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Analysis and risk assessment of fragrances and other organic substances in squishy toys

Survey of chemical substances in consumer products No. 165

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Editors:
Helene Bendstrup Klinke, PhD, MSc, Danish Technological Institute
Birgitte Lange Winther Lund, PhD, MEng, Danish Technological Institute
Søren Ryom Villadsen, MSc, Danish Technological Institute
Sie Woldum Tordrup, MEng, Danish Technological Institute
Gitte Tang Kristensen, MSc, Danish Technological Institute
Poul Bo Larsen, MSc, DHI

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Contents

Preface

This report presents a study and risk assessment of squishy toys carried out for the Danish Environmental Protection Agency in 2018.

This study includes a description of typical sales points, prices, countries of production, target group for squishy toys and the expected contents of chemical substances in the toy. In addition, information on the expected usage of the toy has been collected in this study. This information creates the foundation for this report's description of real-life exposure scenarios regarding children's exposure to substances while using squishy toys.

Chemical analysis of selected squishes was carried out and is reported here. The chemical analysis has been performed in two phases: a screening phase and a phase with quantitative analysis.

The analysis results create background for risk assessment of selected chemical substances from squishies selected in cooperation with the Danish Environmental Protection Agency.

The analyzed products have been purchased by the Danish Environmental Protection Agency during the period from February to March 2018, and the project was carried out from March 2018 to June 2018.

This project is prepared for the Danish Environmental Protection Agency by the Danish Technological Institute with DHI as subcontractor of hazard assessment, exposure scenarios and risk assessment.

Summary and conclusions

Background

Soft foam figures, also called squishies or squishy toys, are popular among children (2017-2018) and are available in many different sizes, colors and models. Playing with the toy involves children e.g. hugging and shaping the foam figure in their hands. When the grip is released, the toy folds out and returns to its original shape, after which the figure can be squeezed and shaped again as a type of stress ball. Squishies are also considered a collectible, e.g. displayed in the child's room, but to a lesser extent used for playing with. Squishies often have a perfumed or chemical smell and are expected to be made of polyurethane foam (PUR), which may potentially contain a number of problematic chemical substances. Until now, only limited information is available on which chemical substances, e.g. fragrances and other organic compounds, are contained in and released from squishy toys.

Aim

The aim of this project is to obtain knowledge about which organic substances, including fragrances, are released from the products and the possible release of substances that give a chemical smell. It must also be assessed whether the substances identified in the products present a risk to children.

Result of the survey

A survey on squishy products for children, which are considered available on the Danish market, has been performed. The mapping includes a description of typical sales points, prices, production countries and the target group for squishy toys. A study on the chemical substances possibly present in the products, including substances originating from the polymer material or added to the toy to obtain a particular fragrance, has also been carried out. Further, information on the expected use of the toys has been collected through a few Danish distributors and their suppliers.

The range of squishies available on the Danish market is large, and the products were found at many retailers in physical Danish stores, Danish webshops and non-EU webshops. China is indicated as the country of production for the vast majority of the identified products. On some of the purchased products it is stated that they are scented, and, therefore, some squishies for children on the Danish market are expected to contain fragrance. Products with comparable designs are found on the market from different providers and with diverse odor/smell. The contacted distributors and importers pay particular attention to the odor of as well as the specific content of fragrance in products, and, in some cases, they deselect products with added fragrance.

Distributors and importers have, in addition to the fragrance substances, been focusing on the content of phthalates, while none of the contacted operators have expressed concerns about the content of substances typically used in the production of the polymeric material, for example, any residues of the monomer which the material consists of or other additives, such as solvents or foaming agents that give the material the properties that characterize squishy toys.

The products are considered collectibles, and it is normal for children to own several different squishies (5-10). Children who collect eagerly can be expected to own even more (between 30 and up to 200 pieces are indicated by distributors / importers for those with the largest collections). The typical use of squishies is described as active play where the products are squeezed, and the restoration to the original shape is observed and compared to other squish-

ies. One of the contacted distributors therefore considers it likely that in case of squishies skin contact occurs longer than with other types of toys. The target audience for the products is generally determined by the contacted importers and distributors from approx. 6 years and upwards. Some types of squishies are expected to be used for role playing, which can last for longer periods.

The information collected in the survey forms the basis for the selected analysis program and this report's description of realistic exposure scenarios of children to substances during their use of squishy toys.

Description of exposure scenarios

Based on information regarding children's play and their use of squishies, a typical scenario was described for the target group of children over 6 years of age. In a scenario for inhalation of vapors, data from emission measurements are used to calculate the concentrations of the substances in a standard children's room of 7 m^2 (17.4 m^3). As a worst-case scenario, it is assumed that up to 40 squishies have been collected in the room and that the child stays in the room for 15 hours. Regarding skin exposure, it is assumed that the child has a skin contact with a squishy for 2 hours daily, and during this time is exposed to substances released from the material over time (through migration).

As a worst-case scenario for an unintentional but possible use, a scenario was described where a 3-year-old child is sleeping 10 hours with a squishy in his arms. In this scenario, the child may breathe relatively concentrated vapors comparable to those measured in the small climate chambers used in the emission experiments. For skin contact, a contact time of 10 hours is used.

Purchasing and selecting samples for analyses

The Danish Environmental Protection Agency purchased 43 different squishies (2-3 of each product) prior to the initiation of this study. The price of products ranged between DKK 7 and DKK 150 with an average price of approx. 60 DKK. Purchasing of products was highly influenced by the high demand, and some products were sold out during the purchase period, while new ones were offered during the same period. Purchases have therefore been limited to the available products during the purchase period (February to March 2018).

The goal for purchasing these samples was that the products should be targeted to children and that most products should be purchased in Danish webshops and non-EU webshops, while purchases in physical Danish stores should constitute a minor part. Due to long delivery times from non-EU webshops, purchases from these types of points of sale became fewer than intended, although still with a majority of products purchased in webshops. Several other criteria were also used in purchasing and selection of samples for analysis, such as popularity, price, material characteristics, packaging, product odor/smell and design.

Eight squishies were selected for initial screening of content and substances that emit to provide an overview of substances that could be relevant for further investigation. The eight samples were selected so that four squishies were purchased in physical Danish stores, two squishies were purchased in Danish webshops and two squishies were bought in non-EU webshops (Chinese producers). In the sample selection, there is an excess of squishies from physical Danish stores compared to the set goals (50% against 10-20%), which is due to the fact that in the selection of samples, priority was also given to samples that smell and their price, as well as it was chosen to include two comparable products from different dealers.

Initial analysis - screening of eight selected samples

Analysis program

The eight products selected for initial screening were analyzed by GC/MS for chemical content and for the emission of volatile chemical substances in a climate chamber test. This method of screening is chosen due to focus in the project on volatile organic compounds, and the same eight products are analyzed for content and emission for comparison of results.

Three out of the eight products are also selected for identification of the material type (IR characterization). The three selected samples are also analyzed for isocyanates which may be present as residual monomer in the PUR material and are highly respiratory irritant.

Results of screening of chemical content.

Approximately 100 chemical substances have been found in each of the eight squishies, and 35 of these substances could be identified with great certainty. Several of the other substances were also identified, but with a higher uncertainty.

The 35 substances identified with the highest degree of certainty are probably predominantly chemical substances originating in the polymer material from which squishies are made of. This applies, for example, to amine compounds (dimethylaminoethanol, dimethylformamide, octadecenamid, triethyldiamine and pentamethyldiethyltriamine) used in the preparation of the polymeric material. There is also triethyl phosphate, which is probably used as a catalyst in the polymerization process. Also, phthalates (DEP and DEHP), cyclohexanone and octadecyl di-tert-butyl-4-hydroxyhydrocinnamate are identified in the products, as well as 4,4'-methylenebis benzeneamine, which is probably a monomer residue.

Among the substances identified with a higher uncertainty are e.g. the fragrances versalid and galaxolide, the organophosphorous-based fire retardant tris(2-ethylhexyl) phosphate (TEHP) and traces of the reactive radical initiator azobisisobutyronitrile, which may indicate that the chemical reaction that is taking place during the manufacturing process is not fully completed (incomplete polymerization). Traces of glycol and silicon compounds were also found in an amount indicating that they may be residues from the polymer chain.

Screening analysis by extraction and subsequent GC/MS analysis results in a dissolution and partial degradation of the polymer which may result in finding substances bound in the product under normal use and therefore not found in emission or migration analyzes. It cannot be denied that some substances could have been added in free form to the material to obtain special material properties, and hence are not chemically bound to the polymer network. Therefore, there may be a risk that some release of the substances during use may occur depending on the physicochemical properties of the individual substances.

Results of screening by emission tests

The emission analyses of the eight selected squishies show that a number of volatile organic compounds, carbonyls and VOCs can be identified in the individual samples. Several fragrances have been found in the emissions: D-limonene, benzyl alcohol, L-linalool, delta-3-carene, alpha-pinene and beta-pinene. In addition, N,N-dimethylformamide (DMF), N,N-dimethylaminoethanol, triethylenediamine, bis(2-(dimethylamino)ethyl)ether, 1,2-ethanediamine and N-[2-(dimethylamino)ethyl]-N,N',N'-trimethyl-cyclohexanone found in high concentrations. Many of these substances are also identified in the screening of chemical content.

In six out of eight squishies, concentrations of formaldehyde, acetaldehyde, propanal, butanal, acrolein and crotonaldehyde are below 10 µg/m^3 of air in the performed emission screenings. This is considered low in comparison to existing limit values for e.g. formaldehyde in indoor climate, which is 100 µg/m^3.

Results of material determination
Material determination has been made using infra-red spectroscopy, which unambiguously shows that the three analyzed squishies consist mainly of polyurethane foam, confirming the knowledge obtained in mapping.

Results of isocyanate screening
Three selected squishies are analyzed for isocyanates, which is one of the monomers that the material is made of. These residues of monomers are found in all three squishies. The complexity of the material interferes with the analysis, but an estimated worst case total value of 1.5 mg/kg isocyanate is found in the squishy having the highest content.

Initial hazard assessment

For the identified substances found in the screening of content analyzes and emission analyzes, hazard classification data were found in the European Chemicals Agency's database (EU harmonized CLP classification and / or classification used in the substance REACH registration).

Subsequently, special attention was paid to substances with serious hazard classifications such as:
• CMR 1A, 1B, 2
• STOT RE 1.2
• STOT SE 1.2
• Acute tox. 1,2,3
• Skin Sens 1
• Resp. Sens 1

Substances with very high emissions or high content levels were also included in the prioritization, although the substances were not prioritized based on their classifications.

For further emission analyzes, 14 substances (including 3 fragrances) were identified, while 26 declarable fragrances in addition to the substances N,N-dimethylformamide (DMF) and N,N-dimethylaminoethanol (DMAE), both found in much high amounts of content, were identified as relevant for migration analysis. The substance N,N-dimethylformamide is furthermore a substance that appears on REACH's candidate list of substances of very high concern due to its classification as toxic for reproduction, Repr. 1B.

Quantitative emission and migration analysis on selected samples

Analysis program
It has not been possible to include all substances with a relevant classification with respect to children's exposure from squishies. An analysis program containing quantitative analyses of emission in a climate chamber and quantitative determination of migration of selected substances was, therefore, designed.

Substance-specific quantification of selected substances has been completed for a total of twelve squishies, the eight were tested during the performed screening analyses and four additional squishies (one purchased in a physical Danish shop, two purchased in Danish webshop and one purchased in a non-EU webshop). For emission tests in the climate chamber and subsequent quantification of volatile substances, attention is put on fragrances, carcinogens, amines and chlorinated substances found in the initial screening. The emission to air from all the squishies of the selected substances after a short period of time (1 hour) and after 3 days (3 days) in the climate chamber is measured to determine how emission is reduced

during the first days after unpacking and to provide information for the risk assessment of children's exposure.

Migration to artificial sweat was also performed with the same 12 squishies with subsequent substance-specific analysis of DMF, 26 fragrances and DMAE in the migration fluid.

Results of migration analysis for artificial sweat
Migration analysis was conducted with a one-hour and 100 mL migration fluid per 10 cm^2 sample as defined in EN 71-10: 2005. The migration is done to artificial sweat at body temperature and on a sample with as high a proportion of the outside surface of the product as possible.

For DMF and DMAE, migration has not been detected under the conditions used for any of the samples tested. The detection limit per surface is 100 $\mu g/cm^2$ for this analysis, which corresponds to 1000 µg/g sample and with an estimated uncertainty of 20% RSD.

None of the 26 fragrances tested were found in a concentration above the detection limit in the 12 selected products. Detection limit per surface area for this analysis is 2 $\mu g/cm^2$, which corresponds to 50 µg/g and with an estimated uncertainty of 20% RSD.

Results of emission testing
The emission of three fragrances is confirmed in the 12 analyzed squishies; limonene and linalool, which must be declared if the content in the toy exceeds 100 mg/kg, and benzyl alcohol, which is not allowed in toys. Limonene is found in concentrations up to 1900 $\mu g/m^3$ in emission tests after one hour, which, however, is reduced to 1100 $\mu g/m^3$ after 3 days. As the declaration obligation is set for content and no content analysis of the limonene in these exact samples has been performed, it can neither be confirmed nor denied if the limit of 100 mg/kg has been exceeded. Benzyl alcohol has been found in low concentrations (< 5 $\mu g/m^3$) in the emissions from four squishies after 1 hour and 3 days, respectively. The Danish Statutory Order on toys permits substances that are not allowed in toys to be present if these are technically unavoidable and below 100 mg/kg. As the low values indicate, this is probably the case. In all squishies, other fragrance-relevant terpenes have also been found: alpha-pinene, beta-pinene and delta-3-carene. Both the alpha-pinene and beta-pinene are among 82 recognized contact allergens identified in cosmetics.

Various chlorinated substances have been found in emission tests: dichloromethane (methylene chloride), chloroform, 1,2-dichloroethane and 1,2-dichloropropane. From 1 hour to 3 days, the concentrations of most substances are reduced in the emission from the squishies.

Three amines have been found: N,N-dimethylaminoethanol (DMAE), triethylenediamine and bis (2- (dimethylamino) ethyl) ether where the concentration either rises or has approximately the same concentration in the air from 1 hour to 3 days. A fourth amine; 1,1,4,7,7-Pentamethyl-diethylenetriamine is found in the emission test of eight of the tested samples. Unlike the other seven samples analyzed after 1 hour of emission, the substance for squishy No. 033 is not seen after one hour, but only after 3 days of emission. Overall, it is thus estimated that amines are released more slowly from the material over time than the other volatile organic compounds measured, which means that children are potentially exposed to this type of substance over a long period of time.

The concentrations of the individual substances vary with the type of squishy and it also indicates that the weight and the corresponding surface area of the squishies are important for the concentrations of volatile organic compounds released in the climate chamber test. It also suggests that the type of substances that are released varies with the manufacturer. Four of the analyzed samples have comparable appearance in sets of two (i.e., look similar with re-

spect to figure, color and design); sample 038 and 061 are similar to each other and sample 034 and 063 are similar to each other. Sample 061 and 063 are from the same retailer (online store in non-EU country) but from two different manufacturers, while samples 034 and 038 are purchased in a Danish online store (manufacturer not specified). There are substances that are identified in all or many of the tested samples, but in general there are great differences in the substances that are released by emission in the climate chamber. At a first glance, there are no apparent trends in content and no conclusions can be reached as to which substances are typically used in production and which fragrances are used. Even for products manufactured by the same producer (samples 051 and 054), significant differences are observed in the chemical content of the two squishies, both in terms of substances and emission concentrations.

Hazard and risk assessment

In the hazard assessment of the emitted substances, data were retrieved on tolerable exposure levels for the substances (the REACH legislation uses the term DNEL, Derived No Effect Level) for the 17 substances considered most problematic. As a starting point, DNEL values derived by expert groups in EU or DNEL values developed in previous environmental management projects were used. For four of the substances where no DNEL value was found, these were derived in this project (Appendix 7).

In the actual risk assessment process, the measured exposure levels were compared to the DNEL values for the substances and a RCR (Risk Characterization Ratio) was calculated:

RCR = Exposure (µg/m^3) / DNEL (µg/m^3)

RCR values above 1 mean that the exposure level exceeds the tolerable DNEL value, which in turn means that the level of protection is too low, and there may be a risk associated with the use.

In the case of emission measurements of 12 different selected squishies, emission of a number of substances was detected at levels that may cause irritation of the eyes and respiratory tract, and which, in the case of repeated exposure, may cause damage to the mucous membranes. This included the following substances where RCR values were found to be significantly greater than 1:

- dimethylaminoethanol, (RCR = 28 as the highest value)
- N,N-dimethylformamide, (RCR = 73 as the highest value)
- cyclohexanone, (RCR = 15 as the highest value)
- triethylenediamine, (RCR = 206 as the highest value)
- bis(2-(dimethylamino)ethyl)ether, (RCR = 200 as highest value)
- 1,1,4,7,7-pentamethyldiethylenetriamine, (RCR = 46 as the highest value)

In an exposure scenario for a small child sleeping with a squishy in his arms, unacceptably high levels of the substances N,N-dimethylformamide, triethylenediamine and cyclohexanone were reached for all 12 squishies based on the emission measurements one hour after unpacking of the toy. For four squishies for which 3-day measurements were also made, the concentrations remained unacceptably high for the substances N,N-dimethylformamid and triethylenediamine.

For other mucosal irritants: bis(2-(dimethylamino)ethyl)ether; 1,1,4,7,7-pentamethyldiethylenetriamine and dimethylaminoethanol the emission level from 6 of the squishies exceeding a tolerable level 1 hour after the unpacking. After three days, the level of bis 2-(dimethylamino)ethyl)ether remained unacceptably high for three out of four squishies.

For substances with other effects, e.g. methylene chloride (carcinogenic) and xylenes (chronic neurotoxic), the tolerable exposure level was only exceeded slightly at 1 hour after unpacking (RCR up to 2.3 for methylene chloride and RCR up to 4.9 for xylenes). Since these adverse effects are associated with long-term exposure above the DNEL value, a short-term exceeded RCR value is considered to be less significant in a risk assessment context.

In a scenario where more squishies are stored in a child's room, unacceptably elevated levels were found in the child's room after three days for the substances N,N-dimethylformamide, N,N-dimethylaminoethanol, triethylenediamine, (bis(2-(dimethylamino)ethyl)ether), 1,1,4,7,7-pentamethyldiethylenetriamine and cyclohexanone.

In migration tests for artificial sweat fluid, no migration of any of the selected substances was found, so a quantitative risk assessment for skin exposure to these substances could not be performed. However, in case of skin contact, the skin will also be exposed to the emitted substances, so the risk of skin irritation cannot be excluded. Similarly, the risk of skin allergy cannot be ruled out due to the emission of substances that can cause skin allergy, which emitted in smaller amounts. Particularly, repeated skin contact may promote the development of skin allergy. If small children are sucking on parts of the squishy, the possible risk of skin irritation and skin allergy is greatest for areas where the skin is thinnest, e.g. on the lips.

1. Introduction

1.1 Background

Soft foam figures, also called squishies or squishy toys, have become very popular among children during the recent years (2017-2018). Squishy toys can be found in many different sizes, colors and models and are made to resemble, among others, animals, different food products, e.g. ice cream, cakes and fruit, and as emojies. Squishies can be purchased in e.g. toy stores, supermarkets, book stores and webshops.

Toys are, for one thing, used by a child squeezing and forming foam figures in her hands. After releasing the grip around the soft toy, the toy unfolds and returns to its initial shape and then the toy can be squeezed and shaped once again. Furthermore, squishies are also considered a collectible. This means that some children own many different toy designs that are, e.g., displayed in children's rooms and only to a lesser extent used as toys. Many toy distributors, among others BR, Toys'R'Us and Squishyshoppen, describe squishy toys as being easy to put in a bag, pocket or the car, and the toy is often found in classrooms, where pupils use the soft squishies as a sort of stress ball.

Squishies are often fragranced or have a chemical smell and are expected to be produced from polyurethane foam (PUR) due to the product's ability to reestablish the initial structure after deformation. The type of material is, however, not decisively confirmed prior to this project, and there is a limited knowledge of the chemical ingredients. PUR, as well as other polymer materials, may contain many different chemical substances (see e.g. Danish Environmental Protection Agency 2014A) such as:

- fragrances
- solvents
- preservatives
- residual monomers (for PUR e.g. isocyanates)
- fire retardants (phosphates as well as chlorinated and brominated compounds)
- coloring agents (e.g. heavy metals)
- softening agents (e.g. phthalates)
- other additives, such as foaming agents, catalysts, stabilizers, antioxidants and flavoring agents (to prevent animals and children from eating them).

Some websites provide information that certain squishies have an odor/smell upon delivery, but that this odor/smell decreases with time and during use, and that the odor/smell is not hazardous. Currently, only limited information is available on which fragrances and other organic compounds are included in and emitted from squishy toys.

1.2 Aim

The aim of this project is to gain knowledge on which organic substances, including fragrances, are emitted from these products as well as possible emission of substances with a chemical smell. It will also be assessed, whether substances identified in products constitute a risk for children.

2. Survey of squishy toys

This survey consists of collecting information on typical sales points, prices, countries of production, target group for squishy toys and expected content of chemical substances in squishy toys on the Danish market. Information on the expected use of toys has also been collected. This information creates background for the description of real-life exposure scenarios regarding children's exposure to substances during use of squishy toys and choice of methods for chemical analysis of selected products.

2.1 Legislation in relation to squishy toys

Squishies sold on the Danish market must comply with the Danish Statutory Order on safety requirements for toys (BEK no. 309 of 3/4/2017, *Legetøjsbekendtgørelsen*), which is the implementation of the Directive of the European Parliament and the Council of 18 June 2009 on the safety of toys (2009/48/EC). Furthermore, certain limitations are in force regarding the specific chemical substances according to EU chemical regulation REACH (1907/2006) and a few other special Danish regulations. In the following sections, limitations for chemical substances expected to be relevant for squishies are described.

Limitations of Danish Statutory Order on safety requirements for toys

According to Danish Statutory Order on safety requirements for toys, the toys must be produced in such a way that they do not constitute a risk for hazardous effect on human health as a result of exposure to chemical substances in toys. The requirements in the statutory order include toys used for the intended purpose or in ways children may be expected to use them.

CMR substances

Generally, substances classified as carcinogenic, mutagenic or toxic for reproduction (CMR substances) may only be used in toy parts that are not accessible to children, including via inhalation. If substances with CMR classification are used in parts accessible to children, their concentration must be lower than the respective classification limit of these substances.

Fragrances

Of particular relevance for squishy toys are the limitations included in the Directive 2009/48/EC regarding the use of many allergenic fragrances. In total, 55 fragrances are prohibited in concentrations exceeding 100 mg/kg, and 11 other fragrances must be declared if added above this concentration. A list of these substances can be found in Appendix 1.

Migration limits for some chemical elements

For toys, there are established migration limits for a long range of chemical elements such as cadmium, nickel and chromium. Migration limits depend on the material of toys, and squishies would mainly be categorized as scraped-off toy material. The complete list of migration limits is given in Appendix 1.

Limitations in toys for children under the age of three and toys intended to be placed in the mouth

Specific limit values are in force for substances in toys for children under the age of three and in toys intended to be placed in the mouth. Substances such as phenol, bisphenol A, formamide, the flame retardants TCEP, TCPP and TDCP as well as the preserving agents benzisothiazolinone, methylchloroisothiazolinone (MCI) and methylisothiazolinone (MI). The specific limit values are given in Appendix 1. In addition to these limitations, there is a national limitation in Denmark on all phthalates in toys and products for small children under the age of three

(BEK no. 855 of 5/9/2009). The limit is 0.05 % and applies to all phthalates except phthalates already regulated in EU. Currently, it is uncertain how squishy toys will be age-determined, since there is no consensus between member states at EU level. According to Danish Statutory Order on toy safety, toys must be safe for children under the age of three unless the toy carries a warning that it is not safe for children under the age of three or that it is clearly not intended for small children. Since it has not been clearly indicated, whether squishy toys are not intended for small children, it may be expected that the product is safe for all age groups unless the products are marked with a warning.

Limitations in REACH

In addition to the mentioned restrictions in Danish Statutory Order on safer toys, the use of chemicals in toys is also subject to limitations in the REACH regulation, Appendix XVII. Limitations in toys include six specific phthalates (entry 51 and 52), benzene (entry 5) and eight PAHs (entry 50). The exact limitations are given in Appendix 1.

2.2 Aim and method

The aim of the screening is to shed light on which materials squishies typically consist of and which possible content substances are expected to be found and emitted from these toys. The Danish Environmental Protection Agency has carried out a screening of toys on the market and have purchased a selection of products prior to project start. The survey takes its departure in information collected by the Danish Environmental Protection Agency when purchasing the toys, and, on this basis, a short description on the following has been made:

- sales points
- price differences
- country of production
- product materials
- ingredient expected to be found in products
- typical age of target group for this product
- reflections of children's play with products regarding exposure, e.g. skin contact, play time and time spent in children's room indicated in hours per day.

Knowledge of sales points and prices has been collected by the Danish Environmental Protection Agency prior to project start and has been processed by the Danish Technological Institut during the survey. Additional knowledge of above-mentioned aspects, e.g. from label insert or description of the purchased products, was also included in the survey and was supplemented to a lesser degree with information found by an internet search.

Since the toy industry constitutes a very important information source, a telephone interview with selected importers and distributors from the toy industry has been conducted with the aim to collect information on material types, potential problematic ingredients and description of how children are expected to play with these types of toys (see questionnaire for phone interview in Appendix 2). During telephone interviews, the contents of fragrances, which constitute a risk in relation to development of allergy (SCCS 2012), and contents of volatile organic compounds that emit smell, such as solvents, were specifically addressed.

