Ministry of Environment and Food of Denmark
Environmental Protection Agency

Substances in household detergents

Survey and environmental and health assessment

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1. Summary and conclusions

A comprehensive environmental and health safety assessment on substances in household detergents and cosmetic detergent products was published by the Danish Environmental Protection Agency (Danish EPA) in 2001. Based on new regulations and customer demands on detergents, the Danish EPA requested an update of the report with a new assessment of the ingredients in the household detergents to reflect the status of the household detergents in 2018.
The objective for the present report is:

- Provide an updated overview of the substances used in the household detergents in Denmark.
- If possible, provide information on the tonnage of the substances
- Provide updated information on environmental and health safety profiles of the substances in the household detergents enabling the Danish EPA to assess, if regulative initiatives or new advice for consumers are relevant within the area

The report covers a survey of the groups of surfactants, complexing agent, bleaching agents, enzymes and fragrance substances for the period from 2001 to 2018. Focus is on products and ingredients in laundry detergents, detergents for dishwashing and all-purpose detergents for consumer use.

For the Danish market, information was collected from Statistic Denmark and the Prodcom Database. The import of washing preparations and cleaning preparations has increased from 30,000 tonnes in 2001 to 85-90,000 tonnes per year for the period 2012-2017, whereas the production decreased from 150,000 tonnes in 2004 to around 80,000 - 85,000 tonnes in the period from 2012 to 2016. Overall, the level of consumption in 2014-2016 is the same as that in the period of 2001-2003, which is around 50,000 tonnes per year.
In general, the number of eco-labelled products has increased during the last ten years. Whereas the number of all-purpose products still increases after 2015, the number of eco-labelled products within the group of laundry detergents and machine dishwashing detergents has declined after 2015 and 2014, respectively. For the hand dishwashing detergents, the number has reached a steady state for the period 2015-2017.
The survey of substances in laundry detergents, detergents for dishwashing and all-purpose detergents was done by questionnaires, interviews and ingredients lists public available.
In general, for the EU and the Danish market, the main trends for innovation of washing and cleaning products focus on:

- Low temperature washing
- Unit dosing
- Compaction
- Controlled dosing
- Resource efficiency and packaging.

Laundry detergents
The results from the present survey of laundry detergents point out the following trends:

- Application of enzymes in detergents for low temperature washing
- Ingredients with a preservative function may be present in cold wash detergents
- Enzyme stabilisers are used together with the enzymes in laundry detergents
- Introduction of gel tabs or pods/capsules to meet demand for easy dosing of laundry detergents

- Environmental-friendly products based on biodegradable ingredients – the eco-labelled products and so-called green products in focus
- Development of substances manufactured from natural sources instead of synthetic sources such as substances with vegetable origin versus petrochemical origin
- Introduction of biosurfactants synthesized by fermentation by microorganisms such as bacteria, fungi and yeast
- Introduction of “colour” laundry detergents to improve colourfastness and washing results of coloured and black fabrics by the use of dye transfer inhibitors.

The results of the survey of the ingredients in laundry detergents indicate the following:

- Surfactants are represented by anionic and nonionic surfactants and amphoteric alkylamidopropylbetain
- Complex binders are represented by phosphates, phosphonates, polycarboxylates, silicates, zeolites and citrate
- New complex binders are methylglycine diacetate (MGDA) and sodium carboxymethyl inulin
- Bleach agents are represented by tetraacetyl ethylenediamine (TAED), perborates and percarbonates
- New bleach agent is hydrogen peroxide
- Enzymes are represented by proteases, lipases, amylases, mannanases, cellulases and pectinases
- Fragrance substances are represented by 25 different substances from the list of 82 fragrance substances that are considered as possible contact allergens for humans (SCCS no 1459, 2011)
- Ingredients with other functions include additives, antifoaming substances, binders, bulking agents, colours, dye transfer inhibitors solvents, optical brighteners, pH adjuster stabilisers, and viscosity controllers among others.

Dishwashing detergents

The results from the survey point out the following trends within dishwashing detergents:

- Tabs and gels for easy dispensing for machine dishwashing
- Tabs for dishwashing with additional functions such as pre-soaking action, machine lime scale protection, low temperature action, filter protection and glass protection
- Gels for dishwashing to reduce washing time due to a faster solubility of the ingredients in the detergent
- Green image and eco-labelled products for dishwashing are in focus.

The results from the survey of the ingredients in dishwashing detergents indicate the following:

- Surfactants are represented by anionic, non-ionic, amphoteric and cationic surfactants
- New surfactants are amphoteric amine oxides and alkyl amidopropyl amine oxides
- Complex binders are represented by phophates, phosphonates, silicates, carbonates and citrate
- New complex binders are MGDA, polyethylene imine, sodium carboxymethyl inulin and a range of organic acids and their salts
- Bleaching agents are represented by perborates, percarbonates and TAED
- Enzymes are represented by amylases and proteases including subtilisin
- Fragrance substances are represented by natural essential oils (no detailed information available), limonene, butylphenyl methylpropional, hexyl cinnamal, linalool, coumarin and glutaral
- Ingredients with other functions include additives, antifoaming agents, antimicrobial substances, binders, fillers, hydrotropes, solvents and viscosity controllers.

All-purpose detergents
The results from the survey point out the following trends within all-purpose detergents:

- Packaging and form of application with focus on application of the cleaning agents in spray products

The results from the survey of the ingredients in all-purpose detergents indicate the following:

- Surfactants are represented by anionic, non-ionic, amphoteric and cationic surfactants
- New surfactants are amphoteric alkyl amines and alkyl amine oxides
- Complex binders are represented by citrates, phosphates, carbonates and acrylic polymers
- New complex binders are MGDA and sodium iminodisuccinate.
- Bleaching agents and enzymes are not used in normal all-purpose detergents
- Fragrance substances are represented by limonene, linalool, citronellol, geraniol, butylphenyl methylpropional, hexyl cinnamal and amy cinnamal
- Ingredients with other functions include antifoaming substances, disinfectants, hydrotrope substances, solvents and viscosity controllers among others.

Environmental and health assessment
The environmental and health assessment was done for selected substances and group of substances prioritized to supplement the report from 2001. The new functional groups: antifoaming agents represented by a group of siloxanes, the dye transfer inhibitors represented by the group of polyvinylpyrrolidone polymers, enzyme stabiliser ((4-formylphenyl) boronic acid) and enzyme activator (manganese-II-oxalate dehydrate) were selected because they were not assessed in the report from 2001. Furthermore the assessments was performed for the new complexing agents including MGDA, sodium carboxymethyl inulin, polyethylene imine and sodium iminodisuccinate, which were not assessed in 2001.

Data on environmental fate, environmental toxicity and human health of the selected substances were retrieved from public available databases and literature. Data from the European Chemicals Agency (ECHA) registration database were used as the primary source of information. If no information available in the ECHA database, data were retrieved from other databases, opinion reports and from literature. Sufficient data were available for the environmental and human health assessment of the substances; however, data were scarce on the environmental properties of the polymers sodium carboxymethyl inulin and polyethylene imine.

2. Introduction

2.1 Background

Household detergents are continuously under development in order to improve effectiveness and to meet market demands on new product types or formulations, as well as improvement of environmental image in terms of sustainability and compliance with EU's regulation on detergents.

With the EU Regulation on detergents (Regulation (EC) no. 648/2004) and its amendments, requirements on the biodegradability of surfactants, limitations on the content of phosphates and other phosphorus compounds[1] as well as requirements on labelling and ingredient datasheets were introduced.

During the period from 1998 to 2000, a comprehensive environmental and health safety assessment was made on substances in household detergents and cosmetic detergent products for the EU market. A report from the Danish Environmental Protection Agency (Danish EPA) presents the results from the assessment (Madsen *et al*., 2001).

Due to the market demands and the regulations within the area, formulations may have changed, and new substances may have been introduced in the household cleaning products, since the overview was made in 2000. Therefore, the environmental and health safety profiles of the detergents may have changed as well. On this background, the Danish EPA requested an update of the survey and the assessment of the ingredients in the household detergents from 2000 to reflect the status of the household detergents in 2018.

This report presents the results of the survey of the market for household detergents. The environmental and health assessment of selected substances and selected groups of substances is intended as a supplement to the Danish EPA's report from 2001 (Madsen *et al*., 2001).

2.2 Objective and scoping

The Danish EPA has defined the following objective for this report:

- Provide an updated overview of the substances used in the household detergents in Denmark.
- If possible, provide information on the tonnage of the substances
- Provide updated information on environmental and health safety profiles of the substances in the household detergents
- Provide information enabling the Danish EPA to assess, if regulative initiatives or new advice for consumers will be relevant within the area.

The report will focus on the following:

- Products and ingredients in laundry detergents, detergents for dishwashing and all-purpose detergents for consumer use
- Surfactants, complexing agent, bleaching agents, enzymes and fragrance substances
- The period from 2001 to 2018.

[1] Consumer laundry detergents shall not be placed on the market if the total content of phosphorus is equal to or greater than 0,5 grams in the recommended quantity of the detergent to be used in the main cycle of the washing process for a standard washing machine load. Consumer automatic dishwasher detergents shall not be placed on the market if the total content of phosphorus is equal to or greater than 0,3 grams in the standard dosage.

2.3 Methodology

2.3.1 Market information

Information on the Danish retail market for laundry and cleaning detergents has been collected from the database Statistics Denmark and Eurostat's Prodcom Database (Statistics Denmark; Prodcom Database). Data on import and export have been retrieved for the period 2001-2017 using the KN kode 34022090 (Detergent preparations including laundry detergents and cleaning products, whether or not containing soap, in retail sale packaging (except organic surfactants, soaps and surfactants and fabrics of preparations for skin washing, in liquid form or as a cream) (Statistics Denmark). Data on production were retrieved for the period 2001-2016 from the Prodcom database using the NACE Code 20413250.

Furthermore, Ecolabelling Denmark was contacted to get information on the market for ecolabelled products.

2.3.2 Information from trade organisations and suppliers

The two relevant trade organisations in Denmark, Kosmetik- og hygiejnebranchen (formerly SPT) and VKH under the Confederation of Danish Industry (DI) were contacted and asked to send the questionnaires to their members in order to retrieve the requested information.

Questionnaires were prepared to collect information on the ingredients in the following products:

- Laundry detergents for machine wash and hand wash for consumers
- Machine dishwashing detergents and detergents in washing-up liquids for consumers
- All-purpose detergents for consumers.

The questionnaires were distributed by the two trade organisations to the relevant suppliers of detergents for the Danish market.

In the questionnaires that were based on the information from the previous environmental project (Madsen *et al.*, 2001), the suppliers were asked to tick the substances in use (2016/2017) and add the chemical name of new ingredients within the following groups:

- Surfactants (divided into anionic, nonionic, cationic and amphoteric surfactants)
- Complexing binders
- Bleaching agents
- Enzymes
- Fragrances (a list of 82 fragrance substances were provided)

The list of fragrance substances was based on the SCCS (Scientific Committee on Consumer Safety) conclusion that 82 fragrance substances can be considered as possible contact allergens for humans, i.e. that in at least two or more independent clinical trials sufficient human evidence has been found that the substances are allergenic (SCCS no 1459, 2011).

Recently, a survey of preservatives in washing and cleaning detergents was carried out by the Danish EPA. The results are published in 2018 (Kjølholt J. *et al*., 2018), and therefore this survey disregard the preservatives.

In addition, the suppliers were asked to describe the development in product types and use of substances within the individual products for the period 2001 – 2018.

The results from the questionnaires were poor as only few questionnaires were returned representing only two suppliers. With an additional follow up by interviews, the outcome of the activity was input from six suppliers covering suppliers of the three product types: Laundry detergents, dishwashing detergents and all-purpose detergents. The number of suppliers providing information is considered to represent only a minor part of the market in Denmark.

Therefore, a supplement to the information from the contacted actors, product information has been searched on websites with available ingredients lists available on the internet on sales websites and company websites. The websites include www.nemlig.com, Mad.coop.dk, www.Unilever.dk, www.rbeuroinfo.com, www.Tingstad.com.

Further information on the ingredients such as function of ingredients has been found via A.I.S.E.'s website www.cleanright.eu (2018), Unilever (2018) supported by Emsley (2015).

The results from the survey of ingredients in laundry detergents (powder, liquid, pods), dishwashing detergents (liquid, powder, gel, tabs) and all-purpose detergents collected from questionnaires (Q), interviews (I) and product information (PI) are shown in Appendix 2 and discussed in chapter 4 to 6.

3. Market information

3.1 The Danish retail market for washing and cleaning detergents

Information on the Danish import, production and export of washing and cleaning detergents to retail for the period from 2001 to 2017 is illustrated in Figure 1 (Statistics Denmark; Prodcom Database). The consumption of washing and cleaning detergents is calculated from the information on import, export and production and shown in the figure as well. A table with detailed volumes is included in Appendix 1.1.

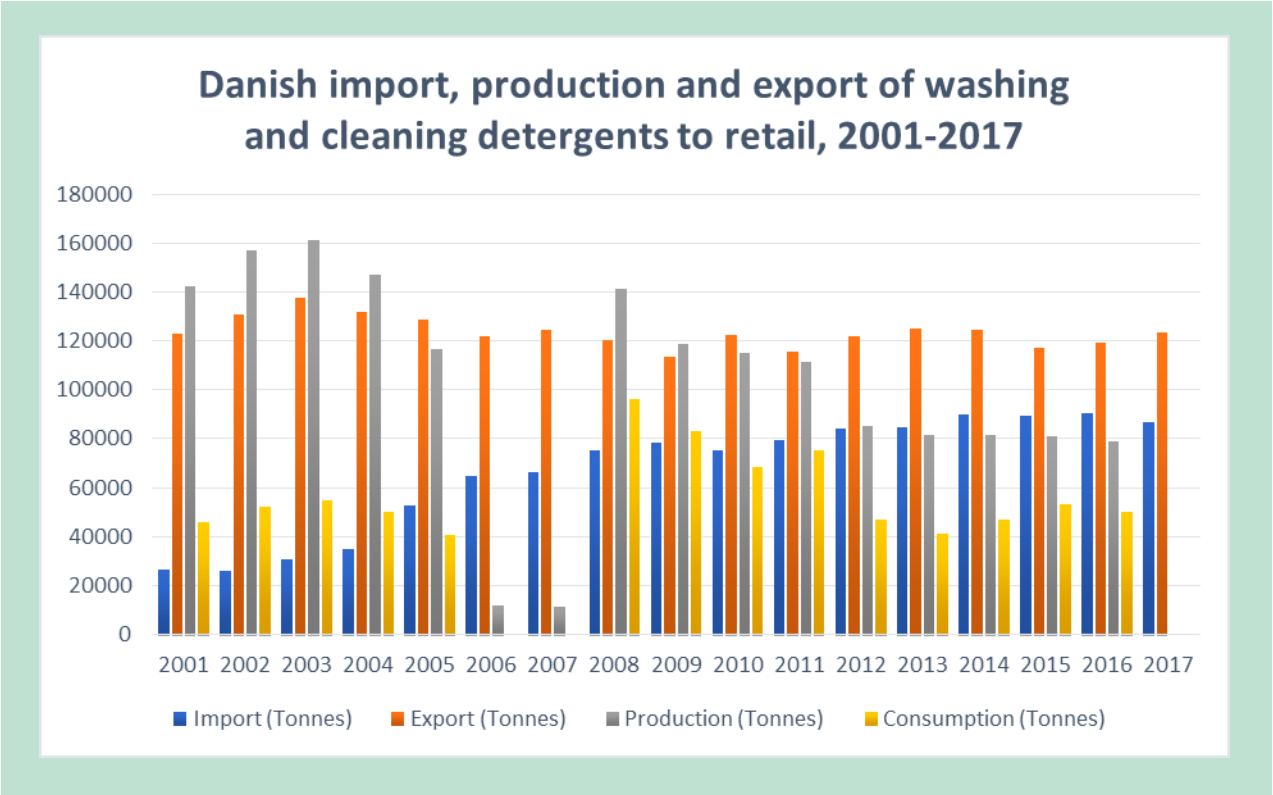


FIGURE 1. Danish import, production and export (in tonnes) of washing and cleaning detergents to retail, 2001-2017. The consumption is calculated as Import + Production – Export. The values for 2006 and 2007 are excluded (see text below).

The available information covers the retail market of the entire group of products for washing and cleaning including laundry detergents, dishwashing detergents and all-purpose detergents. The group therefore also covers products outside the scope of this report such as speciality cleaners and sanitary cleaners.

The import of washing preparations and cleaning preparations has increased roughly by 300 % (30,000 tonnes to 90,000 tonnes) from 2001 to 2017 reaching a steady state of around 85-90,000 tonnes per year for the period 2012-2017. Meanwhile, the export was steady around 120,000 -125,000 tonnes with only small fluctuations throughout the whole period from 2001 - 2017. The Danish production of washing and cleaning detergents increased from 142,000 to 161,000 tonnes in the period 2001 to 2003 where after it decreased from 150,000 tonnes to 80,000 tonnes during the period from 2004 to 2012. In the period from 2012 to 2016 it seems

that the production has reached a steady state around 80,000 - 85,000 tonnes. Overall, the figures indicate that the increase in the import of detergents compensates the decline in the production of washing and cleaning detergents in Denmark.

The production numbers from the Eurostat ProdCom database for the years 2006 and 2007 were about 10-times lower than the average tonnage for the whole period. This is anticipated to be a recording failure and therefore the consumption for the years 2006 and 2007 were not calculated. However, this has no effect on the overall picture for the period from 2001 to 2017. The consumption had some fluctuations during the period, but overall the level of consumption in 2014-2016 is the same as that in the period of 2001-2003, which is around 50,000 tonnes per year.

According to a survey of consumer habits done by the International Association for Soaps, Detergents and Maintenance Products (A.I.S.E.), every third year, the 2017 results were the following (A.I.S.E. 2017):

- The number of laundry washes per two weeks has decreased slightly over the years (from 6.7 in 2008 to 6.1 in 2017), but was stable during the recent years at 3.1 loads a week per household
- Stable loading of washing machine during the recent years (8/10 fully loaded)
- Frequency of use of dishwasher was stable across the years at 4.3 loads a week per household
- Dishwashers were filled to capacity for 92% of the time (9/10 fully loaded).

Provided that all loads are based on liquid detergents, the consumer consumption of laundry detergents in Denmark can be estimated to be 38,300 m^3 per year based on

- 3.1 loads a week per household (A.I.S.E. 2017)
- Dose of 88 ml on average (medium-hard water and average laundry soil levels) (Cleanright, 2018)
- 2,700,000 households in Denmark (Statistics Denmark).

Consumer consumption of dishwashing detergents in automatic dishwasher in Denmark can be estimated to be 9660 tons per year based on

- 4.3 loads a week per household (A.I.S.E. 2017)
- Dose of one tablet of 16 g on average (classic tablet)
- 2,700,000 households in Denmark (Statistics Denmark).

It has not been possible to collect enough information to describe the distribution of the type of products (liquid, powder, pods, tabs, gel) within laundry detergents and dishwashing detergents, which are in focus in this report.

3.2 Eco-labelled products

The general trend within the washing and cleaning detergents is an increasing demand for eco-labelled products. This is a result from a growing environmental awareness from both the consumers' side but also companies seeking a green image.

Figure 2 below shows the number of detergent products for laundry, dishwashing and cleaning having either the EU Ecolabel or the Nordic Swan Ecolabel for the Nordic market for the period from 2007 to 2017 (Ecolabelling Denmark). The number of laundry detergents with the Nordic Swan label includes stain removers, and the number of machine dishwashing detergents with the Nordic Swan label includes rinse aid products. For the hand dishwashing detergents and all-purpose detergents, the figures cover products for consumers and professional users.

