceeded.
2) The product is a toy, which children will be able to put in their mouth. It is regulated by REACH No 1907/2006, Annex XVII, entry 52 with threshold value of 1000 mg/kg (0.1%), which is exceeded.
3) The products cannot be marketed in Denmark as of July 2020, because the content exceeds the threshold value of 1000 mg/kg (0.1%) according to REACH No 1907/2006, Annex XVII, entry 51.
4) The product is regulated by the RoHS Directive, government order BEK no. 720 of 09/07/2019 with threshold value of 1000 mg/kg (0.1%), which is exceeded.

4.4.2 Results for SCCP content

41 products were analyzed to detect SCCP. The analysis results show that five out of 41 products contain SCCP in concentrations from 0.49 - 3.7% (4,900–37,000 mg/kg, see TABLE 10). The content of SCCP in these five products exceeds the threshold value of 0.15% (1,500 mg/kg) as indicated in the POPs Regulation. SCCP was detected in one toy (product 12), whereas no SCCP above the threshold value was detected in the Chemical Inspection Service control campaign in 2018 for control of CMR substances in toys. There is no statistically solid foundation to conclude a difference between the two types of purchases and the violation of the SCCP threshold value. For further information on legislation, see TABLE 14.

Three of the products with detected SCCP were purchased on websites inside the EU (except Denmark), and two were purchased outside the EU. The analysis results indicate, thus, no systematic difference in the violation of the SCCP threshold value in relation to whether the product was purchased inside the EU (except Denmark) or outside the EU.

TABLE 10. Results of detection of SCCP in soft PVC products (1000 mg/kg = 0.1%).

Unit: mg/kg		
Product		Short-chain chlorinated paraffins (SCCP)
No.	Name	CAS No. 85535-84-8
12	Jump rope	37,000
21	Hobby cutting board	4,900
25	Tape	13,000
26	Tape	12,000
30	Car mat	5,800

4.5 Screening analysis by GC-MS

All 41 soft products analyzed for softener content were also investigated for the content of other substances. The products were analyzed using GC-MS as described in Appendix 4. Upon review of the acquired data and comparison with a database with mass spectra, a range of possible substances were identified, as shown in TABLE 12. The concentration was calculated with deuterium-labelled internal standards of phthalate compounds. The identification from the library is considered for guidance only. For a conclusive positive identification, substance-specific analysis would have to be performed with reference substances, which was not included in this project.

The identified substances were looked up by CAS No. in the C&L Inventory database from the European Chemicals Agency.[32] Both harmonized and notified classifications were investigated to identify the substances. Classifications for each substance are indicated in TABLE 12, and it was registered in which product the substance was found. All notified references are included in TABLE 12, which is why it may occur that a substance can be identified as ”not classified”, while having an identified hazard class.

[32] https://echa.europa.eu/da/information-on-chemicals/cl-inventory-database

4.5.1 Results of screening analyses

In general, the GC-MS-screening identified 54 different possible substances with CAS No. for 41 products, see TABLE 12.

All substances found in volumes above 1% have a known softening function, and none of them have a harmonized classification. An overview of the identified softeners is shown in TABLE 11.

TABLE 11. Overview of softeners identified by GC-MS screening.

Name	CAS No.	Content
DINCH	166412-78-8	Up to 49%
Didecan-2-yl phthalate	28029-89-2	Up to 26%
Tributyl acetylcitrate	77-90-7	Up to 10%
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	6846-50-0	Up to 6.8%
Butyl citrate	77-94-1	Up to 6.7%
1-Propene-1,2,3-tricarboxylic acid, tributyl ester	7568-58-3	Up to 1.5%
Diethylene glycol dibenzoate	120-55-8	Up to 2.4%
Tri(2-ethylhexyl) trimellitate	3319-31-1	Up to 0.95%
Hexanedioic acid, bis(2-ethylhexyl) ester	103-23-1	Up to 0.17%

The remaining substances were all found in volumes below 1% (many much lower than 1%) and are not necessarily added as actual additives to PVC.

A large part of the analyzed PVC products indicated the content of phosphorus in the ICP analyses. The two soft PVC products no. 14 and 16 contain substances with phosphorous that were identified by GC-MS screening. Product no. 14 contains two substances belonging to the organophosphite group, which is described as co-stabilizers in the report *Survey of PVC in Denmark (2018)*. Product no. 16 contains octizicer, which is a flame retardant.

From the C&L Inventory database from the European Chemicals Agency, it was discovered that 14 of the substances were not registered, and only one substance was registered with no indication of harmonization or notified classification.

Three of the identified substances have a harmonized classification: BPA, isophorone and 2-[2-(2-butoxyethoxy)ethoxy]-ethanol, which each were detected in no more than two of the product no. 13, 14, 31, 32, and 33. By contrast, most of the substances have a notified classification, see TABLE 12.

Selected substances in TABLE 12 (marked with *) were investigated further in relation to their environmental and health effects in TABLE 15.

TABLE 12. Substances identified by GC-MS screening of soft PVC products. (10,000 mg/kg = 1%)

Name	CAS No.	Function	Harmonized hazard class and category	Notified hazard class and category	Product No.	Content [mg/kg]
2-(2-Butoxyethoxy)ethanol	112-34-5		Eye Irrit. 2	Eye Irrit. 2	2	100
				Acute Tox. 4	3	750
				Skin Irrit. 2	14	20
				STOT SE 3	15	230
				STOT SE 2	33	100
				Not Classified	43	160
4,4'-(1-methylethylidene)-bi-sphenol (BPA)*	80-05-7		Eye Dam. 1 Repr. 1B Skin Sens. 1 STOT SE 3	Skin Sens. 1 Repr. 1B Eye Dam. 1 STOT SE 3 Aquatic Chronic 2 Repr. 2 Skin Sens. 1B Aquatic Chronic 3 Asp. Tox. 1 Muta. 1B Carc. 1B Acute Tox. 4	33	40
Isophorone	78-59-1		Acute Tox. 4 * Carc. 2 Eye Irrit. 2 STOT SE 3	Acute Tox. 4 Carc. 2 Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Acute Tox. 3	13 14	80 40

Name	CAS No.	Function	Harmonized hazard class and category	Notified hazard class and category	Product No.	Content [mg/kg]
Benzoic acid, ethyl ester	93-89-0			Skin Irrit. 2 Eye Irrit. 2 Aquatic Chronic 2	31	100
Butyl citrate*	77-94-1	Softener		Not Classified Eye Dam. 1 Aquatic Acute 1	3 17 19 20 33 41 42	2,200 6,400 8,900 9,200 1,500 66,500 300
Tributyl acetylcitrate*	77-90-7	Softener		Not Classified Aquatic Chronic 3 Flam. Gas 1 Muta. 1B Carc. 1B Eye Irrit. 2 Skin Irrit. 2 Aquatic Chronic 2	3 42	101,000 800
2-Ethylhexyl mercaptoacetate	7659-86-1			Acute Tox. 4 Skin Sens. 1B Aquatic Acute 1 Aquatic Chronic 1 Skin Sens. 1 Flam. Liq. 3 Skin Irrit. 2 Eye Irrit. 2	5 6 42	300 530 580

Name	CAS No.	Function	Harmonized hazard class and category	Notified hazard class and category	Product No.	Content [mg/kg]
				STOT SE 3		
1-Propene-1,2,3-tricarboxylic acid, tributyl ester*	7568-58-3	Softener	-	-	3	15,100
					41	1,300
Nonylcyclopropane	74663-85-7		-	-	4	360
					17	290
					42	350
2-Octyl benzoate	6938-51-8				43	260
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate*	6846-50-0	Softener		Repr. 2	2	590
				Aquatic Chronic 3	3	68,200
				Not Classified	4	280
				Skin Irrit. 2	5	270
				Eye Irrit. 2	6	940
				STOT RE 2	17	500
				Aquatic Chronic 2	25	30
				Repr. 2	42	480
Pentadecane	629-62-9			Asp. Tox. 1	17	280
				STOT SE 3		
				Skin Irrit. 2		
				Eye Irrit. 2		
Tetradecane	629-59-4			Asp. Tox. 1	15	240
				Skin Irrit. 2	17	210
				STOT SE 3		
				Eye Irrit. 2		
				Aquatic Chronic 4		
Tridecane	629-50-5			Asp. Tox. 1	17	130

Name	CAS No.	Function	Harmonized hazard class and category	Notified hazard class and category	Product No.	Content [mg/kg]
				Skin Irrit. 2 Eye Irrit. 2 STOT SE 3 Not Classified Aquatic Chronic 4	33	40
Dibutyl sulfonate	625-22-9			Acute Tox. 4 Acute Tox. 3	42	220
3-Octyl-*trans*-oxiran-octanoic acid, methyl ester	6084-76-0				39	160
Octadecane	593-45-3			Asp. Tox. 1 Skin Irrit. 2 Eye Irrit. 2 STOT SE 3	17	380
Hexadecane	544-76-3			Asp. Tox. 1 Skin Irrit. 2 Eye Irrit. 2 STOT SE 3 Skin Corr. 1B	17	310
Benzoic acid, 2-ethylhexyl ester	5444-75-7			Repr. 1B Aquatic Chronic 4 Not Classified	30	50
15-Octadecadienoic acid, methyl ester	4764-72-1				18	2,800
4-(Prop-2-enoyloxy)octane	42928-87-0				25	20
Dodecanoic acid, phenyl ester	4228-00-6				14	70

Name	CAS No.	Function	Harmonized hazard class and category	Notified hazard class and category	Product No.	Content [mg/kg]
1-Hexadecanol	36653-82-4			Not Classified	4	3000
				Eye Irrit. 2	4	680
				Aquatic Acute 1	17	1,900
				Aquatic Chronic 2	18	1,500
				Aquatic Chronic 3	31	40
				Aquatic Chronic 1	31	30
				Flam. Liq. 2	32	500
				Acute Tox. 4	33	790
				STOT SE 3		
				Skin Irrit. 2		
				Aquatic Chronic 4		
Bis(2-ethylhexyl) hydrogen phosphite	3658-48-8	Co-stabilizer		Skin Irrit. 2	14	100
				Eye Irrit. 2		
				Aquatic Chronic 1		
				Eye Dam. 1		
				STOT SE 3		
				Aquatic Acute 1		
Tris(2-ethylhexyl) trimellitate*	3319-31-1	Softener		Not Classified	17	4,500
				Repr. 2	29	9,500
				Skin Irrit. 2		
				Eye Irrit. 2		
Cyclohexadecane	295-65-8				34	840
Didecan-2-yl phthalate	28029-89-2	Softener			15	260,000
					22	20,000
					35	60,000

Name	CAS No.	Function	Harmonized hazard class and category	Notified hazard class and category	Product No.	Content [mg/kg]
					42	6,000
					56	130
3-Octyl-*cis*-oxiraneoctaoic acid, methyl ester	2566-91-8				17	2,200
3-Octyl-oxiraneoctaoic acid, methyl ester	2500-59-6				11	9,900
					13	210
					17	2,400
					22	580
					42	920
					43	2,700
1,1'-oxybisdecane	2456-28-2			Not Classified	15	300
n-Propyl benzoate	2315-68-6			Not Classified	31	30
1-Propanol, 2-[2-(benzoyloxy)propoxy]-, benzoate	20109-39-1				31	30
(Z)-11-Octadecadienoic acid, methyl ester	1937-63-9			Skin Irrit. 2 Eye Irrit. 2 STOT SE 3	17	2,800
1-Iodotetradecane	19218-94-1				17	380
p-Toluic acid, 2-ethylhexyl ester	16397-65-2				5	60
2-[2-(2-butoxyethoxy)-ethoxy]-ethanol	143-22-6		Eye Dam. 1	Eye Dam. 1	31	10
					32	270
Methyl diphenyl phosphite	138374-09-1	Co-stabilizer			14	340
Butyl benzoate	136-60-7			Not Classified	25	10
				Eye Irrit. 2	26	30