2.3 Information collected from distributors and importers

During the survey, four stakeholders within the industry were contacted: two toy distributors and two toy importers (the one via their distributor, who has forwarded the answers). Products purchased from both of the contacted distributors are included in the analysis. All questions have been answered either by phone or via e-mail in March 2018.

Distributor 1

A Danish squishy distributor confirms that their marketed products are made of polyurethane foam (PUR). The products are made in China, but companies responsible for the production are based outside China (Canada and UK). The distributor is always very attentive when dealing directly with Chinese manufacturers and is always dependent on their trust towards suppliers.

In general, the distributor does not see a risk for a content of problematic substances as being more significant for this type of toys compared to other toy products and thus has not posed stricter requirements for squishies. The documentation for compliance with existing legislation has been collected, and, for instance, test results for phthalates have been documented, where–according to legislation–there are limitations to the substance contents. Among the marketed products from this distributor, there may be products containing declarable fragrances within the permitted concentrations according to Directive 2009/48/EC, i.e. below 100 mg/kg, while other products are entirely without fragrance. In other squishy products, which the distributor has screened during purchase, some products have been found with declarable fragrances that are considered allergenic.

The distributor has received a few inquiries from consumers regarding their concern about the smell typically emitted by squishies. The products have a “chemical” smell, and the distributor considers it highly possible that the inquiries are primarily connected to media coverage of these products. No inquiries have been registered with specific health-related effects. These inquiries are mainly connected to concerns about the experienced smell, where probably one or two customers have indicated that they have been directly annoyed by the smell. There are no inquiries related to allergic reactions. The distributor assessed that the number of inquiries reflects the sales figures and the media coverage of the products during the recent period, and can generally be compared to similar toy products as e.g. fidget spinners.

The distributor considers children between the age of 6-10 years, maybe up to 12 years, to be the typical target group for squishy products. Marketing through e.g. YouTube stories are mostly directed towards older children in this age group. The distributor’s sales figures indicate that children between the age of 6-10 years purchase and use these products (sales peak with 10-year-olds), and the distributor generally recommends the products from the age of 6 and above.

The distributor expects that playing with these products is centered around squeezing and observing the toy while returning to its original shape. These products are usually rubbed in hands and may be included in roleplays, where usually several squishies are involved. Due to the squeezing function, longer skin contact is highly possible compared to other types of toys. However, the toys are mainly expected to be used in waking state and cannot be compared to soft toys or teddy bears, since the material surface does not feel pleasant against skin as e.g. textile materials.

Squishies are available in series, where several designs can be collected, as well as so-called blind bags, where consumers have an opportunity to acquire rare versions. The products remain at the top-ten list of sold products, and no decrease in interest has been observed yet. It is highly unusual to have only one squishy, but 100-200 pcs. as sometimes reported in media, is likewise highly unusual. The trend is that more squishies are purchased and collected, but this has not been investigated by analyzing sales figures.

Distributor 2 and Importer 1

The second Danish distributor of squishies informs that technical documentation on squishies is procured in the same way as for similar types of toy products, and the distributor in general has strict requirements for chemical content in products, and he performs random sample control himself. The distributor has a list of specific substances that he does not allow in toys, and he works closely together with importers to ensure that their products meet all requirements. This distributor has via his importers been confirmed that the squishy toys marketed by this specific distributor consist of PUR and are produced in China. During purchase of squishies, a special focus has been on the potential content of fragrances and phthalates. Squishies with added fragrance have actively been deselected, and, hence, the distributor has no knowledge of which fragrances are typically used for squishies. According to one importer, fragrances, that provide the odor of cream, pineapple and peach are often used.

No inquiries from consumers have been registered regarding health-related complaints when using these products. Only a few inquiries have been registered regarding the hazard of the smell of these products.

The typical target group, as indicated by this distributor, are children between the age of 6-12 years, while their importer has chosen to recommend these products for children between the age of 5 and 14 years. The distributor has assessed that the product does not appeal to small children, since the product cannot be activated, and small children (under the age of 3) do not sit and observe the appearance and expansion of squeezed object. The product does not emit any sound, does not have any effects or moving parts that could catch a small child's attention. The distributor has assessed that the color and design may possibly make a difference and expects that squishies looking like food products could appeal to small children, if the toys are visible to a child under the age of 3. According to the importer, the selection of material for the product may result in the formation of small parts, which is why the use by small children advised against as indicated on the packaging ("not suitable for children under 3 years).

Playing with these products is expected to be of long duration for the target group, i.e. play for hours by comparing the product designs and observing the squeezing and reformation of the original form. The speed for reformation is of main importance for the play, since products taking longer to return to their original shape are preferred. According to importers, roleplay with squishies, which is expected have a longer duration, are also a widespread activity.

Products are undoubtedly seen by both the distributor and its importers as collectibles, and the distributor is aware of a customer who purchased 65 squishies. The Danish distributor still observes a demand for these products, but it seems to be declining. According to the respective distributor's importer, there is still growth on the international market.

Importer 2

A Danish importer of squishies, who covers the Nordic market, screened a long list of possible producers when introducing the product to the market. In the screening, the producers were especially assessed according to the quality of the documentation, they forward, and their professionalism when handling requirements regarding chemical contents. This also relates to requirements that exceed the requirements determined by the legislation. The importer has been in contact with 10-12 producers, which all have their products produced in China, but only a few delivered the required documentation, among others on chemical contents, and could be approved as suppliers. This importer has currently suspended its import as the Danish Safety Technology Authority investigates the products, including investigations regarding possible special safety requirements for this type of products.

The producers have confirmed the importer that the products meet the relevant regulations, e.g. REACH and the special regulations to toys, including the contents of phthalates. Further-

more, it is confirmed that products comply with standards EN71-1 to 71-3. The producers have confirmed that squishies consist of PUR, and that the material contains typical additives that are commonly expected for this type of material, as well as different amine-based catalysts and foaming agents. This importer distributes only squishies with no added fragrance due to customer demands. Thus, the importer does not have a specific knowledge of fragrances that are typically used in squishies.

According to the importer's opinion, the omission of fragrance in the products has resulted in squishies with a strong chemical smell, which–according to the producers–is characteristic for the material (PUR). However, the smell does raise concern among consumers, which is why the importer has received several inquiries regarding this, either directly from the consumers or via distributors. Furthermore, the importer has received 5-7 inquiries regarding concerns about smell via the consumer app "Tjek kemien". Never before has this importer received inquiries via "Tjek kemien", but the importer has concluded that it is due to the chemical smell, and he has not experienced other inquiries relating to specifically health-related complaints. In this relation, the importer suggests degassing the products before use.

According to this importer, a typical target group for squishies is between the age of 8-14. The trend started among older children in the age group, and the younger children are now following the trend, which is a typical pattern. The products are marked with a label 6+, and the importer will not deny the possibility that also smaller children would play with squishies. However, it is not suggested by the importer, whose own experience further indicate that the recommended age group matches the market trend.

The importer has no direct experience with children's play with products, but considers it likely that children play with each squishy for about 15 min. at a time by squeezing, observing and comparing them to other squishies. New forms and designs of squishies are being produced continuously, and the current trends, according to this importer, is more detailed squishy designs, which are more attractive to older children, e.g. for using squishies in roleplays. The importer's products are definitely seen to be collectibles, and it is considered that each child could easily have 5-10 in their possession, and that is not unusual that a child may have up to 30-40 squishies.

New squishy figures are introduced all the time, e.g. as collectibles, and the number of sold products currently exceeds 100,000 pcs. in total. The demand among some of the importer's customers is considered to be declining. The sales of squishies started at toy retailers, but has now spread to many types of retailers and, hence, the total sales figures could still be on the increase.

2.4 Availability of squishies and indicated target group

In relation to this study, squishies have been found at nine out of more than 15 investigated distributors selling products in one or more physical shops in Denmark (toy shops and other shops expected to sell toys) and/or online shops in both Denmark and non-EU countries, where squishies can e.g. be purchased directly from China. The aim of this study has not been to provide a full overview of sales points for squishies, and it is expected that, besides these nine shops, there is a number of other retailers, especially online. At the time of purchase for this survey, the demand for some types of squishies was very high (February – March 2018), meaning it was found not uncommon that products marketed on online shops were soon sold out.

This project has only focused on those squishies aimed at children, i.e. which typically appeal to children due to their design. Squishies can be found in many different sizes, colors and models. They come in different series, which can be collected, and in editions that are rare or

hard to find. For instance, squishies can be formed as cakes, fruit and cute animals, and they may have been added fragrance.

Squishies with country of production given all originate in China, which confirms the information received from the interviewed importers and distributors. Thus, the products of Chinese origin and of low price are highly prioritized in relation to purchase of samples. Some websites provide information that certain squishies have a specific smell upon delivery, but that the smell disappears with time and use and that the smell is not hazardous[1]. In addition, it is stated that squishies are easy to use and that the product can, thus, be used by small children, except children under the age of 3, since the product may contain small parts[2].

2.5 Material type and expected content of fragrance and other volatile organic compounds

Squishy toys are described as being produced from PUR[3], which can be manufactured with the desired properties for *memory foam,* i.e. materials that regain their initial form after being compressed. This is confirmed by the interviewed importers and distributors, who do not have the knowledge of the use of other material types for squishies. However, it cannot be excluded that other forms of polymer materials may be used by other manufacturers.

In the following, monomers, initiators, catalysts and typical additives will be reviewed with focus on substances in the categories of fragrances or other volatile organic compounds.

Monomers, initiators and catalysts

Polyurethane (PUR) generally consists of di- or tripolyisocyanate, which has reacted with a polyol. Both isocyanates and polyols applied in the production of PUR contain on average two or more functional groups in order to create the correct three-dimensional network and cross-linking of the material. The reaction is typically catalyzed by tertiary amines such as 1,4-diazabicyclooctane (CAS no. 280-57-9), dimethylcyclohexylamine (CAS no. 98-94-2), dimethylethanolamine (DMEA) and bis-(2-dimethylaminoethyl) ether (CAS no. 3033-62-3) (Adam et al., 2005). Some amines have in their pure form problematic health-related properties, e.g. they may cause heavy skin burns and eye damage (H314). The choice of catalysts determines the properties of PUR foam, and besides the traditional catalysts, a range of specialized catalysts have been developed (Soto et al., 2014). It is expected that these amines are physically and/or chemically linked in polymer material after termination of the reaction. The release of these substances upon normal usage is expected to be limited; however, dependent on the physicochemical properties of the respective amine.

The properties of PUR foam are to a high degree affected by the type of isocyanates and polyols that are applied in production. There are many accessible isocyanates and polyols as well as additives and process requirements that may vary in relation to PUR production and which contribute to the wide range of properties of PUR, e.g. foam which retakes its form (so-called memory foam or LR/Low-resilience PU).

The mostly applied isocyanates are the aromatic isocyanates diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI), which are more reactive than aliphatic isocyanates such as hexamethylene diisocyanate (HDI) or isoforon diisocyanate (IPDI) (Randal and Lee, 2002). Most isocyanates are difunctional, meaning they have two isocyanate groups per molecule.

[1] E.g. Squishyshoppen.dk – *Hvad er en Squishy eller Squishies* (What is a Squishy or Squishies) [ed.: The page and contents have been removed].

[2] According to descriptions on the retailers' web pages that have later been removed.

[3] https://www.tabletcovers.dk/products/squishy-gadget-large-blue-koala-lysebla states "material: elastic polyurethane" – reached 2018.04.23.

Isocyanates are severely irritant to the respiratory tract, and their possible existence in squishies may cause a potential risk in relation to their use.

Polyols are polymers that on average have two or more hydroxyl groups per molecule. The length of the polyol chain and its functionality contribute to the properties of the final polymer material. The initiators, such as ethylenediamine and triethanolamine, are applied in the production of some polyols. In the same way, diacids of high purity and glycols are used, such as adipic acid (CAS no. 124-04-9) and 1,4-butandiole (CAS no. 110-63-4), to produce some conventional polyols for PUR.

Typical additives

The production of PUR foam requires the formation of a gas simultaneously with the process of polymerization to inflate the material. The gas can be e.g. carbon dioxide either generated by reacting isocyanate with water (a process catalyzed by tertiary amines) or added as gas. The required gas for inflation may also form by volatile compounds evaporating due to increased temperatures caused by the exothermic polymerization reaction. It has been observed that such volatile compounds have been used for foam formation, e.g. 1,1,1,3,3-pentafluoropropane and 1,1,1,2-tetrafluorethane or carbon hydrides, such as n-pentane (Feske, 2004).

Other additives are typically added as well, e.g. surface-active substances designed to create foam with the preferred properties. The examples surface-active substances used in such processes include polydimethylsiloxane-polyoxyalkylene block copolymers, silicone oils and nonylphenolethoxylates, which are, however, not typically volatile compounds.

Traditionally, flame retardants are added to many types of PUR foam, and in an analysis of bicycle helmets from 2018, the chlorine-/phosphorous-based flame retardants TCPP, TDCP, TIBP, TCEP and TPHP were identified in small amounts (Danish Environmental Protection Agency, 2018). Previous studies have also indicated the use of brominated flame retardants (Danish Environmental Protection Agency, 2014A).

Cross-linking agents and substances that prolong polymer chains are often hydroxyl- and amine-terminated compounds with a low molecular weight, and, hence, they have a significant role determining the properties of PUR. The most important are ethylene glycol, 1,4-butanediol (1,4-BDO or BDO), 1,6-hexandiol, cyclohexanedimethanol and hydroquinone bis(2-hydroxyethyl) ether (HQEE). Diethanolamine and triethanolamine are used in foam to build firmness and add catalytic activity.

Several distributors and suppliers express their concerns regarding the possible contents of phthalates in squishy toys. Phthalates are also listed by suppliers as possible plasticizing agents for PUR (Eastman, 2014). Phthalates, such as bis(2-ethylhexyl) phthalate (DEHP), diisononyl phthalate (DINP), dibutyl phthalate (DBP) and bis(2-ethylhexyl) isophthalate (iso-DEHP), have been previously found in PUR matrasses for children (Brandon et al., 2015). The presence of phthalates has also been reported earlier in surveys of carpets by the Danish Environmental Protection Agency, where they could originate from the foam material on the backside, which could e.g. be PUR (Danish Environmental Protection Agency, 2016B). Health-related effects of some phthalates include CMR and hormone-disrupting effects.

Other volatile organic compounds (VOCs) that may be present in PUR foam include e.g. aldehydes, ketones, terpenes and solvents such as xylene, styrene, toluene, dimethylformamide, dichloromethane and benzene. Previously, these compounds/compound groups have been identified in emissions from carpets with foam backsides (Danish Environmental Protection Agency, 2016B). According to the survey of carpets, some these compounds (e.g. aldehydes) may cause obnoxious smells to the annoyance of consumers with varying odor threshold, i.e.

the substance concentration in air, where it is possible to register the smell. Some of the VOCs may also result in health-related effects (e.g. styrene, which is a CMR substance).

On many of the identified products, the content of fragrances (e.g. 'scented') and flavor (e.g. 'contains non-toxic additives designed to taste bad') has been indicated, but no specific substances in products have been stated. In a survey of allergens in products for children carried out by the Danish Environmental Protection Agency, several cosmetic products and toys were analyzed. The analyses showed contents of, among others, terpineol, vanillin, benzaldehyde and camphor as well as limonene and linalool (Danish Environmental Protection Agency, 2016C). Due to the characteristic odor of squishy products, it is expected that some types do contain fragrances that may cause obnoxious smells and odors to the annoyance of consumers. Further, for many fragrances there is a risk that they are allergens (SCCS, 2012).

2.6 Purchase of samples

As a preparation to this study, 43 different squishies (2-3 of each product) were purchased. Two of these were, however, deselected by initiation of the project; one sample deselected due to the purchased product examples not being identical (the squishy itself was inside a plastic cup, which could contain different types of squishies), and the other sample deselected since the purchased product examples had considerably different colors.

The price range for products was between 7 - 150 DKK with an average price of approx. 60 DKK. The purchase of products has been affected by the great demand for squishies, and a few of the identified products on the market were sold-out during the purchase period, while new products have emerged. Thus, the purchase has been limited to products available during the purchase period. The main aim has been to ensure that the number of products purchased from Danish and foreign webshops selling low-price products from Chinese manufacturers constitute a majority of all purchased product samples. The actual proportion was slightly different, but still with the majority of products was purchased in webshops, see TABLE 1.

Criteria for selection of samples for purchase:

- *representativity referring to point of purchase*: products have been purchased to match the proportions described in TABLE 1.
- *representativity referring to price*: products represent different price levels.
- *material*: the purchased products have been made of slow-rising foam, also called memory foam, which is deformed upon pressure and then slowly regains its original form. It is assumed that the material is PUR foam. Thus, products of e.g. PVC or silicone are not part of the survey.
- *packaging*: as far as possible, it is prioritized that products are inside a packaging upon purchase, since it ensures the highest possible presence of volatile or semi-volatile chemical substances and can, thus, be expected to constitute the worst-case scenario regarding children's exposure to the substances.
- *scent/odor*: it is prioritized that products have a scent/odor, since fragrances and other chemical substances that emit odor are the main priority in this study.
- *appealing to children and popularity:* squishies that appeal to children, i.e. products with e.g. cute appearance, faces with large eyes and/or forms that are appealing for playing or hugging, are selected. Further, popular products, i.e. indicated as for example "very popular/best-selling" on company's website, are seeked to be prioritized.
- *"equal appearance"*: In foreign webshops distributing low-price products from Chinese manufacturers, squishies that in form and appearance seem comparable to squishies available in Danish webshops or physical shops are seeked to be prioritized to investigate if the products may also be comparable regarding content and emission of chemical substances.

TABLE 1. Overview of distribution of purchased products in percentage for different distributor types.

Type of retailer	Aim for sample representation by purchase	Actual sample representation
Physical Danish shops (e.g. supermarkets, toy shops, other toy distributors, e.g. book shops)	10-20 %	30 %
Danish webshops	45-55 %	47 %
Webshops from non-EU countries (Chinese manufacturers)	30-35 %	23 %

* Due to very long delivery times, the sample proportion from non-EU webshops is lower than the targeted proportion (23 % vs. 30-35 %).

The packaging and labelling of the purchased products vary considerably. A number of the products are delivered in unlabeled plastic bags (especially those received directly from China) with e.g. no indication of a possible CE label of the product and if the product is suitable for children under the age of 3.

2.7 Summary of the survey

The selection of squishies available on the Danish market is vast, and for the largest part of the identified products, China is indicated as the producing country.

According to importers and distributors, the required documentation on compliance to legislation is delivered through the supplier chain. Some of the contacted players actively set requirements regarding which fragrances may be used in their products, and some even require that the products contain no fragrances, which the manufacturers have complied with. On some of the purchased products, it has been indicated that they are scented, and, thus, some of the squishies on the Danish market are expected to contain fragrances. Products with comparable design have been found on the market from different retailers and with a widely varying odor/smell.

Besides the fragrances, the focus among many suppliers has been on the contents of phthalates, while none of the contacted players have mentioned concerns regarding the potential contents of residue monomers or additives such as solvents or foaming agents used in polymer production. The presence of foaming agents and catalysts used in the polymerization process are, however, indicated in the technical documentation from one manufacturer.

The smell from products has caused several inquiries to importers/distributors from concerned consumers; however, no specific examples of health-related discomfort thereof. The smell is allegedly characteristic for the used polymer material according to a Chinese manufacturer. Based on the collected information and the material properties, the material is highly likely to be PUR.

The products are considered collectibles, and it is normal that children own many different squishies (5-10). Children that are eager collectors are expected to have an even higher number (between 30 and up to 200 pcs. for the largest collectors, as indicated by distributors/importers). The most typical use of squishies is described to be active play, where products are squeezed, observed and compared to other squishies while returning to their original shape. Therefore, one of the contacted distributors considers it possible that playing with squishies involves long-term skin contact compared to other types of toys. The contacted

importers and distributors have determined the target group for products in general to be from approx. 6 years and above, which has been confirmed by the actual sales figures of one Danish distributor; and the nature of the marketing material also indicates this target group. Some types of squishies are expected to be used for roleplays, which also can last for longer periods of time. A use time from 15 minutes at a time and a total use time of up to several hours a day is, thus, considered to be realistic for the target group.

3. Exposure scenarios

Based on the information collected in this survey on the expected use of squishy toys, the following chapter offers a description of the exposure scenarios for children's exposure to substances emitted from toys during use. A range of different scenarios can be presented. The scenarios described here are considered the most relevant in relation to the accessible knowledge before execution of chemical analyses of content and emission of substances.

3.1 Presentation of exposure scenarios

The description of an exposure scenario for squishy toys is based on a real-life worst-case scenario for a child's use of a squishy (see chapter 2.3) and on the principles described in ECHA (2016) regarding consumer exposure. When assessing the products' safety, it is important to ensure that also unforeseen use is included in considerations and assessments. Hence, it is considered relevant as a worst-case scenario to include the possible small children's usage of the toys. It is not deemed impossible that children under the age of 3 years, especially younger siblings, would use the toys due to their appealing appearance and/or due to the sensory experiences they offer.

Besides this scenario, a typical scenario is also described for the target group of squishies that primarily includes children at the age of 6 and above.

3.1.1 Assessment of worst-case scenario

The scenario with the highest possible direct exposure from squishy toys is assessed to be a young 3-year-old child, who sleeps while hugging the squishy toy, and where the toy is very close to the child's nose and mouth. This scenario has the highest possible potential partly for skin contact (migration to child's palms) and partly for inhalation of vapors emitted from the toy.

A scenario for a 3-year-old is assessed to lead to considerably higher exposure to migrating and emitting substances compared to a scenario for e.g. exposure of an older child (see scenario for typical use below).

A realistic worst-case scenario for a young child's exposure may be described using the following relevant parameters:

Body weight, child 3 years old: 14 kg

ECHA (2016) refers to RIVM (2014) that indicate a body weight of 12.4 kg for a 2-3-year-old and 15.7 kg for 3-6-year-olds based on the 25 percentile in the two age groups, which is why an average for these two age groups of 14 kg is applied for a 3-year-old child.

Inhalation volume during rest/sleep: 0.18 m^3/hour

ECHA (2016) refers to RIVM (2014) that indicate an inhalation volume during resting at 0.12 m^3 air/hour for 1-3-year-old children and 0.24 m^3 air/hour for 4-6-year-olds, which is why an average for these two age groups of 0.18 m^3 air/hour is applied for a 3-year-old child.

Duration of exposure: 10 hours/day
This is considered a pragmatic worst-case estimate for a child lying and hugging the toy close to her body during sleep.

Surface area of two palms in contact with the squishy: 150 cm^2
RIVM (2016) indicates 270 cm^2 and 330 cm^2 as palm surface area for 2-3-year-olds and 3-6-year-olds, respectively. The average of 300 cm^2 is thus applied to 3-year-olds. 50 % of this value is applied for palms.

From this, the child's exposure may be calculated as follows:

Inhalation (systemic intake, mg/kg lgv/d) =
measured chamber concentration mg/m^3 x 0.18 m^3/hour x 10 hours/d/14 kg

Inhalation (local exposure eyes/respiratory tract, mg/m^3) =
measured chamber concentration mg/m^3

Skin exposure + sucking (mg/kg lgv/d) =
migration/cm^2 during 10 hours x 150 cm^2/14 kg

In this worst-case context, it is not considered relevant to specifically separate skin exposure and sucking, as it is assumed that the entire migrating amount from the squishy toy is transferred to hands, from where the substance is absorbed through skin or may be absorbed by sucking of hands.

The worst-case scenario will be used for risk assessment of the analysis results from the selected squishy toys, i.e. emission and migration of chemical substances from the toys. With the results of risk assessments, the uncertainties and limitations for applying this worst-case scenario will be assessed together with other uncertainties that are part of the risk assessment, including the uncertainties regarding hazard assessment of each substance.

3.1.2 Scenario for typical use

The information acquired from importers and distributors in chapter 2.2 states that the typical target group is children between the age of 6-12. Generally, the product is considered not to be targeted young children (under 3 years).

Typical playing with the products is expected to involve squeezing and observing the reestablishment of its original form. The products are often squeezed in hands and may be used for roleplays, where many squishies are often involved. Due to the squeezing function, longer-term skin contact is considered to be realistic for this type of product compared to other types of toys.

Some children consider the products collectibles, and the squishies are available both in series, where more designs can be collected, and the so-called blind bags, where one has a chance to acquire rare designs. Thus, it is not considered unusual that children own up to 30-40 squishies.

As a worst-case scenario for the typical use (for target group down to 6 years) based on emission measurements, that/those squishies with the highest emission will be selected, and an equilibrium concentration in the room will be calculated with an assumption that there are 40 squishies in the room. A residence time of 15 hours in the room is applied. For skin contact, a daily play of 2 hours with squishy toys is assumed.

A realistic worst-case scenario for a typical use of squishies may be described with the following relevant parameters:

Body weight, child – 6 years: 20 kg
ECHA (2016) refers to RIVM (2014) that indicate a body weight of 15.7 kg for 3-6-year-olds and 24.3 kg for 6-11-year-olds based on the 25 percentile in the two age groups, which is why an average for these two age groups of 20 kg is applied for a 6-year-old child.

Child's Room, volume: 17.4 m^3
The Danish Environmental Protection Agency (2016) has previously analyzed exposure in children's rooms based on this size of a child's room (corresponding to a floor space of 7 m^2).

Air change: 0.5 times per hour (corresponding to 8.7 m^3 per hour)
According to guidelines in Nordtest Metode NT Build 482.

Number of squishies emitting in the room: 40 pcs.

Child's inhalation volume per day: 12.5 m^3
ECHA (2016) refers to RIVM (2014) that has indicated an inhalation volume during 24 hours of 11 m^3 air for 4-6-year-olds and 14 m^3 air for 7-9-year-olds, which is why an average for these two age groups of 12.5 m^3 is applied for a 6-year-old child.