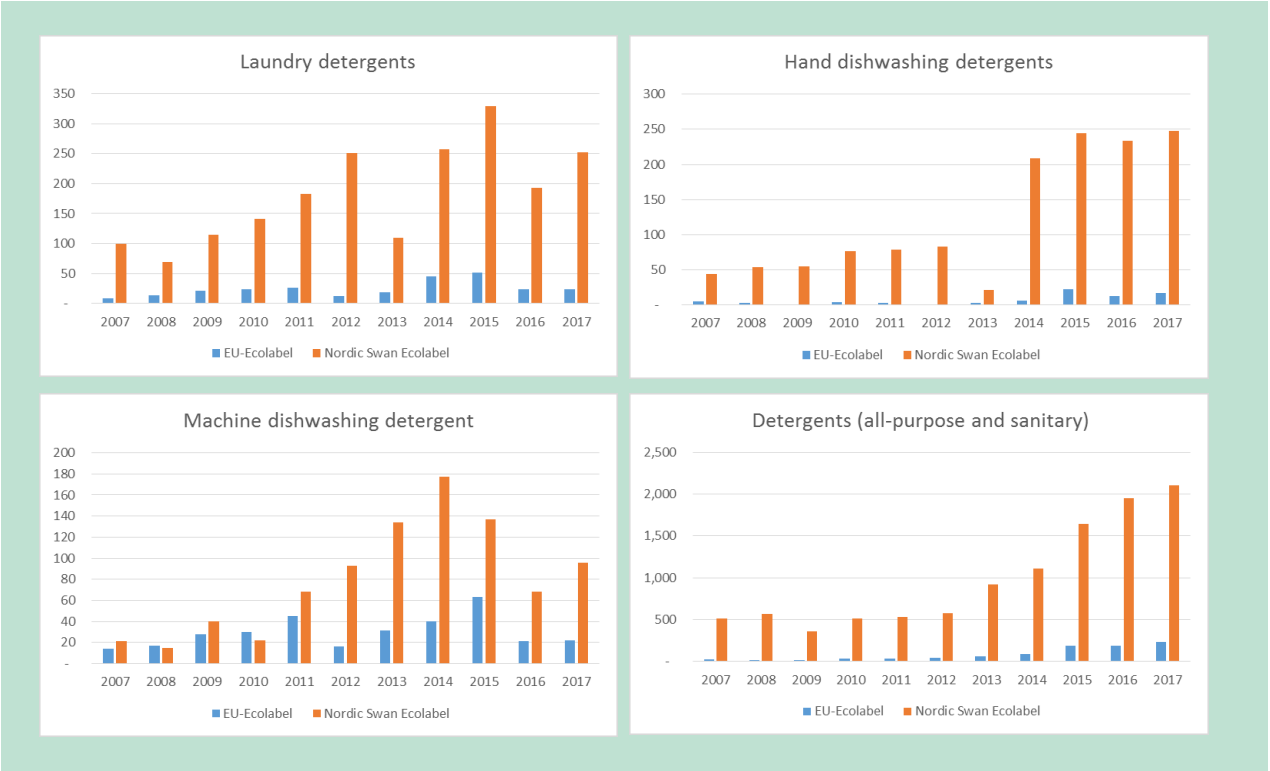


FIGURE 2. Number of products within laundry detergents, hand dishwashing, machine dishwashing and all-purpose cleaning detergents that have either the EU Ecolabel or the Nordic Swan Ecolabel for the period from 2007 to 2017.

The figures show that the number of eco-labelled products has increased since 2007 with some fluctuations during the period. The increase in number has been at least three times and up to more than eight times based on the number in 2007 compared to the number in 2014/2015. Whereas the number of all-purpose products still increases after 2015, the number of labelled products within the group of laundry detergents and machine dishwashing detergents has declined after 2015 and 2014, respectively. For the hand dishwashing detergents, the number has reached a steady state for the period 2015-2017.

Even though the number of products labelled with the Nordic Swan is higher than products having the EU Ecolabel, the numbers seem to follow the same trend.

The number of eco-labelled products may be affected by the development in the ecolabel criteria in addition to the consumer demands to more environmentally friendly products. The trends in the Nordic Swan and EU's Ecolabel criteria for cleaning-, dishwashing-, and laundry detergent for the period from 2001 to 2018 is reviewed and discussed in Appendix 1.2.

3.3 European market for washing and cleaning detergents

A.I.S.E. published an overview of the market value for household care products for the European retail market in their Activity & Sustainability Report for 2017-18 (see table below).

TABLE 1. Market value 2017 for washing and cleaning detergents on the European market for retail. Information from A.I.S.E., 2018a.

Household care	Laundry care	Surface care	Dishwashing	Maintenance products	Bleaches	Total
Market value 2017 (billion EUR)	13.5	6.1	4.4	3.9	0.7	28.6
Market share (%)	47.3	21.2	15.4	13.8	2.3	100

The total European market value in 2017 was 35.9 billion Euros (EUR) with a share for the professional cleaning and hygiene reported to be 7.3 billion EUR. Based on this, the market value for the retail products accounts for 80% (28.6 billion EUR) of the total European market for washing and cleaning products.

In addition, the A.I.S.E. report provides a detailed overview of the product types within washing and cleaning products. The distribution of the products is given as the share of the market value in billion EUR. It is noted that liquid detergents make a total of more than 50 % of the detergents for laundry. Detergents for machine dishwashing form the major part of the dishwashing detergents.

TABLE 2. Market value 2017 for washing and cleaning detergents for retail, distributed in product types. Information from A.I.S.E., 2018a.

Product	Product type	Market value billion EUR
Laundry	Liquid detergents	4.3
	Powder	2.6
	Tabs	1.3
	Other incl. softeners	5.3
Cleaning	All-purpose (surface cleaning)	4.4
	Toilet cleaning	1.7
Dishwashing	Machine dishwashing	2.6
	Hand dishwashing	1.8
Others	Air fresheners, insecticides, polishes, bleaches	4.6

The development and improvement of detergents have been going on for over 150 years focusing on customers' demands and better performance while keeping the costs low.

A.I.S.E. is providing a survey of consumer habit every third year and the results from 2017 report, among others, that consumers prioritize fresh fragrances over whiteness and a general shift to concentrated formats in both dishwashing and laundry.

The main trends for innovation of safe and sustainable use of products include the following areas (A.I.S.E., 2018b):

- Low temperature washing
- Unit dosing
- Compaction

- Controlled dosing
- Resource efficiency and packaging.

The introduction of enzymes (see chapter 4.2.4 for enzymes in laundry detergents) has improved the efficiency of laundry detergents at lower temperatures compared to products without enzymes. An important driver for innovation of detergents products is to develop safe products and improve user safety. User safety is improved by the introduction of products, such as tablets and pods, that are easier to dose and with no direct handling of powders (elimination of inhalation of the products) or liquids (elimination of skin contact).

4. Results of survey of laundry detergents

4.1 Trends in laundry detergents

This chapter describes the trends within the development of laundry detergents since 2001. If no other reference mentioned, the information in this chapter is collected from the questionnaires and interviews supported by the ingredient lists consulted in the survey (www.nemlig.com, Mad.coop.dk, www.Unilever.dk, www.rbeuroinfo.com, www.Tingstad.com).

The Danish suppliers operate together with their raw materials suppliers within the trends described by A.I.S.E. (2018b) including low temperature washing, compaction, dosing, packaging and resource efficiency.

The builder and the surfactant systems in laundry detergents are continuously optimised to improve the washing results in a broader temperature range that includes low temperatures. The primary function of the builder system is to soften the water by extracting and binding the calcium and magnesium ions, and, thus, reducing the water hardness. The builder system also prevents the re-deposition of soils, and it provides alkalinity and buffering capacity. The surfactants are surface-active agents increasing the wettability of surfaces and emulsifying oily soils and keep them suspended and dispersed in the water phase.

Enzymes have a central role in the development of detergents for cold wash laundry. Enzymes are effective at moderate temperature and in the washing process. They degrade the dirt in the fabrics such as proteins, lipids and polysaccharides. The application of enzymes has an important role in the optimisation of the builder and surfactant systems at low temperature, as they promote the solubility and removal of the soils from the fabric surface. At low washing temperatures, microorganisms may survive in the laundry demanding the application of chemical substances for removal of bacteria and inhibition of microbial growth. Therefore, ingredients with an antiseptic function may be present in cold wash detergents.

The trend in relation to product type is towards concentrated products for both powders and liquids. The use of concentrated products, if used correctly, is good for the environment as it saves energy for transport. Theoretically, based on the washing activity contained in the recommended dosing of the concentrated products versus that of the normal products, the environmental impact from the use of concentrated products is the same as from the use of the normal products. The consumer must, however, be aware of correct dossing, to avoid overdosing which may lead to a surplus of washing activity and thus emission of unused chemicals. In addition, it is more convenient for the consumers with smaller packages for the compact products compared to the bigger packages for standard products. The results from industrial projects *A.I.S.E. Product Resource Efficiency Projects* for powder and liquid laundry detergents show that the maximum recommended dosage for liquid decreased from 120 ml in 2009 to 55 ml in 2018, while the same dosage for powder detergents decreased from 110-150 g in 2000 to 75 g in 2018 (A.I.S.E. 2018a).

Furthermore, a demand for easy dosing of the laundry detergent is met by the introduction of gel tabs or pods/capsules. This enables the consumer to dose the liquid detergent avoiding spill and any contact with the detergent. However, with the use of tabs or pods, it is not possible to adjust the dose to the water hardness, the load and the dirtiness of the laundry. This may lead to overdosing when the washing machine is not fully loaded or the laundry is less

soiled. According to the figures from A.I.S.E., only 8 out of 10 loads are fully loaded (A.I.S.E., 2017).

Recently, suppliers have introduced washing balls as an alternative to the traditional laundry detergents. The washing balls are containers filled with laundry pellets, which are hard-pressed laundry powder. According to the suppliers, the washing balls can be used for more than 100 washes but need to be refilled depending on the product (one product claims that refill is needed after 70 washes). During wash, the washing balls release soap to the water that help to remove dirt from the clothes in the same way as ordinary laundry powders (Forbrugerrådet Tænk, 2017). For the washing balls, it is not possible to adjust the dosing of laundry detergents to fit the load and soiling of the laundry.

In addition, dosing of laundry detergent is made easier by washing machines with a self-dosing system. In Denmark, such system is only available for one brand and therefore only very few products are available for the system (Miele, 2018).

According to the Danish suppliers, the main trend in Denmark is towards environmental-friendly products – the so-called green products and eco-labelled products with focus on biodegradable ingredients. The trend is also towards the development of substances manufactured from natural sources instead of synthetic sources. The manufacturing process results in the same chemical structures to ensure the same performance and efficiency of the surfactant. The use of renewable sources is in focus for the group of surfactants. Consumers and retailers are becoming more and more aware of the origin of the raw materials with an increasing demand on renewable sources especially of vegetable origin as an alternative to the petrochemical origin.

During the last decade biosurfactants have also been introduced on the market. Biosurfactants are a diverse group of surface-active substances synthesized by fermentation by microorganisms such as bacteria, fungi and yeast. The manufacturing process is mild and may be 100% based on renewable sources. The hydrophilic moiety of biosurfactants can either be an amino acid, peptide group, phosphate group, carbohydrate (mono-, di-, or polysaccharides), or some other compounds, whereas the hydrophobic group is generally made up of a long hydrocarbon tail. Commonly, biosurfactants are neutral or anionic in nature. Most common are the glycolipids also called alkyl polyglucosides (APG). APG is a nonionic surfactant composed of a fatty alcohol linked by a glycosidic bond to a glucose unit and sourced from plant-based raw materials like starch and vegetable oil.

The development of laundry detergents towards products that are effective at low temperatures has introduced the use of enzymes and substances related hereto such as enzyme stabilisers in the laundry detergents. Furthermore, “colour” laundry detergents have been developed to improve colourfastness and washing results of coloured and black fabrics. In these types of products, dye transfer inhibitors are introduced.

The development of laundry detergent ingredients is described below in section 4.2. Focus is on the substances identified in the current survey and not described in the report from 2001 (Madsen *et al.*, 2001).

4.2 Ingredients in laundry detergents

The list of ingredients identified in laundry detergents on the Danish market is included in Appendix 2.1.

4.2.1 Surfactants

The surfactants used in laundry detergents are primarily anionic and nonionic surfactants. The group of anionic surfactants is represented by linear alkylbenzene sulfonic acid (LAS), alkyl sulfates, (AS), alkyl ether sulfates (AES), alfa-olefine sulfonates (AOS), fatty acids (FA) and soaps. The soaps that are salts of fatty acids may be added to the product in the form of the fatty acids and formed in the product matrix as the salt. Compared to the substances described in the report from 2001 (Madsen *et a*l., 2001), the secondary alkane sulfonates and sulfosuccinates were not identified in the current survey.

Within the non-ionic substances, the most common surfactants are the alcohol ethoxylates. The nonionic surfactants are represented by the traditional alcohol ethoxylates (AE), block polymers and alkylpolyglycosides (APG). Within this group, the alcohol ethoxylates (AE) are characterised by a wide range of molecules with the carbon chain lengths of C11-C18 and 3-25 EO (ethylene oxide). None of the glucose amides or the fatty acid amides described in the report from 2001 have been found in the laundry detergents in this survey.

Besides the use of anionic and nonionic surfactants, use of amphoteric alkylamidopropyl betaine has been identified. The imidazoline derivatives were not identified as part of this survey.

No use of cationic substances were identified in laundry detergents in this survey.

Among the fatty acids and LAS, the types with either monoethanolamine (MEA) or triethanolamine (TEA) seem to be commonly used. These types were not identified in the report from 2001 (Madsen *et al*., 2001).

Over the years, the Danish EPA has focused on the consumption of LAS in detergents and implemented in 1999 an information campaign to get consumers to purchase LAS-free products. LAS was on the Danish EPA's "List of Undesirable Substances (LOUS), 2004" due to lack of anaerobic degradability and toxicity to aquatic organisms. The fact that the substance does not degrade under oxygen-free conditions can lead to high concentrations of LAS in sewage sludge. Therefore, a cut-off criterion of 1300 mg LAS / kg dry matter was set by the Danish EPA. Furthermore, LAS does not comply with the criterion of biological degradability of surfactants for environmentally labelled products, and therefore LAS is not found in eco-labelled products. A survey by the Danish EPA in 2007 indicated a reduction in the LAS consumption in Denmark from 1998 to 2002 (from 4300 tonnes in 1998 to 1500 tonnes in 2002), after which there has been stagnant consumption (Niemann *et al*., 2007). In spite of the focus on the environmental properties of LAS, the use of LAS in detergents is not banned.

In this survey, the use of LAS in washing and cleaning detergents was identified and further examined. Data from the Nordic SPIN Database were retrieved to provide the information on LAS in washing and cleaning agents placed on the Danish market (UCN code 09). It should be noted that the SPIN database only covers professional uses. According to the report from 2007, more than 98% of the LAS used in Europe consists of the benzene sulphonic acid, C10-13 alkyl derivatives, sodium salt with CAS no. 68411-30-3. The HERA risk assessment of LAS includes five CAS numbers, of which REACH registration has been made for two: CAS no. 68411-30-3 and CAS no. 25155-30-0 (sodium dodecylbenzenesulfonate) (HERA, 2013). The use of LAS in cleaning and washing agents in Denmark for the period 2000 to 2015 is shown for the two CAS numbers in Figure 3. The figures show that the use of LAS has decreased since 2000 and has reached a steady level in the period from 2009 to 2015. The use of LAS with CAS no. 68411-30-3 is 2-13 tonnes/year and 76-93 tonnes/year for CAS no. 25155-30-0.

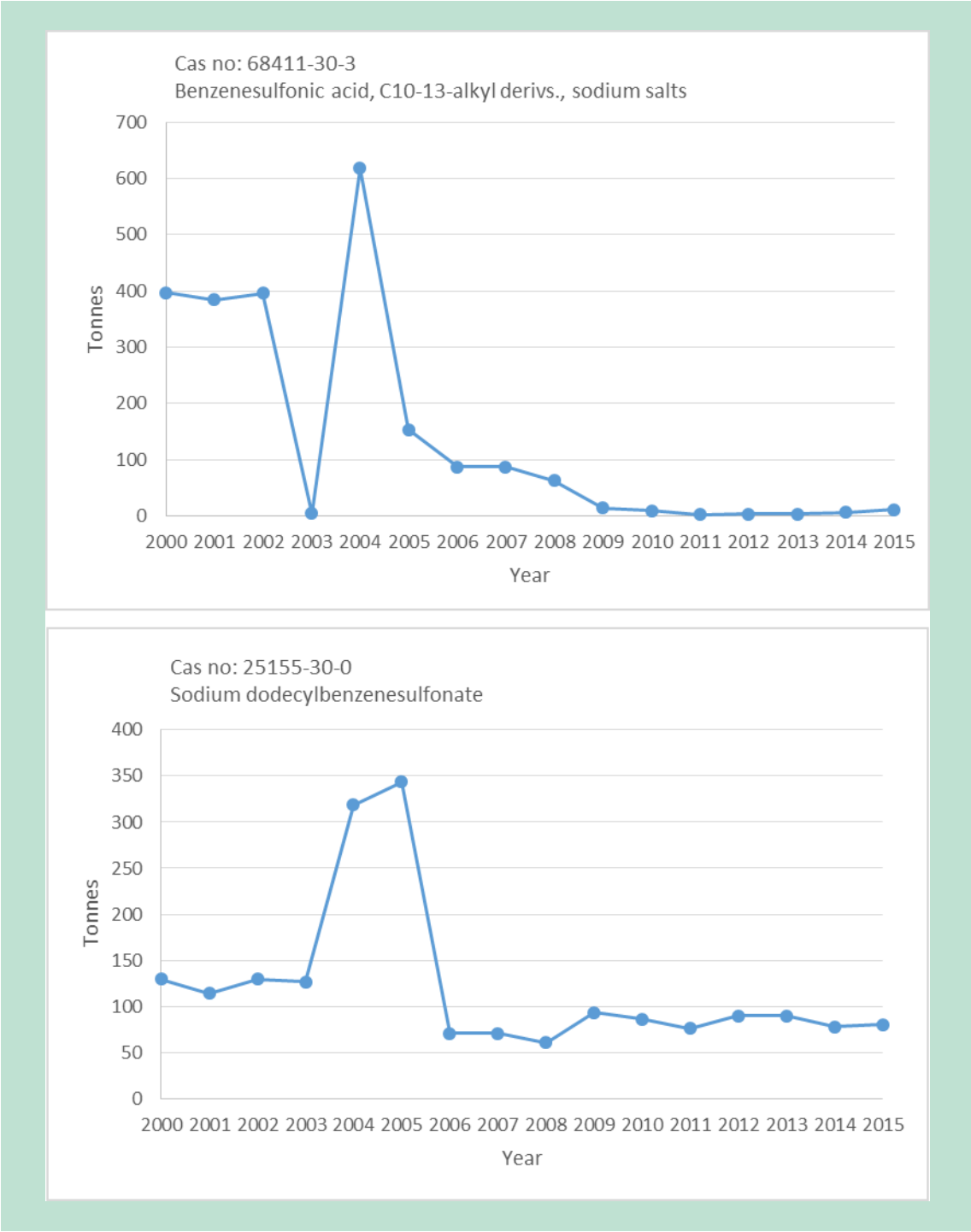


FIGURE 3. LAS recorded as CAS no. 68411-30-3 and CAS no. 25155-30-0 used in washing and cleaning agents placed on the Danish market (UCN code 09) in the period 2000-2015.

Use of LAS with MEA or TEA was also identified in the survey. To retrieve information on the volume of the MEA and TEA dodecylbenzenesulfonates, CAS nos. for these substances were identified in the ECHA database (MEA dodecylbenzenesulfonate: 26836-07-7 and 35465-66-8; TEA dodecylbenzenesulfonate: 27323-41-7, 68411-31-4 and 29061-63-0) (ECHA, 2018). However, none of the MEA and TEA substances were found to be registered in REACH and only the TEA dodecylbenzenesulfonates (CAS no. 27323-41-7, 68411-31-4) were found in the SPIN database. The use of TEA LAS in cleaning and washing agents in Denmark for the period 2000 to 2015 is shown in Figure 4 for the two CAS numbers.

The use of the substance with CAS no 68411-31-4 was 1 tonnes per year or lower except in 2008, where the tonnage was slightly above (1.1 tonnes/year). The use of the substance do-decylbenzenesulphonic acid, compound with 2,2',2''-nitrilotriethanol (1:1) with CAS no. 27323-41-7 seems to be increasing with a use of 6 tonnes in 2014 and in 2015.