Name	CAS No.	Function	Harmonized hazard class and category	Notified hazard class and category	Product No.	Content [mg/kg]
				Skin Irrit. 2	42	830
				Eye Irrit. 2	43	20
				Acute Tox. 4		
				STOT SE 3		
				Skin Sens. 1		
				Resp. Sens. 1		
Butylhydroxytoluene*	128-37-0			Aquatic Chronic 1	14	50
				Aquatic Acute 1	30	380
				Aquatic Chronic 4	36	170
				Not Classified		
				Acute Tox. 4		
				Skin Irrit. 2		
				Eye Irrit. 2		
				STOT SE 3		
				STOT RE 2		
				Skin Sens. 1		
				STOT SE 1		
				Muta. 1B		
				Carc. 2		
				Repr. 2		
				Aquatic Chronic 2		
				Aquatic Chronic 3		
				Resp. Sens. 1		
				Muta. 2		
				Carc. 1B		
				Acute Tox. 3		

Name	CAS No.	Function	Harmonized hazard class and category	Notified hazard class and category	Product No.	Content [mg/kg]
Octicizer*	1241-94-7	Flame retardant		Not Classified Aquatic Acute 1 Aquatic Chronic 1 Aquatic Chronic 2 Acute Tox. 4	14 16	290 730
Hexanedioic acid, dioctyl ester	123-79-5			Skin Irrit. 2 Eye Irrit. 2	23	130
Diethylene glycol dibenzoate*	120-55-8	Softener		Aquatic Chronic 2 Eye Irrit. 2	31	24,000
Benzoic acid, 2-methylpropyl ester	120-50-3			Not Classified	33 34 39	300 430 200
Octadecanol	112-92-5			Not Classified Aquatic Chronic 3 Eye Irrit. 2 Aquatic Chronic 2	32	750
Methyl stearate	112-61-8			Not Classified	13 17 22 42 43	220 1,200 200 210 670
Octadecanol	112-92-5			Not Classified Aquatic Chronic 3 Eye Irrit. 2 Aquatic Chronic 2	32	750

Name	CAS No.	Function	Harmonized hazard class and category	Notified hazard class and category	Product No.	Content [mg/kg]
1-Dodecanol	112-53-8			Eye Irrit. 2 Aquatic Acute 1 Aquatic Chronic 2 Aquatic Chronic 1 Not Classified Aquatic Chronic 3 Flam. Liq. 2 Acute Tox. 4 Eye Dam. 1 STOT SE 3 Skin Irrit. 2 STOT SE 2	17	220
1-Dodecene	112-41-4			Asp. Tox. 1 Skin Irrit. 2 Aquatic Chronic 2 Aquatic Chronic 1 Aquatic Acute 1 Carc. 1B Eye Irrit. 2 STOT SE 3	2 2	150 90
Hexadecanoic acid, methyl ester	112-39-0			Not Classified Skin Irrit. 2 Skin Sens. 1 Eye Dam. 1	11 13 14 16 17 18	6,800 940 170 930 2,900 1,400

Name	CAS No.	Function	Harmonized hazard class and category	Notified hazard class and category	Product No.	Content [mg/kg]
					22	500
					43	1,200
(Z)-9-Hexadecanoic acid, methyl ester	1120-25-8			Skin Irrit. 2	16	880
				Eye Irrit. 2		
				STOT SE 3		
2,2,4,4-tetramethylpentane	1070-87-7			Flam. Liq. 2	33	50
				Asp. Tox. 1		
N-propylbenzamide	10546-70-0			Acute Tox. 4	31	200
				Eye Dam. 1	31	170
Hexadecanoic acid, bis(2-ethylhexyl) ester*	103-23-1	Softener		Not Classified	15	1,200
				Aquatic Acute 1	17	660
				Aquatic Chronic 1	17	610
				Skin Irrit. 2	21	1,500
				Eye Irrit. 2	22	1,000
				Aquatic Chronic 2	42	1,700
				Acute Tox. 4	43	850
				Carc. 2	48	100
				Repr. 2	50	100
				Aquatic Chronic 4		
Acetic acid, 2-ethylhexyl ester	103-09-3			Skin Irrit. 2	5	140
				Eye Irrit. 2		
Triphenyl phosphonate*	101-02-0	Co-stabilizer		Acute Tox. 4	14	110
				Skin Irrit. 2		
				Skin Sens. 1		
				Eye Irrit. 2		

Name	CAS No.	Function	Harmonized hazard class and category	Notified hazard class and category	Product No.	Content [mg/kg]
				STOT RE 2 Aquatic Acute 1 Aquatic Chronic 1 Skin Sens. 1B Skin Sens. 1A STOT SE 2 Skin Corr. 1B		
DINCH (1,2-Cyclohexanedicarboxylic acid, 1,2-diisononyl ester)	166412-78-8	Softener		Not classified	75	490,000

4.6 Violations if products were marketed in Denmark

Products with detected substances in concentrations above the permitted threshold values for marketing in Denmark have been summarized in TABLE 13 (legislation is described in detail in TABLE 14).

In total, 13 out of 54 analyzed products, corresponding to 24%, exceed the permitted threshold values for marketing in Denmark, out of which six products exceed the permitted threshold values in more than one legislation.

TABLE 13. Overview of products, where concentrations are compared to usage restrictions in Danish and European legislation (1000 mg/kg = 0.1%).
GV = threshold value. %RSD is the per cent standard deviation for duplicate determination.

Product			Ingredient substance*			Legislation	GV
No.	PVC	Name	Name	mg/kg	%RSD		[mg/kg]
4	Soft	Bath ducks	DBP DEHP	17,000 103,000	3.2 2.1	REACH No 1907/2006, Annex XVII, entry 51	1,000
			DINP	145,000	9.4	REACH No 1907/2006, Annex XVII, entry 52	1,000
12	Soft	Jump rope	Cd	210	0.9	Government order BEK no. 858 of 05/09/2009	75
			SCCP	37,000	3.1	POPs Regulation (EU), No 2019/1021	1,500
21	Soft	Hobby cutting board	Pb	935	0.2	Government order BEK no. 856 of 05/09/2009	100
			SCCP	4,900	16	POPs Regulation, (EU), No 2019/1021	1,500
23	Soft	Wall sticker	Pb	4,000	3.0	Government order BEK no. 856 of 05/09/2009	100
			Cd	450	2.3	BEK no. 858 of 05/09/2009	75
25	Soft	Tape	Pb	1,050	4.4	Government order BEK no. 856 of 05/09/2009	100
			Cd	130	3.1	REACH no. 1907/2006, Annex XVII, entry 23.	100
			SCCP	13,000	4.9	POPs Regulation (EU), No 2019/1021	1,500
26	Soft	Tape	Pb	1,100	3.4	Government order BEK no. 856 of 05/09/2009	100
			SCCP	12,000	2.2	POPs Regulation (EU), No 2019/1021	1,500
29	Soft	Car mat	Pb	2,600	4.0	Government order BEK no. 856 of 05/09/2009	100
30	Soft	Car mat	Pb	2,600	4.6	Government order BEK no. 856 of 05/09/2009	100

			SCCP	5,800	0.5	POPs Regulation (EU), no. 2019/1021	1,500
36	Soft	Football	Cd	150	1.1	Government order BEK no. 858 of 05/09/2009	75
52	Soft	Garden hose	Pb	850	0.02	Government order BEK no. 856 of 05/09/2009	100
67	Soft	Phone charger	DBP DEHP	13,000 5,400	7.4 4.8	Government order BEK no. 720 of 09/07/2019	1,000
73	Hard	Pipe joint	Pb	9,000	4.7	Government order BEK no. 856 of 05/09/2009	100
74	Hard	Pipe joint	Pb	9,700	3.6	Government order BEK no. 856 of 05/09/2009	100

* Analytic uncertainty for methods: SCCP 35%, metals 15%, phthalates 18% (expanded 35%).
For further details on methods, see Appendix 4.

In Appendix 3, the name of the web shop and country of origin have been indicated for each product. The comparison of countries of origin for products with violations (see TABLE 13) were they purchased from a Danish web shop shows that of the 13 products are six products purchased in the EU (except Denmark), four products purchased outside the EU, and three have an unknown country of origin. Thus, this project has not shown a significant difference in the number of violations of the legislation indicated in TABLE 13 for products purchased inside the EU (except Denmark) and outside the EU.

Furthermore, 22 out of 41 investigated (54%) products contain DIBP, DEHP and DBP in concentrations above 0.1% (1000 mg/kg). Starting from July 2020, marketing of articles with these phthalates is prohibited in the EU according to REACH No 1907/2006, Annex XVII, entry 51 with a threshold value of 0.1%. This concerns the following products:

- Diving goggles (6)
- Jump rope (11 + 12)
- Chew toys for pets (17 + 18)
- Feeding mat (19 + 20)
- Hobby cutting board (21 + 22)
- Wall sticker (23)
- Tape (25 + 26)
- Car mat (29 and 30)
- Yoga ball (33 + 34)
- Football (36)
- Sandal (39)
- Flip-flops (42)
- Rainwear (43)
- Garden hose (52)
- Gloves (55)

Of these products, nine products were purchased inside the EU (except Denmark), 11 were purchased outside the EU and two have an unknown country of origin. Thus, it cannot be concluded that there is a difference between purchases made inside and outside the EU regarding the violation of the upcoming regulations.

5. Hazards and regulation of selected additives

This section provides a more detailed description of a range of additives selected from the analysis results regarding the hazards and regulation of these substances.

Below in **TABLE 14** and **TABLE 15**, the hazards of the substances have been described based on the harmonized EU classification according to Annex VI to CLP Regulation (EC) No

1272/2008 and the notified classifications included in the REACH registrations of the substance.

Thereafter, the status for assessment and regulation is described according to REACH Regulation (EC) No 1907/2006, and hereof the extent to which the substances have one or several of “the five adverse effects” stated in “Political agreement on new joint chemicals initiatives 2018-21” as being specifically problematic in relation to chemical substances. The five adverse effects are valid for substances with:

- carcinogenic, mutagenic or repro-toxic effects
- brain-damaging effects or substances with harmful effects on brain development
- endocrine-disrupting effects
- allergenic effects
- environmentally harmful effects.

Further, the regulatory status valid for the RoHS Directive for electronic articles is included:

- Government order BEK No. 720 of 09/07/2019 on restrictions on import and sales as well as production for export within EU of electrical and electronic equipment containing hazardous substances.

In addition, the regulation of substances enforced for children’s toys, including:

- Government order BEK No. 309 of 03/04/2017 on safety requirements for children’s toys.
- Government order BEK No. 855 of 05/09/2009 on ban on phthalates in toys and articles for young children (valid specifically for products intended for children aged 0-3 yrs.).

In **TABLE 14** below, the hazards and regulation of the PVC additives identified with a high quantitative accuracy in the analyses by use of reference substances are described. The selected additives are additives found in concentrations above 1% as well as selected metal compounds.

TABLE 14. Classification and regulation of selected additives, which are classified after product analysis.