Duration of exposure: *15 hours/day by inhaling*
2 hours by skin contact

Surface area of two palms in contact with the squishy: 230 cm^2
(460 cm^2 is indicated as the surface area for two hands for 6-11-year-old children (RIVM 2016). 50 % of this value is applied for palms).

From this, a child's exposure may be calculated as follows:

Inhalation (systemic intake, mg/kg lgv/d) =
calculated room concentration mg/m^3 x 12,5 m^3/day/20 kg

Inhalation (local exposure eyes/respiratory tract, mg/m^3) =
calculated room concentration mg/m^3

Skin exposure + sucking (mg/kg lgv/d) =
migration/cm^2 during 2 hours x 214 cm^2/20 kg

4. Analyses of squishy toys

The aim of the analysis of squishies is to determine the contents and emission of relevant chemical substances for the subsequent risk assessment.

Different squishies were selected for the chemical analyses. Many squishies have been declared having added fragrance, which is why the products are analyzed with a focus on the fragrances considered to be allergenic by the EU Scientific Committee for Consumer Safety (SCCS, 2012). If children are exposed to allergenic substances, there is a risk that they will develop allergy, which is why there has been a special focus on this type of substances. The specific fragrances, which are detected by the methods selected in this analysis, have been chosen since they are substances typically used industrially, are easily commercially available and there are reference standards available for the analysis. In the introductory survey of squishy toys, other substances that may cause a perfumed chemical odor have been identified. For this reason, other emitting and migrating substances from squishies are of interest, e.g. solvents, foaming agents, flame retardants, preservatives and residue monomers, which may contribute to the odor/smell of squishies and the risk of exposure.

Based on introductory chemical analyses and screenings, it is decided, which quantitative analyses are to be performed in order to assess the risk of playing with the purchased products. A quantitative determination of emitting and migrating fragrances and other substances identified in the introductory screenings and considered to be problematic for a child's health is carried out. The analyses are undertaken, so that migration and emission times are realistic in relation to the exposure scenarios, so that they can be used for risk assessments.

4.1 Analysis program

In this study, an analysis program has been determined for selected squishies based on the established exposure scenarios and the knowledge acquired in the survey regarding material type and expected substance content in squishy toys.

The analysis program was created in cooperation with Danish Environmental Protection Agency and consists of two steps: 1) a screening including analysis of substance content and emission in climate chambers, and 2) a supplementing material identification. Based on the results of the introductory screening, quantitative analyses on substances that emit in the climate chamber and are released by migration were performed. The analysis program scheme is illustrated in FIGURE 1.

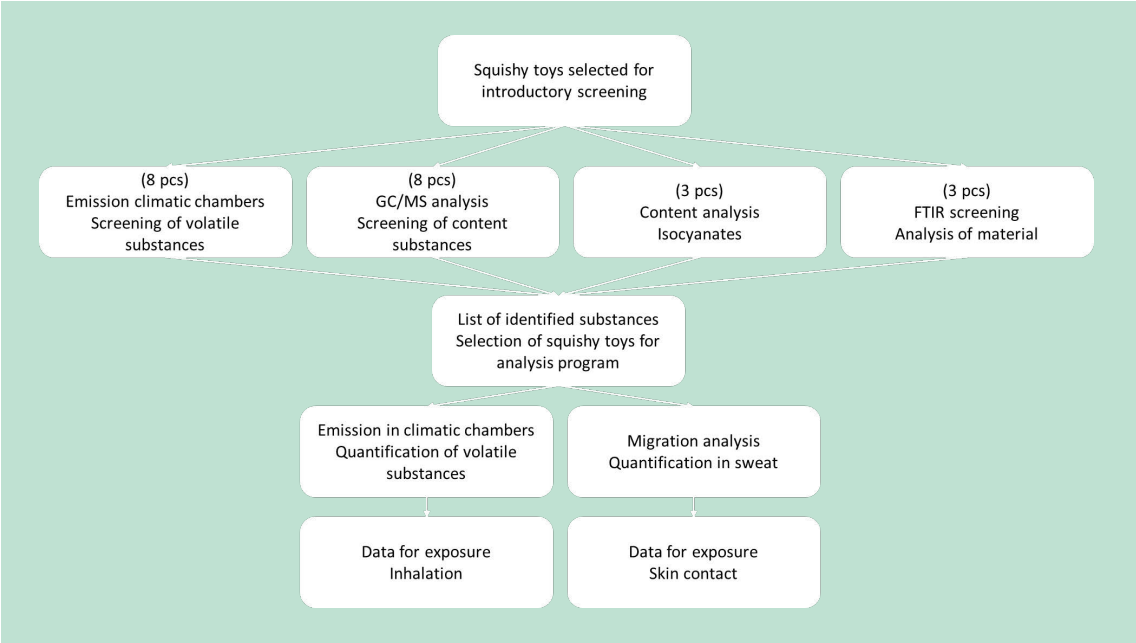

FIGURE 1. Graphic representation of proposals to analysis program in two stages.

4.2 Selection of samples and analyses for introductory screening

By initiation of the analysis, eight products were selected using the same criteria as for purchase of squishies for the introductory analysis of relevant substances present in the products (screening with GC/MS) and emission of volatile chemical substances (climatic chamber test). These analysis methods were chosen due to the project's focus on volatile organic compounds, and it has been chosen that the same eight products will be analyzed for content and emission in order to be able to compare results and assess the emission from products, as far as possible.

The screening analyses by GC/MS cover an extensive number of volatile and semi-volatile organic substances. The method is suitable for aromatic and generally non-polar organic substances with boiling points between 60°C and 500°C, depending on the specific substance. The list of banned fragrances in toys (Appendix 1, TABLE 15) shows that substances belong to many different chemical substance categories, including monoterpenes, aldehydes, alcohols, acids and esters, which all are volatile organic compounds (VOC).

Many fragrances are categorized as allergenic. 26 fragrances, which, among others, are declarable in cosmetic products due to allergenic effects (SCCS, 2012) are likewise included in the 55 regulated substances in Danish Statutory Order on Toys and are either banned or declarable in toys (BEK no. 309 of 3/4/2017). 15 of these substances are banned in toys, and the remaining 11 substances must be declared if they are present in concentrations above 100 mg/kg (see Appendix 1, TABLE 15 with *). SCCS have identified in total 82 fragrance substances as known contact allergens based on clinical experience (SCCS, 2012).

Low-molecular weight aldehydes with 1 to 4 carbon (C1-C4) are very volatile (VVOC) and can, thus, not be analyzed with the same method as VOCs. It has been decided to include analysis of C1-C4-aldehydes in the introductory analysis, since they are both relevant to smell and have a classification of relevance to exposure to children.

Eight squishies have been selected for introductory screening of both substances present in the products and substances that emit in order to create an overview of, which substances could be relevant for further studies. These eight samples have been selected to best possible

represent the sample representation, i.e. point of sales, as decided when purchasing the products, chapter 2.6. Four squishies purchased in physical Danish shops, 2 squishies purchased in Danish webshops and 2 squishies purchased in webshops from non-EU countries (Chinese manufacturers) were selected. In the sample selection, more squishies are from physical Danish shops than the original aim prescribed (50 % against 10-20 %), which is partly due to the very long delivery times from webshops in non-EU countries and partly due to other priority parameters, including scent and price of samples. The eight products and the analyses performed are listed in TABLE 2. Three of the eight products were selected for identification of material type (IR characterization). These three selected samples were further analyzed for isocyanates, which may occur as residue monomers in PUR material and are highly irritant to the respiratory tract.

One product is marked with 'Contains non-toxic additive designed to taste bad', but has no indication of the specific substance (024). Four products are marked with a warning that they may not be eaten or are not food products (048, 051, 054, 056), and two products indicate that they are 'scented' (051, 054). Additionally, three products have been marked to have unique properties such as 'slow rising' (051, 054) and 'improved formula' (024).

TABLE 2. Selected products for screening analyses.

Product No.	Analysis completed	Purchase price in DKK	Weight (grams)	Distributor type
024	Climatic chamber test GC/MS-screening	150.00	94	Physical Danish shop
038	Climatic chamber test GC/MS-screening IR Isocyanate analysis	69.00	63	Danish webshop
043	Climatic chamber test GC/MS-screening	49.00	116	Non-EU webshop
048	Climatic chamber test GC/MS-screening	79.00	102	Danish webshop
051	Climatic chamber test GC/MS-screening	60.00	110	Physical Danish shop
054	Climatic chamber test GC/MS-screening	70.00	52	Physical Danish shop
056	Climatic chamber test GC/MS-screening IR Isocyanate analysis	49.95	45	Physical Danish shop
061	Climatic chamber test GC/MS-screening IR Isocyanate analysis	13.30	76	Non-EU webshop

4.3 Introductory analyses

4.3.1 Material identification with FTIR

Objective

The objective of the analysis is to confirm that the applied material is PUR.

Sample preparation

A piece of foam without painting has been cut out of each of the three squishies (038, 056 and 061). Measurements were performed directly on foam pieces without additional sample preparation.

Analysis method

FTIR spectroscopy was carried out on a 4500a FTIR instrument from Agilent Technologies. Measurements were performed in three locations on the foam on each of the three samples. The spectra were recorded using the ATR (attenuated total reflectance) method with 32 repetitions and a spectral solution of 8 cm^{-1}. Search has been conducted in reference spectra from databases from Agilent, Sigma Aldrich and Smiths Detection.

Results

The spectra from the different locations on each sample are comparable, which makes it probable that the samples are relatively homogeneous. Furthermore, the spectra from the three different samples are almost identical and have a good consistency with a reference spectrum of polyurethane foam, see Figure 3 to Figure 5 in Appendix 3.

4.3.2 Determination of isocyanates

Objective

Isocyanates are used for production of PUR foam. Thus, there is risk that this type of organic compounds may be found as residue monomers in squishy toys made of PUR foam. Three selected squishies are by FTIR confirmed to contain PUR foam. The three squishies have been analyzed for five specific isocyanates that, according to experience, may appear in PUR foam materials.

Sample preparation

Partial samples of the material were weighed out and subsequently extracted with dichloromethane with added internal standard. Partial samples were chosen to contain both the surface of squishy figure and the internal material. Next, extracted isocyanates were derivatized with 9-(N-methylamino-methyl)anthracene (MAMA), which activates the substances for fluorescence detection (FLD). Spiking has been carried out on sample material to examine the presence of positive and negative interferences in the extraction liquid as a result of sample preparation, so-called matrix effects.

Analysis method

The applied analysis method is based on the standard ISO 13130-8 (2004), which has been developed for the analysis of foam materials, e.g. such as PUR foam. The analysis of extracts of squishy toys is performed with HPLC-FLD and quantification of calibration curves by derivatization of the examined isocyanates.

The detection limit for each isocyanate is 0.02 mg/kg. The relative standard deviation for determination in triplicate is normally < 5 % for homogeneous materials and < 20 % for products consisting of several materials and/or decorative surface coating. For analysis of squishy toys, the relative standard deviation is observed from 7 to 51 %, which assign unknown matrix effects from the sample material.

Results

The contents of five different isocyanates in three selected squishies are given in TABLE 3. The results given are the average of three measurements. For two of the isocyanates, the content has been indicated as a sum, as the chromatographic separation of the two substances was unsatisfactory.

TABLE 3. Results from the analysis of selected isocyanates in three squishies. LOD = limit of detection.

Unit: mg/kg		Product no.		
Isocyanate	**CAS no.**	**038**	**056**	**061**
Sum of 2,6-TDI and HDI	91-08-7 and 822-06-0	0.18	<LOD	<LOD
2,4-TDI	584-84-9	0.59	<LOD	<LOD
4,4-MDI	101-68-8	0.06	0.13	0.08
4,4-HMDI	5124-30-1	0.65	0.24	0.56
SUM of isocyanates	-	1.5	0.4	0.6

During the analysis, it was noticed that the extract was cloudy. After centrifugation, the extract a separate, liquid phase was isolated, but not analyzed further. According to experience, extracts from pure PUR foam materials are clear. The isolated phase abated was located below the dichloromethane phase and was fluid. Upon visual observation, it was determined that this phase constituted less than 5% of the total volume.

Retrieval tests for individual isocyanates have been carried out for all analyzed squishies by adding a known concentration of the individual isocyanates during the extraction. The results showed a great variation in the analyzed contents of isocyanates. This variation refers to the high complexity of the analyzed material. Phase separation may lead to an undetermined insecurity in the indicated results. The insecurity cannot be determined within this project, and the phase separation may result in the underestimation of the content of isocyanate, since the partition relation between phases is not fixed.

4.3.3 Screening of content by extraction and GC/MS

Objective

GC/MS screening is a suitable tool for the introductory assessment of a range of different material and product types, including squishies. Screening has been performed with an aim to identify substances that are present at a level relevant for exposure via skin contact or oral intake of the products. GC/MS screening gives an overview of the contents of many organic substances that may have a physiological effect. This could be e.g. fragrances, organic solvents, flame retardants and monomers.

Sample preparation
Partial samples of approx. 1.0 grams (precisely weighed) were divided and extracted during mechanical shaking with 40 ml extraction liquid consisting of a 1:4 mixture of methanol and dichloromethane with added internal standards. The samples were degraded by the extraction except for a small amount of "dust".

Analysis method
The extract was analyzed using gas chromatography combined with mass-selective detection (GC/MS) with a DB-XLB 60m GC column. The content of volatile and semi-volatile organic substances in products may be identified using this method, as the actual mass spectra are compared with mass spectra in the NIST library, i.e. a database with mass spectra for more than 500,000 chemical compounds. For the examination of consistency between a given spectrum and the NIST library, a hit rate is indicated between the unknown substances and the library reference. The hit rate is a mathematical calculation on how close the consistency is between a reference spectrum of a substance in the NIST library and the spectrum of the respective substance in the analysis. The hit rate is calculated based on the relative intensity between the ten most intensive masses measured by mass spectrometry and the ten most intensive masses for all substances in the library. The identification from the NIST library is considered indicative, and, for this reason, substance-specific analysis with reference substances for definitive positive identification of content substances should be performed. Identification based on the NIST library may form the basis for an assessment of whether it is relevant to proceed with a migration test for specific volatile and/or semi-volatile organic substances.

The content of the identified content substances has been calculated as naphthalene equivalents, and the quantification of each component must, thus, be considered as being semi-quantitative, since the component response factor during the analysis may vary from the response factor of naphthalene.

The detection limit has been estimated to 5 - 100 mg/kg, depending on the substance. Some substances will not respond to the chosen analysis equipment. The uncertainty of the analysis has been estimated to a general 30% RSD and is very dependent on the substance.

Results
Gas chromatography analysis has been carried out after dissolving squishy toys in methanol/dichloromethane. Squishies were dissolved, but gave a solid residue product of particles in the liquid. Since PUR is not entirely dissolved in the methanol/dichloromethane mixture, this is an indication that the polymer material used for squishies does not only contain PUR elements, but may also contain side- or backbones of other polymer types.

By extraction, the polymer dissolves and is degraded. This may cause detection of substances, e.g. the amine-containing compounds possibly used as additives to achieve a certain mechanical property, but which are not accessible for release for used migration substances, as these do not degrade the material as do the solvent used for extraction.

The results for contents analysis are presented in Appendix 4.1 – 4.3. Based on a hit rate and assessment, all identifications are categorized under category 1 to 3. Category 1 are substances that are identified with certainty from the NIST library (high hit rate) and confirmed by specialist evaluation. Category 2 are substances evaluated to be identified with certainty by a specialist despite minor unconformity with the NIST library compared to category 1 substances. Category 3 are substances with an uncertain identification, i.e. the listed substances are most probably not identified correctly, but are substances with similar molecular structure and chemical functionality as the listed substances.

Approx. 100 peaks from each of the eight squishies has been evaluated, and it was possible with great certainty to identify (category 1) 35 substances. 16 substances could be evaluated as probably being identified with certainty (category 2). The uncertainty of category 2 could be due to e.g. co-elution with other content substances or a need for manual identification of the degradation. Thus, it was not possible to achieve direct conformity with the MS library. 22 substances could not be identified, but for each the MS spectrum was comparable with the spectrum of another substance. In other words, these are unidentified substances that have a high chemical resemblance to the listed substance (category 3).

The 35 category 1 substances in are general substances that most probably have origin in the polymer system, where there is a large amount of amine compounds that may have been used as copolymer. This includes dimethylaminoethanol, dimethylformamide, octadecenamide, triethyldiamine and pentamethyldiethyltriamine. Also, triethylphosphate is identified, which is presumably a catalyst residue from the polymerization process. In addition to amine compounds, it can be mentioned that there are phthalates (DEP and DEHP), cyclohexanone and octadecyl di-tert-butyl-4-hydroxyhydrocinnamate (Irganox 1076) in the products. Further, 4,4'-methylenebis benzenamine is identified, which is most probably a monomer residue.

The 16 substances in category 2, which have been determined with no direct consistency with the MS library, differ from the above-mentioned by not being just as widely represented in these eight products. This may be due to them disappearing in the co-elution in some of the samples. There are, among others, fragrances such as versalide and galaxolide, where none of these are among the 55 banned or 11 declarable fragrances regulated in the Directive on toy safety (EC 2009/48/EF), and the organophosphor-based flame retardant tris(2-ethylhexyl) phosphate (TEHP) could be found in one of the products. Furthermore, low concentrations (<10-16 mg/kg) of the reactive radical initiator azobisisobutyronitrile (CAS no. 78-67-1) were found in three of the products, which may indicate an incomplete polymerization during production.

The 22 substances not identified (category 3), but whose chemical functionality could be recognized, are of similar chemical character as the substances mentioned above. An interesting substance that could be mentioned is a substance that resembles 4,4'-methylenebis benzenamine, but which has differences in the MS spectrum that indicate that it must be another substance. Presumably, this is also a monomer residue. Other nameworthy substances are an organophosphorus compound that is presumably a flame retardant found in one of the products, a substance that may be a DBP-phthalate, and a substance that could be an ethyl form of DMAE.

No traces of chlorinated substances have been found, and no decay of the characteristic isotope distribution of chlorine has been observed. Thus, it is assessed that there is probably no chlorinated paraffins in the products (SCCP/MCCP).

Traces of glycol and silicone compounds were found in mass spectra from the contents screenings. These can be e.g. parts of the polymer degraded by dissolution, or they could be free solvents added to achieve specific physical properties for the material.

4.3.4 Screening for emission of volatile substances in climatic chamber

Objective

The objective of the screening is to identify which volatile substances are emitted from entire squishies squeezed during playing. The method finds those substances that are released in indoor climate and, thus, identifies the substances that children may be exposed to.

Method

Emission of volatile substances was carried out in 113 L climatic chambers according to modified version of well-established testing methods (ISO 16000-9 and EN 16516) for emission from materials at 23°C, 50 % RH and an air change of ½ times per hour (0.5 h^{-1}). Sampling and analysis of VOC was performed according to ISO 16000-6, while sampling and analysis of aldehydes was performed in accordance with ISO 16000-3.

An air sample was drawn on the relevant sampling medium with calibrated pumps from the empty chamber, and, moreover, air samples were drawn from the chamber with sample material. The sampling volume has been indicated for each substance group and method. Air samples were collected on calibrated GilAir Plus pumps.

One hour after the squishy had been squeezed 10 times inside the climatic chamber, 0.4 liters and 4 liters of air were collected on Tenax tubes with a flow of 80 mL/min. for VOC analysis as well as 30 liters of air on 2,4-dinitrophenylhydrazine-filter (DNPH) with a flow of 650 mL/min. for carbonyl analysis.

Modified ISO 16000-6 Screening analysis for emitted substances from climatic chamber test with TDS-GC/MS: The collected VOCs on Tenax were thermally desorbed (TDS) and analyzed with gas chromatography combined with mass-selective detection (GC/MS) on a Gerstel-Agilent system with a 60 m DB-5 GC column.

The identity of VOCs was determined by searching Wiley W9N by conformity of the MS spectra of more than 80%. The identified VOCs are quantified and reported as toluene equivalents according to EN 16516 for concentrations above 5 µg/m^3. The actual concentrations of the identified substances and the corresponding toluene equivalents will be close to each other if the response of the identified substances to MS signal resembles the response of toluene. This means that e.g. toluene equivalents for aromatic hydrocarbons, BTEX (benzene, toluene, xylene), which resemble toluene in their response to MS signal, would be close to the actual concentration. Limit of detection (LOD) is dependent on the particular substance, but is typically 1 - 10 ng on Tenax medium, which corresponds to 0.25 – 2.5 µg/m^3 in air by collecting 4 liters of air. By collecting 0.4 liters of air, the detection limit would be 2.5 - 25 µg/m^3 air. Air samples of low volume are also collected to quantify substances in high concentrations to avoid exceeding the upper quantification limit. In general, polar substances have higher detection limits, and in special cases, as for e.g. dimethyl aminoethanol, it is even above 24 µg/m^3. The analysis uncertainty for VOC depends on the particular substance, but is within 30% (RSD, relative standard deviation).

Modified ISO 16000-3 Detection of volatile carbonyls (aldehydes and ketones) collected on 2,4-dinitrophenylhydrazine-filter (DNPH): the collected carbonyls are derivatized on the filter and eluted with acetonitrile. Following, they are analyzed with HPLC with UV detection, identified by retention time and UV spectrum, and quantified using calibrated reference substances. The detection limits (LOD) are 0.03 µg for formaldehyde, acetaldehyde, butyraldehyde and acrolein and 0.05 µg for propanal and crotonaldehyde on DNPH medium. Analysis uncertainty for carbonyls is 7.5 % (RSD, relative standard deviation).

Results

The results for emission analysis of volatile organic compounds, carbonyls and VOCs are presented in Appendix 5.1 and Appendix 5.2.

Several fragrances have been found in emissions: D-limonene, benzyl alcohol, L-linalool, 3-carene, alpha-pinene and beta-pinene.

N,N-Dimethylformamide (DMF), N,N-dimethylaminoethanol, triethylenediamine, bis(2-(dimethylamino)ethyl) ether, 1,2-ethandiamine and N-[2-(dimethylamino)ethyl]-N,N',N'-trimethyl-cyclohexanone have been found in high concentrations.

The result of the detection of volatile aldehydes is given in TABLE 4. In addition to the established content of aldehyde, 2-butanone has been found in two squishies (043 and 054), which is detected by aldehyde analysis and TDS-GC/MS analysis (see Appendix 5.2) in very high concentrations. 2-Butanone has a carbonyl group that attaches itself to the collection medium (DNPH), and can thus hamper the collection of other aldehydes on DNPH (samples marked with * in TABLE 4).

TABLE 4. Results of aldehyde analysis in air samples.

Unit: µg/m^3		Product number							
Substance	**CAS no.**	**024**	**038**	**043***	**048**	**051**	**054***	**056**	**061**
Formaldehyde	50-00-0	11	23	8,2	3,1	19	4,6	9,7	6,6
Acetaldehyde (ethanal)	75-07-0	6,6	17	27	8,0	30	8,1	18	10
Propanal	123-38-6	1,5	6,4	19	1,9	5.3	5,2	3,3	2,0
Butanal	123-72-8	1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0
Acrolein	107-02-8	< 1,0	< 1,0	< 1,0	4,0	< 1,0	< 1,0	< 1,0	< 1,0
Crotonaldehyde (butenal)	4170-30-3	< 1,7	< 1,7	< 1,7	< 1,7	< 1,7	< 1,7	< 1,7	< 1,7

*The DNPH capacity of the tube is exhausted, meaning the true content may be higher.

4.4 Summary of results from introductory analysis

The material identification shows that squishies consist mainly of PUR foam (Appendix 3). GC/MS screening analysis shows substances that may indicate the presence of a modified PUR that ensures the characteristic texture of squishies. It is supposedly the PUR type LRPu, which is known from e.g. memory-foam products. The material type may be squeezed together, and it will hold its form for a certain period, where after it will slowly return to its original form. The viscoelastic property of the material may be achieved by having fewer cross-linkages and more non-covalent linkages.

Squishies do not exhibit the characteristics of normal PUR products neither at extraction for isocyanate analysis, nor at content screening. The screening analysis at extraction results in a solution and partly degradation of the polymer, which may give rise to detection of substances that are bound physically and/or chemically in the product under normal use and are thus not possible to find in emission or migration analyses. It cannot be excluded that substances have been added to the material in a free form, and, thus, cannot be chemically bound to the polymer network (covalent binding), in order to achieve the specific material properties. Hence, there can be a risk that a certain degree of substances may occur during use depending on the physicochemical properties of each substance.

The results of GC/MS screening are found in Appendix 4. Approx. 100 tops in each of the eight squishies have been analyzed, which allowed identification (category 1) of 35 substances with great certainty, while 16 substances could be considered being definitely identified (category 2). 22 substances could not be identified, but the respective MS spectra were comparable to the spectrum of another substance, i.e. presumably close chemical resemblance with this listed substance (category 3).

The 35 substances in category 1 are mainly substances originating in the polymer system, e.g. amine compounds (dimethylaminoethanol, dimethylformamide, octadecenamide, triethyldiamine and pentamethyldiethyltriamine), which are used in the production of polymer material. Triethylphosphate was also found, which is supposedly a catalyst residue from the polymerization process. There are also phthalates (DEP and DEHP), cyclohexanone and octadecyl di-tert-butyl-4-hydroxyhydrocinnamate (Irganox 1076) in these products, as well as 4,4'-methylenebis benzenamine, which may be a monomer residue.

Among the 16 substances in category 2, there are, among others, the fragrances versalide and galaxolide, the organophosphorus-based flame retardant tris(2-ethylhexyl) phosphate (TEHP) and traces of the reactive radical initiator azobisisobutyronitrile, which may indicate an incomplete polymerization during production. Additionally, traces of glycol and silicone compounds were found, which elute in volumes indicating that them as residue of the polymer chain.