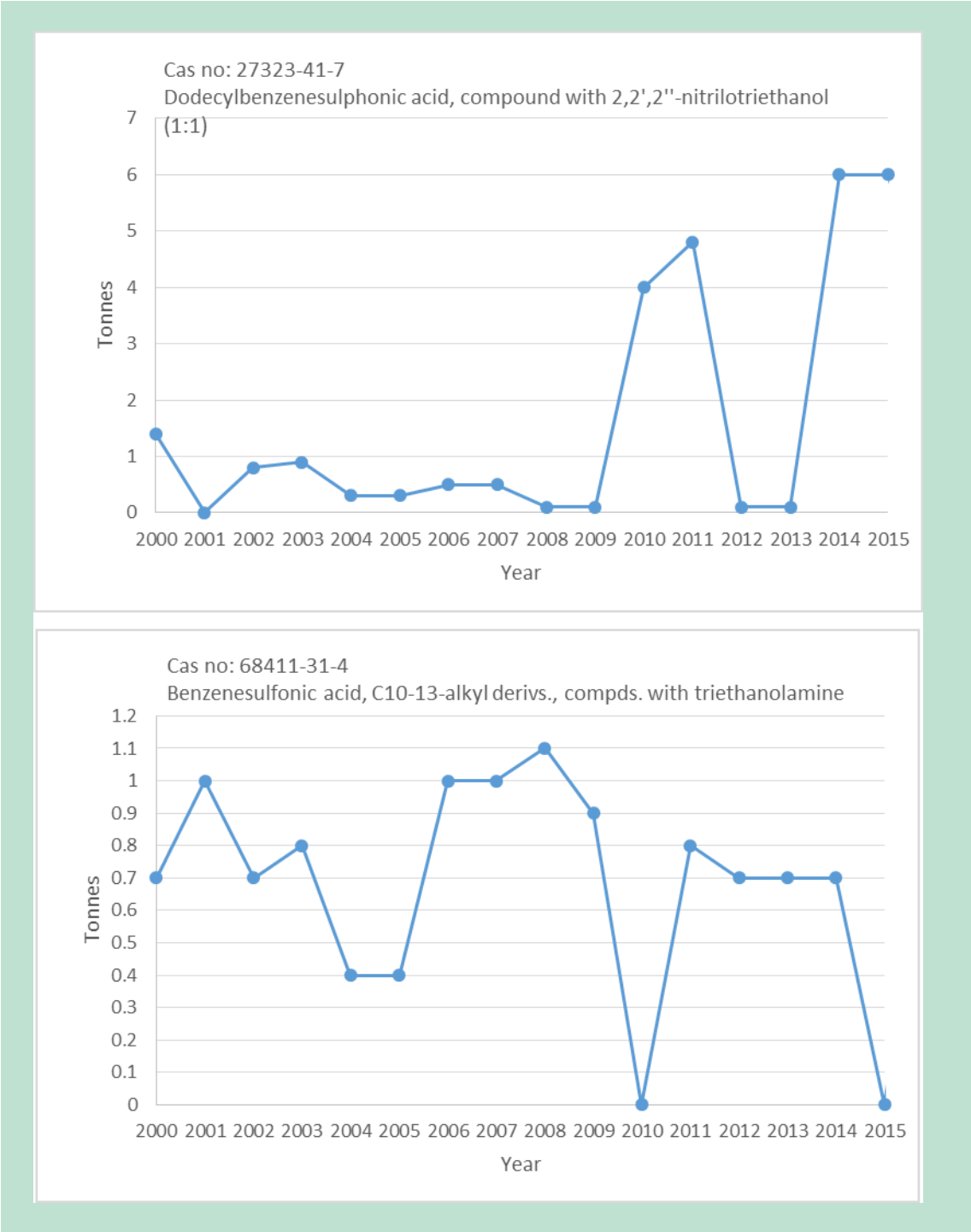


FIGURE 4. TEA-dodecylbenzenesulfonate recorded as CAS no. 27323-41 and 68411-31-4 used in washing and cleaning agents placed on the Danish market (UCN code 09) in the period 2000-2015.

4.2.2 Complex binders/Builders

The building system in laundry detergents consists of a system of substances that reduces the effect of water hardness by binding calcium ions and magnesium ions. This is done by chelation or sequestration, precipitation or by ion exchange.

Phosphates are sequestering builders found in the laundry products on the market. The phosphates and other phosphorus compounds in household laundry detergents is regulated by a restriction on the amount of phosphates and phosphonates used per wash (≥ 0.5 g per standard wash). It is not the aim of the present survey to examine whether the restriction on amount of phosphate per wash is met, as the dosage and the exact content of phosphate in the products have to be known. In most products on the Danish market, other substances substitute the use of phosphates and phosphonates. The systems used are mainly the systems described in the report from 2001 (Madsen *et al*., 2001) including polycarboxylates, silicates, zeolites and citrate.

Some new complex binders have also been developed to substitute phosphates and phosphorous substances in laundry detergents. A commercial product based on methylglycine diacetate (MGDA) has been introduced in addition to sodium carboxymethyl inulin, which is a vegetable scale inhibitor. Both substances are characterised by being biodegradable and thus environmental-friendly. The introduction of MGDA is emphasized by Danish suppliers of laundry detergents.

From the results of the survey, it seems that the use of ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetat (NTA) in laundry detergents has stopped. NTA is on the Danish EPA's List of Undesirable Substances due to a classification as Carc. 2. The use of NTA by consumers has therefore been in focus, and NTA is no longer used in laundry detergents.

4.2.3 Bleach agents

The use of substances for bleaching is represented by tetraacetyl ethylenediamine (TAED), perborates and percarbonates, as in 2001, and furthermore hydrogen peroxide. The use of hydrogen peroxide as bleaching agent was not reported in 2001 (Madsen *et al*., 2001). The bleaching systems may have been improved in order to meet the demand for wash at low temperature. A combination of several bleaching agents expands the temperature range of the laundry detergent. Sodium carbonate is active from about 40 °C and up, whereas TAED (tetraacetyl ethylenediamine) is active at lower temperature.

Use of dichloroisocyanurates and sodium hypochlorite, which was described in the report from 2001 (Madsen *et al*., 2001), has not been identified in this survey on laundry detergents.

4.2.4 Enzymes

Enzymes application in laundry detergents has been further developed during the past 20 years offering a wide range of enzymes for detergents. The enzymes are effective at moderate temperature and pH values that characterise the laundering conditions. Therefore, the application of enzymes improves the washing results and saves energy.

The major classes are proteases, lipases, amylases, mannanases, cellulases and pectinases. The proteases help removing soils consisting of proteins such as stains from blood, egg and grass. The enzyme named Subtilisin is a protease. Lipases degrade lipids and remove stains from grease and grease-containing products. The amylases are effective against sticky stains containing starch and sugars. Mannanases and pectinases are used for hard-to-remove stains, i.e. stains from coloured and greasy food and fruits. Cellulases contribute to fabric care by removing fluff from the fabric surface, maintaining the colour and softness of the fabric (Anglamark, 2018).

4.2.5 Fragrances

The fragrance substances identified in the laundry products are listed in Appendix 2.1. The list includes a total of 25 different substances from the list of 82 fragrance substances that are considered as possible contact allergens for humans based on the conclusions by the SCCS (Scientific Committee on Consumer Safety). The most commonly used fragrances hereof include limonene, linalool, citronellol, geraniol, butylphenyl methylpropional, hexyl cinnamal, coumarin, benzyl salicylate, alpha-isomethyl ionone.

In the report from 2001, the most frequently used fragrances in detergent and cleaning products were described. The present survey did not identify the use of the following fragrances: polycyclic musks, camphene, 2-pinene, camphor, terpineol and eucaluptus oil to be used in laundry detergents. Of the fragrances described in 2001, only limonene, coumarin and hexyl cinnamal were identified in laundry detergents in 2018.

4.2.6 Ingredients with other functions

The list of ingredients with other functions shown in Appendix 2.1 includes additives, antifoaming substances, binders to bind solids together, bulking agents to increase the bulk of the powders, solvents, stabilisers, pH adjusters and viscosity controllers among others. Colours and optical brighteners are also identified in the survey.

The list of ingredients in pods for laundry contains a range of substances that were not identified as part of the project reported in 2001 (Madsen *et al.*, 2001). Just to mention some of the substances, terephthalates are used as suspending agents, di-substituted alaninamide is used as stabilising agent, polyvinyl alcohol is used for the film packaging, and potassium sulfite is used as an antioxidant.

A group of substances of different nature and structure is used as anti-redeposition agents, which prevent dirt in the wash solution being re-deposited on the clothes during the washing cycle. The anti-redeposition agents are represented by cellulose gum, ethoxylated aziridine homopolymer, 1,4-benzenedicarboxylic acid, 1,4-dimethyl ester, polymer, and polyethylene terephthalate.

Dye transfer inhibitors are used in detergents for coloured clothes as they help prevent “free dye” in the wash water being re-deposited on the clothes. The identified dye transfer inhibitors are polyvinylpyrrolidone (PVP), polyvinylpyridine N-oxide (PVPNO) and vinyl imidazole/VP copolymer (PVP/IV). PVP/IV is indicated as PVPI on the ingredient list, but information from the supplier confirmed that the ingredient is the PVP/IV with CAS no. 29297-55-0 and not the iodine form of PVP.

The use of enzymes in the formulations involves the use of enzyme stabilisers. This applies to powders, liquids and pods. The enzyme stabilisers are modified cornstarch, sorbitol, boronic acid (4-formylphenyl) and calcium chloride.

The substance denatonium benzoate is a bitterant used to give a bitter taste to the detergent or to the foil on pods or capsules that may be mistaken as candy in order to avoid intake.

5. Results of survey of dishwashing detergents

5.1 Trends in dishwashing detergents

This chapter describes the trends within the development of dishwashing detergents since 2001. If no other reference mentioned, the information in this chapter is collected from the questionnaires and interviews supported by the ingredient lists consulted in the survey (www.nemlig.com, Mad.coop.dk, www.Unilever.dk, www.rbeuroinfo.com, www.Tingstad.com).

Like the laundry detergents, the trend in relation to the product type is towards the concentrated dishwashing detergents (A.I.S.E. 2018a).

The trend in relation to type of products is aimed at products that are easy to use and easy to dispense. Solutions for easy dispensing for machine dishwashing are the introduction of tabs and gels.

The tabs are either packed in foil that has to be removed before wash or covered by a water-soluble film (polyvinyl alcohol) which dissolves during the washing process. Furthermore, the tabs for dishwashing have been developed to include additional functions such as pre-soaking action, machine lime scale protection, low temperature action, filter protection and glass protection.

With the introduction of gels to be used for machine dishwashing, the washing time may be reduced due to a faster solubility rate of the ingredients in the detergent. The gels are concentrated and easy to dose and have shorter washing cycle/washing time.
As for the laundry detergents, a green image and development of eco-labelled products for dishwashing are in focus. See Chapter 3.2 for description of the market trends for eco-labelled products.

The ingredients used in dishwashing detergents include the substances described below in section 5.2. Focus is on the substances identified in the current survey and not described in the report from 2001 (Madsen *et al.*, 2001).

5.2 Ingredients in dishwashing detergents

The list of ingredients identified in dishwashing detergents on the Danish market is included in Appendix 2.2.

5.2.1 Surfactants

The group of surfactants in dishwashing detergents is represented by anionic surfactants such as fatty acids (FA), soaps and alkyl sulfates (AS), nonionic surfactants such as the alcohol ethoxylates (AE), alcohol alkoxylate (AA), fatty acid amides (FAA), alkylpolyglycosides (APG) and block polymers as well as amphoteric substances including alkyl amine oxides, alkyl amidopropyl amine oxides and betaines. Within the non-ionic alcohol ethoxylates, a wide range of molecules with the carbon chain lengths of C8-C18 and 8-25 EO (ethylene oxide) units characterises the alcohol ethoxylates (AE).

Cationic substances of the type alkyldimethyl benzylammonium chloride (ADMBAC) and dialkyldimethyl ammonium chloride (DADMAC) have been identified as ingredients in gels, powder and tabs for dishwashing. These surfactants may have an additional function as antimicrobial agent (Emsley, 2015).

Compared to the substances described in the report from 2001 (Madsen *et a*l., 2001), the use of the following anionic surfactants were not identified in the current survey: linear alkylbenzene sulfonic acid (LAS), alkyl sulfates, (AS), alfa-olefine sulfonates (AOS) and sulfosuccinates. Within the amphoteric surfactants, no use of the imidazoline derivatives was found and for the cationic surfactants, the type of alkyltrimethylammonium chloride was not identified in detergents for dishwashing.

New substances within the surfactants include the amphoteric amine oxides and alkyl amidopropyl amine oxides, which were not described in the report from 2001.

5.2.2 Complex binders/Builders

Phosphates are sequestering builders found in the dishwashing detergents on the market. The phosphates and other phosphorus compounds in dishwashing detergents is regulated by a restriction on the amount of phosphorus used per standard dosage (≥ 0.3 g per standard dosage). It is not the aim of the present survey to examine whether the restriction on amount of phosphate per dosage is met, as the dosage and the exact content of phosphate in the products have to be known. Furthermore, complexing agents described in the report from 2001 (Madsen *et al*., 2001) are used, including phosphonates, silicates, carbonates and citrate.

For the builders, the commercial MGDA (methylglycine diacetate), is introduced in dishwashing detergents, as well as polyethylene imine and Sodium carboxymethyl inulin.

A range of organic acids and their salts have been identified in the survey, and these may contribute to the system of builders in the dishwashing detergents removing the hardness of the water by binding calcium and magnesium ions.

The survey indicates that EDTA, NTA and zeolites are no longer used in dishwashing agents.

5.2.3 Bleach agents

Bleaching agents are used in tabs for dishwashing, and they are represented by the oxygen-based perborates and percarbonates as well as TAED (tetraacetyl ethylenediamine).

Use of sodium hypochlorite and dichloroisocyanurates was described in the report from 2001, but not found in dishwashing detergents in this survey.

5.2.4 Enzymes

Enzymes application in detergents for machine dishwashing contributes to the development of greener products as the enzymes work under mild conditions. In addition, the use of enzymes in the combination with modified detergent compositions may have contributed to the substitution of phosphates in the building systems.

Enzymes that are applied in dishwashing detergents for machine dishwashing are amylases and proteases including subtilisin. After the dirt has been removed by water jets in the automatic dishwasher, there is usually a thin film of starch/protein-containing soils left behind. The amylases are effective against the starch soils, whereas the proteases remove the protein soils (Novozymes A/S, 2013).

5.2.5 Fragrances

The fragrance substances identified in the survey are listed in Appendix 2.2. Fragrances are used only in detergents for hand dishwashing and not in detergents for automatic dishwashing. The fragrances used are natural essential oils (not further described), limonene, butylphenyl methylpropional, hexyl cinnamal, linalool, coumarin and glutaral.

In the report from 2001, the most frequently used fragrances in detergent and cleaning products were described. The present survey did not identify the use of the following fragrances: polycyclic musks, camphene, 2-pinene, camphor, terpineol and eucaluptus oil to be used in detergents for dishwashing. Of the fragrances described in 2001, only limonene, coumarin and hexyl cinnamal were identified in dishwashing detergents in 2018.

5.2.6 Ingredients with other functions

The list of ingredients with other functions shown in Appendix 2.2 includes additives, antifoaming agents, antimicrobial substances, binders, fillers, solvents and viscosity controllers among others. Colours are also used in dishwashing detergents.

In this survey, antifoaming agents were identified in dishwashing tabs. The substances used are within the group of siloxanes: dimethicone and simethicone. These antifoaming agents were not described in the report from 2001 in which mainly alcohol alkoxylates were mentioned to provide foam-mitigating properties.

Some hand dishwashing detergents contain chemical substances for skin care such as glycerine and PEG-40 glyceryl cocoate and antimicrobial agents such as potassium sorbate, sodium benzoate and sodium levulinate.

A broad group of binders including cellulose, dextrin, sucrose, PEG-9 and PEG-20, is used in tabs to provide adhesive properties to bind the solids in the tabs. Fillers such as bentonite, kaolin and starch are used in tabs for dishwashing as well.

Ethanol and propylene glycol are solvents used in liquid and tabs/gels.

To control the viscosity, polymers are used. The type of polymers includes acrylic polymers and copolymers hereof, 2-propenoic acid homopolymer, sulfonated carboxylate polymers and xanthan gum. The polymers of acrylic acid (polycarboxylates) are also part of the builder system.

The substance sodium xylenesulfonate is used as a hydrotrope in liquid dishwashing detergents. The function of hydrotropes is to ensure homogeneity of the product and preventing the liquid to separate into layers. The hydrotrope was not described in the report from 2001.

The use of enzymes in the formulations involves the use of enzyme coatings such as sodium chloride, calcium chloride and sodium sulfate, enzyme stabilisers (cellulose gum) and enzyme controller (manganese-II-oxalate dehydrate).

A corrosion inhibitor, 1-H-methylbenzotriazole, is used in tabs to protect the dishwasher from corrosion. Polyvinyl alcohol is used in the water-soluble foil for dishwashing tabs.

6. Results of survey of all-purpose detergents

6.1 Trends in development of all-purpose detergents

This chapter describes the trends within the development of all-purpose detergents since 2001. Information in this chapter is from the results collected via the questionnaires and interviews supported by the ingredient lists consulted in the survey (www.nemlig.com, Mad.coop.dk, www.Unilever.dk, www.rbeuroinfo.com, www.Tingstad.com).

For the development of the all-purpose detergents, there has been focus on the packaging and form of application rather than the composition during the past 20 years. Focus has been on application of the cleaning agents in spray products.

The ingredients used in all-purpose detergents include the substances described below in section 6.2. Focus is on the substances identified in the current survey and not described in the report from 2001 (Madsen *et al.*, 2001).

6.2 Ingredients in all-purpose detergents

The list of ingredients identified in all-purpose detergents on the Danish market is included in Appendix 2.3.

6.2.1 Surfactants

The surfactants used in all-purpose detergents are traditional anionic surfactants such as linear alkylbenzene sulfonic acid (LAS), fatty acid (FA) soaps, alkyl sulfates (AS), alkyl ether sulfates (AES) and traditional nonionic surfactants such as alcohol ethoxylates (AE) and alkylpolyglycosides (APG). A wide group of AE with carbon chain lengths of C9-C16 and 3-10 EO (ethylene oxide) units characterises the alcohol ethoxylates (AE).

Cationic surfactants of the type dialkyldimethyl ammonium chloride (DADMAC) and alkyltrimethyl ammonium chloride (ATMAC) are used in all-purpose cleaners. The cationic surfactants may act as a disinfection agent in addition to surface activity.

Use of amphoteric surfactants has been identified for the all-purpose detergents in the current survey. The amphoteric substances are betaines, alkyl amines and alkyl amine oxides. The amphoteric surfactants are also used in personal care products as they are mild to the skin when used in low concentrations.

Compared to the substances described in the report from 2001 (Madsen *et a*l., 2001), the use of the anionic surfactants alfa-olefine sulfonates (AOS) and sulfosuccinates was not identified in all-purpose detergents in the current survey. None of the non-ionic block polymers, glucose amides or fatty acid amides were identified. Within the cationic surfactants, no use of the type of alkyldimethylbenzylammonium chloride was found, and for the amphoteric surfactants, the use of imidazoline derivatives was not identified in detergents for all-purpose cleaning.

The amphoteric alkyl amine oxides and alkyl amines were not described in the report from 2001.

6.2.2 Complex binders/Builders

Detergents for surface cleaning hold chelating agents and builders. Chelating substances include citrates, phosphate, MGDA (methylglycine diacetate) and sodium iminodisuccinate, which all form stable complexes with calcium and magnesium ions hence removing water hardness and enhancing the efficiency of the surfactants. Other builders are carbonates that reduce the water hardness by precipitation. The acrylic polymers and copolymers hereof are also part of the builder system.

The complexing agents EDTA, NTA and zeolites described in the report from 2001 were not found in all-purpose detergents in this survey. However, MGDA (methylglycine diacetate) and sodium iminodisuccinate are substances not described in the report from 2001.

6.2.3 Bleach agents

All-purpose cleaners do not normally contain agents for bleaching. However, bleaching agents such as sodium hypochlorite are applied in speciality cleaners that have a whitening or bleaching purpose.

6.2.4 Enzymes

Enzymes are not applied in all-purpose cleaners.

6.2.5 Fragrances

The fragrance substances identified in the survey include limonene, linalool, citronellol, geraniol, butylphenyl methylpropional, hexyl cinnamal and amy cinnamal.