Substance / **CAS No.** **Highest concentration in this project**	**EU-harmonized CLP classification according to EC No. 1272/2008, Annex VI** **(notified classification in REACH register)**	**REACH (EC), No 1907/2006** **Registration Status** **Other REACH requirements and measures**	**Subject to** **"The five adverse effects"**	**RoHS** **Government order BEK no. 720 of 09/07/2019 (RoHS Directive)**	**Children's toys** **Government order BEK no. 309 of 03/04/2017 (on toys) BEK no. 855 of 05/09/2009 (on phthalates in toys)**
Phthalates and terephthalates					
Bis(2-ethylhexyl)phthalate **(DEHP)** **117-81-7** **37.5%**	Repr. 1B, H360Df (Repr. 1B, H360 Aquatic Chronic 1, H410 Aquatic Acute 1, H401)	Indicated tonnage: 10,000-100,000 tons/year Limited in Annex XVII, entry 51: Restrictions on use in toys and articles for young children in concentrations above 0.1% (includes DIBP, DEHP, DBP, BBP). The same threshold value applies to articles mainly from July 7, 2020 with certain exceptions. On approval list (Annex XIV).	Reprotoxic Endocrine-disrupting Harmful to environment	In Appendix II on prohibited substances in electrical and electronic equipment, the threshold value is set to 0.1%.	In government order on toys, Appendix II, appendix B restrictions are placed substances classified as CMR substances in category 1A,1B or 2 in toys (prohibited for DIBP $\geq$ 0.3%) Government order on phthalates in toys set general restrictions on all phthalates in toys and articles for young children in concentrations above 0.05% (unless they are included in Appendix 1).

Diisobutyl phthalate **(DIBP)** **84-69-5** **47,7%**	Repr. 1B, H360Df Repr. 1B, H360 Aquatic Chronic 1, H410 Aquatic Acute 1, H401)	Indicated tonnage: 1-10 tons/year Limited in Annex XVII, entry 51: Restrictions on use in toys and articles for young children in concentrations above 0.1% (includes DIBP, DEHP, DBP, BBP, where restrictions for DIBP will first come into effect from July 7, 2020). The same threshold value applies to articles mainly from July 7, 2020 with certain exceptions. On approval list (Annex XIV).	Reprotoxic Endocrine-disrupting Harmful to environment	In Appendix II on prohibited substances in electrical and electronic equipment, the threshold value is set to 0.1%.	In government order on toys, Appendix II, appendix B restrictions are placed substances classified as CMR substances in category 1A,1B or 2 in toys (prohibited for DIBP ≥ 0.3%) Government order on phthalates in toys set general restrictions on all phthalates in toys and articles for young children in concentrations above 0.05% (unless they are included in Appendix 1).
Dibutyl phthalate **(DBP)** **84-74-2** **29.7%**	Repr. 1B, H360Df Aquatic Acute 1, H400 (Repr. 1B, H360Df Aquatic Acute 1, H400 Aquatic Chronic 2, H411)	Indicated tonnage: 1000-10 000 tons/year Limited in Annex XVII, entry 51: Restrictions on use in toys and articles for young children in concentrations above 0.1% (includes DIBP, DEHP, DBP, BBP, where restrictions for DIBP will first come into effect from July 7, 2020). The same threshold value applies to articles mainly from July 7, 2020 with certain exceptions. On approval list (Annex XIV).	Reprotoxic Endocrine-disrupting Harmful to environment	In Appendix II on prohibited substances in electrical and electronic equipment, the threshold value is set to 0.1%.	Limited in REACH Annex XVII, entry 51.

Di-(2-ethylhexyl)-terephthalate **(DEHT)** **6422-86-2** **42.2%**	No harmonized classification (not classified)	Indicated tonnage: 100 000-1000 000 tons/year In connection with REACH-registration, the substance has been assessed as unproblematic by national authorities. No initiatives under REACH are necessary. RMOA (2016)	None	Not regulated specifically	Not regulated specifically
Diisononyl phthalate **(DINP)** **28553-12-0** **30.6%**	No harmonized classification Proposal for Repr. 1B H360DF under review. (not classified)	Indicated tonnage: 100,000-1,000,000 tons/year Limited in Annex XVII, entry 52: Restrictions on use in toys and articles for young children, which children will be able to place in their mouth, in concentrations above 0.1 %.	Reprotoxic Endocrine-disrupting	Not regulated specifically	Limited in REACH Annex XVII, entry 52
Other					
SCCP; C10-13 chloroalkanes **85535-84-8** **3.7%**	Carc.2, H351 Aquatic Acute 1, H400 Aquatic Chronic 1, H410 (Not registered in REACH)	Not registered in REACH On candidate list because of PBT and vPvB properties. In 2009, has been suggested to include on Appendix XIV by Chemicals Agency. Subject to POPs Regulation (EU) No. 2019/1021 and production, marketing, and usage of SCCP is prohibited in articles in concentrations above 0.15%.	Harmful to environment	Not regulated specifically	Limited in POPs Regulation. Also includes substance content in toys.
Metals and metal compounds					

Cadmium **7440-43-9** **460 mg/kg** **(0.046%)**	Carc. 1B, H350 Muta. 2, H341 Repr. 2, H361fd Acute Tox. 2, H330 STOT RE 1, H372 Aquatic Acute 1, H400 Aquatic Chronic 1, H410 (uses the harmonized classification)	Indicated tonnage: 1000-10 000 tons/year Limited in Annex XVII, entry 23: Polymer materials produced from a range of specified polymer materials must not include more than 0.01% cadmium or above. Hard PVC materials produced from PVC waste may in some applications contain cadmium not exceeding 0.1%. Government order BEK no. 858 of 05/09/2009 on ban on import, sales and production of cadmium-containing products. Threshold value: 75ppm (corresponding to 75mg/kg = 0.0075%). To a degree where the product is subject Appendix 1, section 4 in government order, otherwise REACH is applicable. On candidate list for approval due to the carcinogenic effect of the substance.	Carcinogenic Mutagenic Reprotoxic Harmful to environment	In Appendix II on prohibited substances in electrical and electronic equipment, the threshold value is set to 0.1%.	In government order on toys, Appendix II, section III, article 13, the migration of cadmium from toys are subject to specific migration limit values depending on the type of toy material.
Lead **7439-92-1** **9,900 mg/kg** **(0.99%)**	Repr. 1A, H360FD, C ≥ 0,03 % Lact., H362 Proposal for further harmonized classification as:	Indicated tonnage: 1 000 000 -10 000 000 tons/year Limited in Annex XVII, entry 63: Prohibited in consumer products with lead concentrations above 0.05% (sv.t. 500 ppm = 500 mg/kg) unless migration can be indicated being below 0.05 µg Pb/cm² per hour. Valid for articles or their parts,	Reprotoxic Causes brain damage Harmful to environment	In Appendix II on prohibited substances in electrical and electronic equipment, the threshold value is set to 0.1%.	In government order on toys, Appendix II, section III, article 13, the migration of cadmium from toys are subject to specific migration limit values depending on the type of toy material.

	Aquatic Acute 1, H400, M-factor=10, Aquatic Chronic 1, M-factor=10 (Repr. 1A, H360FD, C ≥ 0,03 % Lact., H362 STOT RE 1 H372, C ≥ 0,5 %" Aquatic Acute 1, H400, M-factor=10, Aquatic Chronic 1, H410)	which under normal and relatively predictable usage conditions can be placed in mouth by children. In addition, specific Danish regulations: Government order, BEK No 856 of 05/09/2009 (government order on lead). Ban on import and sales of products with lead contents above 100 ppm (corresponding to 0.01%=100 mg/kg).			
Dibutyl tin chloride **683-18-1** **(indicated as representative of several dibutyl tin compounds)** **0.19 mg/kg**	Muta. 2, H4341 Repr. 1B, H360FD Acute Tox. 2, H330 Acute Tox. 3, H301 Acute Tox. 4, H312 STOT RE 1, H372 Skin Corr. 1B, H314 Aquatic Acute 1, H400 Aquatic Chronic 1, H410 (Muta. 2, H4341 Repr. 1B, H360FD Acute Tox. 1, H330	Indicated tonnage: 1 -10 tons/year On candidate list for approval. Limited in Annex XVII, entry 20: Dibutyl tin compounds are prohibited in consumer products at tin-concentrations above 0.1%	Mutagenic Reprotoxic Skin Irritating Harmful to environment	Not regulated specifically	Migration limits for organic tin compounds depends on the toy material.

	Acute Tox. 3, H301 Acute Tox. 4, H312 STOT SE 1, H370 STOT RE 1, H372 Skin Corr. 1B, H314 Eye Damage 1, H318 Skin Sens. 1, H317 Aquatic Acute 1, H400 H410)

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TABLE 15 includes a number of selected additives identified in the screening analysis, i.e. the quantitative data must be seen as highly uncertain, which is why the contents detected in the analysis were divided into intervals instead of providing specific values.

TABLE 15. Classification and regulation of selected additives identified in screening analysis of products.

Substance / CAS No. Highest concentration in this project	**EU-harmonized CLP classification according to EC No. 1272/2008, Annex VI (classification indicated in REACH register)**	**REACH (EC), No 1907/2006 REACH-registration Other REACH requirements and measures**	**Subject to "The five adverse effects"**	**RoHS Government order BEK no. 720 of 09/07/2019 (RoHS Directive)**	**Children's toys Government order BEK no. 309 of 03/04/2017 (on toys)**
Tributyl acetyl citrate **77-90-7** **≥10%**	No harmonized classification (not classified)	Indicated tonnage: 10,000-100,000 tons/year. Conclusion of dossier-evaluation: further reprotoxic tests required to reach Appendix X level. RMOA (2016): no additional initiatives required.	Suspected to be endocrine-disrupting	Not regulated specifically	Not regulated specifically
1-propen-1,2,3-trikarboxylic acid, tributyl ester **7568-58-3** **1-10%**	No harmonized classification (not registered in REACH)	(not registered in REACH)	None	Not regulated specifically	Not regulated specifically

Tributyl citrate **77-94-1** **1-10%**	No harmonized classification (not classified)	Indicated tonnage: 1,000-10,000 tons/year RMOA (2016): substance is not seen as reprotoxic, but inadequate knowledge on endocrine-disrupting effects. The substance is recommended for dossier evaluation.	Suspected to be endocrine-disrupting	Not regulated specifically	Not regulated specifically
Diethylene glycol dibenzoate **120-55-8** **1-10%**	No harmonized classification (not classified)	Indicated tonnage: 1,000-10,000 tons/year At dossier evaluation, further tests are required to comply with requirements in Appendix X. Selected to substance assessment due to suspicion of reprotoxic effects.	None	Not regulated specifically	Not regulated specifically
Bisphenol A **80-05-7** **< 1%**	Repr. 1B, H360F STOT SE 3, H335 Eye Dam. 1, H318 Skin Sens. 1, H317 (Repr. 1B, H360F STOT SE 3, H335 Eye Dam. 1, H318 Skin Sens. 1, H317	Indicated tonnage: 10,000,000-1,000,000 tons/year. Annex XVII, entry 66: Restrictions on usage in cash register receipts (thermal paper). Must not contain 0.02% BPA or above. Assessed to be endocrine-disrupting both regarding environment and health. On candidate list and recommended by the European Chemicals Agency for inclusion on approval list.	Reprotoxic Endocrine-disrupting Harmful to environment	Not regulated specifically	In government order on toys, Appendix II, appendix C, the migration of BPA is restricted to a specific migration limit of 0.1 mg/l in toys for children under 3 yrs. and toys that are intended for putting in mouth.