The 22 substances not identified (category 3), but for which it was possible to make a guess about their chemical functionality, were of similar chemical character as substances described above, among others, amines, organophosphorus-compounds and phthalates.

No traces of chlorinated substances have been found, and no decay with the characteristic isotope distribution of chlorine could be observed. Thus, it can be assumed that there are no chlorinated paraffins in these products (SCCP/MCCP).

Three selected squishies have been analyzed for five specific isocyanates. The results showed that these residue monomers are found in the analyzed squishies. The complexity of the material influences the analyses, but an estimated worst-case total value of 1.5 mg/kg of isocyanate has been found in the squishy with the highest content.

In six of eight squishies, concentrations of formaldehyde, acetaldehyde, propanal, butanal, acrolein and crotonaldehyde, analyzed by emission, are under 10 µg/m^3 air in the performed screenings for emission of volatile substances (Appendix 5.1).

4.5 Introductory hazard assessment of screening results

To focus the following analytical chemical analysis, it is essential to prioritize measurements and assessments on substances identified in the screening analysis that are of the greatest concern. Thus, an introductory hazard assessment was performed to identify those substances that have the most problematic effects. These substances are pointed out based on their harmonized classification or, if this is not possible, on the substance classification indicated in the REACH registry of substances.

The following classifications are prioritized:

- CMR 1A, 1B, 2
- STOT RE 1,2
- STOT SE 1,2
- Acute tox 1,2,3
- Skin sens 1
- Resp sens 1

Thereafter, the relevance of substances is assessed for further prioritization based on the measured levels as substances with very high levels should also be prioritized even if they do not meet the prioritization for classification. Finally, fragrances are prioritized, as these were chosen as a focus in this project beforehand.

With these criteria for prioritization, the results for content analyses and emission analyses have been evaluated. Appendix 4 indicates the results from content analysis and Appendix 5 includes the results for emission analyses, and in both tables the last column shows the result of the prioritization of each identified substance.

TABLE 5. Prioritized substances and concentration estimate (in naphthalene equivalents) based on GC/MS screening in Appendix 4.

Substance	CAS no.	Hazard class	H-statement	Prioritization	Conc. in screening for contents by GC/MS (mg/kg)
Dioxane	123-01-1	Eye Irrit. 2, STOT SE 3, Carc. 2	H319 H335 H351	Yes, classification	10-29
N,N,-Dimethylaminoethanol	108-01-0	Acute Tox. 4 Acute Tox. 4 Skin Corr. 1B Acute Tox. 4	H302 H312 H314 H332	Yes, high concentration	62-421***
N,N-Dimethylformamide	68-12-2	Acute Tox. 4, Eye Irrit. 2, Acute Tox. 4, Repr. 1B	H312 H319 H332 H360d	Yes, high concentration and classification	24-274
Triethylenediamine	280-57-9	Acute Tox. 4 Skin Irrit. 2 Eye Dam. 1	H302 H315 H318	Yes, high concentration, also emission	119-1198***
Bis(2-(dimethylamino)ethyl)ether	3033-62-3	Acute Tox. 4, Acute Tox. 3, Skin Corr. 1B, Eye Dam. 1, Acut Tox 4	H302 H311 H314 H318 H332	Yes, high concentration	288-448***
Phenol*	108-95-2	Acute Tox. 3, Acute Tox. 3, Skin Corr. 1B, Acute Tox. 3, Muta. 2, STOT RE 2	H301 H311 H314 H331 H341 H373	Yes, classification	10-50***
Linalool	78-70-6	Skin sens 1B	H317	Yes, classification	40-60***
Pentamethyldiethylenetriamine	3030-47-5	Acute Tox. 4, Acute Tox. 3, Skin Corr. 1B	H302 H311 H314	Yes, high concentration	44-754***
2-Ethylhexylacid	149-57-5	Repr 2	H361d	Yes, classification	17-24
4-tert-butylcyclohexyl acetate	32210-23-4	Skin sens 1B	H317	Yes, classification	19-47
3-(4-Isopropylphenyl)-2-methylpropionaldehyde	103-95-7	Skin Irrit. 2, Skin Sens. 1B	H315 H317	Yes, classification	22
BHT (butylated Hydroxy-toluene)	128-37-0	-	-	Yes, endocrine-disrupting	23-91
4,4'-Methylenebis benzenamine	101-77-9	Skin sens 1, Muta 2, Carc 1B, STOT SE 1, STOT RE 2	H317 H341 H350 H370 H373	Yes, classification	64-271
2-(2H-Benzotriazol-2-yl)-5-methylphenol or Drometrizol	4998-48-5 or 2440-22-4	Skin sens 1	H317	Yes, classification	44
Bis(2-ethylhexyl) phthalate (DEHP)**	117-81-7	Repr 1B	H360d	Yes, classification	243
Versalide (fragrance)	88-29-9	-	-	Yes, fragrance	138
Galaxolide (fragrance)	1222-05-5	-	-	Yes, fragrance	20-174

** Phenol has been found in very low concentrations and with interference.*

*** Phthalates have extremely low migration rate to aqueous migration liquids*

****also detected by emission, see Appendix 5*

All these substances are interesting with respect to migration due to relatively low volatility. Especially, substances classified for skin allergy (among others, fragrances) are considered relevant, because even a very low exposure to this type of substances can cause a risk for skin sensitization.

N,N-Dimethylformamide (DMF) and N,N-dimethylaminoethanol (DMAE) were identified in relatively high concentrations in both emission and content analyses, and can, therefore, be of interest regarding migration.

Several amines have been detected, among others, triethylenediamine and pentamethyldiethylenetriamine in screening of the extract from squishies. Amines may be problematic in relation to extraction to organic solvent, as amines may become protonated and, thus, less prone to extraction to an organic solvent. The detection of amine signals that it is present and that it can be analyzed using the method, but it is unknown which matrix effect is present and whether the result is underevaluated compared to the measured response. Finally, the substances have been prioritized for emission analyses, where the substances will most likely be more critical due to possible irritation effects of the vapors.

DEHP is considered of less relevance, since the substance, due to its high fat solubility, does not migrate to artificial sweat during migration test.

According to an overall assessment based on classification, content level identified in screening and taking the analytic method into consideration, the project group agreed with the Danish Environmental Protection Agency to focus on the following substances in the subsequent migration test:

- N,N-dimethylformamide (DMF)
- N,N-dimethylaminoethanol (DMAE)
- fragrances (the 26 declarable in cosmetics)

From the emission analysis in Appendix 5, the substances in TABLE 6 have, thus, been prioritized for further assessment.

TABLE 6. Prioritized emission substances and concentration estimate (in toluene equivalents) according to screening results in Appendix 5.

Substance	CAS no.	Classification	H-statement	Prioritization	Conc. in screening by emission (µ/m^3)
Methylene chloride	75-09-2	Carc. 2	H351	Yes, classification	<5-10
N,N-Dimethylaminoethanol	108-01-0	Acute Tox. 4 Acute Tox. 4 Skin Corr. 1B Acute Tox. 4	H302 H312 H314 H332	Yes, high concentration	96-840*
Toluene	108-88-3	Skin Irrit. 2 Asp. Tox. 1 STOT SE 3 STOT RE 2 Repr. 2	H315 H304 H336 H373 H361d	Yes, classification	7-95
N,N-dimethylformamide	68-12-2	Acute Tox. 4 Eye Irrit. 2	H312 H319	Yes, classification SVHC due to Repr	210-3700*

		Acute Tox. 4 Repr. 1B	H332 H360D	1B.	
Benzene, ethyl-	100-41-4	Acute Tox. 4 Asp. Tox. 1 STOT RE 2	H332 H304 H373 (hearing organs)	Yes, classification	16-340
m-Xylene	108-38-3	Acute Tox. 4 Skin Irrit. 2 Acute Tox. 4	H312 H315 H332	Yes, high concentration	<5-510
p-Xylene	106-42-3	Acute Tox. 4 Skin Irrit. 2 Acute Tox. 4	H312 H315 H332	Yes, high concentration	<5-120
Styrene	100-42-5	Skin Irrit. 2 Eye Irrit. 2 Acute Tox. 4 STOT RE 1 Repr. 2	H315 H319 H332 H372 (hearing organs) H361d	Yes, classification	20-40
o-Xylene	95-47-6	Acute Tox. 4 Skin Irrit. 2 Acute Tox. 4	H312 H315 H332	Yes, high concentration	14-460
Cyclohexanone	108-94-1	Acute Tox. 4	H332	Yes, high concentration	630-6800
Alpha-pinene, (-)-	80-56-8	Acute Tox. 4 Asp. Tox. 1 Skin Irrit. 2 Skin Sens. 1	H302 H304 H315 H317	Yes, classification and odorous substance	7-14
Cyclotetrasiloxane, octamethyl-	556-67-2	Repr. 2	H361f	Yes, classification	1-15
2-Beta-pinene	127-91-3	Asp. Tox. 1 Skin Irrit. 2 Skin Sens. 1B	H304 H315 H317	Yes, classification and odorous substance	<5
Delta 3-Carene	13466-78-9	Asp. Tox. 1 Skin Irrit. 2 Skin Sens. 1	H304 H315 H317	Yes, classification and odorous substance	9-19
Phenol	108-95-2	Acute Tox. 3 Acute Tox. 3 Skin Corr. 1B Acute Tox. 3 Muta. 2 STOT RE 2	H301 H311 H314 H331 H341 H373	Yes, classification	1-10*
Triethylenediamine	280-57-9	Acute Tox. 4 Skin Irrit. 2 Eye Dam. 1	H302 H315 H318	Yes, high concentration	480-920*

*Also detected in GC/MS screening of contents, see Appendix 4.

It must be noted that formaldehyde has not been included in further analysis and assessment. This is related to the fact that this substance has been found in relatively low concentration compared to the existing indoor climate value for formaldehyde of 100 µg/m^3. Furthermore, the analysis of formaldehyde and other very volatile aldehydes require a special analysis method compared to the analysis of the remaining substances.

Fragrances have been found in both emission and extraction analyses in different amounts. Linalool has been found by both extraction and emission, while pinene, carene and limonene have been primarily found in emission analyses. The latter has been found in low concentrations, which is most likely the main reason why they are not found by extraction.

4.6 Choice of samples and methods for quantitative analysis of selected substances

It has not been possible to include all substances with the prioritized classification. Thus, an analysis program including quantitative analyses of emissions in climatic chamber and qualitative detection of migration of selected substances has been set up.

A substance-specific quantification of selected substances for 12 squishies in total has been performed; the eight squishies tested in climatic chamber during screening and additional four squishies. For the emission test in climatic chamber and subsequent quantification of volatile substances, the focus is on fragrances (see list of quantified fragrances in Appendix 6.1), carcinogenic substances, amines and chlorinated substances that were found in the introductory screenings (see quantified substances in Appendix 6.2). In total, 12 squishies that have been emission tested.

Migration to artificial sweat is performed with the same 12 squishies with subsequent substance-specific analysis of DMF, 26 fragrances as well as DMAE in migration liquid.

Eventually, the migration liquid is analyzed with GC/MS, while emission tests are performed with collection on Tenax® and subsequent analysis using TD-GC/MS.

Sample selection

Migration analysis is carried out for the eight squishies already tested in both the content screening as well as for emission of volatile substances (VOC and aldehydes) in climatic chamber, so that data can be compared for the exposure assessment.

Further, four products from the remaining purchased squishies are selected according to the same criteria applied for selection of the initial eight squishies. Two products have been marked with warning that they are not edible/are not food products (33, 44), and one product indicates that it is 'scented' (44). These 12 selected products are listed in TABLE 7. The same squishies are selected for emission and migration, so that the results can be compared, and the two analyses of exposure can provide an overall picture of each individual product.

TABLE 7. Products selected for stage 2 in analysis program. Samples that were not analyzed during screening have been marked with [ ].

Product no.	Price in DKK	Weight (g)
024	150	94
038*(A)	69	63
043**	49	116
048*(B)	79	102
051	60	110
054	70	52
056	49.95	45
061**	13.3	76
[033]	49	20
[034]* (A)	79	134
[044]* (B)	79	86
[063]**	54	142

*from Danish webshop; samples are purchased in different shops, A and B, respectively.

** from US webshop that sells low-priced products primarily from Chinese manufacturers.

4.7 Quantitative detection of emissions in climatic chamber

Emission of selected substances to air from entire squishies after a short-term play (1 hour) and after being in a chamber for 3 days (3 nights/days) is measured to determine how emission can be expected to fall during the first days after unpacking and provide the possibility to assess the risk in an exposure scenario, where emission in a large room over a longer period of time is assumed.

Quantification of the selected volatile substances from the 12 selected samples is carried out according to method description in section 4.3.4. VOC compounds have been identified and quantified against reference substances. Carcinogenic substances in category 1 are quantified and reported in concentrations of > 1 µg/m$^{3.}$, and the other problematic substances that were selected based on the screening have been quantified and reported as "< 5" if measured in a concentration below 5 µg/m^3.

Substances that have been shown and quantified in chamber tests are indicated in TABLE 8. All fragrances (according to Appendix 1), except the two last Evernia-extracts, are calibrated and quantified, and the proven fragrances are illustrated in TABLE 8. The presence of Evernia Furfuracea Extract and Evernia Prunastri Extract could not be confirmed or denied, since it was not possible to find reference substances.

Emission has been confirmed for three fragrances (mentioned in Appendix 1) in these 12 squishies; limonene and linalool that are declarable if the content in toys exceeds 100 mg/kg as well as benzyl alcohol that is prohibited in toys. Limonene has been found in very high concentrations during emission from squishy no. 034 and 063, where emission from no. 063 decreases from approx. 1900 to 1100 µg/m^3 between 1 hour and 3 nights/days. Since the obligation of declaration is related to content, and no content analysis of limonene in the respective samples has been performed, it is not possible to either confirm or deny whether the limit of 100 mg/kg has been exceeded. For linalool, the highest emission was found from samples 034 and 063. Just as for limonene, no content analysis for linalool has been performed in the two samples, but linalool has been found in content analysis of samples 048 and 054 at a concentration level of 60 and 40 mg/kg, respectively (stated as naphthalene equivalents). A calculation of the concentration using a rather uncertain one-point calibration using reference substance indicates that the actual concentration may be higher than the result when using naphthalene equivalents, which is why the actual emission may possibly exceed 100 mg/kg. Benzyl alcohol has been found in low concentrations (<5 µg/m^3) in emissions from squishy no. 034, 044, 048 and 061 after 1 hour and 3 days and nights, respectively. The Danish Statutory Order on toys (Legetøjsbekendtgørelsen) opens an opportunity that substances not allowed in toys can be present if it is technically inevitable and below 100 mg/kg, which may be the case as indicated by the low values. In all squishies, additional odor-relevant terpenes have been found: alpha-pinene, beta-pinene and delta-3-carene. Both alpha-pinene and beta-pinene are among 82 known contact allergens identified within cosmetics (SCCS 2012).

Various chlorinated substances were found by emission: dichloromethane (methylene chloride), chloroform, 1,2-dichloroethane and 1,2-dichloropropane. Furthermore, high concentrations of different amines were found: N,N-dimethylaminoethanol, triethylenediamine, bis(2-(dimethylamino)ethyl)ether and 1,1,4,7,7-pentamethyl-diethylenetriamine, which corresponds to the information acquired in the prior survey.

Very high concentrations of several of substances in TABLE 8 have been found, and even despite using Tenax tubes with the lowest air volume for quantification, there is so much substance that the concentration exceeds the tube capacity and the upper linear measuring range. This is marked for each substance and measured concentrations. From 1 hour to 3 days and nights, the concentrations in emissions of most of the substances from squishies

decrease.[4] Three amines have been found: N,N-dimethylaminoethanol (DMAE), triethylenediamine and bis(2-(dimethylamino)ethyl)ether, where concentrations either increase or have somewhat the same concentration in air from 1 hour to 3 days and nights. 1,1,4,7,7-Pentamethyl-diethylenetriamine is found in emissions in eight of the examined samples. In contrast to other seven samples, which all were analyzed after 1 hour of emission, the substance for squishy no. 033 is not observed after an hour, but only in emissions after 3 days and nights.[5] Overall, it is thus evaluated that amines are released from the material slower over time compared to other measured VOCs.

The concentrations of each substance vary according to the type of squishy, and it also indicates the fact that the weight and the consequent surface area of the squishy has an impact on VOC concentrations released in climate chamber test. Further, it indicates that the type of substances that emit varies between manufacturers. Measurements have been carried out on four samples with comparable appearances (i.e. similar to each other regarding form, colors and design by pairs); sample 038 and 061 that resemble each other and sample 034 and 063 that resemble each other, respectively. Samples 061 and 063 are from the same distributor (webshop in non-EU country), but from different manufacturers, while samples 034 and 038 are purchased in a Danish webshop (manufacturer not indicated). It has been evaluated that samples have totally different emission profiles despite the same substances being identified in many of the examined samples. There are no clear tendencies as to the content, and no conclusions can be made on the type of substances typically used for manufacturing or which added fragrances are used. Even products produced by the same manufacturer (sample 051 and 054) exhibit distinct differences in the chemical content of the two squishies both regarding the substances and emission concentration.

[4] When measuring emission from materials, concentrations will initially increase to a given level and then decrease to a constant level, typically over 28 days. I.e., the emissions can in the intervening time from 1 hour to 3 days have been of higher concentrations than the concentrations measured after 1 hour and 3 days, respectively.

[5] The diffusion rate of a substance varies depending on e.g. chemical structure and size of the given molecule, just as materials from which the substance emits can be physically and chemically different, thereby changing the affinity between emitting substance and the host material. For reasons like this, the concentration of slow-emitting substances can increase to a higher concentration after three days than the concentration after 1 hour, even despite a given air renewal. For e.g. triethylenediamine and 1,1,4,7,7-pentamethyl-diethylenetriamine, the emission results may be due to the amines originating from synthesis of the PUR foam, i.e. they are localized inside the polymer material and are expected to have a higher affinity to the material. For this reason, they are not emitted as fast as e.g. limonene, which is added–possibly
after termination of the foam formation process. The ”added substances”, i.e. fragrances and solvents, originating from application of colors to the surface of a squishy are not trapped inside in the polymer matrix and are, therefore, able to emit faster, resulting in lower concentrations after 3 days. DMF emits faster due to e.g. a lower boiling point and lower affinity to the PUR foam. This means that several parameters (boiling point, affinity, size of the emitting molecule and porosity of the hosting material, etc.) in a complex interaction determine the rate of emission.

TABLE 8. Climatic chamber test emission of 12 squishies with measured concentrations of volatile compounds (VOC) after 1 hour and 3 days and nights (4 selected products).

Unit: µg/m3	**Product number (weight)**															
Substance, CAS no. and classification**	024 (94 g)	038 (63 g)	043 (116 g)	048 (102 g)	051 (110 g)	054 (52 g)	056 (45 g)	061 (76 g)	033 (20 g)		034 (134 g)		044 (86 g)		063 (142 g)	
Time	1h	1h	1h	1h	1h	1h	1h	1h	1 h	3 d	1 h	3 d	1 h	3 d	1 h	3 d
Methylene chloride (CAS no.75-09-2) CARC 2		6	22			<5		<5	<5				560		11	
2-Butanone (CAS no.78-93-3) EYE IRRIT 2	<5	1100	3800*	130	85	220	5	66	12		22		2100*	<5	410	
Chloroform (CAS no.67-66-3) CARC 2, REPR 2, STOT RE1		9	8		1	4		1	7				12		8	
1,2-Dichloroethane (CAS no.107-06-2) CARC 1B		3	2			8						3			3	
Propane, 1,2-dichloro- (CAS no.78-87-5) CARC 1B					6			6					3			
N,N-Dimethylaminoethanol (CAS no.108-01-0) (SKIN CORR 1B)	250	1600		34	2900*		970	240	91		1800	1000			6800*	3200*
Toluene (CAS no.108-88-3) REPR 2, STOT RE2	9	54	41	3	120	44	16	120	22		330	22	96	4	230	25

Unit: µg/m3	Product number (weight)															
Substance, CAS no. and classification**	024 (94 g)	038 (63 g)	043 (116 g)	048 (102 g)	051 (110 g)	054 (52 g)	056 (45 g)	061 (76 g)	033 (20 g)		034 (134 g)		044 (86 g)		063 (142 g)	
Time	1h	1h	1h	1h	1h	1h	1h	1h	1 h	3 d	1 h	3 d	1 h	3 d	1 h	3 d
N,N-dimethylformamide (CAS no.68-12-2) REPR 1B	720	2000	14000*	4900*	3000*	4100*	1500	520	4300*	1200	6000*	3600*	4000*	2300	6500*	3000*
Ethylbenzene (CAS nr.100-41-4) STOT RE2	<5	12	270	<5	18	350	15	22	<5		12	<5	44	7	19	<5
m,p-Xylene (CAS no.179601-23-1)	<5	27	770	7	33	920	42	44	24		19	<5	120	19	50	14
o-Xylene (CAS no.95-47-6)	<5	9	490	<5	13	560	25	18	16	<5	7	<5	50	8	15	6
Styrene (CAS no.100-42-5) REPR 2, STOT RE1	2	51	10		21	25		13	2		3	1	11	2	8	3
Cyclohexanone (CAS no.108-94-1)	3500*	3500*	15000*	5200*	5000*	8200*	3900*	1200	4600*	1100*	9100*	5600*	7700*	3900*	5300*	5600*
alpha-Pinene (CAS no.7785-26-4) SKIN SENS 1	8	11	9	8	7	8	16	11	13		11	<5	5		14	<5
Cyclotetrasiloxane, octamethyl (CAS no.556-67-2) REPR 2			3						1		2	2	7	2	2	1
beta-Pinene (CAS no.18172-67-3)	<5	<5	<5	<5	<5	<5	5	<5	<5		6	<5	<5		<5	

Unit: µg/m3	Product number (weight)															
Substance, CAS no. and classification**	024 (94 g)	038 (63 g)	043 (116 g)	048 (102 g)	051 (110 g)	054 (52 g)	056 (45 g)	061 (76 g)	033 (20 g)		034 (134 g)		044 (86 g)		063 (142 g)	
Time	1h	1h	1h	1h	1h	1h	1h	1h	1 h	3 d	1 h	3 d	1 h	3 d	1 h	3 d
SKIN SENS 1																
delta 3-Carene (CAS no.13466-78-9) SKIN SENS 1	6	7	7	5	<5	6	10	8	4	<5	6	<5	6	<5	9	6
Triethylenediamine (CAS no.280-57-9) (EYE DAM 1)	1300	1400	2700*	2400	3200*	2600	2000	1900	450	710	2600	2700*	1900	2700*	3500*	2900*
Limonene (CAS no.5989-27-5) SKIN SENS 1B	<5	<5	<5	6	17	<5		47	<5		310	260			1900*	1100*
Benzyl alcohol (CAS no.100-51-6)				<5				<5				<5	<5	<5		
Bis(2-(dimethylamino)ethyl)ether (CAS no.3033-62-3) (SKIN CORR 1B)	7	390	<5	22	1000		<5		<5	6	260	400			280	340
Linalool (CAS no.78-70-6) SKIN SENS 1	12	44	<5	20	38		6	31			210	200	18	11	480	340
1,1,4,7,7-Pentamethyl-diethylenetriamine (CAS no.3030-47-5) (SKIN CORR 1B)	870	150	220	<5	90	85	100			210						

Unit: µg/m3	Product number (weight)															
Substance, CAS no. and classification**	024 (94 g)	038 (63 g)	043 (116 g)	048 (102 g)	051 (110 g)	054 (52 g)	056 (45 g)	061 (76 g)	033 (20 g)		034 (134 g)		044 (86 g)		063 (142 g)	
Time	1h	1h	1h	1h	1h	1h	1h	1h	1 h	3 d	1 h	3 d	1 h	3 d	1 h	3 d
Butylated hydroxytoluene (CAS no.128-37-0)	<5	<5	6	7	<5	<5	<5		<5	<5		<5	10	8	8	10
Sum of all quantified VOCs	6684	10375	37358	12742	15551	17130	8611	4249	9541	3226	20697	13787	16641	8961	25547	16545

*Due to high concentration of substance, the capacity of collection medium (Tenax) has been exceeded, and the real concentration may be higher.

**Selected classification: CMR Cat. 1A, 1B, 2; STOT RE 1, 2; STOT SE 1, 2; Acute Tox. 1, 2, 3; Skin Sens. 1, Resp. sens 1. Other classifications that are considered relevant have been included in brackets ( ), see chapter 4.5 with introductory hazard assessment.

< 5 indicates that the substances have been quantified in a concentration below 5 µg/m^3. Substances with Carc. 1A and Carc. 1B are quantified down to 1 µg/m^3 according to EN 16516.

4.8 Quantitative analysis results for migration to sweat

Objective

The objective of the analysis is to determine the amount of DMF and DMAE that can migrate from product to artificial sweat under controlled conditions as defined in EN 71-10:2005.

Sample preparation

A piece of sample was cut in the size of 10 - 15 cm^2 material with as high a part of outer surface as possible and transferred to a Schott Duran bottle containing 10 mL/cm^2 artificial sweat heated to 37°C, after which the bottle is closed with a red screw cap with PTFE insert. Thereafter, the migration is continued for 1 hour in a heating cabinet set to 37°C. Then, the migration liquid is transferred to another container.

The migration period was 1 hour and 100 mL of migration liquid per 10 cm^2 sample as defined in EN 71-10:2005. The migration liquid was thereafter taken out and a portion was extracted with dichloromethane, which can be analyzed with GC/MS for contents of the selected substances. The result is indicated in mg/dm^2. The migration according to EN 71-10:2005 has been modified with respect to migration liquid, temperature and sampling, which would be artificial sweat, physiological temperature and partial sample with as much outside surface as possible, respectively.