In the report from 2001, the most frequently used fragrances in detergent and cleaning products were described. The present survey did not identify the use of the following fragrances: polycyclic musks, camphene, 2-pinene, camphor, coumarin, terpineol and eucaluptus oil to be used in all-purpose detergents. Of the fragrances described in 2001, only limonene and hexyl cinnamal were identified in all-purpose detergents in 2018.

6.2.6 Ingredients with other functions

The list of ingredients with other functions shown in Appendix 2.3 includes a range of substances with different functions such as antifoaming substances, disinfectant, hydrotrope substances, solvents and viscosity controllers among others. Colours may also be found in all-purpose products.

A group of siloxanes with a function as antifoaming agents have been introduced. The antifoaming agents used are dimethicone and dimethylsiloxane.

The organic acid lactic acid and its salt sodium L-lactate may be used in all-purpose detergents as a disinfectant. Concerning disinfectants and preservatives, reference is made to the survey of preservatives in washing and cleaning detergents (Kjølholt J. *et al*., 2018).

The substance sodium cumenesulfonate is used as a hydrotrope in the detergents. The function of hydrotropes is to ensure homogeneity of the product and preventing the liquid to separate into layers. Sodium cumenesulfonate was not described in the report from 2001.

Solvents such as alcohols (including butoxypropanol), ethers (PPG-2 Butyl ether) and amines represented by ethanolamine and triethanolamine are used in all-purpose products.

Substances for control of viscosity in all-purpose products include acrylic polymers and copolymers hereof, propylene oxide/ethylene oxide block copolymer and xanthan gum. The polymers of acrylic acid (polycarboxylates) are also part of the builder system.

Calcium carbonate is used as an abrasive agent in specialty products such as products with a scouring purpose.

The bitter taste substance denatonium benzoate has been identified in all-purpose detergents. The purpose of bitter taste is to avoid intake of the products by small children.

7. Environmental and health assessment

7.1 Substances selected for assessment

The environmental and health assessment in this report is a supplement to the Danish EPA's report from 2001 (Madsen *et al*., 2001). A total list of substances selected for potential environmental and health assessment is shown in Appendix 3. The substances have been identified in the survey in this project as ingredients in detergents for the Danish market for laundry, dishwashing and surface cleaning (all-purpose). The selection of the substances is carried out to cover substances and group of substances not previously assessed in the 2001 project. The substances are selected primarily based on their chemical composition. Inorganic substances and substances structurally similar to those previously assessed have not been selected. Substances with antiseptic or antimicrobial properties are disregarded as they are assumed to be part of the survey done by the Danish EPA of preservatives in washing and cleaning detergents (Kjølholt J. *et al*., 2018). Colours, enzymes and by-products, which are not intentionally added, are also disregarded in relation to the environmental and health assessment.

The prioritization of the substances included in the environmental and health assessment was made after consultation with the Danish EPA. It was decided to focus the assessments on antifoaming agents as they were identified in all three product groups: laundry products, dishwashing products and al-purpose detergents, and because this group of substances was not assessed in the report from 2001. In order to complete the assessment of the complexing agents in the previous report it was decided to focus the assessment on the new complexing agents that were not assessed previously. Furthermore, it was decided to focus on dye transfer inhibitors, which is a new group of substances introduced with the "colour" laundry detergents. The use of enzymes has introduced the use of substances that control the enzymes either by stabilisation or by activation. Therefore is was decided to include in the assessment, an enzyme stabiliser and an enzyme activator that were identified in the survey. The selected substances are listed in Table 3 below.

7.2 Data search strategy

Data on the environmental fate and environmental and human health properties of the selected substances were retrieved from public available databases and literature. Where available, data from the ECHA registration database (ECHA, 2018) searched by CAS numbers were applied in the assessment using results from key studies only and the related end-point summaries from the registrations. If the results from key studies were supplemented only studies with Klimish score 1 or 2 are used. It should be noted, that evaluation of the data from the ECHA registration and the Klimish score allocation are done by the registrants, only. From the substance name reported from the product specifications/declarations, a Chemical abstract service (CAS) number was identified by performing an online search. The data search included the following databases:

- ECHA's registration database search by CAS no.;
- TOXNET database;
- Aquire ECOTOX database;
- The Detergent Ingredient Database List (DID-List)
- Online search using Google with the search-terms "(substance name) and toxicity and opinion";
- Public available reports published by the Danish EPA.

TABLE 3. List of substances selected for environmental and health assessment

Substance		CAS no. /EC no.	Function
Polymers of siloxanes. One representative substance within the group of silicone compounds to be assessed	Dimethicone	CAS 63148-62-9 CAS 9006-65-9	Antifoaming agents
	Dimethylsiloxane	CAS 63148-62-9	
	Simethicone	CAS 8050-81-5	
	Phenylpropyl dimethicone	CAS 2076-92-01	
Sodium methylglycine diacetate, MGDA, Trisodium dicarboxymethyl alaninate		CAS 164462-16-2 EC 423-270-5	Complexing agents
Sodium carboxymethyl inulin, Trisodium dicarboxymethyl inulin, Sodium carboxymethyl carbohydrate		CAS 430439-54-6	Complexing agents
Polyethylene imine; aziridine homopolymer		CAS 9002-98-6	Complexing agents
Sodium Iminodisuccinate		EC 429-200-1 (CAS 144538-83-0; EC 604-420-0)	Chelating agent
Group of PVP polymers	PVP, Polyvinylpyrrolidone	CAS 9003-39-8	Dye transfer inhibitor
	PVPNO, Polyvinylpyridine N-oxide	CAS 9045-81-2	
	Vinyl imidazole/VP copolymer, PVP/IV	CAS 29297-55-0 (CAS 999999-02-7, CAS 1027-63-5)	
Boronic acid, (4-formylphenyl)		CAS 87199-17-5	Enzyme stabiliser
Manganese-II-oxalate Dihydrate		CAS 640-67-5	Enzyme activator

8. Antifoaming agents

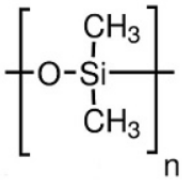
Polymers of siloxanes represent the group of antifoaming agents. According to the survey, the most common siloxanes used in washing and cleaning detergents are polydimethylsiloxane with different modifications. In the present environment and health assessment polydimethylsiloxane, the so-called dimethicone, is chosen as a representative siloxane/polymer for the group of antifoaming agents listed in Table 3.

8.1 Polymers of siloxanes

A report on siloxanes published by the Danish EPA includes information on both cyclic and non-cyclic compounds (Lassen *et al.*, 2005). Data on the non-cyclic compounds are included where relevant. In REACH, polymers are covered by the registration of the monomers only. The hazard and risk assessment is made for the monomers accordingly, and no information is available on the hazard and risks of the polymers in the REACH registrations. However, linear dimethylsiloxanes with up to five dimethylsiloxane units (dodecamethylpentasiloxane) have been registered under REACH and data on this substance will be considered here where relevant.

In general, the properties of the siloxanes and silicone products depend on the length of the Si-O backbone, the chemical groups attached to the backbone and the presence of cross-links between the backbones. As the siloxane polymers are relatively stable towards hydrolysis under most environmental conditions (Lassen *et al*., 2005), the present environmental and health assessment is performed on the silicone polymers and not on the monomers, even though information is available on the monomers. In the current survey, only linear siloxanes were identified in household detergents, and the cyclic siloxane will therefore not be treated further.

ECHA's database identifies the linear polydimethylsiloxane with the synonym name dimethicone by two CAS numbers:
Dimethicone: CAS no.: 9006-65-9 and EC no.: 618-433-4
Dimethyl Siloxane: CAS no.: 63148-62-9 and EC no.: 613-156-5



In the C&L Inventory (2018), a total of 1011 notifiers provided information for CAS no.: 63148-62-9 and 104 notifiers provided information for CAS no.: 9006-65-9. A number of 128 of the 1011 notifiers and 59 of the 104 notifiers reported a notified classification as Eye. Irrit. 2, whereas 30 of the 1011 notifiers reported a classification as Aquatic chronic 2.

ECHA has focus on the linear dimethylsiloxanes. Hexamethyldisiloxane is expected to be CMR, whereas the compounds representing the trisiloxane, tetrasiloxane and pentasiloxane are expected to be PBT/vPvB substances. The substances are all listed on the Community Rolling Action Plan, the CoRAP list, as selected for substance evaluation (ECHA CoRAP, 2018).

8.1.1 Occurrence in the environment

A screening programme investigated the occurrence and distribution of some siloxanes in environmental samples from the Nordic countries (Kay *et al*., 2005). The study included cyclic siloxanes and the linear siloxanes represented by hexamethyldisiloxane and the compounds up to dodecamethylpentasiloxane. The results from the study of the linear compounds indicated that the measured concentrations in sewage, sludge, soil and sediments increase with the number of dimethylsiloxane units.

The study of Kay *et al*. (2005) states that the siloxanes such as linear siloxane hexamethyldisiloxane have high K_{oc} and are expected to be immobile in soil. They adsorb to particles in water and are likely to be enriched in sediments. The study concludes that siloxanes occur as common pollutants in the Nordic environment and in many different matrices. The observed concentrations reported for the environmental compartments were not alarmingly high and many sites were non-contaminated. The study further concludes that extensive use of siloxanes may lead to increased environmental levels, eventually reaching effect concentrations (Kay *et al*., 2005).

8.1.2 Environmental fate

8.1.2.1 Aerobic biodegradability

Siloxanes are very persistent, and once released to the environment, the siloxanes remain in the environment for many years (Lassen *et al*., 2005).

8.1.2.2 Anaerobic biodegradability

No data are available on anaerobic biodegradability.

8.1.2.3 Bioaccumulation

The estimated bioconcentration factors (BCF) of the small siloxanes, which are reported by the Lassen *et al*. (2005) vary in the range from 340 for hexamethyldisiloxane (HMDS, CAS no.: 107-46-0) to 40,000 for a phenylated trisiloxane (phenyl trimethicone). This indicates that the phenyl siloxanes have BCF that are two orders of magnitudes higher than the values for the small linear dimethylsiloxanes. According to the REACH registration of HMDS, the experimentally determined BCFs for HMDS are somewhat higher but also below the cut-off value of 2000 L/kg for bioaccumulation (B) as described in the ECHA guidance Document R.11 PBT/vPvB assessment (ECHA, 2017). Bioconcentration factors for long-chained siloxanes have not been assessed in the report (Lassen *et al*., 2005).

It is assumed, that the potential for bioaccumulation of polydimethylsiloxanes is low, and further that the phenylated polydimethylsiloxanes may have a potential for bioaccumulation. This is based on the assumption that the potential for bioaccumulation of polydimethylsiloxanes is lower than that of the small siloxanes due to the larger molecule size of the polydimethylsiloxanes. However, the presence of phenyl groups increases the potential for bioaccumulation.

8.1.3 Effects on the aquatic environment

Lassen *et al*., (2005) have derived Chronic Values (ChV) for fish for a number of siloxanes by using the U.S. EPA PBT Profiler software. ChV is the same as the chronic no effect concentration (NOEC) and shows at what concentration no long-term effects are expected. Chronic NOEC values were estimated to be 0.062 mg/L, 0.028 mg/L, 0.00082 mg/L and 0.0012 mg/L for hexamethyldisiloxane , octamethyltrisiloxane (CAS no.: 107-51-7), phenyl dimethicone (CAS no.: 56-33-7) and phenyl trimethicone (CAS no.: 2116-84-9), respectively, indicating the highest toxicity to aquatic organisms for the small phenylated siloxanes. The data also indicate that the toxicity is increasing with the number of siloxane units.

It is assumed, that polydimethylsiloxanes are toxic in the aquatic environment.

8.1.4 Effects on Human Health

8.1.4.1 Toxicokinetics

None to minimal absorption was observed for dimethicone when orally fed (single and repeatedly) to beagle dog and rat, and most of the substance passed unaltered through the GI-tract. The same was observed in a human study in four subjects with oral intake of silicone products containing 91% dimethicone. Also, there was no evidence of dermal absorption of dimethicone in five human subjects after dermal exposure to 50 mg dimethicone/kg for 20 hours/day for 10 days (CIR, 2003).

8.1.4.2 Acute toxicity

The acute oral toxicity of dimethicone has been extensively studied in rodent animal models without any signs of acute toxicity. Acute dermal toxicity was investigated in rats and rabbits (CIR, 2003). In an acute dermal toxicity study, rabbits were exposed to a single application of 2000 mg/kg bw (>90% dimethicone) without any mortality (CIR, 2003). In an old study with inhalation of dimethicone (unknown concentration and particle size) for 6 hours caused only mild effects and no mortality in rats and two dogs, whereas three out of six guinea pigs died during exposure. The authors concluded that dimethicone was essentially non-toxic (CIR, 2003).

8.1.4.3 Skin and eye irritation

Eye and skin irritation studies with dimethicone (various concentrations used for eye and skin irritation studies) found it being a minimal to mild eye and skin irritant in rabbits (CIR, 2003).

8.1.4.4 Skin sensitisation

Studies investigating the skin sensitising potential of 70-100% dimethicone in mice and guinea pigs found no reactions and it was concluded to be a non-sensitiser. Same result that dimethicone is a non-sensitiser was also concluded in a human clinical study (repeated-insult patch test) with 5% dimethicone and 10 - 24h patch application (CIR, 2003).

8.1.4.5 Repeated dose toxicity

No treatment-related adverse effects were observed in mice and rats after 90 days of oral dosing up to 10% dimethicone, and no adverse effects were observed after short-term inhalational exposure to dimethicone. In addition, no treatment-related carcinogenicity was observed after twice-weekly dermal exposure (for lifetime) to undiluted dimethicone (CIR, 2003).

8.1.4.6 Toxicity to reproduction and development

In a reproductive toxicity study, food grade dimethicone (0%, 0.5%, 1.0%, and 2.5%) was fed to time-mated rabbits at gestational day 6-19. No maternal or foetal toxicity were observed during the study (CIR, 2003).

8.1.4.7 Genetic toxicity

Several *in vitro* and *in vivo* mutagenicity studies have been performed using pure and trade-mixtures of dimethicone all with same results and conclusion that dimethicone is not mutagenic (CIR, 2003).

8.1.4.8 Overall assessment

In summary, minimal oral absorption was observed in dogs and rats fed with dimethicone. In general, dimethicone exhibit a low to minimal acute toxicity in several species independent of route of exposure. Dimethicone was found to be a non-sensitiser both in a human patch study and animal studies. However, it is reported to be a mild eye and skin irritant in several animal studies. The available data indicates no concern of organ toxicity, carcinogenicity or toxicity towards reproduction and development after either dermal, oral or inhalation exposure in rodents. No mutagenicity was observed for dimethicone *in vitro* and *in vivo* models.

9. Complexing agents

The following chapters describe the complexing agents identified in the survey and not previously described (Madsen *et al*., 2001).

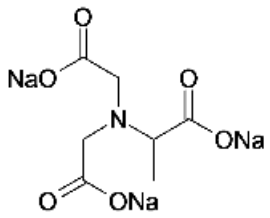
New complex binders include a commercial product based on methylglycine diacetate (MGDA), sodium carboxymethyl inulin, which is a vegetable scale inhibitor, polyethylene imine for use in dishwashing detergents and sodium iminodisuccinate used as chelating agent in all-purpose detergents.

Complexing agents are applied in laundry detergents, dishwashing detergents and all-purpose cleaners to soften water and to remove traces of metals such as iron and manganese. This increases the effectiveness of the surfactants that otherwise would be less active because of the presence of e.g. calcium and magnesium ions.

9.1 Sodium methylglycine diacetate (MGDA)

Sodium methylglycine diacetate and trisodium dicarboxymethyl alaninate, also called MGDA, are organic chelating agents, which are used in household-detergents to control the concentration of metal ions in aqueous systems. MGDA is an aminocarboxylic acid with four functional groups, which is produced from glycine. MGDA can withstand higher temperatures while maintaining a high stability as well as the entire pH range. As a result, the chelating strength of MGDA is stronger than many commercial chelating agents (BASF, 2016).

CAS no.: 164462-16-2 and EC no.: 423-270-5



The REACH registration dossier of MGDA (at the tonnage-level 10,000-100,000 tonnes per annum) suggests no classification of the substance. In the C&L Inventory (2018), two self-classifications are notified by companies. One third of the companies reported the hazard statement code H290 (100%): May be corrosive to metals. The other two third of the companies reported no classification (ECHA, 2018).

Furthermore, the substance used for registration under REACH is a multi-constituent substance consisting of a racemic mixture of both (D) and (L)- enantiomers under the EC number 423-270-5. The same racemic mixture of (D) and (L)- enantiomers of MGDA was used for all toxicological studies (ECHA, 2018).

9.1.1 Occurrence in the environment

Data on the occurrence of MGDA in the environment were not searched, as this was not considered to be important.

9.1.2 Environmental fate

9.1.2.1 Aerobic biodegradability

The biodegradation of MGDA has been studied according to OECD Guideline 301 F (Ready Biodegradability: Manometric Respirometry Test). After 28 days, 80-90% degradation of the test item was determined, and based on the results MGDA is considered as ready biodegradable (> 60% biodegradation after 28 days) (ECHA, 2018). Unlike other complexing substances, MGDA does not require adapted bacteria for decomposition, and is degraded under the standard conditions defined by the OECD.

9.1.2.2 Anaerobic biodegradability

No data on the anaerobic biodegradability of MGDA are available.

9.1.2.3 Bioaccumulation

No experimental data describing the bioaccumulation potential of MGDA were found in the literature. The octanol-water partitioning coefficient (Log Kow) was reported as < -4 and the water solubility was determined to be >500 g/L at 24 °C. MGDA is thus expected to have a low potential for bioaccumulation (ECHA, 2018).

9.1.3 Effects on the aquatic environment

The toxicity of MGDA was determined in studies with fish, invertebrates and algae. Both short-term and long-term results are available and summarised in the table below. Results indicate a low toxicity with E(L)C50 and NOEC-values > 100 mg/L for both fish, invertebrates and algae (ECHA, 2018).

TABLE 4. Effects of MGDA (CAS no.: 164462-16-2) to aquatic organisms

Species	Scientific name	Endpoint/Effect	Test duration	Reference
Fish	*Danio rerio*	LC50> 110 mg/L	96 h	ECHA 2018
	Oncorhynchus mykiss	NOEC = 100 mg/L (Body weight and length)	28 d	ECHA 2018
Crustacean	*Daphnia magna*	EC50> 100 mg/L	48 h	ECHA 2018
	Daphnia magna	NOEC ≥ 100 mg/L	21 d	ECHA 2018
Algae	*Desmodesmus subspicatus*	EC50> 100 mg/L (growth rate)	72 h	ECHA 2018
	Desmodesmus subspicatus	ErC10 > 100 mg/L (growth rate)	72 h	ECHA 2018

9.1.4 Effects on Human Health

9.1.4.1 Toxicokinetics

The substance is a racemate, and oral toxicokinetic studies were performed in rats using both the racemate test substance and the L- and D- isomers separately. The substances were rapidly absorbed via the intestine and excreted rapidly via the kidneys (3-6 hours). There was no indication of bioaccumulation potential (ECHA, 2018).

9.1.4.2 Acute toxicity

In the REACH registration, low acute oral and dermal toxicity was observed for MGDA in the rat. Acute oral toxicity of MGDA in rats was performed under GLP and according to EU.B.1. (Acute toxicity (oral)), and the LD50 was found to be >2000 mg/kg bw. A GLP compliant acute

dermal toxicity study in rats was performed according to OECD TG 402 and a LD50 >2000 mg/kg bw was concluded (ECHA, 2018).

9.1.4.3 Skin and eye irritation

The skin irritation potential of MDGA was assessed on rabbit skin (4h exposure, semi occlusive) in a GLP compliant study according to OECD TG 404 (Acute Dermal Irritation / Corrosion). At 72 hours and 15 days after exposure, no adverse/irritative effects were observed on the exposed skin. The eye irritation potential of MGDA in rabbit was assessed in a GLP complaint study according to OECD TG 405 (Acute Eye Irritation / Corrosion). An amount of 42 mg of the test substance was single ocular applied to three rabbits. No severe effects were observed and all of the minor effects were reversible in all animals. Hence, it was concluded that the test item does not cause eye irritation (ECHA, 2018).