	Aquatic Chronic 2, H411)				
Butylhydroxytoluene **128-37-0** **< 1%**	No harmonized classification (Aquatic Chronic 1, H410)	Indicated tonnage: 10,000-100,000 tons/year Under substance evaluation.	Harmful to environment Suspected to be endo-crine-disrupting	Not regulated specifically	Not regulated specifically
Triphenyl phosphite **101-02-0** **<1%**	Skin Irrit. 2, H315 C ≥ 5 % Eye Irrit. 2, H319 C ≥ 5 % Aquatic Acute 1, H400 Aquatic Chronic 1, H410 (Acute tox. 4, H302 Skin Sens. 1, H317 Skin Irrit. 2, H315 C ≥ 5 % Eye Irrit. 2, H319 C ≥ 5 % Aquatic Acute 1, H400 Aquatic Chronic 1, H410)	Indicated tonnage: 1,000-10,000 tons/year Undergone substance evaluation, which concluded that the substance must be rec-ommended for harmonized classification for Skin Sens. 1 and STOT RE 2 (regarding its effect on the nervous system).	Skin irritating Harmful to environment	Not regulated specifically	Not regulated specifically

2,2,4-Trimethyl-1,3-pentane-diol diiso-butyrate **6846-50-0** **<1%**	No harmonized classification (Repr. 2, H361 Aquatic Chronic 3, H412)	Indicated tonnage: 1,000-10,000 tons/year Dossier evaluation conclusion: further reprotoxic tests required to reach data requirements in Appendix X registration.	Reprotoxic Harmful to environment	Not regulated specifically	Not regulated specifically
Bis(2-ethylhexyl)adipate **103-23-1** **<1%**	No harmonized classification (No classification)	Indicated tonnage: 10,000-100,000 tons/year Selected for substance evaluation.	None	Not regulated specifically	Not regulated specifically
2-ethylhexyldiphenyl- phosphate **1241-94-7** **<1%**	No harmonized classification (No classification)	Indicated tonnage: 1,000-10,000 tons/year After dossier evaluation, further tests required to comply with requirements in Appendix X.	None	Not regulated specifically	Not regulated specifically
tri(2-ethylhexyl)- trimellitate **3319-31-1** **<1%**	No harmonized classification (No classification)	Indicated tonnage: 10,000-100,000 tons/year Substance evaluation: assessment in relation to PBT and endocrine-disrupting effect has not been completed.	None	Not regulated specifically	Not regulated specifically

As seen in **TABLE 14** and **TABLE 15**, there are a number of additives and contaminations / residual concentrations that can be present in small concentrations and are considered to be problematic, since they are already strictly regulated due to their health-related and environmental effects. This concerns the following substances:

- Diisobutyl phthalate (DIBP)
- Dibutyl phthalate (DBP)
- Bis(2-ethylhexyl)phthalate (DEHP)
- Diisononyl phthalate (DINP)
- SCCP; C10-13 chloroalkanes
- Cadmium
- Lead
- Dibutyl tin compounds
- Bisphenol A.

For additives (softeners) with a content of >10% in the analyses, and which are not classified for harmful effects on health or environment, the following can be indicated:

- Di-(2-ethylhexyl)-terephthalate (DEHT)
- Tributyl acetyl citrate.

For additives (softeners) with a content interval of 1-10% in the analyses, and which are not classified for harmful effects on health or environment, the following can be indicated:

- Diethylene glycol dibenzoate
- 1-Propene-1,2,3-trikarboxylic acid, tributyl ester
- Tributyl citrate.

The substance DEHT, which has been assessed under REACH, may according to this screening be considered an adequate additive based on its effects on health and environment, as no missing measures or data necessary for the substance were identified during REACH registration.

The substances tributyl acetyl citrate and tributyl citrate are suspected to have endocrine-disrupting effects, and in relation to REACH regulation more tests were requested to clarify the possible reprotoxic effects of these substances. Here, it is also important to evaluate additional data on the substances before their suitability as PVC additives can be further assessed.

For the substance diethylene glycol dibenzoate, additional data / tests have also been requested in relation to the REACH regulations due to the suspicions on the reprotoxic effects of the substance.

No data have been found for the substance 1-propene-1,2,3-tricarboxylic acid, tributyl ester in the European Chemicals Agency's database, since it is not registered in REACH. Also, it means that the usage of this substance is below 1 ton per year, which is why the substance may be considered as less relevant as a potential additive.

Other substances indicated in **TABLE 15** have been found in the PVC material in concentrations below 1%. Thus, these cannot be seen as an actual additive for PVC, because the content of these substances is most likely the result of residual concentrations of substances, or the usage of these substances has been related to reasons other than as additive or having an impact on the technical properties of the PVC material. Thus, the discussion of these substances can be considered less relevant.

6. The impact of additives on recyclability of PVC-products

6.1 Method for assessment of recyclability

In the project *Chemical substances contained in consumer products which may prevent recycling – development of a method* (2016),[33] a general method for assessing whether chemical substances can impede the recyclability of consumer products. The method is, thus, relevant for the consumer products made of PVC as analyzed in this survey. This method divides the assessment into five activities described as follows:

- Activity 0: Delimitation and scope
  - Which consumer products, materials and chemicals are included?
- Activity 1: Problematic chemical substances
  - Prevalence and environmental and health effects of problematic chemical substances
- Activity 2: Opportunities for recycling
  - Current disposal possibilities, legislation, opportunities for recycling, including steps / processes and future scenarios
- Activity 3: Assessment of exposure and risks
  - Exposure of employees, consumers, and environment as well as risks
- Activity 4: Conclusion/summary

Activities 0-1 as well as 3 are described in preceding chapters and are shortly summarized or referred to in the review below, while activities 2 and 4 specifically on recyclability will be described in chapter 6.2.

6.2 Assessment of recyclability

TABLE 16 provides a general assessment of the product recyclability according to the described method. Since the purchased and analyzed consumer products belong to many different product types and applications, the assessment has been created as a general analysis of consumer products containing PVC, but the recyclability of the specific products can also be impeded by factors such as other materials, product design or other unwanted chemicals not included in this project.

TABLE 16. Assessment of recyclability.

Activity 0: Delimitation and scope	
Which consumer products?	Delimitation and scope have been defined as part of the project, as the selection of consumer products was described in chapter 3 and includes a broad range of different consumer products purchased on European (not Danish) websites and on websites outside the EU.
Which materials and chemicals?	The analyzed consumer products consist entirely or partially of PVC. The aim of this project is to identify and analyze specific added additives, where some of these are considered as problematic substances. This assessment only includes a specific assessment of the substances in the table on selected additives (**TABLE 14**) that are currently regulated, as there is generally no barrier

[33] Christensen et al.: Kemiske stoffer i forbrugerprodukter, der kan hindre genanvendelse, Kortlægning af kemiske stoffer i forbrugerprodukter nr. 146, 2016.

Activity 0: Delimitation and scope	
	for recycling materials containing non-hazardous substances. In the cases where some of the substances will be regulated in the future, a specific assessment should be performed for these, as well.
Activity 1: Problematic chemical substances	
Occurrence of problematic chemical substances	The occurrence of selected additives is shown in the analysis results, in sections 4.3-4.5. However, it must be emphasized that products may contain other problematic chemicals that have not been identified and analyzed in this project.
Environmental and health effects	The environmental and health effects of the analyzed additives are described in **TABLE 14**.
Activity 2: Recycling opportunities	
Current disposal	The current waste treatment of PVC products has been described in *Survey of PVC in Denmark 2018*.[8] Most of the analyzed consumer products are small and will most likely end up in waste incineration together with residual waste from households, or as residual fractions after separation of household plastic waste. Hard PVC products, which are disposed of at waste recycling centers, are collected for recycling, for example through the WUPPI-scheme,[34] while fractions of soft PVC are deposited at waste recycling centers.
Legislation	Since the incineration of PVC is problematic, PVC products must be collected either for recycling or disposal in landfills according to Danish government order on waste (BEK No 224 of 08/03/2019).
Recycling opportunities	As described in Survey of PVC in Denmark 2018[Fejl! Bogmærke er ikke defineret.] , hard PVC can be recycled after shredding or regranulation. However, this requires control on whether the additives are problematic according to their processing properties, and if they comply with requirements (both technical properties of materials and legislation), which are made to those products, in which the material will be recycled. Thus, special attention should be paid to the usage of regranulate in toys and electronic products, since a general regulation of the usage of lead, cadmium and dibutyltin is in force, for example, among substances and compounds found in consumer products in this project. Similarly, the usage of SCCP and a range of other phthalates is regulated according to **TABLE 14**. Recycling of soft PVC products is generally more problematic due to often high content (up to 50%) of, among others, softeners. These can cause difficulties in controlling the properties of recycled materials in relation to, for example, processing and technical properties of the material. In general for PVC recycling, additives may cause challenges in controlling the material properties, because PVC products may have high concentrations of additives, and depending on the age of the products, these may be substances that are now unwanted and/or illegal to use both in general and in specific applications. Regranulation and remelting may dilute specific additives; however, most often products and/or materials, which are similar, will be recycled together, which means that one can only be sure of “dilution” of additives if the recycled material is mixed with virgin PVC with a known additive combination. An opportunity to recycle soft PVC in the future could be to extract softeners from PVC plastic matrices and, thereafter, recycle the PVC material. This can be done by solvent extraction or supercritical extraction of CO_2.[35]
Activity 3: Assessment of exposure and risks	

[34] Kaysen et al.: Genanvendelse af hård PVC i Denmark. Miljøprojekt nr. 1717, 2015.

[35] Joint R&D project funded by the Danish Environmental Protection Agency: Sikker og effektiv genanvendelse af blød PVC fra medicinsk udstyr ved miljøvenlig superkritisk kuldioxid ($scCO_2$) teknologi, 2016-2019.

Activity 0: Delimitation and scope	
Exposure and environment	In general, additives present in PVC products before recycling will also be present during processing and recycling in new products. Thus, additives that are problematic with regard to exposure and environment (as described in **TABLE 14**) may still pose the same unwanted effects during and after recycling.
Risks	The risks when recycling the products with additives are, as mentioned earlier, the same as when using the additives in a product during its first life cycle.
Activity 4: Conclusion/summary	
Summary	The specific additives described in **TABLE 14** should not create technical barriers for the recycling, except for the lack of control of properties when remelting or regranulating, for example, a mixed fraction of different soft PVC products. This is typically related to the fact that additives in the recycled PVC fraction are unknown due to the lack of traceability and / or because the fraction is mixed. However, the challenge is to use the processed PVC in products, where the content of the specific additive does not exceed the permitted threshold value or violates the existing legislation. In this project, specific examples have been found on the content of substances in concentrations above the threshold value in specific products or general products if these were marketed on the Danish market. If these products were recycled as clean fractions, new products would be produced that would also exceed the threshold values for the specific additives. The identified examples include the additives lead and cadmium, while the regulated dibutyltin has been found in concentrations below the threshold value. Similarly, SCCP was found in several products and phthalates in children's toys, which makes them illegal to market in Denmark (section 4.4). However, there are other additives that do not impede recycling according to existing legislation.
Conclusion	The chemical substances and additives found in PVC products before recycling will also be present during processing and recycling in new products, which means that existing classifications, threshold values and application restrictions will be valid for the new products. This means that as long as the unwanted substances are used in PVC products, these cannot be recycled responsibly with dilution as the best-case scenario. The circular economy of plastic products requires that unwanted and classified substances are not used in products, and it also requires that materials can be reused again in similar products. Recycled plastic is challenging to use in the production of products such as toys and food contact materials as it is important to trace this plastic and ensure safety of substances in previous products.

7. Discussion of recommendations for future measures on problematic substances in PVC products

The aim of this project was to acquire information on many consumer products covering a wide range of product types. As a result, it provided a deep insight into the many examples of additives in specific products. However, it was not possible to observe explicit trends, e.g. within one single group of products.