DMF and DMAE have an estimated detection limit of 1 mg/L in synthetic solution with an uncertainty of 10-20 % RSD. The quantification will take place against an external calibration curve. The matrix is examined by addition of a known amount of analysis that is, thereafter, attempted to be recovered with the analysis method. The 26 regulated fragrances have a detection limit of 0.1 mg/L in migration liquid except for two natural extracts, where a qualitative assessment will be performed to determine whether they are present or not. The uncertainty is 10-20 % RSD in relation to synthetic injections. The quantification is performed against an external calibration curve. Spike of the matrix shows that an uncertainty of up to 30% RSD may be expected.

Analysis method

For DMF and DMAE analysis, an alkaline regulation of pH 10 is performed, and a shaking of dichloromethane is performed with added internal standard. The shaking effectiveness is investigated by spike of samples. Spiking is carried out using volumes that are expected to be relevant based on results from the introductory tests. Thereafter, the shaken liquid is injected on GC/MS, where identification and quantification against authentic reference substances is carried out set up using a calibration curve in the interval around the expected concentration.

The shaking effectiveness is determined by spiking, and a recovery of 20-50% is present by identification of a detection limit level. The level of the recovery is possibly due to the water/dichloromethane partition of the substances in the samples, and the quantification with external calibration curve is performed in pure dichloromethane.

Spiking is performed on migration liquid from samples at the level of the detection limit, and a response from samples with spike was observed, but not from samples without spike. Thus, it can be concluded with certainty that the contents in migration liquid are below the stated detection limit.

For DMF and DMAE:
Detection limit per surface: 100 $\mu g/cm^2$ corresponding to 10 mg/dm^2
Detection limit per mass: 1000 µg/g
Estimated uncertainty: 20 % RSD

For the analysis of fragrances, shaking with dichloromethane has been performed, and, thereafter, the extract was analyzed according to EN 16274:2012 *Methods for analysis of allergens. Quantification of suspected fragrance allergens in consumer products. Step 1: GC analysis of ready-to-inject sample.* The analysis has been performed with specific calibration for each individual fragrance. According to the standard, no quantification of the two natural extracts from Evernia Furfuracea and Evernia Prunastri has been performed, and these are merely indicated as detected or not detected as defined. For the 24 quantified fragrances, there was a recovery between 70-94% in the spike of migration liquid from samples, except for benzyl alcohol, where the recovery percentage was 50%.

For fragrances:
Detection limit per surface: 2 µg/cm^2 corresponding to 0.2 mg/dm^2
Detection limit per mass: 50 µg/g
Estimated uncertainty: 20 % RSD

Results
None of the examined fragrances (Appendix 6.1) were identified in a concentration above detection limit in the 12 examined products.

For DMF and DMAE, no content above the detection limit in none of the samples has been indicated.

Chromatograms for the analyzed squishies were mainly the same. Since it has not been possible to review all chromatograms in detail, one chromatogram was selected for closer review (038). 36 tops were identified, where there are mainly tops that represent substances that could not be identified with using the NIST database. The mass spectra from the dominant part of the tops measured by area may be from glycol-like substances of unknown complexity. In total, 36 individual substances are identified, and in total 110 mg/L of organic substance were found in the migration liquid quantified as naphthalene equivalents. This corresponds to 25,000 mg/kg corresponding to 2.5 % of the total mass that has migrated to the liquid. If converted to migration per area, it corresponds to 110 mg/dm^2.

One substance listed in EN 71-9 + A1:2007 was identified. It was cyclohexanone, and calculated as naphthalene equivalents the concentration was 1 mg/L, which is below the listed limit of 46 mg/L.

According to the information above, it was attempted to weigh the test sample again to evaluate mass loss during the 24-hour migration, which was determined to be a loss of 15% of the test sample (squishy 038). The difference between weight loss and the chemical analysis is due to migration of components outside the measuring range for GC/MS as well as the uncertainty in detection as naphthalene equivalents. The migrated amount of glycol-like organic substances may be the phase that was observed and interrupted the analysis of isocyanates.

4.9 Substances found by emission and content comparison of selected squishies

In TABLE 9, only results for the substances with concentrations above 50 µg/m^3 for emission or 50 mg/kg for content, respectively, and with one or more of the prioritized classifications is given.

As expected, the climatic chamber test shows a higher detection of low-boiling substances (VVOC)[6], while the content analyses show more high-boiling substances (SVOC) and other

[6] VVOC's cannot be detected by applied GC/MS for content screening.

less volatile substances. There is an overlap, where VOC in an adequately high concentration is found by both emission in chamber and in content analyses, e.g. from N,N-dimethylaminoethanol (DMAE) to 1,2-ethandiamine and N-[2-(dimethylamino)ethyl]-N,N',N'-trimethyl as well as N,N-dimethylformamide (DMF). There is a long range of substances found in both products, but also distinctive differences between the two squishies. Sample 038 (purchased in a Danish webshop) has, e.g., higher emission of N,N-dimethylformamide and linalool, but a lower emission of toluene and limonene.

Regarding the contents, differences are observed as well, since 038 contains more 4,4'-methylene-bis benzenamine than 061 purchased in a non-EU webshop. In the screening analysis of content substances in 061, there is an indication of finding a phthalate in the sample (possibly DEHP), but no quantitative analysis has been performed to confirm its presence.

Limonene and linalool are the most widely used fragrances in toys (Danish Environmental Protection Agency, 2016C), which means that their presence in many of the examined squishies is not surprising. Limonene and linalool are observed by emission from 10 out of 12 examined squishies at levels of up to 1900 µg/m^3 for limonene and 480 µg/m^3 for linalool. In the content screening, linalool was identified in two squishies at levels between 40-60 mg/kg. This corresponds well with previously reported values for linalool in toys (e.g. 63 mg/kg in erasers; Danish Environmental Protection Agency 2006).

TABLE 9. Comparison of selected screening results from emissions in climatic chamber (concentration indicated as toluene equivalents) and content analyses with GC/MS (concentration indicated as naphthalene equivalents). Substances identified in concentrations above either 50 µg/m^3 or 50 mg/kg as well as with at least one of the following classifications are included in this table: CMR 1A, 1B, 2, STOT RE 1,2, STOT SE 1,2, Acut tox 1,2,3, Skin sens 1, Resp sens 1.

		038*		061**		
Substance	**CAS no.**	**Emission (µg/m^3)[1]**	**Content (mg/kg)[2]**	**Emission (µg/m^3)[1]**	**Content (mg/kg)[2]**	**Classification*** **
Toluene	108-88-3	57		95		Flam. Liq. 2 Skin Irrit. 2 Asp. Tox. 1 STOT SE 3 STOT RE 2 Repr. 2
N,N-Dimethylformamide	68-12-2	710	60	210	94	Acute Tox. 4 Eye Irrit. 2 Repr. 1B
D-Limonene	5989-27-5	9		52		Liq. 3 Skin Irrit. 2 Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1
L-Linalool	78-70-6	84		47		Skin Sens. 1B
4,4'-Methylenebis benzenamine	101-77-9		136		64	Skin Sens. 1 Muta. 2 Carc. 1B STOT SE 1 STOT RE 2 Aquatic Chronic

		038*		061**		
Substance	**CAS no.**	**Emission ($\mu g/m^3$)[1]**	**Content (mg/kg)[2]**	**Emission ($\mu g/m^3$)[1]**	**Content (mg/kg)[2]**	**Classification*** **
						2
Bis(2-ethylhexyl) phthalate (DEHP) coeluted with (possibly DINCH)	117-81-7 + (166412-78-8, if DINCH)				243	Repr 1B

*squishy purchased in a Danish webshop

** squishy purchased in an US webshop that sells low-priced products primarily from Chinese manufacturers

***harmonized classification or classification according to REACH registration of substances

5. Risk assessment

In this chapter, risk screening is performed for the exposure scenarios described in chapter 3, and the measurement results described in chapter 4 with a focus on the prioritized substances.

5.1 Risk assessment of inhalation scenarios

5.1.1 Hazard assessment of prioritized substances

For the substances prioritized in the emission analysis (see TABLE 6), data on tolerable exposure limits have been collected from the following sources:

- Recent consumer projects/limit value projects from the Danish Environmental Protection Agency
- The EU-LCI list "Agreed LCI values"
- WHOs limit values for indoor and outdoor air
- Opinions from ECHA's risk assessment committee, RAC
- The US EPA IRIS database (given as reference concentrations, RfC).

The EU-LCI list constitutes an important source, since it provides exposure levels for a number of individual substances. Lowest Concentration of Interest (abbrev. LCI) is a concentration determined to limit emission of chemical substances from building materials. In a report from the European Commission from 2013, LCI values have been composed for a total of 21 substances based on the same method as is used in the REACH regulation for establishment of DNEL values. The EU LCI list "Agreed LCI values" is continuously updated and can be downloaded on their website (EU-LCI 2016).

According to a search in the above-mentioned sources, TABLE 10 shows relevant DNEL values for the prioritized substances in relation to emission. DNEL values have been established to protect against the most critical effects of substances, i.e. effects that occur at the lowest exposure levels to the substances. This way, the DNEL value, which is based on mucous membrane irritation as the most critical effect, will also protect against other possible severe effects, which may be caused by the substance at higher exposure levels. It must be noted that after the follow-up emission analyses, new priority substances have been added to the list in TABLE 10 compared to TABLE 6, since some substances from TABLE 6 are excluded due to relatively low emission levels (e.g. octamethylcyclotetrasiloxane and phenol).

TABLE 10. DNEL values and critical effects for prioritized substances*.

Substance	CAS no.	Classification**	DNEL µg/m^3	Reference, DNEL	DNEL, critical effect if inhaled
Methylene chloride	75-09-2	Carc. 2	**100**	US EPA 2011	Estimate for 10^{-6} cancer risk,
			600	US EPA 2011	affects liver
2-Butanone	78-93-3	Eye Irrit. 2	**5.000**	US EPA 2003	Affects the development of the unborn child
			20.000	EU-LCI 2016	Unspecified
N,N-Dimethylaminoethanol	108-01-0	Skin Corr. 1B Acute Tox. 4	**100**	Appendix 7	Affects the cornea and irritates respiratory tract

Substance	CAS no.	Classification**	DNEL µg/m^3	Reference, DNEL	DNEL, critical effect if inhaled
Toluene	108-88-3	Skin Irrit. 2 Asp. Tox. 1 STOT SE 3 STOT RE 2 Repr. 2	2.900 **725**	EU-LCI 2013 Danish EPA 2016D	Neurotoxicity Neurotoxicity
N,N-Dimethyl-formamide	68-12-2	Acute Tox. 4 Eye Irrit. 2 Repr. 1B	100** **80**	CICAD 2001 Danish EPA 2014B	Affects liver Mucous membrane irritation
Ethylbenzene	100-41-4	Acute Tox. 4 Asp. Tox. 1 STOT RE 2	850 **200**	EU-LCI 2013 Danish EPA 2016D	Neurotoxicity + affects liver Neurotoxicity
Xylenes	1330-20-7	Acute Tox. 4 Skin Irrit. 2	500 **125**	EU-LCI 2013 Danish EPA 2016D	Neurotoxicity + mucous membrane irritation Neurotoxicity
Styrene	100-42-5	Skin Irrit. 2 Eye Irrit. 2 Acute Tox. 4 STOT RE 1 Repr. 2	250 **175**	EU-LCI 2013 Danish EPA 2016D	Neurotoxicity + mutagenicity Neurotoxicity
Cyclohexanone	108-94-1	Acute Tox. 4 Skin Irrit 2 Eye damage 1	**410**	EU-LCI 2013	Mucous membrane irritation
Triethylenedia-mine	280-57-9	Acute Tox. 4 Skin Irrit. 2 Eye Dam. 1	**7**	Appendix 7	Mucous membrane irritation
Bis(2-(dimethyl-amino)ethyl)ether	3033-62-3	Acute Tox. 4 Acute Tox. 3 Skin Corr. 1B Eye Dam. 1 Acute Tox. 4	**2**	Appendix 7	Mucous membrane irritation
1,1,4,7,7-Pentamethyl-diethylenetri-amine	3030-47-5	Acute Tox. 3 Skin Corr. 1B	**8**	Appendix 7	Mucous membrane irritation
Terpenes:					
delta 3-Carene	13466-78-9	*all:* Asp. Tox. 1 Skin Irrit. 2 Skin Sens. 1B	**1.500**	EU-LCI 2013	Unspecified
Linalool	78-70-6		-	-	-
Limonene	5989-27-5		4.500	Danish EPA 2013	Mucous membrane irritation
alpha-Pinene	7785-26-4		2.500	EU-LCI 2013	Affects kidneys
beta-Pinene	18172-67-3		-	-	-

* Harmonized classification/classification in REACH-registration of substance.

** an EU LCI-value of 15 µg/m^3 is included in the proposal, but is not approved yet. Background documentation for this value is not available.

All DNEL values are based on 24-hour daily, continuous exposure. However, it was not possible to find data on the tolerable exposure limit for four substances. For these substances, data was searched in the REACH registrations in order to establish a tolerable exposure limit. The substances are:

- N,N-dimethylaminoethanol (DMAE)
- triethylenediamine
- bis(2-(dimethylamino)ethyl)ether
- 1,1,4,7,7-pentamethyldiethylenetriamine

Evaluation of data and calculation of DNEL values for the four substances has been performed in Appendix 7. The calculation has been performed using guidelines in the ECHA guideline for calculation of DNEL values, and, thus, do not necessarily reflect the DNEL values reported by the registrant in the REACH registration.

The critical effects of the four substances are their effect on the respiratory tract or eye mucous, and, for all substances, very low DNEL values have been reached, as given in TABLE 15.

It must be noted that the substance N,N-dimethylformamide has been included on the REACH candidate list as a substance of very high concern (SVHC) due to the classification of the substance as reprotoxic. However, this effect is not the basis for the indicated tolerable exposure limits, since the effects on liver and mucous membrane irritation occur at lower exposure levels compared to reprotoxic effects.

In the risk screening of squishy toys, the lowest DNEL value identified, if more values for a substance are found, has been used for precautionary reasons.

5.1.2 Risk assessment of exposure scenario for small children

As stated in chapter 3, small children lying and sleeping with a squishy toy could be exposed to the highest concentration of the emitting substances, since the toy is within the child's inhalation zone.

Therefore, emission tests in the small climatic chambers (113 L) were set up in a way, so that measured concentrations in chambers could simulate inhalation concentrations of a sleeping child.

By risk screening of this scenario, the measured levels for emission are compared to the stated tolerable exposure limits and a risk characterization coefficient is calculated:

RCR = Exposure (µg/m^3) / DNEL (µg/m^3)

RCR values exceeding 1 mean that the exposure limit exceeds the tolerable DNEL value, which again means that the protection level is too low and that there may be a risk.

It should be noted that all DNEL values in TABLE 10 have been expressed in the unit µg/m^3. The values for the substances with neurotoxicity as the critical effect (ethylbenzene, xylenes, styrene) are established in the report Danish Environmental Protection Agency (2016d) based on the EU-LCI values for the substances. Further, for each of the substances, there has been paid regard to small children possibly being particularly sensitive to effects on the central nervous system and that small children at a given concentration in the air inhale a larger amount of substances compared to their body weight. For these substances, the described aspects have been included by applying an extra factor of 4 compared to the EU-LCI values (see Danish Environmental Protection Agency, 2016d). In relation to other effects, such as

mucous membrane irritation, children are not considered more sensitive than adults, as these effects depend on the dosage to which the mucous membrane is exposed.

Finally, there is no need, as mentioned in chapter 3, to include calculations regarding the child's weight and inhalation volume, when DNEL is expressed in µg/m^3, and this value is also considered to be valid for children. Weight and inhalation volume would have been relevant if the DNEL value was indicated in the unit mg/kg body weight per day, since this value is based on the child's weight, and inhalation volume should be converted to a DNEL value in the unit µg/m^3.

In TABLE 11, RCR values are calculated for the highest measured values for each of the prioritized substances to clarify which substances can constitute a risk when emitted from squishy toys.

Note that DNEL values in TABLE 11 have been translated from DNEL values for 24-hour daily exposure to 10-hour daily exposure by multiplying the 24-hour value with 2.4. This is considered of relevance, since calculation of the 24-hour DNEL values is performed by scaling proportionally from experiments with animals, where exposure duration is typically six hours daily, and where scaling for 24 hours is performed by multiplying the exposure level for six hours with 6h/24h.

TABLE 11. Risk assessment and calculation of RCR values for 10-hour daily exposure (RCR = max. exp./DNEL (10h)).

Substance	**CAS no.**	**Max. measured exposure level µg/m^3 1 hour/3 days**	**DNEL (24t) µg/m^3**	**DNEL (10 t) µg/m^3**	**RCR** (10 h) **Based on exposure level measured after 1 hour / 3 days**	**DNEL, critical effect**
Methylene chloride	75-09-2	560/0	100	240	**2.3**/0	Estimate for 10^{-6} cancer risk
2-Butanone	78-93-3	3,800/0*	5.000	12.000	0.32/0	Affects the development of the unborn child
N,N-Dimethylaminoethanol	108-01-0	6,800/3,200*	100	240	**28**/13	Affects the cornea and respiratory tract irritation
Toluene	108-88-3	330/25*	725	1.740	0.19/0.01	Neurotoxicity
N,N-Dimethylformamide	68-12-2	14,000/3,600*	80	192	**73**/**19**	Mucous membrane irritation
Ethylbenzene	100-41-4	350/7*	200	480	0.73/0.01	Neurotoxicity
Xylenes	1330-20-7	1,480/27*	125	300	**4.9**/0.09	Neurotoxicity
Styrene	100-42-5	51/3*	175	420	0.3/0.02	Neurotoxicity
Cyclohexanone	108-94-1	15,000/5,600*	410	984	**15**/**5.7**	Unspecified (most likely eye and respiratory tract irritation)
Triethylenediamine	280-57-9	3,500/2,900	7	17	**206**/**171**	Mucous membrane irritation

Substance	CAS no.	Max. measured exposure level µg/m^3 1 hour/3 days	DNEL (24t) µg/m^3	DNEL (10 t) µg/m^3	RCR (10 h) Based on exposure level meas-ured after 1 hour / 3 days	DNEL, critical effect
Bis(2-(dimethyla-mino)ethyl)ether	3033-62-3	1000/400*	2	5	200/80	Mucous mem-brane irritation
1,1,4,7,7-Pentamethyl-diethylenetriamine	3030-47-5	870/210*	8	19	**46/11**	Mucous mem-brane irritation
Terpenes:						
delta 3-Carene	13466-78-9	10/6*	1.500	3.600	~0/~0	Unspecified
Linalool	78-70-6	480/340	-	-	-	-
Limonene	5989-27-5	1,900/1,100	4.500	10.800	0.18/0.10	Mucous mem-brane irritation
alpha-Pinene	7785-26-4	16/0*	2.500	6.000	~0/~0	Affects liver
beta-Pinene	18172-67-3	6/0	-	-	-	-

* Indicates that 1-hour and 3-day measurement results are not associated, i.e. from the same squishy.

In the table, the RCR values above 1 are marked with **bold** letters. The table shows that the emissions of substances:

- N,N-dimethylformamide,
- N,N-dimethylaminoethanol
- triethylenediamine
- bis(2-(dimethylamino)ethyl)ether
- 1,1,4,7,7-pentamethyldiethylenetriamine
- cyclohexanone

may be seen as particularly critical, because RCR values after an hour are all in the interval 15 (cyclohexanone) - 206 (triethylenediamine), while values after three days are in the interval 5,7 (cyclohexanone) - 171 (triethylenediamine). These RCR values are very high, and, thus, it is possible that there may be a risk for other effects that the substances may have at higher exposure levels. This type of analysis is, however, outside the scope of this project.

A limited overstepping of RCR of 1 for methylene chloride is assessed to be less critical, since there is a fast emission of methylene chloride, and after 3 days the RCR is below 1. Since DNEL for methylene chloride is based on a cancer risk for daily exposure throughout the entire life, a very short-term and limited overrun is not considered serious. Also for xylenes the RCR > 1 for 1-hour measurements. However, the risk of chronic neurotoxic effects is related to long-term exposure above the DNEL level. For the squishies with 3-day measurements of xylenes, it is observed that xylenes emit rather fast, but certain knowledge of emission after 3 days for the respective squishy is not available.

Since the focus is on the six substances with the highest RCR values from TABLE 11, and emissions from each of the squishies are evaluated, the following overview has been obtained

for the squishies with emissions exceeding the DNEL value (i.e. RCR > 1) after 1 hour and after 3 hours (TABLE 12).

TABLE 12. Overview of squishies with RCR > 1 for selected substances

Substance	CAS no.	DNEL µg/m3 (10 t)	Squishies with RCR > 1 after 1 hour	Squishies with RCR > 1 after 3 days
N,N-Dimethylaminoethanol	108-01-0	240	024, 034, 038, 051, 056, 061, 063	034, 063
N,N-Dimethyl-formamide	68-12-2	192	024, 033, 034, 038, 043, 044, 048, 051, 054, 056, 061, 063 (all squishies)	033, 034, 044, 063 (all squishies with 3-day-measurements)
Cyclohexanone	108-94-1	984	024, 033, 034, 038, 043, 044, 048, 051, 054, 056, 061, 063 (all squishies)	033, 034, 044, 063 (all squishies with 3-day-measurements)
Triethylenediamine	280-57-9	17	024, 033, 034, 038, 043, 044, 048, 051, 054, 056, 061, 063 (all squishies)	033, 034, 044, 063 (all squishies with 3-day-measurements)
Bis(2-(dimethyla-mino)ethyl)ether	3033-62-3	5	024, 034, 038, 048, 051, 063	033*,034, 063
1,1,4,7,7-Pentamethyl-diethylenetriamine	3030-47-5	19	024, 038, 043, 051, 054, 056	033*

* Only overrun at 3-day measurements and not at 1-hour measurements (the reason for higher emission after 3 days is unknown).

For all substances, the critical effect is mucous membrane irritation related to eye and respiratory tract irritation, which is why emission of several substances simultaneously will contribute to an intensified and, most likely, additive effect.

To highlight the risk of a concrete squishy, a risk assessment is performed of squishy no. 063 below, see results in TABLE 13. This squishy represents a rather high emission with many substances, and both 1-hour and 3-day measurements are carried out for this squishy.

TABLE 13. Risk assessment of squishy no. 063.

Substance	Conc. (µg/m^3) 1 hour/3 days	DNEL (10 t) µg/m^3	RCR 1 hour/3 days	DNEL, critical effect
Methylene chloride	11/0	240	0.05/0	Estimate for 10^{-6} cancer-risk
2-Butanone	410/0	12,000	0.03/0	Affects the development of the unborn child
N,N-Dimethylaminoethanol	6,800*/3,200*	240	**>28/>13**	Affects the cornea and respiratory tract irritation
Toluene	230/25	1,740	0.13/0.01	Neurotoxicity

N,N-Dimethylformamide	6,500*/3,000*	192	**>34/>16**	Mucous membrane irritation
Ethylbenzene	19/<5	480	0.04/<0.01	Neurotoxicity
Xylenes	65/20	300	0.22/0.07	Neurotoxicity
Styrene	8/3	420	0.02/0.01	Neurotoxicity
Cyclohexanone	5,300*/5,600*	984	**>5.4/>5.7**	Unspecified (most likely eye and respiratory tract irritation)
Triethylenediamine	3,500*/2,900*	17	**>206/>171**	Mucous membrane irritation
Bis(2-(dimethylamino)ethyl)ether	280/340	5	**56/68**	Mucous membrane irritation
1,1,4,7,7-Pentamethyl-diethylenetriamine	0/0	19	0/0	Mucous membrane irritation
Terpenes:				
delta-3-Carene	9/6	3,600	~0/~0	Unspecified
Linalool	480/340	-	-	-
Limonene	1,900*/1,100*	10,800	0.18/0.10	Mucous membrane irritation
alpha-Pinene	14/<5	6,000	~0/~0	Affects kidneys
beta-Pinene	<5/0	-	-	-

* Minimal values, because sampling tubes were saturated with VOCs.

The table shows that RCR exceeds the value 1 in the interval 5.4 – 206 after 1 hour and in the interval 5.7 – 171 after 3 days for the substances:

- cyclohexanone
- N,N-dimethylformamide
- N,N-dimethylaminoethanol
- triethylenediamine
- bis(2-(dimethylamino)ethyl)ether

For all these substances, the critical effect is mucous membrane irritation related to the eye and respiratory tract, which is why emission of several substances at the same time will contribute to an enhanced and, most likely, additive effect. No RCR values above 1 are observed for substances with other effects, e.g. carcinogenic or neurotoxic effects.

Thus, it can be concluded that there is a significant risk for eye and respiratory tract irritation/effects in a scenario, where a young child sleeps with squishy 063.

5.1.3 Risk assessment of scenario for older children

As the worst-case scenario for the typical use (for target group down to six years and others, who may stay in the room), a squishy with a high emission will be selected from the emission

measurements, and an equilibrium concentration in the room will be calculated under the assumption that there are 40 squishies in the room and that the child stays in the room for 15 hours daily for periods of time.

The scenario with measuring a squishy in the small climatic chamber (with ventilation rate of 0.5 times per hour) with volume of 0.113 m^3 can be scaled up to a "standard" child's room of 17.4 m^3 (with ventilation rate of 0.5 times per hour), because a factor of 0.113 m^3 / 17.4 m^3 = 0.0065 is applied against the measurement results in the small climatic chamber. If 40 squishies are put in the room, the factor becomes 40 x 0.0065 = 0.26.

Note that DNEL values in TABLE 14 are translated from DNEL values for 24-hour daily exposure to 15-hour daily exposure by multiplying the 24-hour value with 1.6.

TABLE 14. Risk assessment and calculation of RCR for 40 squishies corresponding to no. 063 in a child's room.