9.1.4.4 Skin sensitisation

MGDA was assessed for its skin sensitising effect using a Guinea Pig Maximisation Test (GPMT) in a GLP complaint study according to OECD guideline 406. Intradermal induction performed with 5 % test substance preparations showed slight to well-defined signs of irritation. However, the challenge (21 days after induction) did not cause positive reactions 24 hours after test patch removal. Hence, it was concluded that MGDA does not exert a skin sensitising effect (ECHA, 2018).

9.1.4.5 Repeated dose toxicity and carcinogenicity

The chronic oral toxicity of MGDA was assessed in a combined chronic toxicity/carcinogenicity study in Wistar rats performed according to GLP & OECD TG 453. Rats were daily fed with 0, 1000, 5000, and 19200 ppm MGDA for 24 months (Corresponding to 0, 54, 262, and 1132 mg/kg bw/day for male rats, corresponding to 0, 66, 334 and 1317 mg/kg bw/day for female rats); in addition, a satellite group (12 month) was included. No treatment related observations were observed for MGDA, and the No Observed Adverse Effect Level (NOAEL) was determined to be 262 mg/kg bw/day (male) and 334 mg/kg bw/day (female) (ECHA, 2018).

9.1.4.6 Toxicity to reproduction and development

The effect of oral administration of MGDA on the reproductive performance of rats was assessed in a GLP complaint study according to OECD TG 421 (Reproduction/Developmental Toxicity Screening Test). Administration of 0, 50, 200, and 1000 mg/kg bw/day did not affect the reproductive function or performance. Thus, NOAEL was concluded to be 1000 mg/kg bw/day (ECHA, 2018).

The developmental toxicity of oral administration of MGDA was assessed in rats in a GLP complaint study according to OECD TG 414 (Prenatal Developmental Toxicity Study). Administration of 0, 100, 300, and 1000 mg/kg bw/day did not cause any maternal toxicity or embryotoxic/teratogenic effects. Thus, a NOAEL of 1000 mg/kg bw/day was concluded for maternal as well as for developmental toxicity (ECHA, 2018).

9.1.4.7 Genetic toxicity

The mutagenic potential of MGDA was investigated in three *in vitro* and one *in vivo* studies. In Ames test (according to GLP & OECD guideline 471), *S. typhimurium TA 1535, TA 1537, TA 98 and TA 100 E. coli WP2 uvr A* were exposed to concentrations of 0, 100, 500, 2500, 5000 and 7500 µg MGDA /plate with and without metabolic activation. No genotoxic effects were observed. (ECHA, 2018).

In a HPRT test (according to GLP & OECD guideline 476) Chinese hamster Ovary (CHO) cells were exposed for 4 hours to (0 - 1,750.00 µg MGDA /mL without S-9 mix) and (0 - 3,500.00 µg MGDA/mL withS-9 mix). (ECHA, 2018).

In a chromosome aberration test (GLP & OECD guideline 476) Chinese hamster lung fibroblasts (V79 cells) were exposed for 4 hours to (900; 1800; 2700 µg MGDA /ml with and without S-9 mix) or (1800; 2250; 2700 µg MGDA /ml without S-9 mix). Cytotoxicity was observed at 2700 µg MGDA /mL without S-9 mix. MGDA caused a significant increase in the number of structurally aberrant metaphases without S-9 mix and after adding a metabolizing system the test substance exhibited only a weak clastogenic activity. Hence, under the experimental conditions of the study MGDA is a chromosome damaging (clastogenic) agent in V79 cells. However, it was concluded that it cannot be ruled out that these findings are the result of an indirect mechanism due to the chelating properties of the test substance which might interfere with cellular cationic pools (ECHA, 2018).

In a mammalian erythrocyte micronucleus test (GLP & OECD TG 474) mice were orally treated with a single dose of (0, 500, 1000, and 2000 mg MGDA/kg bw). No genotoxic effects were observed after 24 h (0 - 2000 mg/kg bw); 48 h (0 mg/kg bw and 2000 mg/kg bw) (ECHA, 2018).

Overall, the *in vitro* and *in vivo* studies indicated no genotoxic potential of MGDA (ECHA, 2018).

9.1.4.8 Overall assessment

MGDA is rapidly absorbed after ingestion, without any noteworthy accumulation and is excreted via the kidneys within 3-6 hours. MGDA displays low toxicity in rats with an oral and dermal LD50 >2000 mg/kg bw. MGDA was not observed to cause any skin or eye irritation, or any skin sensitising effect. In rats, chronic oral intake of MGDA caused no carcinogenicity or other treatment-related adverse effects at dose-levels relevant for consumer exposure, and a NOAEL of 262 mg/kg bw/day (males) and of 334 mg/kg bw/day (female) were concluded. No toxicity was observed towards reproduction and development at the highest dose-level and a NOAEL of 1000 mg/kg bw/day was concluded. Finally, the conclusion of several in vitro studies was that MGDA has no genotoxic potential.

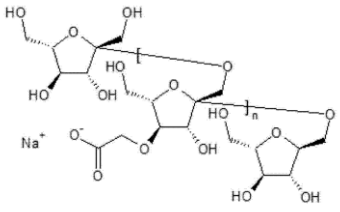
9.2 Carboxymethyl inulin (CMI)

Carboxymethyl inulin (i.e. carboxymethyl carbohydrates) polymers are relatively new ingredients used as complexing agents in dishwashing and laundry detergents. They are alternatives to phosphorous agents, and synergistic effects with CMI and sodium citrate, chelating agents and polyacrylates have been reported (R. Nolles, 2013). In this chapter, the effects of both CMI and inulin are described when data were available.

CMI

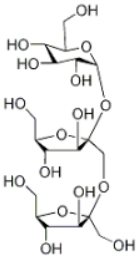
Sodium carboxymethyl inulin and trisodium dicarboxymethyl inulin is the sodium salts of the product obtained by the reaction of chloroacetic acid with inulin. It is used as a chelating and complexing agent or as a viscosity Increasing agent in aqueous solutions.

CAS no.: 430439-54-6 and EC / List no.: 610-102-2



No REACH registration dossier is available as the substance is a polymer and no C&L information is available from ECHA's website.

Inulin
Inulin is a polysaccharide with the molecular weight of 6179.
CAS no.: 9005-80-5 and EC/ List no.: 232-684-3



No REACH registration dossier is available for the polysaccharide inulin. From ECHA's C&L Inventory (2018), information is provided by nine companies in one notification as not classified.

9.2.1 Occurrence in the environment

Data on the occurrence of CMI in the environment were not searched, as this was not considered to be important.

9.2.2 Environmental fate

9.2.2.1 Aerobic biodegradability

CMI is included in the Detergent Ingredient Database (DID) list (entry no. 2514) where CMI is reported as being not biodegradable under aerobic conditions but inherently biodegradable according to OECD guidelines.

9.2.2.2 Anaerobic biodegradability

CMI is not biodegradable under anaerobic conditions (DID-list part A, 2016).

9.2.2.3 Bioaccumulation

No information on the bioaccumulation potential of CMI was found in literature.

9.2.3 Effects on the aquatic environment

No data on the aquatic toxicity of CMI could be retrieved from literature. According to information on aquatic toxicity included in the DID-list, the acute toxicity of CMI is E(L)C50 = 1000 mg/L and the chronic toxicity is NOEC = 423 mg/L. These values indicate a low aquatic toxicity of CMI.

9.2.4 Effects on Human Health

9.2.4.1 Toxicokinetics

No information was available on the toxicokinetics of CMI. Inulin, the major component of CMI is completely inert towards hydrolysis in human beings. Hence inulin is commonly used as in medicine to assess the kidney function by determination of the Glomerular Filtration Rate (GFR). Furthermore, if Inulin passes through the gastrointestinal tract it may undergo bacterial hydrolysis in the colon to yield fructose and glucose (Carabin and Flamm 1999).

9.2.4.2 Acute toxicity

No information available.

9.2.4.3 Skin irritation and Skin sensitisation

The skin sensitisation potential of CMI (31.1% aqueous) was evaluated in the guinea pig maximisation test. No local reactions or symptoms of systemic toxicity were observed. Thus, no evidence of dermal sensitisation was observed (CIR, 2014).

9.2.4.4 Repeated dose toxicity

Repeated dose oral toxicity of CMI was investigated in a 28 days study where groups of rats received CMI (31.1% aqueous), by gavage, at doses of 0, 50, 150 and 1000 mg/kg bw/day. No treatment-related effects were observed at all dose-levels except effects on motor activity in high-dosed females, but it was not considered toxicologically significant. Thus, the NOAEL was determined to 1000 mg/kg bw/day (CIR, 2014).

9.2.4.5 Carcinogenicity

The role of inulin as an anti-carcinogen or pro-carcinogen is controversial. In a mechanistic study in a cancer mouse model, groups of 10 -15 mice (Min/+ mouse model) were fed a control diet or an inulin-enriched diet (10% w/w) from the ages of 5 weeks to 8 or 15 weeks. The animals were killed at 8 or 15 weeks of age. Wild-type mice were included as controls and fed the same diets until the age of 8 weeks. The findings were that Inulin-enriched dietary may activate the normal-appearing mucosa β-catenin signalling, which, in the presence of Adenomatous polyposis coli mutation, induces adenoma growth (CIR, 2014). However, an anti-carcinogenic effect of inulin was observed in a 28 week dietary study. Here 4 months old rats were treated with dimethylhydrazine to induce colon cancer. The results of this 28 week study indicated that dietary intake of inulin prevented preneoplastic changes and inflammation that otherwise could promote colon cancer development (CIR, 2014).

9.2.4.6 Toxicity to reproduction and development

No information available.

9.2.4.7 Genetic toxicity

In an Ames test, *Salmonella typhimurium strains (TA98, TA 100, TA 1535, and TA 1537)* and *E. coli* strain (*WP2uvrA*) were exposed to CMI in concentrations up to 5,000 µg/plate, with and without metabolic activation. No genotoxic potential was observed (Johannsen, F. R. 2003). In another genotoxicity study using the chromosome aberrations assay, CHO cells were exposed to CMI concentrations up to 5,060 µg/ml with and without metabolic activation. No significant increases in chromosomal aberrations were observed (Johannsen, F. R. 2003).

9.2.4.8 Overall assessment

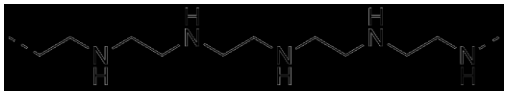
There was no information available on the toxicokinetics of CMI. However, the significant component of CMI is inulin that is inert towards hydrolysis in humans and therefore poses no risk of toxic metabolites. CMI caused no dermal sensitization in guinea pigs or mutagenicity *in vitro.* Furthermore, no repeated dose toxicity was observed in rats after oral exposure to 1000 mg/kg bw/day which was therefore also considered the NOAEL. No toxicity data are available for CMI on acute toxicity, eye irritation, reproduction and development and carcinogenicity. However, limited data on the anti- and pro-carcinogen effect of inulin are available but these are rather controversial and inconclusive.

9.3 Polyethylene imine (PEI)

PEI is polymers of ethylene imine either linear or highly branched with a formula of $(C_2H_5N)_n$ for the linear form. PEI is also called aziridine homopolymer and has a range of commercial names, such as Corcat P, Epomin, Lupasol, Pei, among others. PEI is used as a complexing agent in dishwashing gel and tabs.

CAS no.: 9002-98-6 and EC no.: 618-346-1

Branched polyethylene imine



Linear polyethylene imine

Polymers are exempted from the provisions on registration of Title II of REACH, and no REACH registration dossier is thus available for the polymer PEI. PEI has no harmonised classification. From the C&L Inventory (2018), information was provided by 807 companies in 17 aggregated notifications. Among the self-reported notifications, a number of 775 companies have assigned the classification H411 (Toxic to aquatic life with long lasting effects), which applies to a substance that is either bioaccumulative or not readily biodegradable (C&L Inventory, 2018). A notified classification as Acute Tox. 4 was reported by 751 companies, Eye. Irrit.2 reported by 503 companies, Eye. Dam. 1 reported by 193 companies, and Skin Sens 1 reported by 186 companies.

9.3.1 Occurrence in the environment

Data on the occurrence of PEI in the environment were not found.

9.3.2 Environmental fate

Data on environmental fate are not available.

9.3.3 Effects on the aquatic environment

The notified classification available indicates a classification of PEI with H411 (Toxic to aquatic life with long lasting effects). The classification applies to substances that are either bioaccumulative or not readily biodegradable and have an ecotoxicity (EC50) of 1-10 mg/L (C&L Inventory, 2018). According to the Annex III report available for the substance in ECHA's database (2018), the substance is suspected to be hazardous to the aquatic environment. The prediction is based on the EPA Daphnia Magna toxicity model in VEGA (Q)SAR platform predicting that the chemical has a 48h EC50 of 15.6 mg/L (good reliability).

9.3.4 Effects on Human Health

9.3.4.1 Toxicokinetics

No information available.

9.3.4.2 Acute toxicity

The acute oral toxicity of three types of PEI Corcat P-12, Corcat P-18, and Corcat 600 was tested in rats (no information given about guideline) with an LD50 in the range of 1990 - 7500 mg/kg bw (JECFA, 1985). In mouse the acute oral toxicity of an unspecified type of PEI was LD50 = 2800 - 8000 mg/kg bw. It was not possible to test the oral LD50 in cat and dog due to vomiting within 30 minutes when dosed with 100 - 500 mg/kg bw (JECFA, 1985),

9.3.4.3 Skin and eye irritation

No information available.

9.3.4.4 Skin sensitisation

No information available.

9.3.4.5 Repeated dose toxicity

In a study, rats were fed with 0, 250, 500, or 1000 mg/kg bw/day of PEI via the diet for 8.5 months without any significant treatment-related effects.
In another study, dogs were fed 0, 250, 500, or 1000 mg/kg bw/day. PEI via the diet for 9 months. A decrease in body weight) was observed in high-dose males and females. Severe degenerative changes were observed in the kidneys of all the high-dosed animals, and less severe effects were observed in all animals dosed with 500 mg/kg bw/day while very slight effects were observed in females dosed with 250 mg/kg bw/day. Effects were also observed in the livers (brown pigmentation of Kupffer's cells) of animals of both sexes increasing from very slight to moderate with increasing dose (JECFA, 1985),
A study in rabbits showed that treatment with 500 mg PEI/kg bw/week did not cause any signs of toxicity (period of treatment ≥6 weeks). However, the rabbits tolerated only 6 weeks of treatment when increasing the dose to 1000mg PEI/kg bw/ week; no further details were given (JECFA, 1985), JECFA concluded that since absorption and distribution studies are not available to show uptake of this high-molecular-weight compound, the mechanisms of action of the kidney and liver lesions are unknown.

9.3.4.6 Toxicity to reproduction and development

No information available.

9.3.4.7 Genetic toxicity

PEI (P-1000) MW 70,000 was tested for mutagenicity in Ames test with or without metabolic activation using *S.typhimurium*: *TA1535, TA1537, TA1538, TA98, and TA100* and *E. coli: wp2 uvrA*. No mutagenic activity was found using concentrations of up to 5000 µg/plate (JECFA, 1985),

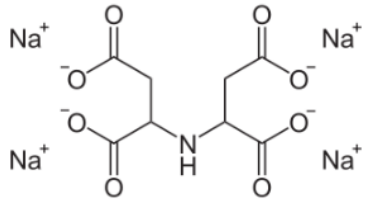
9.3.4.8 Overall assessment

There is no information available on the toxicokinetics of PEI, but as this substance has a high molecular weight limited absorption is expected. PEI has low acute oral toxicity LD50 1990 – 8000 mg/kg bw in rodents and causes vomiting at lower doses in cat and dogs. Some adverse effects were observed in the kidneys and liver in dogs after nine months repeated oral exposure (250 – 1000 mg/kg bw/day). However, no effects were observed in rats with similar dose-level and exposure period. Since low absorption is expected from oral intake of this high-molecular-weight substance, the mechanisms of action of the kidney and liver lesions are unknown. PEI was tested negative for mutagenicity in the Ames test. No data are available on skin and eye irritation, sensitization, and reproduction and development toxicity. However, since PEI is a high-molecular-weight substance with no to very low dermal uptake, it is not expected to be a skin sensitizer.

9.4 Sodium iminodisuccinate

The substance sodium iminodisuccinate (sodium IDS) is identified by two EC numbers with registrations under REACH. One full registration (100+ tonnes per annum) as IDS, Na-Salz (EC no.: 429-200-1) and one registration for intermediate use as tetrasodium;2-(1,2-dicarboxylatoethylamino) butanedioate (Cas no.: 144538-83-0 and EC no.: 604-420-0). Data from the full registration of IDS, Na-Salz registration are used in the assessment of the substance in the present report.

CAS no.: not available and, EC / List no.: 429-200-1



According to the REACH registration of sodium IDS, the substance is not classified. This is supported by the notifications by 37 companies in the C&L Inventory (2018). However, intention for a proposed harmonised classification (CLH intention) is noted for the substance. According to the information in the Registry of CLH intentions on ECHA's website, a proposal for harmonised classification as Carc.2, H351 is planned to be submitted to ECHA End 2018.

9.4.1 Occurrence in the environment

Data on the occurrence of sodium iminodisuccinate in the environment were not searched, as this was not considered to be important.

9.4.2 Environmental fate

9.4.2.1 Aerobic biodegradability

Registration data on the ready biodegradability of sodium IDS (EC no.: 429-200-1) are available (EU Method C.4-B). According to the results obtained, 79% of the sodium IDS was degraded after 28 days, and thus the test substance was considered readily biodegradable (ECHA, 2018).

The Australian government has also published a report on Aspartic acid, N-(1,2-dicarboxyethyl)-, tetrasodium salt (CAS no.: 144538-83-0) where IDS with a variable number of sodium has been studied. According to the information reported, IDS sodium salt is readily biodegradable (97% biodegradation after 28 days) fulfilling the criteria stated in the OECD Guideline 301E (NICNAS, 2002).
Furthermore, IDS is included in the Detergent Ingredient Database (DID) list (entry no. 2555) where it is reported as readily biodegradable under aerobic conditions.

9.4.2.2 Anaerobic biodegradability

IDS is not anaerobically biodegradable according to information reported in the DID-list (2016).

9.4.2.3 Bioaccumulation

No experimental data on the bioaccumulation potential of sodium IDS were found in the literature. A water solubility of 564 g/L was determined experimentally and together with a calculated Log Kow of -3.93 this indicates a low potential for bioaccumulation (Log Kow < 3) (ECHA, 2018).

9.4.3 Effects on the aquatic environment

The toxicity of sodium IDS was determined in studies with fish, invertebrates and algae and reported in the REACH registration. Short-term studies are available for three trophic levels and long-term results for crustacean and algae. Results are summarised in the table below and show an acute toxicity above 82.6 mg/L (ECHA, 2018). Data are similar to the information on ecotoxicity of IDS reported in the DID-list (entry no. 2555, DID 2016). The toxicity values together with the readily biodegradability indicate that the substance is not toxic to aquatic organisms.

TABLE 5. Effects of sodium IDS (EC no.: 429-200-1) to aquatic organisms

Species	Scientific name	Endpoint/Effect	Test duration	Reference
Fish	*Danio rerio*	NOEC > 82.6 mg/L	96 h	ECHA 2018
Crustacean	*Daphnia sp.*	EC0 > 84 mg/L	48 h	ECHA 2018
	Daphnia magna	NOEC ≥ 11.7 mg/L	21 d	ECHA 2018
Algae	NA	EC50 > 94.5 mg/L (growth rate)	72 h	ECHA 2018
	NA	ErC10 > 22.8 mg/L (growth rate)	72 h	ECHA 2018
NA	NA	EC50 = 8 mg/L	NA	DID 2016
NA	NA	NOEC = 11.7 mg/L	NA	DID 2016

Based on the available data, the substance is assessed as not hazardous in the aquatic environment.

9.4.4 Effects on Human Health

9.4.4.1 Toxicokinetics

One oral toxicokinetic study in rats (OECD TG 417) has been used in the registration of the substance. No metabolites were identified; however, the kinetic data are not public available (ECHA, 2018).