In order to gain additional knowledge based on the results acquired in this project, it would be valuable to design a targeted analysis program based on a more focused selection of additives and products. The starting point of this program could be either the specific additives, which are assessed as relevant, or within a very narrow selection of products. Irrespective of the chosen approach, the additive function must be linked to the product type to ensure that the additive is relevant for the specific product and, thus, perform analyses for the substances expected to be found (see illustration in FIGURE 2).

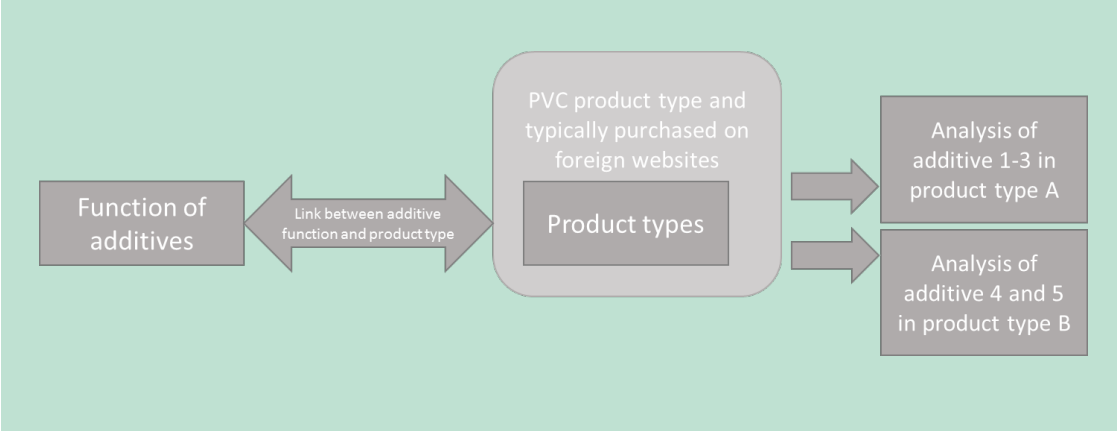

FIGURE 2. Illustration of the design of a targeted analysis program for additives in PVC.

The choice of products and product types, as in this project, should be based on the knowledge that the consumer products often consist of PVC and are purchased on foreign websites. Furthermore, the products can be prioritized according to special criteria, for example, the usage of highly exposed groups, frequent / high degree of exposure or similar. The choice of several comparable products could provide information on the tendencies in additive content.

As for the choice of additives, a proposal for the prioritization of additives analyzed to a greater or lesser degree in this project has been described below.

If the analysis is based on the selection of concrete product types, the relevant functions in each product type must be established, and a group of additives belonging to the PVC material is expected to be able to derive according to the information from, for example the PLASI database, the industry and literature. These additives must be assessed and prioritized to ensure that these are worth collecting more knowledge on. However, the focus on the choice of relevant additives will require the creation of a survey of the individual functions of additives to be able to link them to product types among those types which most often consist of PVC and are purchased on foreign websites.

Both approaches require that the analysis of additive groups with the same function are not necessarily performed using the same analysis method, which must be taken into consideration in the analysis program.

7.1 Approach based on selection of product types

The range of products in this project has provided several examples of additives but has shown no general tendencies for each product type. An approach with the selection of product types will, thus, require creating a survey based on single examples to investigate the likelihood of a general occurrence of the identified additives in other products of the same type. This survey would collect knowledge, which would create the foundation for the selection of products. Further criteria can be added, such as products that cause frequent exposure or that are targeted e.g. children.

7.2 Approach based on selection of additives

This project has provided knowledge about the identified additives, and this knowledge, be it about concrete data and assessments or the lack of it, can constitute a foundation to focus on additives to be further evaluated.

7.2.1 Additives prioritized from the PLASI database

According to the assessment of the 32 additives selected from the PLASI database, 10 substances were prioritizes as described in chapter 2 based on their inherent properties or suspicion of inherent properties regarding:

- Carcinogenic, mutagenic and reprotoxic effects
- Effects on the central nervous system and its development
- Endocrine-disrupting effects
- Allergenic effects
- Environmental effects.

10 prioritized substances, which all are marketed in a tonnage of more than 100 tons per year, include the following substances:

- Disodium tetraborate
  CAS No. 1330-43-4; 1303-96-4;12179-04-3
  Function: Antistatic, flame retardant, other stabilizer
- Ethanol, 2,2'-iminobis-, N-C12-18-alkyl derivs
  CAS No. 71786-60-2
  Function: Antistatic
- Phenol, isopropylated, phosphate
  CAS No. 68937-41-7
  Function: Flame retardant, softener
- Alkanes, C14-17, chloro
  CAS No. 85535-85-9
  Function: Flame retardant, softener

- Reaction mass of tris(2-chloropropyl) phosphate and tris(2-chloro-1-methylethyl) phosphate and phosphoric acid, bis(2-chloro-1-methylethyl) 2-chloropropyl ester and phosphoric acid, 2-chloro-1-methylethyl bis(2-chloropropyl) ester
  EC no. 911-815-4
  Function: Flame retardant, softener
- 6,6'-di-tert-butyl-4,4'-butylidenedi-m-cresol
  CAS No. 85-60-9
  Function: Antioxidant, other stabilizer
- 2-(2H-benzotriazole-2-yl)-p-cresol
  CAS No. 2440-22-4
  Function: UV / light stabilizer, other stabilizer
- Ethanol, 2,2'-iminobis-, N-(C13-15-branched and linear alkyl) derivates
  CAS No. 97925-95-6
  Function: Antioxidant, antistatic
- Azodicarbonamide
  CAS No. 123-77-3
  Function: Flame retardant, foaming agent
- 1,1'-(isopropylidene)bis[3,5-dibromo-4-(2,3-dibromo-2-methylpropoxy)benzene]
  CAS No. 97416-84-7
  Function: Flame retardant

However, due to reasons related to analysis techniques, it was not effective to include these substances in the analysis program of this project. Thus, knowledge must still be acquired on the application of these substances as additives in PVC, as well as the specific occurrence of additives in PVC products on the market.

As described in chapter 2, it is suggested to establish the connection between concrete substances and their function as well as application, among others based on the information from the PLASI database and the industry. This way, only a few product types can be selected, where this function is relevant, and it is expected that these substances can be included with an aim to complete a focused analysis program. Since these 10 substances require different analysis methods, it is necessary to perform a thorough preparation in relation to analysis methods for each additive, additive function, and corresponding product groups to create an effective analysis program as described above. Thus, the resources are used to investigate specific additives in products, where these are expected to be detected due to their relevant function.

7.2.2 Prioritization of additives identified by GC-MS screening

For additives identified in specific consumer products in this project and described in detail due to their inherent properties and their regulatory status in **TABLE 14** and **TABLE 15**, it is considered relevant to follow up on the substances detected in concentrations indicating an intentional addition. Concentrations of 1% or more are a relevant limit for prioritization. In this project, this can be specifically assessed for additives measured quantitatively in products (i.e. specific heat stabilizers, phthalates and SCCP), while additives detected in the GC-MS screening are determined with a high uncertainty as it has been done by a screening, and the identification has not been verified with a reference substance. For additives indicated by the screening, the estimated content shown in TABLE 12 is suggested, even though the actual content can deviate from the estimated content. Also, it is important that the substance is registered in REACH, as the application of substances not registered in REACH can be considered as limited due to the requirements for tonnage for registration. In addition, it is also relevant to prioritize additives with missing information on their inherent properties, among others environmental and health effects, and additives not subject to regulatory requirements. This way, it is considered not relevant to prioritize well-known problematic substances if their harmful effects are known, and they are already subject to regulatory requirements (e.g. several phthalates, SCCP, lead, cadmium, and organotin compounds).

Therefore, the following substances are suggested to be prioritized for further follow-up (see occurrence in TABLE 17):

- Di-(2-ethylhexyl)-terephthalate, DEHT (CAS 6422-86-2)
  This substance was found in concentration of 1% or above in 15 out of 41 consumer products of soft PVC, among others, in two children's toys. DEHT was also found in high concentrations in products during the Chemical Inspection Service control campaigns as described in chapter 4.
- Diisononyl phthalate, DINP (CAS 28553-12-0)
  This substance was found in concentration of 1 % or above in 11 out of 41 consumer products, among others, in one children's toy product.
- Tributyl acetyl citrate (CAS 77-90-7)
  This substance was found in a concentration of 1 % or above in one out of 41 consumer products, which was a children's toy.
- 1,2-cyclohexandi-carboxylic acid dinonylester, DINCH (EC no. 431-890-2)
  This substance was found in a concentration of 1 % or above in one out of 41 consumer products.
- Tributyl citrate (CAS 77-94-1)
  This substance was found in a concentration of 1 % or above in one out of 41 consumer products.

TABLE 17. Overview of the occurrence of suggested additives, country of sales and country of production.

Product No.	Product name	DEHT	DINP	Tributyl-acetyl citrate	DINCH	Tributyl citrate	Country of sales[1]	Country of production[2]
2	Bathing ring	x					Germany	China
3	Trump bath duck			x			England	China
4	Bath ducks		x				Unknown	China
5	Diving goggles	x					Holland	China
13	Bag		x				Spain	China
14	Bag		x				(China)	(China)
16	Pencil case	x					England	Unknown
17	Chew toys for pets	x					China	China
19	Feeding mat	x					Malaysia	(China)
20	Feeding mat	x					England	China
21	Hobby cutting board	x					Unknown	Unknown
22	Hobby cutting board	x					(China)	(China)
29	Car mat	x					England	Unknown
31	Yoga mat	x					Germany	Unknown
32	Yoga mat	x					Unknown	China
35	Football	x					Holland	Unknown
36	Football		x				China	Unknown
39	Sandal	x					Sweden	China
41	Flip-flops					x	Holland	China
43	Rainwear	x					(China)	(China)
48	Cover for garden furniture		x				England	Unknown
50	Tarpaulin	x					Italy	Unknown
56	Gloves		x				Sweden	China
67	Phone charger		x				China	China

Product No.	Product name	DEHT	DINP	Tributyl-acetyl citrate	DINCH	Tributyl citrate	Country of sales[1]	Country of production[2]
75	Sex toys, arm				x		Unknown	China

[1] Country, where the seller belongs to; in some cases this is ”Unknown” and, in such cases, the shipping country has been indicated in brackets instead to the extent it was possible.

[2] Country of production if this has been indicated on the product; if it has not been indicated on the product, the language used on the product has been shown in brackets to the extent it was possible.

According to the results on substance contents acquired in this project, it has not been possible to observe any tendencies related to which product types one or several additives are predominant or often seen in (TABLE 17), except for the fact that they all are soft PVC, as the suggested substances are all softening additives. Similarly, it can be concluded that the suggested additives are found to a great extent in products produced in Asia: 17 are produced in China, while seven products have an unknown country of origin, and none have been indicated as produced in the EU. Only one product out of 54 analyzed products was indicated as produced in the EU, while the country of origin for 14 products is unknown disregarding the country of the web shop. Two products are produced in USA (se Appendix 3). There is no basis to conclude if this result would be different when purchasing similar products in Danish web shops.