Substance	**Conc. (µg/m^3) Small climatic chamber 1 hour/3 days**	**Conc. (µg/m^3) 40 squishies in child's room 1 hour/3 days**	**DNEL (24 h) (µg/m^3)**	**DNEL (15 h) (µg/m^3)**	**RCR Based on exposure levels measured after 1 hour / 3 days**	**DNEL, Critical effect**
Methylene chloride	11/0	2.9/0	100	160	0.02/0	Estimate for 10^{-6} cancer risk
2-Butanone	410/0	107/ 0	5,000	8,000	0.01/0	Affects the development of the unborn child
N,N-Dimethylaminoethanol	6,800*/3,200*	1,768/832	100	160	**>11/>5.2**	Affects the cornea and respiratory tract irritation
Toluene	230/25	60/ 6.5	725	1.160	0.05/0.01	Neurotoxicity
N,N-Dimethylformamide	6,500*/3,000*	1,690/780	80	128	**>13/>6.1**	Mucous membrane irritation
Ethylbenzene	19/<5	4.9/1.3	200	320	0.02/~0	Neurotoxicity
Xylenes	65/20	17/ 5.2	125	200	0.09/0.03	Neurotoxicity
Styrene	8/3	2.1/0.8	175	280	0,01/~0	Neurotoxicity
Cyclohexanone	5,300*/ 5,600*	1,378/1,456	410	656	**>2.1/>2.2**	Unspecified (most likely eye and respiratory tract irritation)
Triethylenediamine	3,500*/ 2,900*	910/754	7	11	**>83/>69**	Mucous membrane irritation
Bis(2-(dimethylamino)ethyl)ether	280/340	73/88	2	3.2	**23/28**	Mucous membrane irritation

Substance	Conc. (µg/m^3) Small climatic chamber 1 hour/3 days	Conc. (µg/m^3) 40 squishies in child's room 1 hour/3 days	DNEL (24 h) (µg/m^3)	DNEL (15 h) (µg/m^3)	RCR Based on exposure levels measured after 1 hour / 3 days	DNEL, Critical effect
1,1,4,7,7-Pentamethyl-diethylenetriamine	0/0	0/0	8	13	0/0	Mucous membrane irritation
Terpenes:						
delta-3-Carene	9/6	2.3/1.6	1,500	2,400	~0/~0	Unspecified
Linalool	480/340	125/88	-	-	-	-
Limonene	1,900*/1,100*	494/286	4,500	7,200	0.07/0.04	Mucous membrane irritation
alpha-Pinene	14/<5	3.6/<1.3	2,500	4,000	~0/~0	
beta-Pinene	<5/0	<1.3/0	-	-	-	Affects kidneys
						-

* Minimal values, because sampling tubes were saturated with VOCs.

The table indicates that RCR exceeds the value 1 in the interval 2.1 – 83 after 1 hour and in the interval 2.2 – 69 after 3 days for the substances:

- cyclohexanone
- N,N-dimethylformamide,
- N,N-dimethylaminoethanol
- triethylenediamine
- bis(2-(dimethylamino)ethyl)ether

For all five substances, the critical effect is mucous membrane irritation related to eye and respiratory tract, which is why emission of several substances at the same time will contribute to an enhanced and, most likely, additive effect. Thus, it can be concluded that there is a significant risk for eye and respiratory tract irritation in a scenario, where 40 squishies are stored in a child's room, and where the child resides in the room a full day.

Even with only one squishy, the RCR value would equal 1.7 for the substance triethylenediamine after 3 days' storage in a child's room.

5.2 Risk assessment of scenario with skin contact

No substances have been detected above the indicated detection limits in the performed migration tests. It is, thus, not possible to perform a quantitative risk assessment on the basis of migration data with calculation of RCR values.

As tables for emission analysis indicate, emission of several substances hazardous to health takes place, which is why a child will be exposed to these vapors by skin contact with a squishy. It is assessed that particularly substances that can cause skin irritation and skin allergy will be able to constitute a potential risk.

The following eight substances, which can cause skin irritation, have been found in relatively high concentrations in the emission test and can, thus, have an impact on potential risk by skin contact:

- cyclohexanone
- N,N-dimethylaminoethanol

- triethylenediamine
- bis(2-(dimethylamino)ethyl)ether
- 1,1,4,7,7-Pentamethyldiethylenetriamine
- toluene
- xylenes
- styrene

Furthermore, a risk for skin allergy cannot be excluded, since the examined squishy products can emit or contain the following seven skin allergy-causing substances:
- delta-3-carene
- linalool
- limonene
- alfa-pinene
- beta-pinene
- 3-(4-isopropylphenyl)-2-methylpropionaldehyde
- 4-tert-butylcyclohexylacetate

In general, relatively low emissions have been detected for the allergy-causing substances except for the substances limonene and linalool, which in a single squishy (no. 063) emitted in relatively high levels (limonene: 1900 µg/m^3 and linalool: 480 µg/m^3 at 1-hour measurements).

Even though the risk of these effects cannot be quantified, it is assessed that the greatest risk of these effects may occur in case of a scenario where a young child lies down and hugs a squishy toy during sleep (up to 10 hours). The young child's contact can be of significantly longer duration compared to an older child's skin contact during play with squishies (approx. 2 hours).

A possible risk of skin irritation/allergy is evaluated to be greatest in areas, where the skin is particularly thin, which means that if young children suck on parts of the squishy, the area around lips with be particularly exposed.

5.3 Limitations and uncertainties

5.3.1 Exposure scenario

The basis for the inhalation scenario for a 3-year-old child is that the child lies down and sleeps holding the squishy in the inhalation area, and that measurement results performed after 1 hour and 3 days in a small climatic chamber of 113 liters reflect an inhalation concentration for a child (partly directly after unpacking of the toy and partly after 3 days). The experiment design itself with a small chamber is considered to reflect the concentration in the child's inhalation area in a realistic way.

At the same time, the exposure estimates based on 1-hour and 3-day measurements will as a rule overestimate the exposure over a longer period of time, since emission of a wide range of substances decreases fast after unpacking, which can be seen, among others, after 1-hour measurements and 3-day measurements for e.g. hydrocarbons (toluene, xylenes, ethylbenzene, styrene). It is also worth mentioning that particularly critical substances (cyclohexanone, N,N-dimethylformamide, N,N-dimethylaminoethanol and triethylenediamine), which produce high RCR values, preserve a rather high concentration from the 1-hour to 3-days measurements, which indicates that the emission of these substances will last over a longer period of time.

To acquire better knowledge of the period of time at which RCR values are above 1, follow-up measurements over a longer period of time will be necessary.

It is assessed that there is a greater uncertainty regarding the exposure scenario for older children, since there are more variables that must be taken into consideration, including the number and choice of squishies actually stored in the child's room, the size of the child's room, ventilation and the length of stay in the room. Initially in the emission analyses, each squishy is squeezed 10 times inside the climatic chamber. In case of a scenario with exposure to 40 squishies, the likelihood that all squishies are squeezed ten times would be low, which is why the concentration may be overestimated. It is also worth indicating that some substances retain a rather high concentration after 1-hour to 3-day measurements, which indicates that the emission of these substances will last over a longer period of time with no additional physical action. It is, thus, assessed that even the storage of relatively few squishies within the established scenarios will result in RCR values above 1.

5.3.2 Establishment of DNEL values and risk assessment

It must be mentioned that for some of the most critical substances: N,N-dimethylaminoethanol, triethylenediamine, bis(2-(dimethylamino)ethyl)ether and 1,1,4,7,7-pentamethyldiethylenetriamine, no expert assessments were available indicating a tolerable exposure limit. For this reason, DNEL values were estimated from inhalation experiments on animals reported in REACH registration of the substances. Especially, DNEL values for triethylenediamine vapors may be considered as uncertain, since the value is calculated on the basis of a study, where animals were exposed to the substance in the form of an aerosol, which will most likely create a stronger response in animals in comparison to vapors.

Furthermore, it has not been possible within this project to perform a more detailed assessment of these studies or to find additional data for these substances, which might potentially have an impact on determining the DNEL value.

Hence, there is some uncertainty regarding the determination of DNEL values for these substances, and in order to reach a more precise risk assessment, a more thorough assessment of these substances is required. Likewise, this applies to the substance cyclohexanone, which emitted in large volumes, and for which the background for the used LCI value is unknown.

In the risk assessment, focus is put on the risk of substance effects that occur at the lowest exposure levels (the critical effects for the DNEL value). However, in case of very high RCR values it cannot be excluded that there is a risk for other, possibly more critical, effects that may occur at higher levels. An analysis of this aspect is not included in this project, as no assessment of each substance regarding the dosage-response and DNEL values for any other possible effects has been carried out.

5.4 Final conclusion, risk assessment

In emission measurements of 12 selected, different squishies, emission was measured for a range of substances at levels that–based on the risk screening performed in the report–may cause irritation of eyes and respiratory tract, and that may cause damage to mucous membranes during exposure of a longer period of time.

This included the following substances that showed RCR values considerably higher than 1:

dimethylaminoethanol, (RCR = 28 as highest value)
N,N-dimethylformamide, (RCR = 73 as highest value)
cyclohexanone, (RCR = 15 as highest value)
triethylenediamine, (RCR = 206 as highest value)
bis(2-(dimethylamino) ethyl) ether), (RCR = 200 as highest value)
1,1,4,7,7-pentamethyldiethylenetriamine, (RCR = 46 as highest value)

In an exposure scenario of a young child lying and sleeping while hugging a squishy, on the basis of measurements performed 1 hour after unpacking the toy, for *all 12 squishies* unac-

ceptably high levels of the substances N,N-dimethylformamide, triethylenediamine and cyclohexanone were measured. For four squishies, which also underwent follow-up 3-day measurements, the concentrations remained at unacceptably high levels for the substances N,N-dimethylformamide and triethylenediamine.

For other mucous membrane, irritant substances: bis(2-(dimethylamino)ethyl)ether; 1,1,4,7,7-pentamethyldiethylenetriamine and dimethylaminoethanol, emissions from six squishies resulted in exceeding the tolerable limit 1 hour after unpacking. After three days, the levels of bis(2-(dimethylamino)ethyl)ether were still unacceptably high for three out of four squishies.

For substances with other effects, e.g. methylene chloride (carcinogenic) and xylenes (chronically neurotoxic), minor overstepping of the tolerable exposure level was detected 1 hour after unpacking (RCR up to 2.3 for methylene chloride and RCR up to 4.9 for xylenes). Since these hazardous effects are related to a long-term exposure above the DNEL value, a short-term overstepping of the RCR value in a risk assessment context is considered to be less significant.

In a scenario, where several squishies are stored in a child's room, unacceptably increased levels were detected in the child's room of the substances: N,N-dimethylformamide, N,N-dimethylaminoethanol, triethylenediamine, bis(2-(dimethylamino)ethyl)ether, 1,1,4,7,7-pentamethyldiethylenetriamine and cyclohexanone.

After execution of migration tests to an artificial sweat liquid, no migration of any of the selected substances was detected, which is the reason why no quantitative risk assessment for skin exposure for these substances can be carried out. Upon skin contact, the skin will also be exposed to the emitted substances, which does not exclude the risk of skin irritation. In the same way, the risk of skin allergy cannot be excluded due to the emission of skin allergy-causing substances, though emissions in smaller amounts, but in the case of recurrent skin contact can cause development of skin allergy. If young children suck on part of the squishy toy, a potential risk of skin irritation and skin allergy would be greatest in areas with the thinnest skin, e.g. lips.

6. List of abbreviations

CAS	Chemical Abstracts Service
DBP	Dibutyl phthalate
DEHP	Diethylhexyl phthalate
DEP	Diethyl phthalate
DMAE	Dimethylaminoethanol
DMF	Dimethylformamide
DNPH	2,4-Dinitrophenylhydrazine
DOP	Dioctyl phthalate
ECHA	European Chemicals Agency
FLD	Fluorescence detector
FTIR	Fourier Transformed Infrared Spectroscopy
GC/MS	Gas Chromatography / Mass Spectrometry
HDI	Hexamethylene diisocyanate
HMDI	Hydrogenated methylene diphenyl diisocyanate
HPLC	High-pressure liquid chromatography
LRPu	Low-resilience polyurethane
MAMA	9-(N-Methylamino-methyl)anthracene
MCCP	Medium-chained chlorinated paraffins
MDI	Methylene diphenyl diisocyanate
NIST	National Institute of Standards and Technology
OPFR	Organophosphorous flame retardants
pH	-log([H3O+])
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PUR	Polyurethane
PVC	Polyvinylchloride
RCR	Risk characterization ratio
REACH	Registration, Evaluation, Authorisation and Restriction of Chemical Substances
RH	Relative humidity
RSD	Relative standard deviation
SCCP	Short-chained chlorinated paraffins
STOT RE	Specific Target Organ Toxicity Repeated Exposure
STOT SE	Specific Target Organ Toxicity Single Exposure
SVHC	Substances of very high concern
SVOC	Semi-volatile organic compound, boiling point > approx. 287°C (n-hexadecane)
TDI	Toluene diisocyanate
TDS	Thermal desorption system
TEHP	Tris(2-ethylhexyl) phosphate
VOC	Volatile organic compound
VVOC	Very volatile organic compound, boiling point < 68°C (n-hexane)

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Appendix 1. Substances restricted in toys by existing legislation

Appendix 1.1 Allergenic fragrances listed in EU's Toy Safety Directive 2009/48/EC

According to EU's Toy Safety Directive 2009/48/EC, toys may not contain the 55 allergenic fragrances listed in TABLE 15.

TABLE 15. 55 allergenic fragrances banned in toys according to EU Toy Safety Directive 2009/48/EC.

No.	Name of the allergenic fragrance	CAS no.
1	Alanroot oil (Inula helenium)	97676-35-2
2	Allylisothiocyanate	57-06-7
3	Benzyl cyanide	140-29-4
4	4-tert-Butylphenol	98-54-4
5	Chenopodium oil	8006-99-3
6	Cyclamen alchohol	4756-19-8
7	Diethyl maleate	141-05-9
8	Dihydrocumarin	119-84-6
9	2,4-Dihydroxy-3-methylbenzaldehyde	6248-20-0
10	3,7-Dimethyl-2-octen-1-ol (6,7-Dihydrogeraniol)	40607-48-5
11	4,6-Dimethyl-8-tert-butylcoumarin	17874-34-9
12	Dimethyl citraconate	617-54-9
13	7,11-Dimethyl-4,6,10-dodecatrien-3-on	26651-96-7
14	6,10-Dimethyl-3,5,9-undecatrien-2-on	141-10-6
15	Diphenylamine	122-39-4
16	Ethyl acrylate	140-88-5
17	Fig leaf, fresh and preparations	68916-52-9
18	trans-2-Heptenal	18829-55-5
19	trans-2-Hexenal diethyl acetal	67746-30-9
20	trans-2-Hexenal dimethyl acetal	18318-83-7
21	Hydroabietyl alcohol	13393-93-6
22	4-Ethoxy-phenol	622-62-8
23	6-Isopropyl-2-decahydronaphthalenol	34131-99-2
24	7-Methoxycoumarin	531-59-9
25	4-Methoxyphenol	150-76-5
26	4-(p-Methoxyphenyl)-3-buten-2-one	943-88-4
27	1-(p-Methoxyphenyl)-1-penten-3-one	104-27-8

No.	Name of the allergenic fragrance	CAS no.
28	Methyl trans-2-butenoate	623-43-8
29	6-Methylcumarin	92-48-8
30	7-Methylcumarin	2445-83-2
31	5-Methyl-2,3-hexanedione	13706-86-0
32	Costus root oil *(Saussurea lappa Clarke)*	8023-88-9
33	7-Ethoxy-4-methylcumarin	87-05-8
34	Hexahydrocumarin	700-82-3
35	Peru balsam, crude (Exudation of Myroxylon pereirae (Royle) Klotzsch)	8007-00-9
36	2-Pentylidene-cyclohexanone	25677-40-1
37	3,6,10-Trimethyl-3,5,9-undecatrien-2-one	1117-41-5
38	Verbena oil *(Lippia citriodora Kunth)*	8024-12-2
39	Musk ambrette (4-tert-Butyl-3-methoxy-2,6-dinitrotoluene)	83-66-9
40	4-Phenylbut-3-en-2-on	122-57-6
41*	Amyl cinnamal	122-40-7
42*	Amylcinnamyl alcohol	101-85-9
43*	Benzyl alcohol	100-51-6
44*	Benzyl salicylate	118-58-1
45*	Cinnamyl alcohol	104-54-1
46*	Cinnamal	104-55-2
47*	Citral	5392-40-5
48*	Coumarin	91-64-5
49*	Eugenol	97-53-0
50	Geraniol	106-24-1
51*	Hydroxy-citronellal	107-75-5
52*	Hydroxy-methylpentylcyclohexencarboxaldehyde	31906-04-4
53*	Isoeugenol	97-54-1
54*	Oakmoss extracts	90028-68-5
55*	Treemoss extracts	90028-67-4

* Declarable substance in cosmetics according to Regulation on cosmetic products EC 1223/2009.

However, the presence of traces of these 55 fragrances shall be allowed provided that such presence is technically unavoidable under good manufacturing practice and does not exceed 100 mg/kg.

In addition, the names of the following allergenic fragrances shall be listed on the toy, on an affixed label, on the packaging or in an accompanying leaflet, if added to a toy, as such, at concentrations exceeding 100 mg/kg in the toy or components thereof. See TABLE 16.

TABLE 16. 11 allergenic fragrances, which according to EU's Toy Safety Directive 2009/48/EC shall be listed if they are used in toys in concentrations above 100 mg/kg.

No.	Name of the allergenic fragrance	CAS no.
1*	Anisyl alcohol	105-13-5
2*	Benzyl benzoate	120-51-4
3*	Benzyl cinnamate	103-41-3
4*	Citronellol	106-22-9
5*	Farnesol	4602-84-0
6*	Hexyl cinnamaldehyde	101-86-0
7*	Lilial	80-54-6
8*	d-Limonene	5989-27-5
9*	Linalool	78-70-6
10*	Methyl heptine carbonate	111-12-6
11*	3-methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one	127-51-5

* Declarable substance in cosmetics according to Regulation on cosmetic products EC 1223/2009.

Appendix 1.2 Restrictions in Appendix II, Annex C in Toy Safety Directive: toys intended for children under 3 years and toys intended to be placed in mouth

TABLE 17. Specific limit values for chemicals used in toys intended for use by children under 36 months or in other toys intended to be placed in mouth.

Substance	**CAS no.**	**Limit value**
TCEP	115-96-8	5 mg/kg (limit value for content)
TCPP	13674-84-5	5 mg/kg (limit value for content)
TDCP	13674-87-8	5 mg/kg (limit value for content)
Bisphenol A	80-05-7	0.04 mg/l (migration value) according to methods established in EN 71-10:2005 and EN 71-11:2005
Formamide	75-12-7	20 µg/m^3 (limit value for emission) after at most 28 days from the beginning of emission analysis of foam materials in toys that contain more than 200 mg/kg (limit value based on contents)
1,2-Benzisothiazol-3(2H)-one	2634-33-5	5 mg/kg (limit value for content) in water-based toy materials according to methods EN 71-10:2005 and EN 71-11:2005
Reaction mixture of: 5-chlor-2-methyl-4-isothiazolin-3-one [EC no. 247-500-7] and 2-methyl-2H -isothiazol-3-one [EC no. 220-239-6] (3:1)	55965-84-9	1 mg/kg (limit value for content) in water-based toy materials
5-Chlor-2-methyl-isothiazolin-3(2H)-one	26172-55-4	0.75 mg/kg (limit value for content) limit value for content in water-based toy materials
2-methylisothiazolin-3(2H)-one	2682-20-4	0.25 mg/kg (limit value for content) in water-based toy materials
Phenol	108-95-2	5 mg/l (limit value for migration) in polymer materials according to methods established in EN 71-10:2005 and EN 71-11:2005. 10 mg/kg (limit value for content) as preservative according to methods in EN 71-10:2005 and EN 71-11:2005

Appendix 1.3 Restrictions according to REACH

PAHs
(a) Benzo[a]pyrene (BaP)
CAS No 50-32-8
(b) Benzo[e]pyrene (BeP)
CAS No 192-97-2
(c) Benzo[a]anthracene (BaA)
CAS No 56-55-3
(d) Chrysene (CHR)
CAS No 218-01-9
(e) Benzo[b]fluoranthene (BbFA)
CAS No 205-99-2
(f) Benzo[j]fluoranthene (BjFA)
CAS No 205-82-3
(g) Benzo[k]fluoranthene (BkFA)
CAS No 207-08-9
(h) Dibenzo[a,h]anthracene (DBAhA)
CAS No 53-70-3

Toy plastic and rubber components that have a direct long-term or short-term repeated skin contact shall not contain any of the above-mentioned PAHs in concentrations above 0.5 mg/kg.

Benzene
Toys and toy components shall not contain benzene in concentrations above 5 mg/kg.

Phthalates
DEHP, DBP and BBP shall not be present in toys at concentrations above 0.1 %. DINP, DNOP and DIDP shall not be found in concentrations above 0.1 % in toys that can be placed in mouth.

National restrictions of phthalates: concentration of phthalates in toys for children under 3 years shall be lower than 500 mg/kg. Phthalates, which are regulated by EU-regulations, are not included in the national restrictions.

Appendix 2. Questionnaire guide used for industry contacts

Example of initial contact:
I am calling from Danish Technological Institute, and we are conducting an analysis of squishy toys for the Danish Environmental Protection Agency. Hence, we would like to interview selected Danish distributors and importers of this type of toys to gain knowledge about these products. Danish Environmental Protection Agency have selected you for this purpose. Would you be willing to participate? The interview will take approximately 15 minutes. Do you have time now, or should we find another time, where I could call you?

We will sum up the information in a report to be published by the Danish Environmental Agency, but it will be in an anonymous form. We will send a draft of the text to you for review prior its publication, so that you have an opportunity to provide comments.

Question guide during the interview (is forwarded before, if desired):

1. Have you been and/or are you concerned or particularly aware of any substances when purchasing squishies? Which ones?
2. Do you have knowledge of specific substances in squishies, about which you have asked questions or acquired information (legislative regulation and requirements for businesses)? Which information have you asked about and did you receive confirmation of the contents of squishies?
3. Have you acquired information on the content of fragrances, other substances with an odor or which originate from surface coating or similar? What answers did you receive?
4. Squishies are expected to be made of polyurethane foam, which has been confirmed in an analysis of samples. Are you able to provide supplementary knowledge on material types used in squishies? Are e.g. other types of polymer materials used and which?
5. Where are squishies that you sell produced?
6. Have you received inquiries about squishies from consumers regarding health-related effects or risks? What are consumers' inquiries usually about?
7. Who do you consider the primary target group (age-related)?
8. Would you consider it possible that also young children (e.g. <3 years of age) play with squishies?
9. Knowledge of usage among consumers, e.g. how long and how do children usually play with squishies?
10. How many squishies do children typically purchase? Are they seen as collectables, so that it can be expected that each child owns several squishies?
11. Are you able to provide some information in the demand – is it still increasing/levelled out/decreasing? Do you see changes or new derived trends?

It must be noted, whether the participant is a distributor or an importer.

Appendix 3. FTIR-analysis of foam in squishies

Sample preparation
A piece of foam without paint was cut out of each of the three squishies (802708-38, 802708-56 and 802708-61). Measurements have been conducted directly on foam pieces with no additional sample preparation.

Analysis method
FTIR spectroscopy is conducted on a 4500a FTIR-instrument from Agilent Technologies. Spectra are produced with ATR method (attenuated total reflectance) with 32 repetitions and a spectral solution of 8 cm^{-1}.

Search in reference spectra has been performed from databases by Agilent, Sigma Aldrich and Smiths Detection.

Results
Measurements have been performed in three places on the foam from each of the three samples. Spectra from different areas are comparable, which confirms that these samples are relatively homogenous. Furthermore, spectra from these three samples are close to identical. All spectra are shown in Figure 2.

For all three samples, the best match is a reference spectrum from polyurethane – see Figure 3 to Figure 5.

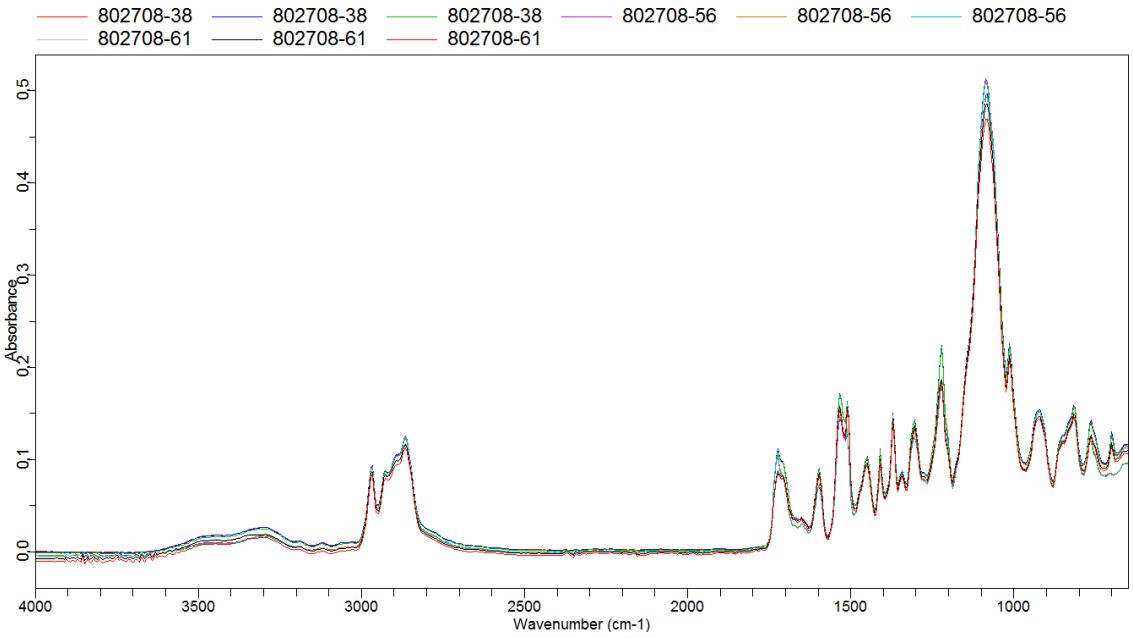

Figure 2: FTIR spectra of the three samples.