9.4.4.2 Acute toxicity

The substance has relatively low acute toxicity. In an acute oral toxicity study (OECD TG 423), an LD50 > 2000 mg/kg bw and in an acute dermal toxicity study (EU Method B.3), an LD50 of 1893 mg/kg bw were obtained. No information was available for acute inhalational toxicity (ECHA, 2018).

9.4.4.3 Skin and eye irritation

From the REACH registration dossier, one study on eye- and one on skin irritation were extracted. A semi occlusive skin irritation test (OECD TG 404) and an Acute Eye Irritation/Corrosion test (OECD TG 405) were performed using the rabbit. Data on the results of both studies were insufficiently reported, and no classification was concluded for both studies (ECHA, 2018).

9.4.4.4 Skin sensitisation

In a skin sensitisation study in guinea pig (OECD TG 406) obtained from the REACH registration on the substance, no skin sensitisation potential was concluded, as no reactions were observed up to 48 hours after challenge (ECHA, 2018).

9.4.4.5 Repeated dose toxicity

A sub-chronic 90 days OECD TG 408 study (Repeated dose oral toxicity study) was performed in rats exposed via the drinking water. Treatment-related effects were observed in the bladder, and a NOAEL = 100 mg/kg bw/day (male) and NOAEL = 300 mg/kg bw/day (female) were concluded (ECHA, 2018).

9.4.4.6 Toxicity to reproduction and development

In a prenatal developmental toxicity study (OECD TG 414), rats were exposed to the test substance via oral gavage (data on dose not available from the REACH dossier). No foetal abnormalities or developmental toxicity were observed, and a NOAEL > 1000 mg/kg bw/day was

concluded for the foetuses and maternal animals. Further, no effects were found on reproduction, and a NOAEL of 16.000 ppm (dose levels in mg/kg bw/day not indicated) was concluded for maternal animals and offspring (ECHA, 2018).

9.4.4.7 Genetic toxicity

No mutagenic potential was observed for the substance *in vitro* in AMES test (OECD TG 471) or *in vivo* in mammalian Erythrocyte Micronucleus Test (OECD TG 474). (ECHA, 2018).

9.4.4.8 Overall assessment

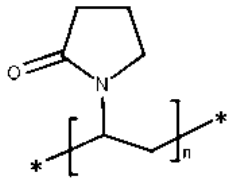
No metabolites were identified after oral intake of IDS, sodium salt. The substance has a low acute oral and dermal toxicity with an oral LD50 >2000 mg/kg bw and a dermal LD50 of 1893 mg/kg bw. Adverse effects were observed on the bladder after repeated oral exposure in rats and a NOAEL of 100 mg/kg bw/day (male) and NOAEL = 300 mg/kg bw/day (female) were concluded. No treatment-related effects were observed on reproduction and development in rats, and a NOAEL > 1000 mg/kg bw/day was concluded for the fetuses and maternal animals. There were no observed effects leading to a classification for skin and eye irritation, skin sensitization or genotoxicity.

10. Dye transfer inhibitors

Dye transfer inhibitors are used in laundry detergents for coloured laundry (liquid-, powder and pods) to avoid re-deposition of “free” dyes or colourants in the wash water. The identified dye transfer inhibitors are Polyvinylpyrrolidone (PVP), Polyvinylpyridine N-oxide (PVPNO) and Vinyl imidazole/VP copolymer (PVP/IV).

10.1 PVP polymers

The group of dye transfer inhibitors are assessed as a group of Polyvinylpyrrolidone (PVP). The chemical structure shown below is representative for the polymers of vinylpyrrolidone.



- Polyvinylpyrrolidone (PVP), 2-Pyrrolidinone, 1-ethenyl-, homopolymer:
  CAS no.: 9003-39-8 and, EC / List no.: 618-363-4.
- Polyvinylpyridine N-oxide (PVPNO), 2-Ethenyl-1-oxidopyridin-1-ium:
  CAS no.: 9045-81-2 and, EC / List no.: not available.
- Vinyl imidazole/VP copolymer, PVPI, PVP/IV polymer, 2-Pyrrolidinone, 1-ethenyl-, polymer with 1-ethenyl-1H-imidazole:
  CAS no.: 29297-55-0, and EC / List no.: 677-778-9.
  Alternative CAS no.: 999999-02-7 and CAS no.: 1027-63-5 have been identified.

According to the majority of notifications provided by companies to ECHA in the C&L Inventory (2018) for PVP (CAS no.: 9003-39-8), no hazards have been classified. At least one company has indicated that the substance classification is affected by impurities or additives. A number of six companies has notified the classification of PVP as Acute Tox.4; H302, Acute Tox. 1; H310, Skin Irrit. 2, Eye Irrit. 2 and Repr. 1B. raising a concern for toxicity to reproduction.
No information on classification has been found for PVPNO (CAS 9045-81-2).
The classification of the PVP/IV polymer (CAS 29297-55-0) was notified with Skin Irrit. 2 in the C&L Inventory (2018).

10.1.1 Occurrence in the environment

Data on the occurrence of PVP polymers in the environment were not searched, as this was not considered to be important.

10.1.2 Environmental fate

10.1.2.1 Aerobic biodegradability

According to information on 2-Pyrrolidinone, 1-ethenyl-, homopolymer given in a safety data sheet for the substance, the substance is poorly eliminated from water. Reference is made to test results showing < 10 % DOC reduction in a 15 days test following OECD Guideline 302 B (aerobic, activated sludge, industrial) (BASF, 2018).

Information on 2-Pyrrolidinone, 1-ethenyl-, polymer with 1-ethenyl-1H-imidazole indicates a poor elimination from water. The information is based on experimental results showing a DOC

reduction <20% in a 24 hours test (OECD 303A; ISO 11733; 92/69 EEC,V, C.10) (BASF, 2015).

10.1.2.2 Bioaccumulation

According to information on 2-Pyrrolidinone, 1-ethenyl-, homopolymer available in a safety data sheet for the substance, accumulation in organisms is not to be expected. This is according to the safety datasheet based on the substances' structural properties indicating that the polymer is not biologically available. This means that the structure has low potential for passing biological membranes.

10.1.3 Effects on the aquatic environment

Assessment of aquatic toxicity is done based on information on 2-Pyrrolidinone, 1-ethenyl-, homopolymer available in a safety data sheet for the substance. Information on aquatic toxicity to fish and microorganisms is available.

TABLE 6. Effects of PVP (CAS no.: 9003-39-8) to aquatic organisms

Species	Scientific name	Endpoint/Effect	Test duration	Reference
PVP (CAS no.: 9003-39-8)				
Fish	*Leuciscus idus*	LC50 > > 10,000 mg/l	96 h (DIN 38412 Part 15, static)	BASF 2018
Microorganisms	aerobic activated sludge, industrial	EC20 > 1,995 mg/l	0.5 h OECD Guideline 209	BASF 2018
PVP/IV polymer (CAS no.: 29297-55-0) – data derived from substances/products of a similar structure or composition.				
Fish	*Brachydanio rerio*	LC50 > 100 mg/l	96 h	BASF 2015
Crustacean	NA	EC50 > 100 mg/l	48 h	BASF 2015
Algae	NA	EC50 > 100 mg/l	72 h	BASF 2015

The assessment in the safety data sheet concludes that there is a high probability that the product is not acutely harmful to aquatic organisms. The inhibition of the degradation activity of activated sludge is not anticipated when introduced to biological treatment plants in appropriate low concentrations.

Based on the available data on the group, it is anticipated that PVP polymers are not harmful in the aquatic environment.

10.1.4 Effects on Human Health

10.1.4.1 Toxicokinetics

The absorption, distribution, metabolism, and excretion of PVP and its copolymers are dependent on molecular weight, dose and dose frequency, and route of administration. Polymers with a weight < 25,000 are eliminated through the kidneys (Andersen, 1998).

10.1.4.2 Acute toxicity

The oral toxicity of PVP and VP, PVP polymers and VP-copolymers is considered low. In a study with VP- copolymers, mice and rats survived the maximum dose of 5000 mg/kg bw containing 12.5% VP/VA-copolymer, although showing signs of decreased activity and ataxia (CIR, 2018).

The least toxic of the substances was PVP (average MW of 40,000) with a LD50 >100 g/kg bw in rats and guinea pigs (CIR, 2018).

In an acute dermal toxicity study, a single dose of 2000 mg Triacontanyl PVP /kg bw was applied to rabbit skin under an occlusive wrap for 24 hours. At 14 days post the test substance application, no clinical signs or toxicity were observed and the acute dermal LD50 was > 2000 mg/kg bw (CIR, 2018).

10.1.4.3 Skin irritation and sensitisation

Most evidence on skin irritation and skin sensitisation of PVP and VP polymers originates from animal models or human trial.

In one *in vitro* study the skin irritation potential of 21% solid hydrolysed wheat protein PVP crosspolymer was evaluated in the Episkin™ reconstituted human epidermis model (OECD TG 431 accepted model) and concluded no classification (CIR, 2018).

PVP and VP/VA Copolymers have been tested on rabbit skin at various concentrations and formulations with mixed results both being irritative and non-irritative. However, in most of the positive studies the polymers were diluted in alcohol, which might have caused the irritation observed (CIR, 2018).

In one human study, 14.95% VP/Hexadencene Copolymer was applied in an occlusive path test to health subjects and subjects with known allergy, eczema or sensitive skin for 48 hours. 48 hours and 72 hours post application, no reactions were observed in any of the test subjects.
Several human and animal studies (guinea pig and rabbit) have investigated the skin sensitisation potential of VP/PVP, modified PVP, and VP-and PVP copolymers. In all the studies, the same conclusion that these monomers and polymers are non-sensitisers was concluded (CIR, 2018).

10.1.4.4 Eye irritation

In albino rabbits VP/VA copolymers caused moderate to severe eye irritation at concentrations >50%, while mild eye irritation was observed at lower concentration, whereas no irritation was observed at concentrations <1.75% (CIR, 2018).
In two *in vivo* studies with instillation of Triacontanyl PVP and a VP crosspolymer into the rabbit eye (concentrations not known), the result was classification as slight eye irritation (CIR, 2018).

10.1.4.5 Repeated dose toxicity and carcinogenicity

Several studies have investigated the effect of oral intake of VP/VP copolymers on systemic toxicity, all with more or less the same conclusion for low toxicity.

The sub-chronic oral toxicity of VP/VA copolymers was investigated in rats fed (in the diet) 0-, 100, 300, or 1000 mg/kg bw/day for 90 days. No clinical signs, local- or systemic toxicity were observed, and a NOAEL of 1000 mg/kg bw/day was concluded (CIR, 2018).

Furthermore, spray inhalation of 5.4 mg/m^3 (4.0% VP/VA copolymer i.e. a concentration of 0.22 mg/m3 of VP/VA) in rats and hamsters 4 hours per day 54 days per week for 13 weeks caused no local or systemic toxicity (CIR, 2018).

In a 52 week feeding study, beagle dogs were fed with 0, 510, 1518, or 2522 mg VP/VA copolymers/kg bw/day. Clinical observations and various gross and histopathological investigations were performed, and no treatment-related toxicity was observed. A NOAEL of 2500 mg/kg bw/day (target dose for the highest dosed group) was concluded. (CIR, 2018).

Similar findings with VP/VA copolymer were observed in two 24-months feeding studies where rats were daily fed with doses of 0, 700, 1400, and 2800 mg/kg bw/day (first study) or 450 mg/kg bw/day (second study). Also, in these two studies no signs of any treatment-related toxicity or treatment-related neoplastic events were observed, and a NOAEL of 2800 mg/kg bw/day was concluded for the first study, no NOAEL was derived in the second study (CIR, 2018).

10.1.4.6 Toxicity to reproduction and development

There is only one old study investigating the effect of PVP (MW 11,500) on the development. Here the Yolk-sac method was used to determine the teratogenic effects of PVP injected into rabbit yolk-sacs. No PVP-related teratogenic effects were observed (Andersen, 1998).

10.1.4.7 Genetic toxicity

The mutagenicity of PVP and PVP copolymers has been evaluated in *in vitro* tests with negative results on mutagenicity.

Unmodified PVP was tested negative in the mouse lymphoma assay up to 100 mg/ml and in Ames test up to 10 mg/plate both with and without metabolic activation (CIR, 2018). Furthermore, both triacontanyl PVP and VP cross-polymers were concluded non-mutagenic in Ames test (CIR, 2018).

10.1.4.8 Overall assessment

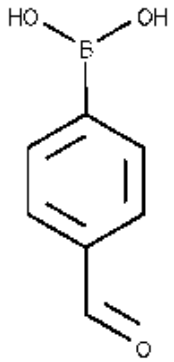
In general, little absorption is expected from high molecular weight polymers, and polymers with a weight < 25,000 are eliminated through the kidneys. PVP and VP, PVP polymers and VP-copolymers are in general considered to have low toxicity for local as well as systemic effects. Several human trials and animal studies indicate PVP/VP polymers to be non-sensitisers. However, eye irritation has been reported for Triacontanyl PVP and a VP in rabbits and therefore a classification as slight eye irritation was suggested. Further, PVP and PVP co-polymers were both tested negative in an *in vitro* test for mutagenicity, and no teratogenic effects were observed for PVP injected into rabbit yolk-sac.

11. Enzyme stabiliser and enzyme activator

11.1 Boronic acid, (4-formylphenyl)

Boronic acid, (4-formylphenyl) also called (4-formylphenyl)boronic acid is used in liquid laundry detergent as an enzyme stabiliser.

CAS no.: 87199-17-5, and EC / List no.: 438-670-5.



The substance has full registration under REACH (10+ tonnes per annum). Further (4-formylphenyl)boronic acid has a harmonised classification as Skin Sens. 1 (H317).

11.1.1 Occurrence in the environment

Data on the occurrence of (4-formylphenyl)boronic acid in the environment were not searched, as this was not considered to be important.

11.1.2 Environmental fate

11.1.2.1 Hydrolysis

According to REACH registration data on (4-formylphenyl)boronic acid a preliminary test on hydrolysis indicated that <10% of the test substance had been hydrolysed after 5 days incubation at 50 °C. Therefore, it is concluded that (4-formylphenyl)boronic acid is hydrolytically stable (ECHA, 2018).

11.1.2.2 Aerobic biodegradability

According to information in the registration dossier, (4-formylphenyl)boronic acid is readily biodegradable under aerobic conditions (weight of evidence) (ECHA, 2018).

11.1.2.3 Anaerobic biodegradability

No data available.

11.1.2.4 Bioaccumulation

No data on the bioaccumulation potential of (4-formylphenyl)boronic acid are available; however, in the registration dossier data on the partitioning between water and octanol is available and a Log Kow = 1.36 at 20°C reported (below cut-off value of 3). Furthermore, the water solubility is reported as 810.1 mg/L at 20°C. The substance (4-formylphenyl)boronic acid is thus expected to have a low potential for bioaccumulation (ECHA, 2018).

11.1.3 Effects on the aquatic environment

Data on the acute toxicity are available for (4-formylphenyl)boronic acid and summarised in the table below. The highest toxicity is observed for algae where an EC50 of 10.7 mg/L and a NOEC of 0.75 mg/L are observed.

TABLE 7. Effects of (4-formylphenyl)boronic acid (CAS no.: 87199-17-5) to aquatic organisms

Species	Scientific name	Endpoint/Effect	Test duration	Reference
Fish	*Onkorhynchus mykiss*	LC50 = 56.7 mg/L	96 h	ECHA 2018
Crustacean	*Reported as aquatic crustacean DM*	EC50 = 61.1 mg/L	48 h	ECHA 2018
Algae	*Pseudokirchneriella subcapitata*	EC50 = 10.7 mg/L (growth rate)	72 h	ECHA 2018
	Pseudokirchneriella subcapitata	NOEC = 0.75 mg/L (growth rate)	72 h	ECHA 2018

Based on the available data, the substance is assessed to have chronic toxicity in the aquatic environment.

11.1.4 Effects on Human Health

11.1.4.1 Toxicokinetics

No information available.

11.1.4.2 Acute toxicity

The acute toxicity of (4-formylphenyl)boronic acid is considered relatively low. In rats the LD50 was >2000 mg/kg bw after oral exposure to (4-formylphenyl)boronic acid. Low acute dermal toxicity was also observed in a rat study with a LD50 >2000 mg/kg bw. No study was available on acute inhalational toxicity (ECHA, 2018).

11.1.4.3 Skin and eye irritation

Skin irritation of (4-formylphenyl)boronic acid was investigated using semi-occlusive dressing on rabbit skin (500 mg for 4 hours). No substance-related skin irritation was observed at 24, 48 or 72 hours post exposure (ECHA, 2018).

The eye irritation of (4-formylphenyl)boronic acid was investigated in rabbits using eye instillation of 100 mg per animal. Slight tear secretion was observed in all three animals at 1 hour post instillation, and still present in one animal 48 hours post instillation. All changes were fully reversible in three animals within 5 days (ECHA, 2018).

11.1.4.4 Skin sensitisation

The skin sensitisation potential of (4-formylphenyl)boronic acid was investigated in a Guinea Pig Maximisation Test (GPMT). For intradermal induction: 1% in 0,5% carboxymethylcellulose (CMC) and for dermal induction: 50% in 0,5% CMC were used. For the first challenge 40% in 0,5% CMC and the second challenge 40%, 5% and 0,5% in 0,5% CMC were used. Readings were performed at 24, and 48 hours post challenge. All animals in the 40% challenge group had reactions/effects at 24 and 48 hours post challenge, and 3 out of 5 animals had reactions after re-challenge. Thus, (4-formylphenyl)boronic acid met the classification criteria for Category 1 (skin sensitising) based on GHS criteria (ECHA, 2018).

11.1.4.5 Repeated dose toxicity

In a 28-day repeated oral gavage study (OECD TG 407) in compliance with GLP, rats were gavaged with 0, 50, 250 or 1000 mg (4-formylphenyl)boronic acid /kg/ bw/day. At highest dose-level (1000 mg/kg bw/day) several effects were observed in haematological and clinical biochemistry parameters, increased liver, spleen, lung and ovary weight in female rat, histopathological changes were also observed in liver and lymph nodes in both sex. NOEL was determined to 50 mg/kg bw/day and the NOAEL was determined to 250 mg/kg bw/day based on the non-histopathological findings, as histopathology was not performed on animals treated at 50 and 250 mg/kg bw/day (ECHA, 2018).

11.1.4.6 Toxicity to reproduction and development

Toxicity to reproduction was assessed in a reproduction/developmental toxicity screening study (OECD TG 421, GLP) in rats gavaged with 0 - 1000 mg/kg bw/day. Based on the results of this study the NOAEL parental reproductive toxicity is ca. 250 mg/kg bw/day in relation to gestation length. A LOAEL of 250 mg/kg bw/day was determined for offspring (F1) based on reduced live birth and viability indices of this group. Based on these findings, it was concluded that no fertility-influencing effects were detected and that the developmental toxicity effects were associated with maternal toxicity (ECHA, 2018).

11.1.4.7 Genetic toxicity

The genotoxicity of (4-formylphenyl)boronic acid was assessed in two *in vitro* studies, both with negative results suggesting that substance is not genotoxic under the conditions given in the studies. The first study, a chromosome aberration test was performed using human lymphocytes and in accordance to OECD TG 473 and GLP. Cells were exposed to (4-formylphenyl)boronic in DMSO for 3 hours in concentrations 734.6 – 1499 µg/ml or 355.7 - 632.4 µg/ml with or without metabolic activation, respectively. Negative results were obtained at all the given conditions (ECHA, 2018).
In the second study, a mammalian cell gene mutation study was performed using mouse lymphoma L5178Y cells according to OECD TG 476 and GLP. Cells were exposed to (4-formylphenyl)boronic in DMSO for 3 hours in concentrations 200 – 1400 µg/ml and 1500µg/ml without and with metabolic activation, respectively. Negative results were obtained at all the given conditions (ECHA, 2018).