7.3 Activities in future surveys

Regardless of the choice of the approach described above, including delimitation of the number of additives and product types, all future surveys include the following activities to achieve a broader knowledge:

- Application:
  - Linking additives with function and product types, as well as applied concentrations.
  - Acquire information on development in consumption/tonnage of the additive during recent years.
  - Acquire information on expected development in consumption/tonnage of the additive during the next 3-5 years.
- Technical and inherent properties:
  - Acquire knowledge on how the additive is embedded in the PVC material and the evaluation of migration potential.
  - A detailed assessment of the toxicological and ecotoxicological data for the additive. Are the data adequate for an assessment? Are some data missing?
  - Execution of relevant migration tests to assess environmental and / or consumer exposure.
- Survey:
  - Preparation of a targeted analysis program.
  - Targeted survey of the content of the additive in relevant product types via analysis program.
- Recycling:
  - Analysis of the potential and challenges for recycling of PVC materials from product types with the occurrence of additives can be relevant. However, it is expected that most of this type of small consumer products purchased on the internet will end up as residual waste or sorted plastic waste from households after usage. PVC is not sorted for recycling at the Danish waste sorting plants as it occurs in a very limited amount. PVC products will typically end up in residue fractions from waste sorting plants and will either be incinerated or exported for further sorting/reprocessing.

8. Literature

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Control campaign from the Chemical Inspection Service: ”REACH: Kontrol af art. 33.2 informationspligten i byggemarkeder – 2018”, 2018 (translated title: REACH: Control of Art. 33.2 on duty to communicate information on substances in articles in building markets – 2018).

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Ministry of Environment and Food of Denmark: Political Agreement on new joint chemicals initiatives 2018-21, 2017. **https://mst.dk/media/143466/kemiindsats-engelsk.pdf**

The Danish Government: Plastics without waste – The Danish government’s plastics action plan, 2018. **https://en.mfvm.dk/fileadmin/user_upload/ENGLISH_FVM.DK/Regeringens_plastikhandlingsplan_UK.pdf**

Appendix 1. Assessment of 32 substances from the PLASI database

TABLE 18. Overview of screening results for environmental and health effects of 32 selected substances from the PLASI database.

No.	EC number	CAS number	Public Name	Classification	CMR	Endocrine disruptor	Allergen	Brain-damaging	Environmental	REACH initiatives	Priority
11	215-540-4	1330-43-4; 1303-96-4; 12179-04-3	Disodium tetraborate, anhydrous	Repr. 1B;H360-Eye Irrit. 2;H319 Repr. 1B;H360FD (C ≥ 4,5%)	R	ED				Proposed for Appendix XIV	+++
21	276-014-8	71786-60-2	Ethanol, 2,2'-iminobis-, N-C12-18-alkyl derivs.	Aquatic Chronic 1;H410-Aquatic Acute 1;H400-Acute Tox. 4;H302-Skin Corr. 1C;H314-Repr. 2;H361	r				a	Additional information requested: 90-day study, pre-natal dev study OECD 414 and extended one-gen OECD 443 based on information gaps and indication	+++
27	273-066-3	68937-41-7	Phenol, isopropylated, phosphate (3:1)	Repr. 2;H361-STOT RE 2;H373; Aquatic Chronic 4;H413	r	ed			a	Additional data requested on ED and reprotoxic dev. OECD TG 443 - indications of effects	+++

29	287-477-0	85535-85-9	Alkanes, C14-17, chloro	Lact.;H362-Aquatic Acute 1;H400-Aquatic Chronic 1;H410 Aquatic Chronic 1;H410-Lact.;H362				a (P)	CoRAP list for evaluation due to high tonnage and possible PBT/vPvB - information requested. No conclusion	+++
31	911-815-4		Reaction mass of tris(2-chloropropyl) phosphate and tris(2-chloro-1-methylethyl) phosphate and Phosphoric acid, bis(2-chloro-1-methylethyl) 2-chloropropyl ester and Phosphoric acid, 2-chloro-1-methylethyl bis(2-chloropropyl) ester	Acute Tox 4;H302		ed		(P)	CoRAP list for evaluation as Suspected Carcinogenic, Suspected Reprotoxic, Potential endocrine disruptor, Suspected PBT/vPvB, Consumer use, Cumulative exposure, Exposure of environment, High (aggregated) tonnage, Wide dispersive use	+++
1	201-618-5	85-60-9	6,6'-di-tert-butyl-4,4'-butylidenedi-m-cresol	not classified		ED		(P)	CoRAP list for evaluation due to high tonnage and possible PBT/vPvB, rep ED - information requested	++
16	219-470-5	2440-22-4	2-(2H-benzotriazole-2-yl)-p-cresol	Aquatic Chronic 1;H410-Skin Sens. 1B;H317		ed	Ss	a	CoRAP substance concluded no further action	++
20	308-208-6	97925-95-6	Ethanol, 2,2'-iminobis-, N-(C13-15-branched and linear alkyl) derivs.	Acute Tox. 4;H302-Repr. 2;H361-Skin Corr. 1B;H314-Eye Dam. 1;H318	r				Proposed rep 1B harmonized classification	++
25	204-650-8	123-77-3	Azodicarbonamide	Resp. Sens. 1;H334 Resp. Sens. 1;H334			Sr		Proposed as SVHC reps. Sens.	++
30	306-832-3	97416-84-7	1,1'-(isopropylidene)bis[3,5-dibromo-4-(2,3-dibromo-2-methylpropoxy)benzene]	not classified		ed		(P)	CoRAP list for evaluation as possible ED, suspected PBT/vPvB, and exposure of environment	++
2	217-420-7	1843-03-4	4,4',4''-(1-methylpropanyl-3-ylidene)tris[6-tert-butyl-m-cresol]	Skin Sens. 1B;H317			Ss		nothing	+

7	406-040-9	125643-61-0	reaction mass of isomers of: C7-9-alkyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	Aquatic Chronic 4;H413 Aquatic Chronic 4;H413			a	nothing	+
9	406-750-9	129757-67-1	A mixture of: bis(2,2,6,6-tetramethyl-1-octyloxypiperidin-4-yl)-1,10-decanedioate; 1,8-bis[(2,2,6,6-tetramethyl-4-((2,2,6,6-tetramethyl-1-octyloxypiperidin-4-yl)-decan-1,10-dioyl)piperidin-1-yl)oxy]octane	Aquatic Chronic 4;H413			a	nothing	+
10	307-055-2	97489-15-1	Sulfonic acids, C14-17-sec-alkane, sodium salts	Acute Tox 4;H302-Eye Dam 1;H318-Skin Irrit. 2;H315-Aquatic Chronic 3;H412			a		+
12	215-222-5	1314-13-2	Zinc oxide	Aquatic Acute 1;H400-Aquatic Chronic 1;H410 Aquatic Acute 1;H410-Aquatic Chronic 1;H410			a	CoRAP initiatives for more data on nanoform	+
14	204-398-9	120-46-7	1,3-diphenylpropane-1,3-dione	Skin Sens. 1;H317	ed	Ss		further testing required- not in compliance	+
15	217-421-2	1843-05-6	Octabenzone	Skin Sens. 1B;H317		Ss		nothing	+
22	620-539-0	1218787-30-4	2,2'-(C16-18 (evennumbered) alkyl imino) diethanol	Aquatic Acute 1;H400-Aquatic Chronic 1;H410-Eye Irrit. 2;H319-Skin Irrit. 2;H315			a	nothing	+
23	620-540-6	1218787-32-6	2,2'-(C16-18 (even numbered, C18 unsaturated) alkyl imino) diethanol	Skin Corr. 1C;H314-Aquatic Acute 1;H400-Acute Tox. 4;H302-Aquatic Chronic 1;H410			a	further testing may be required- not in compliance	+
24	800-029-6	1290049-56-7	Amines, N-(C16-18 (even numbered) and C18-unsatd. alkyl) trimethylenedi-, ethoxylated(NLP)	Skin Corr. 1B;H314-STOT RE 1;H372-Aquatic Acute 1;H400-Aquatic Chronic 1;H410-Acute Tox. 4;H302			a	nothing	+

26	215-175-0	1309-64-4	Diantimony trioxide	Carc. 2;H351-STOT RE 2;H373 Carc. 2;H351	c			nothing	+
3	218-216-0	2082-79-3	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	not classified				further testing required - not in compliance	
4	229-722-6	6683-19-8	Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)	not classified		ed			
5	251-156-3	32687-78-8	2',3-bis[[3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionyl]]propionohydrazide	not classified					
6	253-039-2	36443-68-2	Ethylenebis(oxyethylene) bis[3-(5-tert-butyl-4-hydroxy-m-tolyl)propionate]	not classified and no notified hazards by manufacturers, importers or downstream users				Additional data requested on env. and OBT, vPvB due to information gap	
8	274-570-6	70321-86-7	2-(2H-benzotriazole-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol	not classified			(P)	Additional data requested on env. PBT concern (2015), RMOA ED and persistence (2014). No conclusion	
13	215-138-9	1305-78-8	Calcium oxide	Eye Dam. 1;H318-Skin Irrit. 2;H315-STOT SE 3;H335				nothing	
17	223-445-4	3896-11-5	Bumetrizole	not classified				Additional data requested. RMOA 1, concern for CMR, ongoing	
18	245-950-9	23949-66-8	N-(2-ethoxyphenyl)-N'-(2-ethylphenyl)oxamide	not classified					
19	411-380-6	147315-50-2	2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-((hexyl)oxy)phenol	Aquatic Chronic 4;H413 Aquatic Chronic 4;H413			a	nothing	

28	284-366-9	84852-53-9	1,1'-(ethane-1,2-diyl)bis[pentabro-mobenzene]	not classified	CoRAP list for evaluation due to high tonnage and possible PBT/vPvB - in-formation requested
32	264-150-0	63449-39-8	Paraffin waxes and Hydrocarbon waxes, chloro	not classified	Additional data requested on env.due to inconsistency between data and classification, should be classified as Aquatic Chronic 1;H410 based on data. Concluded (but not classified?)

Abbreviations:

R - repro-toxic cat. 1

r - repro-toxic cat. 2

C - carcinogenic cat 1

c - carcinogenic cat 2

Ss - skin sensitizer

Sr - respiratory sensitizer

ed - indications of ED properties

ED - strong indications of ED properties

a - classification for aquatic toxicity

(P) - Concern for PBT/vPvB in REAC

Appendix 2. Screening for endocrine-disrupting effects

TABLE 19. Result of screening for endocrine-disrupting effects (ed).