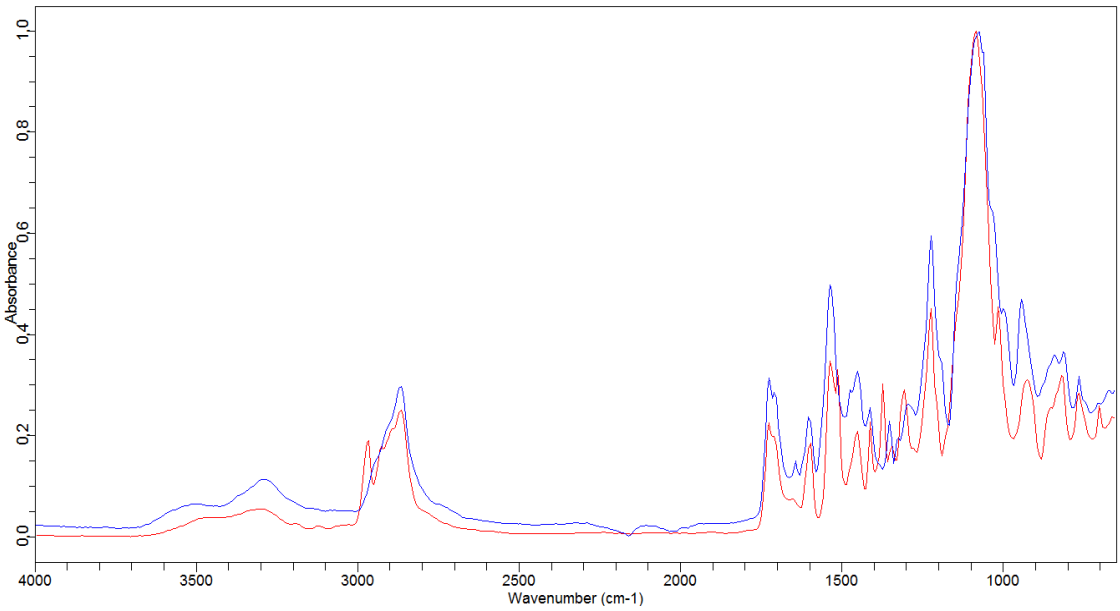

Figure 3: FTIR spectrum of 802708-38 (red) compared with database spectrum of polyurethane (blue).

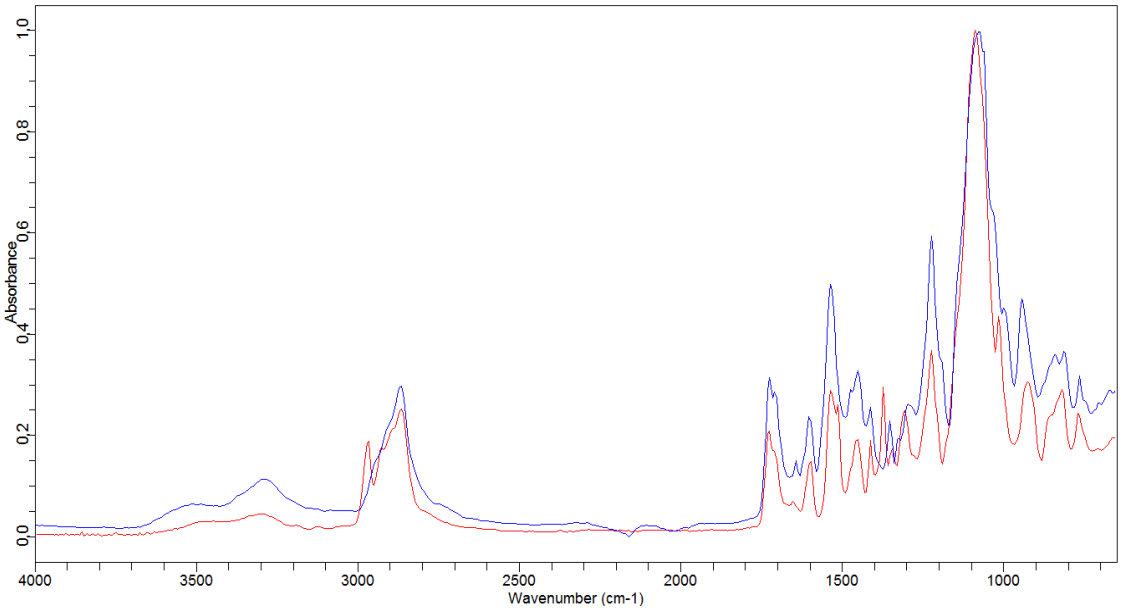

Figure 4: FTIR spectrum of 802708-56 (red) compared with database spectrum of polyurethane (blue).

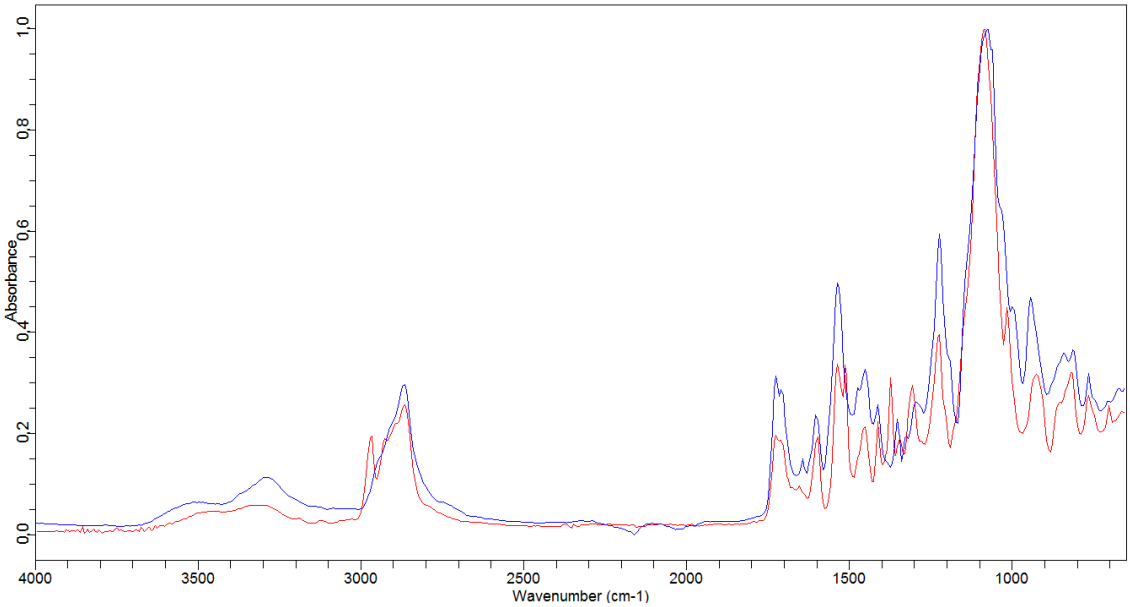

Figure 5: FTIR spectrum of 802708-61 (red) compared with database spectrum of polyurethane

Appendix 4. Screening results of content substances in partial samples from eight squishies with GC/MS

Appendix 4.1 Content substances with certain identification from library (category 1)

Unit: mg/kg	Product number											
Substance	**CAS no.**	**024**	**038**	**043**	**048**	**051**	**054**	**056**	**061**	**Hazard class**	**Hazard state-ment**	**Prioritization**
Ethylene glycol	107-21-1	-	-	-	-	-	-	40	-	Acute Tox. 4	H307	no
Dioxane	123-91-1	-	-	12	-	-	-	29	< 10	Flam. Liq. 2 Eye Irrit. 2 STOT SE 3 Carc. 2	H225 H319 H335 H351	Yes Class.
N,N-Dimethylaminoethanol	108-01-0	62	330	421	-	400	105	89	-	Flam. Liq. 3 Acute Tox. 4 Acute Tox. 4Skin Corr. 1B Acute Tox. 4	H226 H302 H312 H314 H332	Ja High concentration
Propylene glycol	57-55-6	-	-	-	-	-	-	-	16	Not Classified	-	No
(2-Chloroethyl)dimethylamine	107-99-3	-	19	-	-	<10	-	-	-	Acute Tox. 3 Skin Irrit. 2 Skin Sens. 1	H301 H315 H317	No Low concentration

Unit: mg/kg	Product number											
Substance	**CAS no.**	**024**	**038**	**043**	**048**	**051**	**054**	**056**	**061**	**Hazard class**	**Hazard state-ment**	**Prioritization**
										Eye Irrit. 2 Muta. 2 Carc. 2 Aquatic Chronic 3	H319 H341 H351 H412	
Dimethylformamide	68-12-2	-	60	-	274	24	-	53	94	Acute Tox. 4 Eye Irrit. 2 Acute Tox. 4 Repr. 1B	H312 H319 H332 H360D	Yes Class. High concentration
Xylene	106-42-3	-		17	-	-	-		49	Flam. Liq. 3 Acute Tox. 4 Skin Irrit. 2 Acute Tox. 4	H226 H312 H315 H332	No
Cyclohexanone	108-94-1	89	140	868	896	115	59	241	683	Flam. Liq. 3 Acute Tox. 4	H226 H332	No
1,4-Butanediol	110-63-4	171	-	-	-	-	-	-	-	Acute Tox. 4 STOT SE 3	H302 H336 (Central nervous) (Inha-lation)	No
Diethylene glycol	111-46-6	-	44	-	-	29	150	-	-	Acute Tox. 4	H302	No
Bis(2-hydroxypropyl) ether	110-98-5	-	-	-	-	-	36	-	-	-	-	No
Triethylenediamine	280-57-9	119	620	522	1085	606	1198	878	738	Flam. Sol. 1 Acute Tox. 4 Skin Irrit. 2 Eye Dam. 1	H228 H302 H315 H318	Yes High concentration
Bis(2-(Dimethylamino)ethyl) ether	3033-62-3	-	288	-	-	448	-	-	-	Acute Tox. 4 Acute Tox. 3	H302 H311	Yes

Unit: mg/kg	Product number											
Substance	**CAS no.**	**024**	**038**	**043**	**048**	**051**	**054**	**056**	**061**	**Hazard class**	**Hazard state-ment**	**Prioritization**
										Skin Corr. 1B Eye Dam. 1 Acute Tox. 4	H314 H318 H332	High Conc.
Linalool	78-70-6	-	-	-	60	-	40	-	-	Skin Sens. 1B	H317	Yes Class.
2-ethylhexyl acid	149-57-5	17	-	-	-	-	-	24	23	Repr. 2	H361d	Yes Class.
Triethyl phosphate	78-40-0	-	115	111	-	120	-	-	104	Acute Tox. 4	H302	No
Methyl 2-oxocyclopentanecarboxylate	10472-24-9	-	-	-	42	79	49	-	-	-	-	No
Pentamethyldiethylenetriamine	3030-47-5	693	89	558	-	44	-	754	672	Acute Tox. 4 Acute Tox. 3 Skin Corr. 1B	H302 H311 H314	Yes High concentration
Acetic acid, 2-phenylethyl ester	103-45-7	-	-	-	-	-	60	-	-	Eye Dam. 1	H318	No
1,2-Diacetine	102-62-5	-	838	-	191	782	-	-	-	-	-	No No data on class
Triethanolamine	102-71-6	-	-	-	192	-	-	-	-	Not classified	-	No
3-(4-Isopropylphenyl)-2-methylpropionaldehyde	103-95-7	-	-	-	22	-	-	-	-	Skin Irrit. 2 Skin Sens. 1B Aquatic Chronic 3	H315 H317 H412	Yes Class.
BHT (Butylated Hydroxytoluene)	128-37-0	31	-	38	91	-	-	72	23	Aquatic Chronic 1	H410	Yes Endocrine-disrupting
γ-n-Heptylbutyrolactone (peach scent)	104-67-6	-	104	-	-	71	-	-	-	Aquatic Chronic 3	H412	No

Unit: mg/kg	Product number											
Substance	**CAS no.**	**024**	**038**	**043**	**048**	**051**	**054**	**056**	**061**	**Hazard class**	**Hazard state-ment**	**Prioritization**
Diethylphthalate	84-66-2	-	-	1271	761	-	192	-	582	Not Classified	-	No
Triethanolamine borate	283-56-7 + 15277-97-1	-	-	-	165	-	-	-	-	-	-	No Missing class.
Methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	6386-38-5	< 20	-	-	-	-	-	-	-	Aquatic Chronic 2	H411	no
2-(2H-Benzotriazol-2-yl)-5-methylphenol eller Drometrizole	4998-48-5 or 2440-22-4	-	-	-	44	-	-	-	-	Skin Sens 1B Aquatic Chronic 1	H317 H410	Yes Class.
Tri(2-ethylhexyl) phosphite	301-13-3	-	-	67	-	-	-	-	-	-	-	No
4,4'-methylenebis benzenamine	101-77-9	262	136	271	-	133	114		64	Skin Sens. 1 Muta. 2 Carc. 1B STOT SE 1 STOT RE 2 Aquatic Chronic 2	H317 H341 H350 H370 ** H373 ** H411	yes Class.
Octadecenamide	301-02-0	622	853	645	1001	902	507	748	438	-	-	No No data on class.
Bis(2-ethylhexyl) phthalate (DEHP) co-eluted with (probably DINCH)	117-81-7 + (166412-78-8 if DINCH)	-	-	-	-	-	-	-	243	Repr 1B	H360FD	yes class.
2-((2H-benzotriazo)-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol (UV absor-bent)	3147-75-9	-	-	-	42	-	-	-	13	Not classified	-	No
Sucrose Octaacetate	126-14-7	166	-	-	-	-	-	-	-	-	-	No

Unit: mg/kg	Product number											
Substance	**CAS no.**	**024**	**038**	**043**	**048**	**051**	**054**	**056**	**061**	**Hazard class**	**Hazard state-ment**	**Prioritization**
Irganox 1076	2082-79-3	69	61	< 20	-	40	74	<30	< 20	Not classified	-	no

Appendix 4.2 Content substances assessed with relatively large certainty to be the component, but no direct match from library (category 2)

Unit: mg/kg		Product number										
Substance	**CAS no.**	**024**	**038**	**043**	**048**	**051**	**054**	**056**	**061**	**Hazard class**	**Hazard statement**	**Prioritization according to chapter 4.5**
Ethylene glycol and dioxan co-elution	123-91-1	-	-	-	74	-	-	-	-	Flam. Liq. 2 Eye Irrit. 2 STOT SE 3 Carc. 2	H225 H319 H335 H351	Yes (dioxane classification)
Phenol	108-95-2	-	-	10-50	-	-	-	-	-	Acute Tox. 3 Acute Tox. 3* Skin Corr. 1B Acute Tox. 3 Muta. 2 STOT RE 2	H301 H311 H314 H331 H341 H373	yes class
Azodi(isobutyronitrile)	78-67-1	< 10	-	16	-	-	-	-	37	Self-react. C Acute Tox. 4 Acute Tox. 4 Aquatic Chronic 3	H242 H302 H332 H412	no
α-Monoacetine	106-61-6	-	-	-	-	32	-	-	-	-	-	no
4-tert-Butylcyclohexyl acetate	32210-23-4	-	-	-	47	-	19	-	-	Skin Sens. 1B	H317	yes class
γ-n-Amylbutyrolactone	104-61-0	-	-	-	-		15	-	-	Not classified	-	No
Ethylene glycol diphenyl ether	104-66-5	-	-	-	-	-	-	-	21	Aquatic Chronic 2	H411	No
Versalide (fragrance)	88-29-9	-	-	-	-	-	138	-	-	-	-	Yes fragrance
Galaxolide (fragrance)	1222-05-5	-	-	-	20-100	174	-	-	-	Aquatic Acute 1 Aquatic Chronic 1	H400 H410	Yes fragrance
Salicylic acid, benzyl ester	118-58-1	-	-	-	-	-	-	-	< 12	Skin Sens. 1B	H317	no

Unit: mg/kg		Product number										
Substance	**CAS no.**	**024**	**038**	**043**	**048**	**051**	**054**	**056**	**061**	**Hazard class**	**Hazard statement**	**Prioritization according to chapter 4.5**
										Eye Irrit. 2 Aquatic Chronic 3	H319 H412	
Tetradecanamide	1120-16-7	< 20	26	26	31	35	-	-	-	-	-	no
Docosane	629-97-0	-	89	-	-	81	95	-	-	-	-	no
Hexadecanamide	629-54-9	28	42	39	62	74	65	57	30	-	-	no
Octadecanamide	124-26-5	122	175	-	206	59	-	28	-	Not classified	-	no
Phosphoric acid, tris(2-ethylhexyl) ester	78-42-2	-	-	63	-	-	-	-	-	Not classified	-	no
p,p-Dioctyldiphenylamine or Benzenamine, 4-(1,1,3,3-tetramethylbutyl)-N-[4-(1,1,3,3-tetramethylbutyl)phenyl]-	101-67-7 or 15721-78-5	-	-	28	-	-	-	-	25	Aquatic Chronic 3 or Not classified	H412 or none	no

Appendix 4.3 Content substances with uncertain assessment of identification. Possibly incorrect ID. May be a similar molecule or other (category 3)

Unit: mg/kg		Product number									
Substance	**CAS no.**	**024**	**038**	**043**	**048**	**051**	**054**	**056**	**061**	**Hazard class**	**Hazard statement**
N,N-Diethyl-2-aminoethanol	100-37-8	101	110	40	72	129	190	190	102	-	-
Terpeniol	10482-56-1	-	-	-	21	-	-	-	-	-	-
Tripropylene glycol	1638-16-0	32	47	-	35	47	113	34	35	-	-
γ-Decalactone	706-14-9	-	-	-	-	-	37	-	-	**Not classified**	-
Tripropylene glycol	1638-16-0	61	71	0,5	57	95	102	67	39	-	-
Tripropylene glycol	1638-16-0	128	77	4	58	115	125	109	40	-	-
Phthalate (possibly DBP)	84-74-2	-	-	-	-	-	30-80	Positive, but unknown amount	Positive, but unknown amount	-	-
4-[Ethyl(phenyl)amino]benzaldehyde	?	14	-	49	16	-	-	-	-	-	-
Glycol compound with possible silane functionality	-	-	28	34	-	21	44	251	18	-	-
Not identified	-	-	-	-	-	305	452		309	-	-
Not identified	-	-	-	-	-	455	-	-	476	-	-
Not identified (amine compound)	-	-	-	-	63	-	-	-	-	-	-
4,4'-methylenebis benzenamine	-	153	103	197	-	75	75	-	91	-	-

Unit: mg/kg		Product number									
Substance	**CAS no.**	**024**	**038**	**043**	**048**	**051**	**054**	**056**	**061**	**Hazard class**	**Hazard statement**
Hexadecenamide (unknown db)	-	32	45	39	78	69	31	52	30	-	-
p,p'-Diphenylmethane diisocyanate	101-68-8	-	-	-	-	-	-	Positive, but unknown amount	8,9	-	-
Organophosphorus compound	-	-	-	93	-	-	-	-	-	-	-
Octadecenamide (possibly another db or trans)	301-02-0	102	39	< 124	166	108	83	90	37	-	-
4,8,12,16-tetraoxaeicosan-1-ol (glycol)	?	148	-	-	477	-	-	-	-	-	-
Organophosphorus compound	-	-	-	51	-	-	-	-	-	-	-
Dodecanoic acid, undecyl ester	3658-44-4	-	35	-	-	30	37	-	-	-	-
Not identified (DINCH??)	(166412-78-8 if DINCH)	592	197	193	475	204	179	169	-	-	-
2-[2-Methoxy-5-(1,1,3,3-tetramethylbutyl)phenyl]-2H-benzotriazole	?	90	-	144	41	-	-	-	126	-	-

Appendix 5. Volatile substances from eight whole squishies measured in climatic chamber test

Appendix 5.1 Concentration of carbonyls: C1-C4 aldehydes in air: ISO 16000-3

Unit: µg/m^3		Product number										
Substance	**CAS no.**	**024**	**038**	**043***	**048**	**051**	**054***	**056**	**061**	**Classification**	**H-statement**	**Prioritization according to chapter 4.5**
Formaldehyde	50-00-0	11	23	8,2	3,1	19	4,6	9,7	6,6	Carc. 1B Muta. 2 Skin Sens. 1	H350 H341 H317	No Low concentration
Acetaldehyde (ethanal)	75-07-0	6,6	17	27	8,0	30	8,1	18	10	Carc. 2	H351	No Low conc.
Propanale	123-38-6	1,5	6,4	19	1,9	5.3	5,2	3,3	2,0	-	-	No Low conc.
Butanale	123-72-8	1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	< 1,0	-	-	No Low conc.
Acrolein	107-02-8	< 1,0	< 1,0	< 1,0	4,0	< 1,0	< 1,0	< 1,0	< 1,0	Acute tox. 1	H330	No Low conc.
Crotonaldehyde (butenal)	4170-30-3	< 1,7	< 1,7	< 1,7	< 1,7	< 1,7	< 1,7	< 1,7	< 1,7	Muta. 2	H341	No Low conc.

Appendix 5.2 Screening of volatile organic compounds (VOCs) in air: ISO 16000-6

Substance screening on the basis of criteria stated in chapter 5.5

Unit: µg/m^3 as toluene equivalents		Product number										
Substance	**CAS no.**	**024**	**038**	**043***	**048**	**051**	**054***	**056**	**061**	**Classification**	**H-statement**	**Prioritization according to chapter 4.5**
Ethanol	000064-17-5	nd		<5					9	Flam. Liq. 2	H225	no
1,1-Dichloro-1-fluoroethane **	001717-00-6		11	25		6	14		23	Aquatic Chronic 3 Ozone 1	H412 H420	no
Ethane, 1,2-dichloro-1-fluoro- **	000430-57-9		23									no
2-Propanone	000067-64-1	<5		67						Flam. Liq. 2 Eye Irrit. 2 STOT SE 3	H225 H319 H336	no
Acetic acid, methyl ester	000079-20-9		42	100			6			Flam. Liq. 2 Eye Irrit. 2 STOT SE 3	H225 H319 H336	no
Methylene chloride	000075-09-2		<5	10			<5			Carc. 2	H351	Yes, class.

Unit: µg/m^3 as toluene equivalents		Product number										
Substance	**CAS no.**	**024**	**038**	**043***	**048**	**051**	**054***	**056**	**061**	**Classification**	**H-statement**	**Prioritization according to chapter 4.5**
Ethan, 1,1-dichloro-	000075-34-3			<5						Flam. Liq. 2 Acute Tox. 4 * Eye Irrit. 2 STOT SE 3 Aquatic Chronic 3	H225 H302 H319 H335 H412	no
2-butanon	000078-93-3		230	490	61	34	80		31	Flam. Liq. 2 Eye Irrit. 2 STOT SE 3	H225 H319 H336	no
Ethene, 1,1-dichloro-	000075-35-4			<5						Flam. Liq. 1 Acute Tox. 4 * Carc. 2	H224 H332 H351	No Low concentration
Acetic acid ethyl ester	000141-78-6		<5	53			5			Flam. Liq. 2 Eye Irrit. 2 STOT SE 3	H225 H319 H336	no
Carbonic acid, dimethyl ester	000616-38-6			8		<5			<5	Flam Liq 2	H225	no
Trichloromethane	000067-66-3						<5			Acute Tox. 4 Skin Irrit. 2 Eye Irrit. 2 Acute Tox. 3 Carc. 2 STOT RE 1 Repr. 2	H302 H315 H319 H331 H351 H372 H361d	No Low concentration
1-Propanol, 2-methyl-	000078-83-1			19	<5		8			Flam. Liq. 3 Skin Irrit. 2 Eye Dam. 1 STOT SE 3 STOT SE 3	H226 H315 H318 H335 H336	no
Ethan, 1,2-dichloro-	000107-06-2		1				3			Flam. Liq. 2 Acute Tox. 4 * Skin Irrit. 2 Eye Irrit. 2 STOT SE 3	H225 H302 H315 H319 H335	No Low concentration

Unit: µg/m^3 as toluene equivalents		Product number										
Substance	**CAS no.**	**024**	**038**	**043***	**048**	**051**	**054***	**056**	**061**	**Classification**	**H-statement**	**Prioritization according to chapter 4.5**
										Carc. 1B	H350	
Benzene **	000071-43-2		4							Flam. Liq. 2 Skin Irrit. 2 Eye Irrit. 2 Asp. Tox. 1 Muta. 1B Carc. 1A STOT RE 1	H225 H315 H319 H304 H340 H350 H372 **	No Low concentration
1-Butanol	000071-36-3								5	Flam. Liq. 3 Acute Tox. 4 * Skin Irrit. 2 Eye Dam. 1 STOT SE 3 STOT SE 3	H226 H302 H315 H318 H335 H336	No
Ethanamine, N,N-diethyl-	000121-44-8					<5				Flam. Liq. 2 Acute Tox. 4 * Acute Tox. 4 * Skin Corr. 1A Acute Tox. 4 *	H225 H302 H312 H314 H332	No
Heptane	000142-82-5	<5	<5			<5	<5			Flam. Liq. 2 Skin Irrit. 2 Asp. Tox. 1 STOT SE 3 Aquatic Acute 1 Aquatic Chronic 1	H225 H315 H304 H336 H400 H410	No
Propane, 1,2-dichloro-	000078-87-5					3			2	Flam. Liq. 2 Acute Tox. 4 * Acute Tox. 4 * Carc. 1B	H225 H302 H332 H350	No Low concentration
N,N-Dimethylaminoethanol	000108-01-0		816			840			96	Flam. Liq. 3 Acute Tox. 4 * Acute Tox. 4 * Skin Corr. 1B Acute Tox. 4 *	H226 H302 H312 H314 H332	Yes High concentration
Toluene	000108-88-3	8	57	32	7	93	39	11	95	Flam. Liq. 2 Skin Irrit. 2	H225 H315	Yes Class.