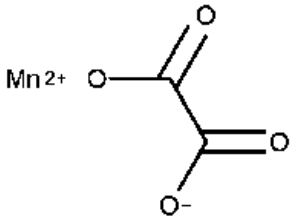
11.1.4.8 Overall assessment

There is no information available on the toxicokinetics of (4-formylphenyl)boronic acid, but it was tested to be hydrolytic stable at 50 degrees celsius. Thus, no toxic metabolites (e.g. boric acid that is toxic to reproduction) are expected to be formed due to oral ingestion. The substance (4-formylphenyl)boronic acid is considered to have relatively low acute oral and dermal toxicity with an LD50 >2000 mg/kg bw. Data on skin and eye irritation suggests no classification. However, (4-formylphenyl)boronic acid fulfil the classification criteria as a skin sensitizer Category 1 (skin sensitizing) based on GHS criteria. In a repeated oral dose study (28 days) several effects were observed at highest dose-level (1000 mg/kg bw/day) and a NOEL of 50 mg/kg bw/day and a NOAEL of 250 mg/kg bw/day were concluded. Toxicity to reproduction was assessed in a reproduction/developmental toxicity screening study where developmental toxicity effects were observed and associated with maternal toxicity. A NOAEL of 250 mg/kg bw/day in relation to gestation length and a LOAEL of 250 mg/kg bw/day was determined for offspring. Further, (4-formylphenyl)boronic acid was test negative for mutagenicity *in vitro*.

11.2 Manganese-II-oxalate dihydrate

Manganese oxalate is used in dishwashing tabs as an enzyme activator.

CAS no. 640-67-5 and EC no. 211-367-3



Manganese oxalate has a full registration dossier under REACH (10 – 100 tonnes per annum). From the C&L Inventory (2018), information was provided by 29 companies in one aggregated notification. From the self-reported notified classification, a classification as Acute Tox. 4 (H302 & H312) is suggested, although experimental toxicological findings in the registration dossier do not support that suggestion.

11.2.1 Occurrence in the environment

Data on the occurrence of manganese-II-oxalate dihydrate in the environment were not searched, as this was not considered to be important.

11.2.2 Environmental fate

11.2.2.1 Aerobic biodegradability

The biodegradation of manganese-II-oxalate dihydrate has been studied according to OECD Guideline 301 B (Ready Biodegradability: CO_2 Evolution Test). After 28 days, 84% degradation of the test item was determined and based on the results obtained, manganese-II-oxalate dihydrate was considered as readily biodegradable (> 60% biodegradation after 28 days) (ECHA, 2018).

11.2.2.2 Anaerobic biodegradability

The anaerobic biodegradation of manganese-II-oxalate dihydrate has been studied according to OECD Guideline 311 (Anaerobic Biodegradability of Organic Compounds in Digested Sludge: Measurement of Gas Production) and ECETOC Guideline on Anaerobic Biodegradation (Technical Report No. 28). After 60 days, the test item attained 53% degradation calculated from the volume of gas produced and 147% total degradation calculated from the sum of the gas produced and the dissolved inorganic carbon (DIC) formation. According to OECD Guideline 311, complete anaerobic biodegradation can be assumed to occur if 75%-80% of theoretical gas production is achieved. The difference between the degradation rates calculated from the volume of gas produced and DIC formation was considered to be due to sampling and/or analytical variation associated with the DIC analysis where small variations in the DIC concentration lead to relatively large variations in the calculated biodegradation values and also values above 100% (ECHA, 2018).

11.2.2.3 Bioaccumulation

No experimental data describing the bioaccumulation potential of manganese-II-oxalate dihydrate were found in the literature. The octanol-water partitioning coefficient (Log Kow) was reported as <<0, and the water solubility was determined to be 0.3 g/L at 20 °C. Manganese-II-oxalate dihydrate is thus expected to have a low potential for bioaccumulation (ECHA, 2018).

11.2.3 Effects on the aquatic environment

The toxicity of manganese-II-oxalate dihydrate was determined in studies with fish, invertebrates and algae. Both short-term and long-term results are available and summarised in the table below (ECHA, 2018).

TABLE 8. Effects of manganese-II-oxalate dihydrate (CAS no.: 640-67-5) to aquatic organisms.

Species	Scientific name	Endpoint/Effect	Test duration	Reference
Fish	*Danio rerio*	LC50 > 75 mg/L (59.9 mg/L)	96 h	ECHA 2018
Crustacean	*Daphnia magna*	EC50 > 90 mg/L (71.9 mg/L)	48 h	ECHA 2018
Algae	*Pseudokirchneriella subcapitata*	EC50: 86 mg/L (68.7 mg/L) (growth rate)	72 h	ECHA 2018
	Pseudokirchneriella subcapitata	NOEC: 3.2 mg/L (2.6 mg/L) (growth rate)	72 h	ECHA 2018

Numbers in parenthesis are values where a correction factor of 1.252 has been applied and where results are adjusted to the anhydrous form of the substance.

Based on the available data on toxicity in the aquatic environment, the substance is not hazardous to aquatic organisms.

11.2.4 Effects on Human Health

11.2.4.1 Toxicokinetics

No information available.

11.2.4.2 Acute toxicity

The acute toxicity of manganese oxalate, dihydrate is considered relatively low. A single oral gavage administration to female rats at 2000 mg/kg bw did not cause any mortality and the LD50 was determined to be >2000 mg/kg bw. In an acute dermal toxicity study, manganese oxalate, dihydrate did not cause mortality to male and female rats when administrated at 2504 mg/kg bw. Thus, the LD50 was calculated to be >2000 mg/kg bw. No study was available on acute inhalational toxicity (ECHA, 2018).

11.2.4.3 Skin and eye irritation

Skin irritation or corrosion was tested *in vitro* according to OECD TG 439 (*In vitro* Skin Irritation: Reconstructed Human Epidermis Test Method) and 435 (*In vitro* Membrane Barrier Test Method for Skin Corrosion). For manganese oxalate, a relative absorbance value of 92.2% was found in the In vitro Skin Irritation Test (Human skin Model Test). This value is well above the threshold for irritancy of <=50%. However, since the acute dermal toxicity study showed no signs of skin corrosion it was concluded that the test item did not induce significant or irreversible damage to the skin (ECHA, 2018).

The eye irritation of manganese oxalate was investigated using rabbits with eye instillation of 100 mg per animal (OECD TG 405). Reddening and chemosis were observed immediately after instillation, but fully reversible within 72 hours post instillation. Thus, it was concluded that manganese oxalate did not induce significant irritation or irreversible damage to the rabbit eye (ECHA, 2018).

11.2.4.4 Skin sensitization

Manganese oxalate, dihydrate suspended in propylene glycol was assessed for its possible skin sensitisation potential in the Local Lymph Node Assay (OECD TG 429) using concentrations of 2.5%, 5%, and 10% (w/v). No reactions were observed during the study. Thus, it was concluded that manganese oxalate, dihydrate was not a skin sensitiser under the test conditions of this study (ECHA, 2018).

11.2.4.5 Repeated dose toxicity

In a 28-day repeated oral gavage study (OECD TG 407) in compliance with GLP, rats were gavaged with 0, 100, 300, or 1000 mg manganese oxalate/kg bw/day. No substance-related deaths, clinical signs or symptoms of toxicity were observed and a NOAEL of 1000 mg/kg bw/day was concluded (ECHA, 2018).

11.2.4.6 Toxicity to reproduction and development

Reproduction and developmental toxicity of manganese oxalate was assessed via oral gavage in a reproduction/developmental toxicity screening study (OECD TG 421, GLP) where rats were gavaged with 0, 100, 300, or 1000 mg/kg bw/day. No test-substance related reproduction or developmental toxicity were observed. Thus, based on the results of this study, the NOAEL was considered to be 1000 mg/kg bw/day (ECHA, 2018).

11.2.4.7 Genetic toxicity

A battery of *in vitro* tests (Bacterial Reverse Mutation Test, Mammalian Chromosome Aberration Test, and Mammalian Cell Mutation assay) was used to assess the genotoxic potential of manganese oxalate in according to the respective OECD test guidelines. The results in all three tests were negative suggesting that manganese oxalate is not mutagenic under the conditions given in the studies (ECHA, 2018).

11.2.4.8 Overall assessment

There is no information available on the toxicokinetics of manganese oxalate. Manganese oxalate is considered to have relatively low acute oral and dermal toxicity with an LD50 >2000 mg/kg bw. Data on skin and eye irritation suggests no classification, and manganese oxalate did not show any skin sensitizing properties when tested in the LLNA assay. No systemic toxicity was observed after repeated oral exposure at doses up to 1000 mg/kg bw/day and a NOAEL of 1000 mg/kg bw/day was concluded. No toxicity was observed in relation to reproduction and developmental and a NOAEL of 1000 mg/kg bw/day was concluded. Further, there was no observed mutagenic effect of manganese oxalate when tested *in vitro.*

12. Remarks on other substances

12.1 Enzymes

The group of enzymes was not included in the environmental and health assessment in this project. Instead, reference is made to general studies and reviews of the effects from the use of enzymes in household detergents. Human & Environmental Risk Assessment is reported by HERA on subtilisins (protease) and the group of amylases, cellulases and lipases (HERA 2007; HERA 2005). Furthermore, a comprehensive study of the environmental effects of enzymes concludes that there are no risk to the aquatic environment from the normal use of household detergents (Madsen et al., 2011). The main concern to human health is the potential induction of respiratory allergies. This has been handled by encapsulation of the enzymes in liquid and powder detergents containing enzymes, which thereby prevent the respiratory exposure (HERA 2005; HERA 2007; A.I.S.E. 2018c).

12.2 Surfactants

For the group of surfactants, ECHA has raised concern on the group of alkyl dimethyl betaine and the alkyl dimethyl amine oxides (ECHA CoRAP, 2018).

Alkyl dimethyl betaine is listed on the ECHA CoRAP list (2018) because of suspected reprotoxicity in addition to high aggregated tonnage and wide dispersive use. The alkyl dimethyl amine oxide (C12-14 even numbered) is also listed on the CoRAP list, as the substance is expected to be reprotoxic.

Furthermore, the cationic substances di-C16-18-alkyldimethyl ammonium chlorides are subject for substance evaluation based on high aggregated tonnage and the need for more information on the environmental exposure (ECHA CoRAP, 2018).

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Appendix 1. Market information

Appendix 1.1

Table 1. Danish import, production and export of washing and cleaning detergents to retail, 2001-2017[1]. Numbers for import and export are for packages sold in retail[2].

Year	Import (T)	Export (T)	Production (T)	Consumption (T)[3]
2001	26303,837	122814,47	142347	45837
2002	26003,871	130946,66	156932	51990
2003	30769,557	137419,62	161417	54767
2004	34903,164	131677,94	146988	50213
2005	52502,294	128484,27	116832	40850
2006	64686,991	121831,66	*11992**	----
2007	66242,683	124570,64	*11216**	----
2008	74977,961	120188,26	141312	96102
2009	78155,661	113434,27	118591	83313
2010	75324,182	122383,08	115259	68201
2011	79491,483	115594,84	111549	75445
2012	84284,228	122068,4	84944	47159
2013	84597,786	125128,26	81490	40959
2014	90144,58	124546,44	81521	47119
2015	89498,142	117334,05	80971	53135
2016	90151,787	119395,1	79115	49871
2017	86729,434	123606,47	----	----
Average (2006 &2007 excluded)	65508	123673	115662	57497

[1] Data source: Statistics Denmark https://www.statistikbanken.dk/VARER1 and Eurostats Prodcom Database http://ec.europa.eu/eurostat/web/prodcom/data/excel-files-nace-rev.2

[2] Data on washing and cleaning detergents to retail using KN code 34022090 (import and export) and NACE code 204 13250 (production)

[3] Consumption is calculated as Import + Production – Export.

*** Numbers reported for 2006 and 2007 are 10-times lower than the average tonnage for the period 2001-2016.**

Appendix 1.2 Trends in the Nordic- and EU's Ecolabel criteria for cleaning-, dishwashing-, and laundry detergent from 2001 to 2018

The Nordic Swan Ecolabel (the swan) and EU's Ecolabel (the flower) criteria are the most used ecolabels for laundry detergents, dishwashing detergents (hand and machine) and of cleaning products on the Danish retail market. The criteria for the two ecolabels are similar with some minor exceptions.

The specific criteria for the Nordic Ecolabel and EU's Ecolabel for the products categories; laundry detergents, dishwashing detergents (hand and machine) and of cleaning products can be found at the Ecolabelling Denmark website (https://www.ecolabel.dk/da/in-english/criteria-documents), or directly via links in the reference list at the end of the document.

Common to all the four product categories, the prohibition of substances that are carcinogenic, mutagenic or toxic to reproduction (CMR) and the limitation of environmentally hazardous substances are standard Nordic Ecolabelling requirements for chemical products.

Laundry detergents

Laundry detergents were one of the first product groups to become ecolabelled according to the Nordic Ecolabelling system. The EU Ecolabel Scheme also has criteria for laundry detergents. These criteria are similar to the Nordic Ecolabel criteria in their structure. However, stain removers are not covered by the EU Ecolabel criteria. The criteria have been extensively revised with the focus on regulating the ingoing chemicals. In 2006 a harmonisation of the chemical calculations was introduced to align with the principles used in the EU Ecolabel (such as integration of Critical Dilution Volume (CDV) and the DID-list) and a major change of the performance test was performed. In addition, the requirements were adjusted so that they enabled ecolabelling of liquid detergents. In 2008, more stringent requirements for fragrances were introduced. From 2011 mandatory requirements of performance at low temperature (i.e., 30°C) were introduced together with more stringent requirements to dose and limitation on the use of substances classified as environmentally harmful (e.g., phosphorous). In the latest criteria from 2017, a new weighted approach for limitation of environmentally hazardous substances was introduced, and adaptation to new regulations on CMR substances was made.

Dishwashing detergents

Hand dishwashing detergents

In the period 2001 - 2005, the environmental matrix was introduced and from now on all surfactants had to be anaerobically biodegradable. Furthermore, health requirements for sensitising substances were introduced for fragrances, and antibacterial products were excluded from the criteria. From 2006 -2009, the new DID-list for chemicals was introduced as well as a tightening of the CDV requirement. In the same period, focus was on requirements of allergenic fragrances, substances of very high concern (SVHC), and substances that may have a long-term effect on the environment. In the following period 2009 to 2016, stricter CDV limits were implemented. In the same period a ban on APD (alkylphenol derivatives), SVHC, endocrine disruptors and potential endocrine disruptors, vPvB (very persistent and very bioaccumulative) and PBT (persistent, bioaccumulative and toxic) substances was introduced. The newest requirements from 2017 include a ban on sensitising preservatives and more sustainable and renewable raw materials.

Dishwasher detergents and Rinsing agents

In the period 2002 to 2009, the use of perborates in dishwashing detergents was prohibited, and the requirement on phosphates was tightened. Furthermore, the CDV and a point score system were introduced. From 2009 to 2013, most focus was on the classifications in accordance with CLP, and the requirements on fragrances were tightened. In the following period, 2014 to 2017, most focus was on more strict requirements on fragrances and allergens, and a

ban on sensitising substances (except fragrances and enzymes) in dishwashing detergents. Further, the use of CDV-chronic instead of CDV-acute and with data from the DID-list was introduced.

All-purpose cleaning products

Previously the criteria for cleaning products were divided into separate criteria documents for all-purpose cleaners and sanitary cleaning products, but they are now merged as one product category. In the period 1999 - 2004, an environmental matrix was introduced in which the requirements are interconnected (toxicity, degradation, non-potentially degradable substances, and phosphorus) resulting in a stricter function test. In the period 2003 – 2007, much focus was on reducing substances with relatively high toxicity, including health-related requirements for fragrance and low degradability. Further, antibacterial products were excluded, and products that served only as decalcifying agents were no longer encompassed by the criteria. During 2007 – 2013, stricter limitations and use were introduced on substances classified as environmentally hazardous. In this period product toxicity and biodegradability (according to the DID-list) were replaced by CDV and the limit values tightened. For the human health, stricter requirements were introduced for sensitising substances, and CMR substances were now prohibited. Overall, stricter requirements came on the use of fragrances. From 2013 to 2018, new products such as oven cleaners and wash polish were included in the product group.

Conclusion

The overall trend from 2001 to 2018 in ecolabel requirements for the laundry detergents, dishwashing detergents (hand and machine) and of cleaning products is the continuous introduction of stricter environmental and human health criteria. The introduction of the environmental matrix considering multiple variables (eco-toxicity, environmental fate, and phosphorus) and stricter requirements led to more holistic evaluations. With the integration of Critical Dilution Volume (CDV) and the DID-list, higher ecotoxicity standards were set for Ecolabel products. Another important trend for all the product groups was the ban on CMR substances and the limiting/ban of sensitising substances including some fragrances. Additionally, a general trend across the entire product group is a strong focus on environmentally hazardous substances (PBT / vPvB) and adaptation to CLP regulation. Finally, another trend not discussed herein is the inclusion of sustainability in relation to raw materials but also to packaging.

References:

Nordic Swan Ecolabelled Laundry detergents and stain removers Criteria Version 7 Background document 7 February 2017 https://www.ecolabel.dk/-/criteriadoc/2378

Nordic Swan Ecolabelled Hand dishwashing detergents Version 6.0 14 March 2018, Background document https://www.ecolabel.dk/-/criteriadoc/3383

Nordic Swan Ecolabelled Dishwasher detergents and Rinsing agents Version 6.4 Background to ecolabelling 07 February 2017 https://www.ecolabel.dk/-/criteriadoc/2389

Nordic Ecolabelling of Cleaning Products - Background to ecolabelling, 15 March 2018, https://www.ecolabel.dk/-/criteriadoc/3395

Appendix 2. Survey of household substances

Appendix 2.1 Laundry detergents

The results on ingredients in laundry detergents (powder, liquid, pods) collected from questionnaires (Q), interviews (I) and product information (PI) are presented in the tables below.