EC number	CAS No	Public Name	CIRCABC	Candidate List	CoRAP from European Chemicals Agency	EU Priority list	Toxcast screening	Score
204-398-9	120-46-7	1,3-diphenylpropane-1,3-di-one					Positive in several in vitro test for ER, AR and THR activity	ed
620-539-0	1218787-30-4	2,2'-(C16-18 (even numbered) alkyl imino) diethanol						
620-540-6	1218787-32-6	2,2'-(C16-18 (even numbered, C18 unsaturated) alkyl imino) diethanol						
204-650-8	123-77-3	Azodicarbonamide		Yes - Respiratory sensitizing properties (Article 57(f) - human health)			Screened, positive in one ER assay, negative in remaining	
406-040-9	125643-61-0	reaction mass of isomers of: C7-9-alkyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate						
800-029-6	1290049-56-7	Amines, N-(C16-18 (even numbered) and C18-unsatd.						

		alkyl) trimethylenedi-, ethoxylated(NLP)				
406-750-9	129757-67-1	A mixture of: bis(2,2,6,6-tetramethyl-1-octyloxypiperidin-4-yl)-1,10-decanedioate; 1,8-bis[(2,2,6,6-tetramethyl-4-((2,2,6,6-tetramethyl-1-octyloxypiperidin-4-yl)-decan-1,10-dioyl)piperidin-1-yl)oxy]octane				
215-138-9	1305-78-8	Calcium oxide	23 hits; no relevant for ED			
215-175-0	1309-64-4	Diantimony trioxide			1 hit, on CoRAP for Carcinogenic potential	
215-222-5	1314-13-2	Zinc oxide	3 hits, not relevant for ED		1 hit, on CoRAP list for evaluation due to wide use and high exposure and insufficient available information	
215-540-4	1330-43-4;1303-96-4;12179-04-3	Disodium tetraborate, anhydrous	3 hits: Identified as potential ED in screening report file:///C:/Users/tam/Downloads/CA-June16-Doc.3.3%20-%20%20ED%20Impact%20Assessment.pdf NB! Difference in whether it is just anhydrate	Yes -Toxic for reproduction (Article 57c)		ED

411-380-6	147315-50-2	2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-((hexyl)oxy)phenol				
217-420-7	1843-03-4	4,4',4''-(1-methylpropanyl-3-ylidene)tris[6-tert-butyl-m-cresol]				
217-421-2	1843-05-6	Octabenzone	1 hit; screened not identified as ED in screening	1 hit, on CoRAP list for being a potential ED but data showed that there are no evidence of ED or reproductive toxicity	Screened, negative in ER, AR (except 1) and THR assays	
218-216-0	2082-79-3	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate				
245-950-9	23949-66-8	N-(2-ethoxyphenyl)-N'-(2-ethylphenyl)oxamide				
219-470-5	2440-22-4	2-(2H-benzotriazole-2-yl)-p-cresol		1 hit, on CoRAP list for evaluation for sensitizing potential and due to wide use and high exposure and insufficient available information	Positive in 4 in vitro test for ER activity	ed
251-156-3	32687-78-8	2',3-bis[[3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionyl]]propionohydrazide				

253-039-2	36443-68-2	Ethylenebis(oxyethylene) bis[3-(5-tert-butyl-4-hydroxy-m-tolyl)propionate]		Screened, negative in ER, AR and THR assays	
223-445-4	3896-11-5	Bumetrizole		Screened, negative in ER, AR and THR assays	
264-150-0	63449-39-8	Paraffin waxes and Hydrocarbon waxes, chloro			
229-722-6	6683-19-8	Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxy-phenyl)propionate)		Positive in 5/25 in vitro test for ER activity (agonistic)	ed
273-066-3	68937-41-7	Phenol, isopropylated, phosphate (3:1)		Positive in 3/17 in vitro test for ER activity and 1 AR assay	ed
274-570-6	70321-86-7	2-(2H-benzotriazole-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol		Screened, negative in ER, AR and THR assays	
276-014-8	71786-60-2	Ethanol, 2,2'-iminobis-, N-C12-18-alkyl derivs.			
284-366-9	84852-53-9	1,1'-(ethane-1,2-diyl)bis[pentabromobenzene]	1 hit, on CoRAP list for evaluation due to high tonnage and possible PBT/vPvB		
287-477-0	85535-85-9	Alkanes, C14-17, chloro	1 hit, on CoRAP list for evaluation due to		

				high tonnage and possible PBT/vPvB		
201-618-5	85-60-9	6,6'-di-tert-butyl-4,4'-butyl-idenedi-m-cresol	1 hit; screened not identified as ED in screening	1 hit, on CoRAP list for being a potential ED. Evaluation ongoing	Positive in in vitro test for ER, AR and GR (glucocorticoid receptor) activity	ED
306-832-3	97416-84-7	1,1'-(isopropylidene)bis[3,5-dibromo-4-(2,3-dibromo-2-methylpropoxy)benzene]		1 hit, on CoRAP list for being a potential ED. Evaluation ongoing		ed
307-055-2	97489-15-1	Sulfonic acids, C14-17-sec-alkane, sodium salts				

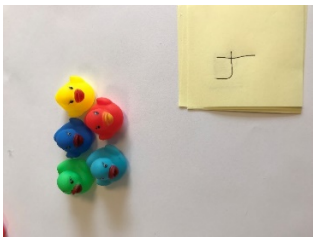
Abbreviations:

ed - indications of ED properties

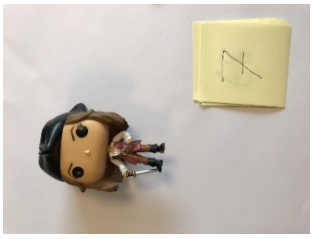
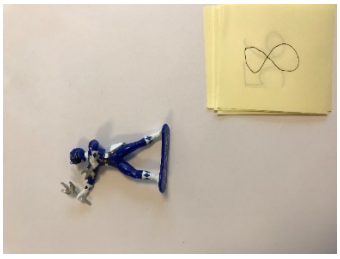
ED - strong indications of ED properties

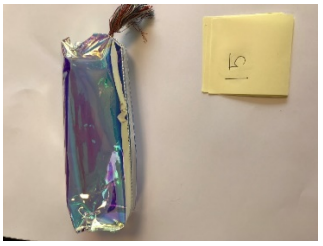
Appendix 3. List of purchased products

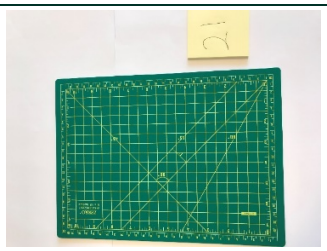
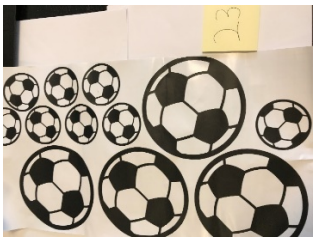
TABLE 20. List of purchased products. Product no. 1 (float) and no. 46 (umbrella) were not received for analysis within the stipulated time frame and were, therefore, not included in further work.

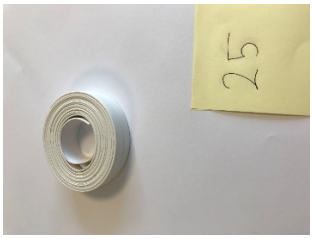
No	Product name	Photo	Online market place	Country of sales*	Country of production**
Swimming equipment, e.g. beach toy animals, beach toys, swimming and paddle pools					
2[a]	Float		German-toys.com	Germany	China
3[a]	Trump bath duck		Ebay.com	England	China
4[a]	Bath ducks		Wish.com	Unknown	China
5	Goggles		Internet-sportandcasuals.com	Holland	China

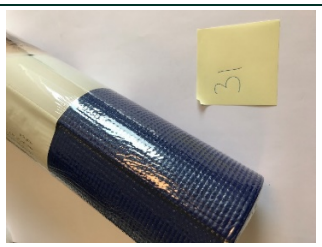
6	Goggles		Aliex-press.com	China	China

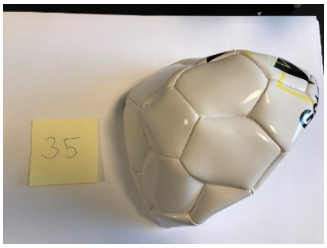
Dolls and toy figures					
7 [a]	Toy figure		Ebay.com	Ireland	China
8 [a]	Toy figure		Ebay.com	USA	China
9 [a]	Toy figure		Ebay.com	Ireland	China
10 [a]	Toy figure		Ebay.com	China	China
Outdoor toys					
11 [a]	Jump rope		Ebay.com	China	China
12 [a]	Jump rope		Internet-sportandcasu-als.com	Holland	Unknown

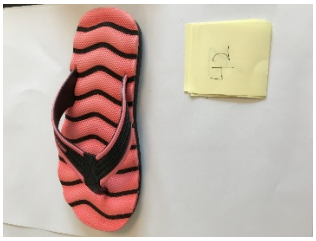
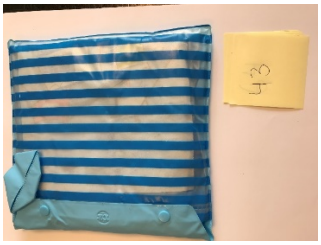
Bags, suitcases, pencil cases					
13	Bag		Scubas-tore.com	Spain	China
14	Bag		Wish.com	(China)	(China)
15	Pencil case		Aliex-press.com	China	China
16	Pencil case		Ebay.com	England	Unknown
Articles for pets, e.g. squeaky toys, equipment					
17	Chew toys		Aliex-press.com	China	China
18	Chew toys		Ebay.com	England	Unknown

19	Feeding mat		Ebay.com	Malaysia	(China)
20	Feeding mat		Ebay.com	England	China
Hobby articles, e.g. beads, pegboards, foils, tape					
21	Hobby cutting board		Amazon.com	Unknown	Unknown
22	Hobby cutting board		Aliex-press.com	(China)	(China)
23	Wallsticker		Wish.com	Unknown	China
24	Wallsticker		Wish.com	Sweden	Unknown

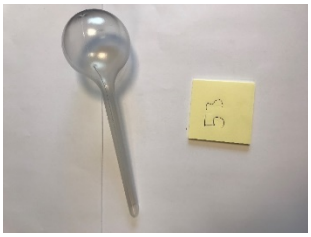
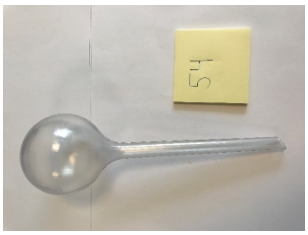
25[b]	Tape		Ebay.com	England	(China)
26[b]	Tape		Wish.com	(China)	(China)

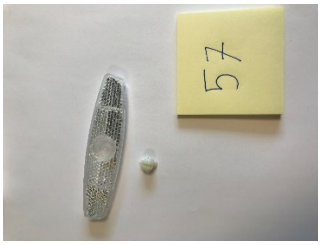
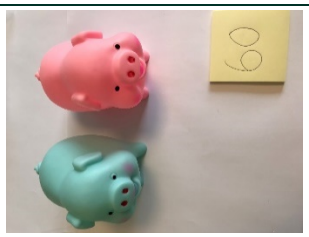
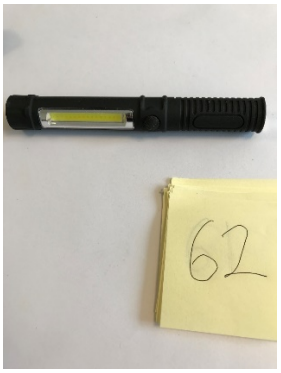
Home textiles, e.g. shower curtains, oil cloth					
27[b]	Oil cloth		Wish.com	(China)	China
28[b]	Oil cloth		Ebay.com	England	China
Rugs, mats, mattresses					
29[b]	Car mat		Ebay.com	England	Unknown
30[b]	Car mat		Internet-sportandcasu-als.com	Holland	China
31[b]	Yoga mat		Amazon.com	Germany	
32[b]	Yoga mat		Amazon.com	Unknown	China

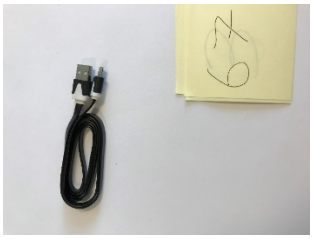
Balls, e.g. yoga balls, footballs					
33[b]	Yoga ball		Ebay.com	Germany	China
34[b]	Yoga ball		Ebay.com	China	China
35[a]	Football		Internet-sportandcasu-als.com	Holland	Unknown
36[a]	Football		Aliex-press.com	China	Unknown
Clothes with print, e. men's, women's and children's clothes (not rainwear)					
37	T-shirt with print		Ebay.com	China	China
38	T-shirt with print		Asos.com	England	Turkey