Unit: µg/m^3 as toluene equivalents		Product number										
Substance	**CAS no.**	**024**	**038**	**043***	**048**	**051**	**054***	**056**	**061**	**Classification**	**H-statement**	**Prioritization according to chapter 4.5**
										Asp. Tox. 1 STOT SE 3 STOT RE 2 * Repr. 2	H304 H336 H373 ** H361d ***	
1,2-Ethanediol	000107-21-1				36					Acute Tox. 4*	H307	no
Formamide, N,N-dimethyl-	000068-12-2	250	710	3700	2000	790	1300	520	210	Acute Tox. 4 * Eye Irrit. 2 Acute Tox. 4 * Repr. 1B	H312 H319 H332 H360D ***	Yes Class.
1,2-Propanediol	000057-55-6						12			Not Classified	-	no
Butanoic acid, ethyl ester	000105-54-4		36			18			10	Flam. Liq. 3	H226	no
Cyclotrisiloxane, hexamethyl-	000541-05-9		11		<5	11	10	5		Flam. Sol. 1	H228	no
Acetic acid, butyl ester	000123-86-4	48								Flam. Liq. 3 STOT SE 3	H226 H336	no
Heptane, 2,4-dimethyl-	002213-23-2					6			9	-	-	no
2-Furancarboxaldehyde	000098-01-1				4					Tox. 3 * Acute Tox. 4 * Skin Irrit. 2 Eye Irrit. 2 Acute Tox. 3 * STOT SE 3 Carc. 2	H301 H312 H315 H319 H331 H335 H351	No Low concentration
2,4-Dimethyl-1-heptene	019549-87-2					<5			6	-	-	no
Benzene, chloro-	000108-90-7		<5				<5			Flam. Liq. 3 Skin Irrit. 2 Acute Tox. 4 Aquatic Chronic 2	H226 H315 H332 H411	no
2-Propanol, 1-(2-propenyloxy)-	021460-36-6				21							no
Piperazine, 1,4-dimethyl-	000106-58-1			63				14		Flam. Liq. 2 Acute Tox. 4 Skin Corr. 1C Eye Dam. 1	H225 H302 H314 H318	no
Benzene, ethyl-	000100-41-4		16	270		34	340	16	28	Flam. Liq. 2 Acute Tox. 4 * Asp. Tox. 1 STOT RE 2	H225 H332 H304 H373 (hear-	Yes Class.

Unit: µg/m^3 as toluene equivalents		Product number										
Substance	**CAS no.**	**024**	**038**	**043***	**048**	**051**	**054***	**056**	**061**	**Classification**	**H-statement**	**Prioritization according to chapter 4.5**
											ing organs)	
m-Xylene	000108-38-3	<5	11		7	32	510		12	Flam. Liq. 3 Acute Tox. 4 * Skin Irrit. 2 Acute Tox. 4 *	H226 H312 H315 H332	Yes High concentration
p-Xylene	000106-42-3	<5	25	85	<5	<5	120	35	28	Flam. Liq. 3 Acute Tox. 4 * Skin Irrit. 2 Acute Tox. 4 *	H226 H312 H315 H332	Yes High concentration
Cyclopentanone, 2-methyl-	001120-72-5				<5					-	-	no
Styrene	000100-42-5		40¤			20¤				Flam. Liq. 3 Skin Irrit. 2 Eye Irrit. 2 Acute Tox. 4 * STOT RE 1 Repr. 2	H226 H315 H319 H332 H372 (hearing organs) H361d	Yes Class.
o-Xylene	000095-47-6		19¤	450		14¤	460	26		Flam. Liq. 3 Acute Tox. 4 * Skin Irrit. 2 Acute Tox. 4 *	H226 H312 H315 H332	Yes High concentration
Cyclohexanone	000108-94-1	1500	1700	6800	2500	1900	4300	1700	630	Flam. Liq. 3 Acute Tox. 4 *	H226 H332	Yes High concentration
Acetic acid, 2-(dimethylamino)ethyl ester	001421-89-2	5	26			37		5	<5	-	-	no
Acetic acid, pentyl ester	000628-63-7		55			29				Flam Liq 3	H226	no
Alpha-pinene, (-)-	000080-56-8	9	11	9	8	7	10	14	10	Flam. Liq. 3 Acute Tox. 4 Asp. Tox. 1 Skin Irrit. 2 Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H226 H302 H304 H315 H317 H400 H410	Yes Class. Odorous substance
Benzene, (1-methylethyl)-	000098-82-8			<5			17			Flam. Liq. 3 Asp. Tox. 1 STOT SE 3	H226 H304 H335	no

Unit: µg/m^3 as toluene equivalents		Product number										
Substance	**CAS no.**	**024**	**038**	**043***	**048**	**051**	**054***	**056**	**061**	**Classification**	**H-statement**	**Prioritization according to chapter 4.5**
										Aquatic Chronic 2	H411	
Gamma. Valerolactone	000108-29-2				<5					-	-	no
Benzene, propyl-	000103-65-1					<5	<5		<5	Flam. Liq. 3 Asp. Tox. 1 STOT SE 3 Aquatic Chronic 2	H226 H304 H335 H411	no
Benzene, 1-ethyl-2-methyl-	000611-14-3		<5			<5	<5			-	-	no
2-Cyclopenten-1-one, 3-methyl-	002758-18-1							<5		-	-	no
Benzaldehyde	000100-52-7		6	<5	<5	7	<5		9	Acute Tox. 4 *	H302	no
Mesitylene **	000108-67-8								<5	Flam. Liq. 3 STOT SE 3 Aquatic Chronic 2	H226 H335 H411	no
Benzene, 1,2,3-trimethyl- **	000526-73-8					<5				-	-	no
Cyclotetrasiloxane, octamethyl-	000556-67-2		6	15	1	4	7	2		Aquatic Chronic 4 Repr. 2	H413 H361f ***	Yes Class.
2-Beta-pinene	000127-91-3	<5	<5		<5	<5	<5	<5	<5	Flam. Liq. 3 Asp. Tox. 1 Skin Irrit. 2 Skin Sens. 1B Aquatic Acute 1 Aquatic Chronic 1	H226 H304 H315 H317 H400 H410	Yes Class.
Propylene Carbonate	000108-32-7				<5					Eye Irrit. 2	H319	no
Benzene, 1,2,4-trimethyl- **	000095-63-6								5	0	0	no
Benzene, 1,2,3-trimethyl- **	000526-73-8		<5			5				-	-	no
Hexanoic acid, ethyl ester	000123-66-0				<5					Flam. Liq. 3 Skin Irrit. 2	H226 H315	no
Benzene, 1,3,5-trimethyl- **	000108-67-8						<5			Flam. Liq. 3 STOT SE 3 Aquatic Chronic 2	H226 H335 H411	no
Decan	000124-18-5		<5	<5		<5	<5	<5	<5	Flam. Liq. 3 Asp. Tox. 1	H226 H304	no
Dipropylene glycol monomethyl ether isomer	000000-00-0	14										no
3-Hexen-1-ol, acetate, (Z)-	003681-71-8								13	Flam. Liq. 3	H226	no
Delta 3-Carene	013466-78-9	9		9	9		19	11		Flam. Liq. 3 Asp. Tox. 1	H226 H304	Yes Class.

Unit: µg/m^3 as toluene equivalents		Product number										
Substance	**CAS no.**	**024**	**038**	**043***	**048**	**051**	**054***	**056**	**061**	**Classification**	**H-statement**	**Prioritization according to chapter 4.5**
										Skin Irrit. 2 Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H315 H317 H400 H410	Odorous substance
Acetic acid, hexyl ester	000142-92-7					36				Flam. Liq. 3	H226	no
Phenol	000108-95-2	1		10						Acute Tox. 3 * Acute Tox. 3 * Skin Corr. 1B Acute Tox. 3 * Muta. 2 STOT RE 2 *	H301 H311 H314 H331 H341 H373 **	Yes Class.
Triethylenediamine	000280-57-9	480	700	810	870	920	890	780	770	Flam. Sol. 1 Acute Tox. 4 Skin Irrit. 2 Eye Dam. 1	H228 H302 H315 H318	Yes High concentration
Propanenitril, 2,2'-azobis[2-methyl-]	000078-67-1	27								Self-react. C Acute Tox. 4 * Acute Tox. 4 * Aquatic Chronic 3	H242 H302 H332 H412	no
Tetramethylsuccinonitril	003333-52-6						88			-	-	no
D-Limonene	005989-27-5	<5	9	5	6	28	<5	<5	52	Liq. 3 Skin Irrit. 2 Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H226 H315 H317 H400 H410	Yes Class. Odorous substance
Triethylenediamine	000280-57-9		<5							Flam. Sol. 1 Acute Tox. 4 Skin Irrit. 2 Eye Dam. 1	H228 H302 H315 H318	no
Benzyl alcohol	000100-51-6					<5			5	Acute Tox. 4 * Acute Tox. 4 *	H302 H332	no
Butanoic acid, 3-methyl-, butyl ester	000109-19-3								27	-	-	no
2(3H)-Furanone, 5-ethyldihydro-	000695-06-7		21				10			-	-	no
Naphthalene, decahydro-, trans-	000493-02-7		<5					<5		-	-	no
1,4-Dioxaspiro[4.5]decane	000177-10-6			35						-	-	no

Unit: µg/m^3 as toluene equivalents		Product number										
Substance	**CAS no.**	**024**	**038**	**043***	**048**	**051**	**054***	**056**	**061**	**Classification**	**H-statement**	**Prioritization according to chapter 4.5**
9-Methylbicyclo[3.3.1]nonane	025107-01-1							<5		-	-	no
Hexanoic acid, 2-propenyl ester	000123-68-2		190		9				15	Acute Tox. 3 Acute Tox. 3 Acute Tox. 3 Aquatic Acute 1 Aquatic Chronic 3	H301 H311 H331 H400 H412	Yes Class.
Cyclopropane, 1,2-dibutyl-	041977-32-6		<5							-	-	no
Undecane	001120-21-4			<5					7	Asp. Tox. 1	H304	no
Bis(2-(Dimethylamino)ethyl) ether	003033-62-3		310		15	440				Acute Tox. 4 Acute Tox. 3 Skin Corr. 1B Eye Dam. 1 Acute Tox. 4	H302 H311 H314 H318 H332	Yes High concentration
L-Linalool	000078-70-6		84		16	68			47	Skin Sens. 1B	H317	Yes Class. Odorous substance
Nonanal	000124-19-6			<5						Aquatic Chronic 3	H412	no
Benzene, 1-bromo-2-chloro-	000694-80-4	<5								-	-	no
Triethyl phosphate	000078-40-0		100	100		78	84			Acute Tox. 4 *	H302	no
Cyclopentasiloxane, decamethyl-	000541-02-6	<5	29	11	<5	10	<5	<5	<5	Not Classified	-	no
1H-Pyrazole, 4,5-dihydro-5,5-dimethyl-4-isopropylidene-	106251-09-6	12								-	-	no
Naphthalene, decahydro-2-methyl-	002958-76-1		10							-	-	no
Propylene glycol trimer	000000-00-0								7			no
2-Propanol, 1-[1-methyl-2-(2-propenyloxy)ethoxy]-	055956-25-7		50	62	36	40		33				no
1,2-Ethanediamine, N-[2-(dimethylamino)ethyl]-N,N',N'-trimethyl-	003030-47-5	580	150	230	<5	120	250	200		Acute Tox. 4 * Acute Tox. 3 * Skin Corr. 1B	H302 H311 H314	Yes Class High concentration
Benzoic acid, ethyl ester	000093-89-0			<5		<5	<5			Registrering 1: Not Classified Registrering 2: Skin Irrit. 2 Eye Irrit. 2	 H315 H319	no
Naphthalene, decahydro-2,3-dimethyl- **	001008-80-6								<5	-	-	no

Unit: µg/m^3 as toluene equivalents		Product number										
Substance	**CAS no.**	**024**	**038**	**043***	**048**	**051**	**054***	**056**	**061**	**Classification**	**H-statement**	**Prioritization according to chapter 4.5**
Naphthalene, decahydro-1,6-dimethyl- **	001750-51-2		11			<5				-	-	no
Dodecane	000112-40-3	<5	72	11	<5	19	18		10	Asp. Tox. 1	H304	no
Naphthalene, decahydro-2,6-dimethyl- **	001618-22-0		7			<5				-	-	no
Benzene, ethyl-1,2,4-trimethyl-	054120-62-6						<5			-	-	no
cis, cis-3-Ethylbicyclo[4.4.0]decane	066660-42-2		5			<5				-	-	no
Acetic acid, 2-phenylethyl ester	000103-45-7								14	Eye Dam. 1	H318	no
Caprolactam	000105-60-2							<5	<5	Acute Tox. 4 * Skin Irrit. 2 Eye Irrit. 2 Acute Tox. 4 * STOT SE 3	H302 H315 H319 H332 H335	no
Cyclohexasiloxane, dodecamethyl-	000540-97-6			6		<5	<5	<5	<5	Not Classified	-	no
Anethol	000104-46-1			18			6			-	-	no
Tridecane	000629-50-5		17	<5	<5	9	5		<5	Asp. Tox 1	H304	no
Naphthalene, 2-methyl- **	000091-57-6					<5	8			-	-	no
Naphthalene, 1-methyl- **	000090-12-0					<5	<5			-	-	no
Triacetin	000102-76-1		47			57				Not Classified	-	no
Tetradecane	000629-59-4		<5	<5	<5	<5	<5		<5	Asp. Tox 1	H304	no
Isolongifolene	001135-66-6			<5						Registrering 1: Aquatic Acute 1 Registrering 2: Not Classified	H400	no
Naphthalene, 1,7-dimethyl-**	000575-37-1						<5			-	-	no
2(3H)-Furanone, 5-hexyldihydro-	000706-14-9		<5			<5			<5	Not Classified	-	no
trans-.beta.-Ionone	000079-77-6		5			6				Aquatic Acute 2 Aquatic Chronic 2	H401 H411	no
pentadecane	000629-62-9				<5					Asp. Tox 1	H304	no
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-	000128-37-0	6	<5	8	11	<5	<5	6		Aquatic Chronic 1	H410	no
Diethyl Phthalate	000084-66-2			36			9			Not Classified	-	no
Benzophenone	000119-61-9	<5								STOT RE 2 Aquatic Chronic 3	H373 (liver, kidney) (Oral) H412	No Low concentration
1,2-Benzenedicarboxylic acid,	000084-69-5		2							Repr. 1B	H360Df	No

Unit: µg/m^3 as toluene equivalents		Product number										
Substance	**CAS no.**	**024**	**038**	**043***	**048**	**051**	**054***	**056**	**061**	**Classification**	**H-statement**	**Prioritization according to chapter 4.5**
bis(2-methylpropyl) ester												Low concentration
Phenol, 4-(1-methyl-1-phenylethyl)-	000599-64-4		<5							Acute Tox. 4 Eye Dam. 1 STOT RE 2 Aquatic Acute 1 Aquatic Chronic 1	H302 H318 H373 (Kidney) H400 H410	No Low concentration
Sum of unidentified VVOC	Rt up to C6	10	24	19	25	33		16	20			
Sum of unidentified VOC	Rt C6 to C16	150	540	470	58	280	170	490	180			
Sum of unidentified SVOC	Rt after C16						2					
Sum of all measured VVOC*	Rt up to C6	10	100	220	25	38	20	16	53			
Sum of all measured VOC*	Rt C6 to C16	3100	6200	10000	5700	6000	8800	3800	2300			
Sum of all measured SVOC*	Rt after C16		2	36			11					
TVOC (Toluene equivalents)		3100	6200	10000	5700	6000	8800	3800	2300			

* Calibrated compounds + Toluene equivalents of unidentified

** Must be quantified

*** Toluene equivalents

¤ Styrene + o-xylene coeludes

Prioritization according to chapter 4.5.
Yes: prioritized either due to classification and/or high concentration
No: not prioritized either due to missing classification, low concentration or relevant classification, but low concentration.
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Appendix 6. Substances quantified in emission test

Appendix 6.1 Fragrances

Name	CAS no.
Phenylacetaldehyde	122-78-1
Citral (Neral isomer) 1	5392-40-5
Citral (Geranial isomer) 2	5392-40-5
Cinnamal	104-55-2
3,7-Dimethyl-7-Hydroxyoctanal	107-75-5
Lilial	80-54-6
alpha-Amylcinnamaldehyde isomer 1	122-40-7
alpha-Amylcinnamaldehyde isomer 2	122-40-7
Lyral isomer 1	31906-04-4
Lyral isomer 2	31906-04-4
alpha-Hexylcinnamaldehyde isomer 1	101-86-0
alpha-Hexylcinnamaldehyde isomer 2	101-86-0
Benzyl alcohol	100-51-6
Linalool	78-70-6
Citronellol	106-22-99
Geraniol	106-24-1
4-Methoxybenzyl alcohol	105-13-5
Cinnamyl alchohol	104-54-1
Eugenol	97-53-0
Methyl eugenol	93-15-2
Isoeugenol	97-54-1
alpha-Amylcinnamic Alcohol	101-85-9
Farnesol isomer 1	4602-84-0
Farnesol isomer 2	4602-84-0
d-Limonene	5989-27-5
1,8-Cineole	470-82-6
Camphor	76-22-2
Methyl 2-octynoate	111-12-6
4-Allylanisole(Estragole)	140-67-0
Safrole	94-59-7
Methyl 2-nonyate	111-80-8
Courmarin	91-64-5
iso-alpha-Methylinone	127-51-5
Benzyl benzoate	120-51-4

Benzyl salicylate	118-58-1
Benzyl Cinnamate	103-41-3

Appendix 6.2 Other substances quantified in emission test

Name	CAS
Methylene chloride #	75-09-2
Ethane, 1,2-dichloro- #	107-06-2
Benzene ? (must be quantified) #	71-43-2
Propane, 1,2-dichloro- #	78-87-5
N,N-Dimethylaminoethanol #	108-01-0
Toluene #	108-88-3
Formamide, N,N-dimethyl- #	68-12-2
Benzene, ethyl- #	100-41-4
m-Xylene #	108-38-3
p-Xylene #	106-42-3
Styrene #	100-42-5
o-Xylene #	95-47-6
Cyclohexanone #	108-94-1
Alpha-pinene #	80-56-8
Cyclotetrasiloxane, octamethyl- #	556-67-2
2-Beta-pinene #	127-91-3
Delta 3-Carene #	13466-78-9
Phenol #	108-95-2
Triethylenediamine #	280-57-9
D-Limonene #	5989-27-5
Bis(2-(Dimethylamino)ethyl) ether #	3033-62-3
L-Linalool	78-70-6
1,2-Ethanediamine, N-[2-(dimethylamino)ethyl]-N,N',N'-trimethyl- #	3030-47-5

Appendix 7. Calculation of DNEL values

N,N-Dimethylaminoethanol

In the REACH registration for the substance, the following relevant data for DNEL release has been given: in an inhalation test rats were exposed to vapors of N,N-dimethylaminoethanol at concentrations 0; 29; 88 and 277 mg/m^3. Animals were exposed for 6h/day 5 days per week for 13 weeks. NOAEC was 29 mg/m^3. Cornea opacity was observed at the medium exposure level, and mucous membrane irritation and damage in mucous membrane cells in the respiratory tract were observed at the highest exposure level.

For consumers, a DNEL value is calculated at continuous exposure:
NOAEC is converted to 24h = 29 mg/m^3 x 6/24 x 5/7 = 5.2 mg/m^3

DNEL = NOAEC / (AF1 x AF2 x AF3 x AF4)
AF1 (interspecies animal to human) = 2,5 (for local irritation effects)
AF2 (intraspecies, difference in human sensitivity) = 10
AF3 (duration of experiments, subchronic to chronic exposure) = 2
DNEL = 5.2 mg/m^3 / (2.5 x 10 x 2) = **0.1 mg/m^3**

Triethylenediamine

In the REACH-registration for the substance, the following data for DNEL release have been given: in an inhalation experiment rats were exposed to aerosols of triethylenediamine at concentrations 0; 0.0058; 0.063 or 0.62 mg/L. Animals were exposed 6h/da 5 days per week for 4 weeks. NOAEC was 0.006 mg/L corresponding to 6 mg/m^3, since at higher concentrations the irritation of respiratory tract, hazardous effects and wounds on the mucous membrane and pneumonia occurred.

For consumers, a DNEL value is calculated at continuous exposure:
NOAEC konverteres til 24h = 6 mg/m^3 x 6/24 x 5/7 = 1.1 mg/m^3

DNEL = NOAEC / (AF1 x AF2 x AF3 x AF4)
AF1 (interspecies animal to human) = 2.5 (for local irritation effects)
AF2 (intraspecies, difference in human sensitivity) = 10
AF3 (duration of experiments, subchronic to chronic exposure) = 6

DNEL = 1.1 mg/m^3 / (2.5 x 10 x 6) = **0.007 mg/m^3**

Exposure to vapors must be expected to be less critical than for aerosols, which is why this DNEL value may be seen as relatively restrictive, as it is based on effects achieved after exposure to aerosols. Further, the large difference between the exposure levels applied results in uncertainty regarding the NOAEC value.

Bis(2-(dimethylamino)ethyl)ether; N,N,N',N'-tetramethyl-2,2'-oxybis(ethylamine)

In the REACH-registration for the substance, the following data for DNEL release have been given: in an inhalation experiment rats were exposed to vapors of bis(2-(dimethylamino)ethyl)ether at concentrations 0; 1.5; 8.2 and 38 mg/m^3. Animals were exposed 6h/day 5 days per week for 14 weeks. LOAEC was 1.5 mg/m^3, since at this concentration signs of irritation in eyes and respiratory tract occured.

For consumers, a DNEL value is calculated at continuous exposure:
LOAEC is converted 24h= 1.5 mg/m^3 x 6/24 x 5/7 = 0.27 mg/m^3

DNEL = LOAEC / (AF1 x AF2 x AF3 x AF4)
AF1 (interspecies animal to human) = 2,5 (for local irritation effects)
AF2 (intraspecies, difference in human sensitivity) = 10
AF3 (duration of experiments, subchronic to chronic exposure) = 2
AF4 (LOAEC to NOAEC extrapolation) = 3

DNEL = 0.27 mg/m^3 / (2.5 x 10 x 2 x 3) = **0.002 mg/m^3**

1,1,4,7,7-Pentamethyldiethylenetriamine; bis(2-dimethylaminoethyl) (methyl)amine

In the REACH-registration for the substance, the following data for DNEL release have been given: in an inhalation experiment rats were exposed to vapors of 1,1,4,7,7-pentamethyldiethylenetriamine at concentrations 0; 21; 85; 340 mg/m^3. Animals were exposed 6h/day, 5 days per week in 2 weeks. LOAEC was 21 mg/m^3, since at this concentration irritation of and effect on the mucous membrane cells in the respiratory tract occured.

For consumers, a DNEL value is calculated at continuous exposure:
LOAEC is converted to 24h = 21 mg/m^3 x 6/24 x 5/7 = 3.75 mg/m^3

DNEL = LOAEC / (AF1 x AF2 x AF3 x AF4)
AF1 (interspecies animal to human) = 2.5 (for local irritation effects)
AF2 (intraspecies, difference in human sensitivity) = 10
AF3 (duration of experiments, subchronic to chronic exposure) = 6
AF4 (LOAEC to NOAEC extrapolation) = 3

DNEL = 3.75 mg/m^3 / (2.5 x 10 x 6 x 3) = **0.008 mg/m^3**[Tekst]

Analysis and risk assessment of fragrances and other organic substances in squishy toys

The aim of this project has been to investigate whether it is possible to detect the contents of fragrances and other organic substances, which can be hazardous to children, in squishy toys. In the project, a total of 12 squishies were analyzed. Screening analyses of content as well as emission showed several problematic substances, such as N,N-dimethylformamide and various fragrances and amines. Quantitative analysis was performed on selected substances by emission after 1 hour and 3 days after unpacking the squishy from packaging and by migration test to artificial sweat. Migration of selected problematic substances was not detected, while emission analysis once again showed high concentrations of some problematic substances both after 1 hour and 3 days. The analysis results for emission have been used for the assessment of health-related risks of selected substances if a child uses these products in two scenarios. In an exposure scenario, where a young child lies down and sleeps while hugging a squishy, the measurements performed 1 hour after unpacking the toy showed unacceptably high levels of the substances N,N-dimethylformamide, triethylenediamine and cyclohexanone in all 12 squishies. In a scenario, where several squishies are kept in a child's room, also unacceptably levels of substances N,N-dimethylformamide, N,N-dimethylaminoethanol, triethylenediamine, bis(2-(dimethylamino)ethyl)ether, 1,1,4,7,7-pentamethyldiethylenetriamine and cyclohexanone were detected in the child's room after 3 days. In case of skin contact, the skin will also be exposed to the emitted substances, which is why a risk for skin irritation cannot be excluded. At the same time, the risk of skin allergy cannot be excluded either due to emission of skin allergy-causing substances that emitted in lower volumes, but which can still, cause the de-velopment of skin allergy in case of recurrent skin contact.

The Danish Environmental
Protection Agency
Haraldsgade 53
DK-2100 København Ø

www.mst.dk