Surfactant		Ingredients	Product	Source
Anionic	LAS	Dodecylbenzenesulfonate	Liquid, powder	Q, PI
Anionic	LAS	MEA-dodecylbenzenesulfonate	Liquid, pods	PI
Anionic	LAS	TEA-dodecylbenzenesulfonate	Liquid	PI
Anionic	AS	Sodium Lauryl sulfate	Powder, Liquid	PI
Anionic	AES	Sodium laureth sulfate Sodium pareth sulfate	Liquid, pods	PI
Anionic	AOS	-	Liquid	Q
Anionic	FA and soaps	Sodium tallowate, stearic acid	Liquid, powder	Q, PI
Anionic	FA and soaps	Sodium stearate, sodium palmitate	Powder	PI
Anionic	FA and soaps	Sodium palm kernelate	Liquid	PI
Anionic	FA and soaps	Potassium cocoate, potassium soyate	Liquid	PI
Anionic	FA and soaps	TEA cocoate, TEA laurate, TEA soyate, TEA oleate, MEA-cocoate	Liquid, pods	PI
Anionic	FA and soaps	TEA-hydrogenated cocoate MEA-hydrogenated cocoate	Liquid, pods	Pi
Anionic	FA and soaps	Sodium hydrogenated cocoate	Liquid	Pi
Anionic	-	MEA-sulfate	Liquid, pods	PI
Nonionic	AE	C11-15 Sec-pareth-12, C12-15, C12-18, C13/15, C14/16, C13-15 Pareth-11, C12-15 Pareth-7, C14-15 Pareth-7, Laureth-3, Laureth-5, Laureth-7, Laureth-9, trideceth-8, trideceth-3, Ceteareth-25, PPG-4-Laureth-3, PPG-4-Laureth-5	Liquid, powder, pods	Q, PI
Nonionic	-	2-ethylhexanol Ethoxylate	Liquid	PI
Nonionic	Block Polymer	-	Liquid	Q
Nonionic	APG	-	Liquid	Q
Amphoteric	Betaine	Cocoamidopropyl Betaine	Liquid	PI

LAS: linear alkylbenzene sulfonic acid; AS: alkyl sulfates; AES: alkyl ether sulfates; AOS: alfa-olefine sulfonates; FA: fatty acids; AE: alcohol ethoxylates; APG: alkyl polyglucosides; MEA: monoethanolamine; TEA: triethanolamine; PPG: polypropylene glycol

Ingredients with other functions	Function	Product	Source
Silica	Additive	Powder	PI
Talc	Additive	Pods	PI
Polyvinyl alcohol	Additive/film packaging	Pods	PI
Phenylpropyl dimethicone	Antifoaming agent	Powder	PI
Potassium sulphite	Antioxidant	Pods	PI
Polyethylene terephthalate	Anti-redeposition Agent	Powder	PI
Cellulose gum	Anti-redeposition Agent	Powder	PI
aziridine homopolymer ethoxylated	Anti-redeposition Agent	Liquid, pods	PI
1,4-benzenedicarboxylic acid, 1,4-dimethyl ester, polymer:…	Anti-redeposition Agent	Liquid	PI
Sucrose	Binder	Powder	PI
PEG-75	Binder/Nonionic surfactant	Powder	PI
Dextrin	Binder	Powder	PI
Cellulose	Binder	Powder	PI
Denatonium benzoate	Bitter taste, bitterant	Liquid, pods	PI

Sodium sulfate	Bulking agent/by-product	Powder, liquid	PI
Kaolin	Bulking agent	Powder	PI
Calcium carbonate	Bulking agent	Powder	PI
Sodium acetate	By-product	Liquid	PI
Peptides, salts, sugars from fermentation process	By-product	Powder, liquid	PI
Sodium thioglycolate	By-product	Powder	PI
Lauryl alcohol	By-product	Powder	PI
Sodium polyaryl sulphonate	By-product	Powder	PI
CI 42051, CI 61585, CI 45100	Colour	Liquid	PI
Polymeric blue colorant	Colour	Liquid, pods	PI
Polymeric yellow colorant	Colour	Liquid, pods	PI
Polymeric violent colorant	Colour	Liquid	PI
Titanium dioxide	Colour	Powder	PI
PVP, Polyvinylpyrrolidone	Dye transfer inhibitor	Powder, pods	PI
PVPNO, Polyvinylpyridine N-oxide	Dye transfer inhibitor	Liquid	PI
Vinyl imidazole/VP copolymer	Dye transfer inhibitor	Pods	PI
PVP/IV, vinyl polymer	Dye transfer inhibitor	Powder	PI
Corn starch modified	Enzyme stabiliser	Powder	PI
Sorbitol	Enzyme stabiliser	Liquid, pods	PI
Boronic acid, (4-formylphenyl)	Enzyme stabiliser	Liquid	PI
Calcium chloride	Enzyme stabiliser	Liquid, pods	PI
Polyether/polyester copolymer	Emulsifier/binder?	Powder	PI
Glycereth-6 laurate	Emulsifier	Pods	PI
Glyceryl Stearates	Emulsion stabiliser	Powder	PI
Propylene glycol	Hydrotrope	Liquid, pods	PI
Sodium cumenesulfonate	Hydrotrope	Liquid	PI
Styrene/acrylates copolymer	Opacifier	Liquid	PI
Disodium distyrylbiphenyl disulfonate	Optical brightener	Powder, Liquid, pods	PI
Disodium Anilinomorpholinotriazinyl-aminostilbenesulfonate	Optical brightener	Powder	PI
Sodium hydroxide	pH adjuster	Liquid	PI
Potassium hydroxide	pH adjuster	Liquid	PI
Potassium carbonate	pH adjuster/buffering agent	Liquid	PI
Sodium sulphite	Preservative	Liquid	PI
Triethanolamine	Solvent/Solubiliser/surfactant	Liquid	PI
Ethanolamine	Solvent	Pods	PI
Dipropylene glycol	Solvent	Powder	PI
Alcohol denat.	Solvent	Liquid	PI
Alcohol	Solvent	Liquid	PI
Glycol	Solvent	Pods	PI
Bentonite	Softness extender	Powder	PI
Di-substituted alaninamide	Stabilising agent	Liquid, pods	PI
Sodium formate	Stabilising agent	Pods	PI
Polypropylene terephthalate	Suspending Agent	Pods	PI
Polyoxyethylene terephthalate	Suspending Agent	Pods	PI
Sodium acrylic acid/MA copolymer	Viscosity control, Structurant, anti-redeposition agent	Powder, liquid	PI
Sodium Polyacrylate	Viscosity control, Structurant	Powder	PI
Sodium acrylates copolymer	Viscosity control	Liquid	PI

Glycerine	Viscosity control/ Humectant	Liquid, pods	PI
Sodium chloride	Viscosity control	Liquid, pods	PI

PEG: polyethylene glycol; MA: methacrylate; CI: Colour Index

Complexing agents/Builders	**Product**	**Source**
Phosphates	Powder, liquid	PI
Phosponates	Liquid	Q
Tetrasodium Etidronate, 1-Hydroxyethylene bisphosphonic acid, sodium salt	Liquid, powder	I, PI
MEA etidronate (1-hydroxyethane 1,1-di-phosphonate MEA)	Liquid	PI
Sodium diethylenetriamine pentamethylene phosphonate	Liquid, pods	PI
Calcium sodium EDTMP (ethylenediamine tetra methylene phosphonic acid)	Powder	PI
Polycarboxylates	Powder-handwash	PI
Sodium carbonate/sodium bicarbonate	Powder	PI
Zeolites (sodium silicoaluminate)	Powder	Q, I, PI
Silicates, (sodium, aluminum*)	Powder	I, PI
Sodium citrate, Citric acid	Tabs, powder, liquid	I, PI
Trisodium citrate	Liquid	PI
Potassium citrate	Liquid	PI
MEA citrate	Liquid	PI
Sodium methylglycine diacetate, MGDA	Liquid, Tabs	I, PI
Trisodium dicarboxymethyl alaninate, MGDA	Powder	PI
Sodium carboxymethyl inulin**	Liquid	PI
Trisodium dicarboxymethyl inulin**	Liquid	PI
Sodium carboxymethyl carbohydrate	Liquid	PI

MEA: monoethanolamine

*anticaking agent/scale inhibitor

**vegetable scale inhibitor

Bleaching agents	**Product**	**Source**
Hydrogen peroxide	Liquid	Q
Perborates/Percarbonates	Powder	Q
TAED (tetraacetyl ethylenediamine)	Powder	I, PI
Sodium Percarbonate/sodium carbonate per-oxide	Powder	I, PI

Enzymes	**Product**	**Source**
Proteases	Liquid, powder	Q, PI
Subtilisin	Powder, liquid, pods	PI
Amylases, alpha-amylase	Liquid, powder, pods	Q, PI
Lipases	Powder, liquid, pods	Q, PI
Pectate lyase	Powder, liquid	I, PI
Pectinase	Liquid	PI
Mannanase	Powder, liquid, pods	I, PI
Cellulase (carezyme)	Powder, liquid	I, PI

Fragrances	Product	Source
Amyl cinnamal	Liquid	Q
Amyl cinnamyl alcohol	Liquid	Q
Anise alcohol	Liquid	Q
Benzyl alcohol	Liquid	Q
Benzyl benzoate	Liquid	Q
Benzyl cinnamate	Liquid	Q
Cinnamal	Liquid	Q
Cinnamyl alcohol	Liquid	Q
Citral	Liquid	Q
Farnesol	Liquid	Q
Hydroxyisohexyl 3-cyclohexene carboxaldehyde (hicc)	Liquid	Q
Hydroxycitronellal	Liquid	Q
Isoeugenol	Liquid	Q
Methyl 2-octynoate	Liquid	Q
Evernia furfuracea extract	Liquid	Q
Evernia prunastri extract	Liquid	Q
Butylphenyl methylpropional	Liquid, pods	PI, Q
Benzyl salicylate	Liquid, Pods	PI, Q
Citronellol	Liquid, pods	PI, Q
Coumarin	Liquid, Pods	PI, Q
Geraniol	Liquid	PI, Q
Hexyl cinnamal	Liquid, Pods	PI, Q
Alpha-isomethyl ionone	Liquid, Pods	PI, Q
Linalool	Liquid, Pods	PI, Q
Limonene	Pods	PI

Appendix 2.2 Dishwash detergents

The results on ingredients dishwashing detergents (liquid, powder, gel, tabs) collected from questionnaires (Q), interviews (I) and product information (PI) are shown in the tables below.

Surfactants		Ingredients	Product	Source
Anionic	FA	C12-18	Hand, Gel, tabs	Q, PI
Anionic	FA	Magnesium stearate	Tabs	PI
Anionic	AES	Sodium laureth sulfate	Hand, Tabs	Q, PI
Nonionic	AE	C10 Pareth-8, Deceth-8, trideceth-8 C8-10 Alcohol Ethoxylate, C16-18 Alcohol Ethoxylate, Hexyl Alcohol Ethoxylate Alipharic alcohol c8-14 ethoxylate, Ceteareth-25 Sorbitan ester	Hand, Gel, powder, tabs	Q, PI
Nonionic	AA	C8-14 Alcohol Alkoxylate	Tabs, gel	PI
Nonionic	APG	-	Hand	PI
Nonionic	FAA	-	Gel, tabs	Q
Nonionic	Block polymers	-	Tabs	Q
		Poloxamer 124	Hand	PI
Cationic	ADMBAC	Alkyldimethylbenzylammonium chloride	Gel, powder, tabs	Q
Cationic	DADMAC	Diallyldimethylammonium chloride	Tabs	PI
Amphoteric	Alkyl amine oxide	Lauramine oxide	Hand	PI
Amphoteric	Alkyl amidopropyl amine oxide	Lauramidopropylamine oxide Myristamidopropylamine oxide	Hand	PI
Amphoteric		Sodium Carboxymethyl Cocopolypropylamine	Hand	PI
Amphoteric	Betaine	Lauryl Betaine Cocoamidopropyl betaine	Hand	PI

FA: fatty acids; AS: alkyl sulfates; AE: alcohol ethoxylates; AA: alcohol alkoxylate; APG: alkyl polyglucosides;

Ingredients with other functions	Function	Product	Source
Polyvinyl alcohol	Additive/film packaging	Tabs	PI
Dimethicone	Antifoaming agent	Tabs	PI
Simethicone	Antifoaming agent	Tabs	PI
Potassium sorbate	Antimicrobial agent	Hand	PI
Sodium benzoate	Antimicrobial agent	Hand	PI
Sodium levulinate	Antimicrobial agent, Buffer	Hand	PI
Cellulose	Binder	Tabs	PI
Dextrin	Binder	Tabs	PI
Sucrose	Binder	Tabs	PI
PEG-9	Binder/Nonionic surfactant	Tabs	PI
PEG-20	Binder/Nonionic surfactant	Tabs	PI
CI 47005, CI 18965, CI 42051	Colour	Hand	PI
CI 10020, CI 77891	Colour	Tabs	PI
Titanium dioxide	Colour	Tabs	PI
1-H-Methylbenzotriazole	Corrosion inhibitor	Tabs	PI
Sodium chloride, calcium chloride	Enzyme coating; viscosity control	Hand, Tabs, gel	PI
Sodium sulfate	Enzyme coating; filler	Tabs	PI
Manganese-II-oxalate Dihydrate	Enzyme activator	Tabs	I, PI

Cellulose gum	Enzyme stabiliser	Tabs	PI
Magnesium sulfate	Filler	Hand	PI
Bentonite	Filler	Tabs	PI
Kaolin	Filler	Tabs	PI
Avena sativa starch	Filler	Tabs	PI
Silicon dioxide	Filler, anti-caking agent	Tabs	PI
Glycerine	Humectant	Hand, gel	PI
Sodium xylenesulfonate	Hydrotrope	Hand	PI
PEG-40 glyceryl cocoate	Skin care	Hand	PI
Ethanol	Solvent	Hand	PI
Propylene glycol	Solvent	Tabs, gel	PI
Xanthan gum	Viscosity control	Gel	PI
Polycarboxylates: Sodium Polyacrylate, Sodium Arylic/MA Copolymer, Acrylic/Sulphonic Acid Copolymer	Viscosity control	Tabs	PI
Acrylic/maleic copolymer, acrylate copolymers, acrylic/sulphonic copolymer	Viscosity control	Tabs, gel	PI
2-Propenoic acid, homopolymer, sodium salt; 2-Propenoic acid, homopolymer, sodium salt, sulfonated	Viscosity control	Tabs	PI
Sulfonated carboxylate polymer	Viscosity control	Gel	PI

PEG: polyethylene glycol; CI: Colour Index;

Complexing agents/Builders	**Product**	**Source**
Phosphates	Gel, powder, tabs	PI
Tetrasodium etidronate, (1-hydoxyethylidene) bisphosphonic acid, sodium salt (phosphonate)	Tabs, gel	PI
Sodium carbonate, sodium bicarbonate	Tabs	PI
Calcium carbonate	Tabs	PI
Trisodium dicarboxymethyl alaninate, MGDA	Hand, Gel, Tabs	PI
Polyethylene imine; aziridine homopolymer	Gel, Tabs	PI
Sodium carboxymethyl inulin	Gel	PI
Sodium silicate	Tabs	PI
Sodium Citrate	Hand, Gel, powder, tabs	Q, PI
Citric acid	Hand, Gel, Tabs	PI
Sodium formate	Hand	PI
Formic acid	Hand	PI
Sodium lactate	Hand	PI
Lactic acid	Hand	PI

Bleaching agents	**Product**	**Source**
Perborates/Percarbonates, Sodium carbonate peroxide	Tabs	Q, PI
TAED (tetraacetyl ethylenediamine)	Tabs	PI

Enzymes	**Product**	**Source**
Amylases, alpha-amylase	Gel, powder, tabs	Q, PI
Proteases	Gel, powder, tabs	Q, PI
Subtilisin	Gel, Tabs	PI

Fragrances	Product	Source
Natural essential oils	Hand	PI
Limonene	Hand	PI
Butylphenyl methylpropional	Hand	PI
Hexyl Cinnamal	Hand	PI
Linalool	Hand	PI
Coumarin	Hand	PI
Glutaral	Hand	PI

Appendix 2.3 All-purpose detergents

The results on ingredients in all-purpose detergents collected from questionnaires (Q), interviews (I) and product information (PI) are shown in the tables below.

Surfactants		Ingredients	Source
Anionic	LAS	C10-13, Sodium C10-14 Alkyl Benzenesulfonate, Sodium dodecylbenzenesulfonate	Q, PI
Anionic	FA (Fatty Acid soap)	C12-18, Sodium Cocoate, Sodium oleate	Q, PI
Anionic	Anionic - other	Substance name confidential information	Q
Anionic	AS	Sodium laureth sulfate	PI
Anionic	AES	Alcohols, C12-14, ethoxylated, sulfates, sodium salts	PI
Nonionic	AE	C9-11 Pareth-8, C9-11 Pareth-3, Lialet 111 10EO, Laureth-5, PPG-4-Laureth-5, deceth-8 (C10 Pareth-8), C10 Pareth-3 , C12-15 Pareth-5, C10-16, C10	Q, PI
Nonionic	APG	C6-16	Q
Cationic	DADMAC	dialkyldimethyl ammonium chloride	Q
Cationic	ATMAC	Tallow, alkyltrimethyl ammonium chloride	Q
Amphoteric	Betaine	Cocamidopropyl Betaine	
Amphoteric	Alkyl amine oxide	LDAO (Lauryl Dimethyl amine oxide), Amines, C10-16-alkyldimethyl, N-oxides;	Q, PI
Amphoteric	Alkyl amines	Amines C12-14 alkyl dimethyl	PI
Amphoteric	Amphoteric - other	Substance name confidential information	Q

LAS: linear alkylbenzene sulfonic acid; FA: fatty acids; AS: alkyl sulfates; AES: alkyl ether sulfates; AE: alcohol ethoxylates; APG: alkyl polyglucosides;

Ingredients with other functions	Function	Source
Calcium carbonate	Abrasive	PI
Dimethicone	Antifoaming agent	PI
Dimethylsiloxane	Antifoaming agent	PI
Denatonium benzoate	Bitter taste, bitterant	PI
Sodium bicarbonate	Buffering, cleaning agent	PI
CI 45100, CI 42051, CI 19140, CI 47005	Colour	PI
Sodium -L-lactate	Disinfectant	PI
Lactic acid	Disinfectant	I
Sodium Cumenesulfonate	Hydrotrope	PI
Ethanolamine	Solvent	PI
Triethanolamine	Solvent	PI
Alcohol	Solvent	PI
Butoxypropanol	Solvent	PI
PPG-2 Butyl Ether	Solvent	PI
Sodium C4-12 Olefin/Maleic Acid Copolymer	Viscosity control	PI
Styrene/Acrylates Copolymer	Viscosity control	PI
Acrylic polymer	Viscosity control	PI
Propylene Oxide/Ethylene Oxide Block Copolymer	Viscosity control	PI
Xanthan gum	Viscosity control	Q
Sodium Polyacrylate	Viscosity control	Q

CI: Colour Index; PPG

Complexing agents/Builders	Note	Source
Sodium citrate	Builder	PI
Citric acid	Builder	PI
Sodium carbonate	Builder	PI
TKPP (Tetra Potassium Pyro Phosphate)	Builder	Q
Trisodium dicarboxymethyl alaninate, MGDA (Methyl Glycine Diacetic Acid, Trisodium salt)	Chelating agent	PI
Sodium Iminodisuccinate	Chelating agent	PI

Bleaching agents	Note	Source
Sodium hypochlorite	Special cleaning product	Q

Fragrances	Source
Limonene	PI
Linalool	PI
Citronellol	PI
Geraniol	PI
Butylphenyl Methylpropional	PI
Hexyl Cinnamal	PI
Amyl Cinnamal	PI

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Appendix 3. Total list of substances for assessment

Substance	**Function**	**L: laundry D: Dishwash A: All-purpose**
Phenylpropyl dimethicone	Antifoaming agent	L: Powder
Dimethicone	Antifoaming agent	D: Tabs; A
Simethicone	Antifoaming agent	D: Tabs
Dimethylsiloxane	Antifoaming agent	A
Polyethylene terephthalate	Anti-redeposition Agent	L: Powder
Cellulose gum	Anti-redeposition Agent	L: Powder
aziridine homopolymer ethoxylated	Anti-redeposition Agent	L: Liquid, pods
1,4-benzenedicarboxylic acid, 1,4-di-methyl ester, polymer:…	Anti-redeposition Agent	L: Liquid
Sodium methylglycine diacetate, MGDA	Complexing agents	L: Liquid, Tabs
Trisodium dicarboxymethyl alaninate, MGDA	Complexing agents	L: Powder D: Hand, Gel, Tabs; A
Sodium carboxymethyl inulin	Complexing agents	L: Liquid D: Gel
Trisodium dicarboxymethyl inulin	Complexing agents	L: Liquid
Sodium carboxymethyl carbohydrate	Complexing agents	L: Liquid
Polyethylene imine; aziridine homopol-ymer	Complexing agents	D: Gel, Tabs
Sodium Iminodisuccinate	Chelating agent	A
PVPNO, Polyvinylpyridine N-oxide	Dye transfer inhibitor	L: Liquid
PVP, Polyvinylpyrrolidone	Dye transfer inhibitor	L: Powder, pods
Vinyl imidazole/VP copolymer	Dye transfer inhibitor	L: Pods
Boronic acid, (4-formylphenyl)	Enzyme stabiliser	L: Liquid
Manganese-II-oxalate Dihydrate	Enzyme activator	D: Tabs
Sodium cumenesulfonate	Hydrotrope	L: Liquid; A
Sodium xylenesulfonate	Hydrotrope	D: Hand
Polypropylene terephthalate	Suspending Agent	L: Pods
Polyoxyethylene terephthalate	Suspending Agent	L: Pods
Polyvinyl alcohol	Additive/film packaging	L: Pods D: Tabs
Denatonium benzoate	Bitter taste, bitterant	L: Liquid, pods; A
1-H-Methylbenzotriazole	Corrosion inhibitor	D: Tabs
Di-substituted alaninamide	Stabilising agent	L: Liquid, pods

Substances in household detergents
This report contains a survey of ingredients in deter-gents on the Danish market during the period 2001-2018, as well as a health and environmental assessment of selected ingredients. The report addresses the following three main categories of detergents; laundry detergents, dishwashing detergents and all-purpose detergents, in which the following functional groups in the three main categories are included: surfactants, complexing agents, bleaching agents, enzymes, fragrances, as well as other ingredients in the individual main categories.

The report is supplement to the Environmental Project No. 615 (2001); a comprehensive environmental and health safety assessment on substances in household detergents and cosmetic detergent products.

The environmental and health assessment included selected substances and group of substances prioritized to supplement the report from 2001. The new functional groups were selected: antifoaming agents, represented by a group of siloxanes; the dye transfer inhibitors, represented by the group of polyvinylpyrrolidone polymers; enzyme stabiliser ((4-formylphenyl) boronic acid); and enzyme activator (manganese-II-oxalate dehydrate). Furthermore, assessments were performed for the new complexing agents including: MGDA, sodium carboxymethyl inulin, polyethylene imine, and sodium iminodisuccinate.

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