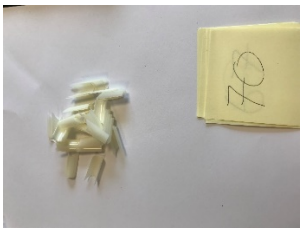
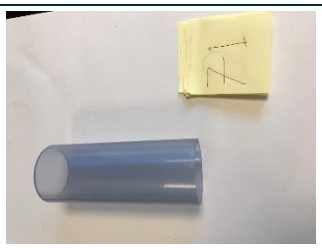
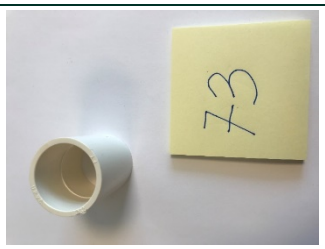
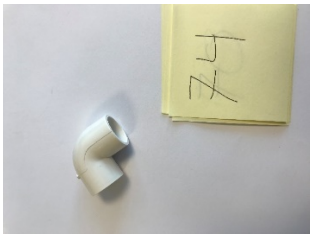
Footwear (artificial leather and soles), e.g. sports shoes, sandals, shoes, boots					
39	Sandal		Cdon.com	Sweden	China
40	Sandal		Aliex-press.com	China	Unknown
41	Flip-flops		Internet-sportandcasu-als.com	Holland	China
42	Flip-flops		Wish.com	(China)	(China)
Rainwear, ponchos, rubber boots, umbrellas					
43[b]	Rainwear		Aliex-press.com	(China)	(China)
44[b]	Rainwear		Internet-sportandcasu-als.com	Holland	Unknown

45	Umbrella		Cdon.com	Sweden	Unknown
Tarpaulins (incl. various protective wrappings for camping and outdoor equipment)					
47[b]	Cover for garden furniture		Wish.com	(China)	China
48[b]	Cover for garden furniture		Ebay.com	England	Unknown
49[b]	Tarpaulin		Aliex-press.com	(China)	China
50[b]	Tarpaulin		Ebay.com	Italy	Unknown
Garden hoses					

51[b]	Garden hose		Amazon.com	England	England
52[b]	Garden hose		Ebay.com	China	(China)
Garden/home articles					
53	Self-irri-gation		Wish.com	(China)	China
54	Self-irri-gation		Ebay.com	England	(China)
Gloves (protective/garden)					
55[b]	Gloves		Aliex-press.com	China	(China)
56[b]	Gloves		Cdon.com	Sweden	China
Cycling equipment (saddles, pads, tape)					

57	Bicycle reflectors		Ebay.com	China	China
58	Bicycle reflectors		Holland-bikeshop.com	Holland	Portugal
Electronic items, e.g. gadgets, shavers and electric toothbrushes					
59	Lamp		Cdon.com	Sweden	China
60	Lamp		Ebay.com	China	China
61	Flash light		Aliex-press.com	Spain	Unknown
62	Flash light		Ebay.com	China	China
Equipment for mobile phones, iPads, etc.					

63	Mobile cover		Ebay.com	China	China
64	Mobile cover		Ebay.com	England	Unknown
65	iPad cover		Cdon.com	Sweden	China
66	iPad cover		Aliex-press.com	China	Unknown
67	Phone charger		Ebay.com	England	Unknown
68	Phone charger		Amazon.com	Unknown	China
Personal care items					

69	Artificial nails		Ebay.com	China	China
70	Artificial nails		Mini-inthebox.com	(China)	(China)
Building materials					
71	Pipe		Ebay.com	USA	USA
72	Pipe		Ebay.com	England	USA
73	Pipe joint		Ebay.com	China	Unknown
74	Pipe joint		Ebay.com	Lithuania	Unknown
Sex toys					

75	Sex toys, arm		Wish.com	Unknown	China
76	Sex toys, arm		Ebay.com	Italy	China

* Unknown sales country. Brackets indicate country of shipping
** Unknown country of production. Brackets indicate language printed on the product.

[a] Compares to products from the control campaign from the Chemical Inspection Service in 2018 on children's toys: "Kontrol af CMR-stoffer i legetøj"

[b] Compares to products from the control campaign from the Chemical Inspection Service in 2018 in DIY retailer products: "REACH: Kontrol af art. 33.2 informationspligten i byggemarkeder – 2018"

Appendix 4. Description of method

Method 1: EDXRF screening

Screening was carried out on sub-samples using Energy Dispersive X-ray Fluorescence (EDXRF) on the instrument EDAX Eagle III. In EDXRF, radiation is directed at the sample, and X-rays specific to the chemical elements are emitted from the sample. This radiation is detected simultaneously for all chemical elements. The diameter of the examined area is 100 µm. The depth of the analysis is dependent on matrix and chemical element. Chemical elements with a higher atomic number than that of neon (10) can be detected, from Na to U. The screening is qualitative and was used to test for presence of Cl (PVC) and possibly other selected metals. For each product, a small sub-sample was taken, for which a single screening was performed.

The samples are analyzed in accordance with Danish Technological Institute's method:
UA 291
Detection limit: 1%

Method 2: Quantitative determination of specific chemical elements

The analysis is performed by means of ICP-MS and ICP-OES in accordance with Danish Technological Institute's method UA 268, which is based on reference method DS/EN 17294-2:2016 (ICP-MS) and DS/EN ISO 11885:2009 (ICP-OES).

By means of microwave induced heating, a weighed quantity sample (0.25 g sample, carefully weighed) was prepared with a mix of concentrated nitric acid (HNO_3), concentrated hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2). The resulting solution was diluted to 50 ml using Milli-Q water and subsequently diluted 10–20 times using 2.8 M HNO_3. Duplicate determination of the sample was performed. Blind samples were prepared similarly.

Quantitative analysis by means of ICP-MS (Cd, Pb, Sn, Sb and B)
Samples and blind samples were analyzed for content of selected chemical elements by means of ICP-MS with CCT in KED mode and with He as collision gas. Ge, Rh and Re were used as internal standards. The quantification by ICP-MS was performed against traceable external standards of the chemical elements. The calibrations were verified against independent traceable control solutions.

Quantitative analysis by means of ICP-OES (P)
Samples and blind samples were analyzed for content of selected chemical elements by means of ICP-OES. Y was used as internal standard. The quantification by means of ICP-OES was performed against traceable external standards of the chemical elements. The calibrations were verified against independent traceable control solutions.

The detection limit is indicated in the table below (component dependent).
Analytic uncertainty: 15% RSD

TABLE 21. Detection limits for analyzed chemical elements

Chemical element	Detection limit [mg/kg]
B	400

Cd	2
P	100
Pb	2
Sb	2
Sn	2

Method 3: Organotin compounds

Sub-samples were extracted in duplicate and determined by means of gas chromatography with mass-selective detector (GC-MS). This method is based on reference method DIN CEN ISO/TS 16179. It is identified and quantified against reference substances.

Detection limit: 0.1-0.05 mg/kg
Analytic uncertainty: 27%

Method 4: OA-500, Quantitative determination of phthalates by means of GC-MS

The analysis is performed by means of gas chromatography with mass-selective detector (GC-MS) in accordance with Danish Technological Institute's accredited method of analysis OA-500, which is based on DS/ISO 16181. The specific phthalates covered by the accreditation are indicated in the table. Any other phthalates found are reported by integration above m/z 149 TIC (total ion count), as DEHP equivalent.

A weighed amount of sample is extracted with solvent (*n*-hexan / acetone with deuterium-labeled internal standards). The extract is analyzed by means of capillary gas chromatography combined with mass spectrometry. Duplicate determination of the sample has been performed.

The detection limit is given in the table below (component dependent).

Expanded analytic uncertainty (k=2): 35% RSD (this corresponds to a relative standard deviation for duplicate determination of about 18%).

TABLE 22**.** Reference substances applied for quantitative determination of phthalates.

Phthalate	Abbreviation	CAS No.	Detection limit [mg/kg]	Accrediting
Bis (2-ethylhexyl) phthalate	DEHP	117-81-7	5	x
Dihexyl phthalate	DHxP	84-75-3	5	x
Dipentyl phthalate	DPP	131-18-0	5	x
Diisopentyl phthalate	DIPP	605-50-5	5	
n-Pentyl-isopentyl phthalate	nPIPP	776297-69-9	5	
Bis(2-methoxyethyl) phthalate	D2MEP	117-82-8	5	x
Diisobutyl phthalate	DIBP	84-69-5	5	x
Dibutyl phthalate	DBP	84-74-2	5	x
Butyl benzyl phthalate	BBP	85-68-7	5	x
Diisonoyl phthalate	DINP	28533-12-0 68515-48-0	20	x
Diisodecyl phthalate	DIDP	26761-40-0 68515-49-1	20	x
Di-n-octyl phthalate	DNOP	117-84-0	5	x

Dicyclohexyl phthalate	DCHP	84-61-7	5
Diisooctyl phthalate	DIOP	27554-26-3	5

Method 5: Quantitative determination of SCCP by means of GC-MS

Sub-samples were extracted in duplicate with dichloromethane, and SCCP is determined by means of gas chromatography with mass-selective detector (GC-MS). It is identified and quantified against reference substances. Duplicate determination of the sample has been performed.

Detection limit: 50 mg/kg
Analytic uncertainty: 35% RSD

Method 6: Screening analyses by means of GC-MS

Products made from soft PVC material have been screened in connection with analysis for phthalates, see method 4. By reviewing the data obtained and comparing with a database with mass spectra, a number of probable substances have been identified.

The individual substances were identified by comparing the current mass spectra with the mass spectrum from the NIST library (version 17).[36] The NIST library is a database with mass spectra of more than 500,000 chemical compounds. To examine the correspondence between a given spectrum and the NIST library, a hit rate between unknown substance and the library reference is given. The hit rate is a mathematical calculation of how close a correspondence there is between the reference spectrum of a substance in the NIST library and the spectrum of that substance in the analysis. Identification from the NIST library is considered indicative. For definitive positive identification, substance-specific analysis should be performed with reference substances, which is not included in the present project.

Screening analysis by means of GC-MS covers a comprehensive number of volatile and semi-volatile organic substances, but the method is not equally suitable for all substances. For certain substances, the hit rate may be low, and, thus, identification may be misleading, because the setup of a screening program by means of GC-MS may not be optimal for all substances. All identifications with hit rates greater than 70% from the NIST library have been reported.

The concentration is calculated using deuterium-labeled internal standards of phthalate compounds. Some of the substances' response factor in the analysis is close to the response factor of the internal standard, while the response factor of other substances is far from it and will, therefore, result in a more uncertain determination of the concentration in the sample.

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

Survey of unwanted additives in PVC products imported over the internet

A primary goal for this project was to investigate if Danish consumers risk exposure to problematic substances when purchasing PVC products in online stores outside Denmark. The focus was on the PVC material's content of two types of additives: heat stabilizers added to stabilize the PVC material during the manufacturing process and plasticizers added to adjust the softness of the PVC. The following problematic substances were identified 1) cadmium and lead, which are part of heat stabilizer additives and 2) various phthalate-type plasticizers and chlorinated paraffins (SCCP). A total of lead containing (nine products), cadmium (four products), the phthalate DBP (in one product) and SCCP (5 products) were found in a concentration that prevents them being marketed in the Danish market. A total of 13 products out of 54 products examined (=24%) contained above substances in concentrations which exceeded threshold values for marketing in Denmark Out of these, six products exceeded threshold values in more than one piece of legislation. In addition, 22 out of 41 tested soft PVC products (=54%) contained the phthalates DIBP, DEHP and DBP in concentrations that have been banned under brand new REACH restrictions introduced after the purchase of the products. No systematic differences was found between the above two groups of infringements in relation to whether the product was purchased or produced within the EU (excluding Denmark) versus outside the EU.

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