Danish Ministry of the Environment
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Survey of 2,5-Di-tert-butylhydroquinone in Cosmetics, Paint, Lacquer and Varnish for the Consumer

A LOUS 2012-2015 follow-up project

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Survey of 2,5-Di-tert-butylhydroquinone in Cosmetics, Paint, Lacquer and Varnish for the Consumer

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Foreword

The project ”Survey of 2,5-Di-tert-butylhydroquinone in Cosmetics, Paint, Lacquer and Varnish for the Consumer” was carried out from September till December 2013. The project is part of the Danish EPA's LOUS project 2012-2015.

The List of Undesirable Substances (LOUS) was established by the Danish Environmental Protection Agency (EPA) as a guide for enterprises. It indicates substances of concern, based on their use tonnage and dangerous properties.

During the period 2012-2015, all substances listed on LOUS will be surveyed and the necessity for further risk management measures will be evaluated. In certain cases implementation projects will be launched to achieve the goals laid down in the strategies for these substances.

This report describes the procedure and the results of a survey of the substance 2,5-di-tert-butylhydroquinone in consumer products including Cosmetics, Paint, Lacquer and Varnish in Denmark.

The project was carried out by Danish Technological Institute. Participants from Danish Technological Institute were Eva Jacobsen (project manager), Inge Bondgaard Nielsen, Karen Krzywkowski and Ulla Christensen.
Quality assurance was carried out by Eva Jacobsen.

The progress, development and results of the project were assessed by a advisory group consisting of the following persons:

Lea Stine Tobiassen, the Danish Environmental Protection Agency (the Danish EPA)
Jette Heltved, the Danish Environmental Protection Agency (the Danish EPA)
Eva Jacobsen, Danish Technological Institute (DTI)

Summary and Conclusion

The substance 2,5-Di-tert-butylhydroquinone has been included on the Danish Environmental Protection Agency's List of Undesirable Substances (LOUS). A survey conducted under the project of the Danish EPA LOUS 2012-15 "Survey of 2,5-Bis(1,1-dimethyl ethyl)-1,4-benzenediol (2,5-Di-tert-butylhydroquinone)", Environmental Project No. 1477, 2013 [DEPA 2013a], stated that in cosmetics, 2,5-Di-tert-butylhydroquinone can be used as an antioxidant. In paint, lacquer and varnish the survey reported the substance mainly to be used for antifouling paint and possibly also in UV metallic inks.

Based on this information the Danish EPA wanted to carry out a survey of the use of 2,5-Di-tert-butylhydroquinone specifically in cosmetics and in paint, lacquer and varnish on the Danish consumer market. The Danish EPA asked Danish Technological Institute to be in charge of the survey.

The main approaches for the survey were contacts to relevant sector specific associations and manufacturers of cosmetics, paint, lacquer and varnish. Other approaches were internet searches for relevant information, information retrievals, database searches and searches in material safety data sheets (MSDS).

In most cases, the associations were contacted by phone and the phone conversations were followed up by e-mails with detailed information about the survey in general with questionnaires included. Most of the associations offered to forward the questionnaires to their members.

Additional information was drawn from the database called "Substances in Preparations in Nordic Countries" (SPIN) for 2,5-Di-tert-butylhydroquinone together with information from the Danish Product Register (PR).[1]

According to the SPIN database (with data from 2000 to 2011) the use of 2,5-Di-tert-butylhydroquinone peaked in Denmark in 2006 with 20.6 tonnes. This amount decreased to 0.3 tonnes in 2011. However, the data from SPIN or PR does not provide a complete picture of the presence of 2,5-Di-tert-butylhydroquinone in mixtures on the Danish market i.a. as the requirement for notification only covers products for professional use.

Information from industry and comprehensive search on databases for cosmetic products leads to conclusion that the substance is not commonly used in cosmetics. Only one cosmetic product on the Danish market with a content of 2,5-Di-tert-butylhydroquinone was identified based on ingredient information on the label. In consultation with the Danish EPA it was decided that no cosmetic products would be analysed for 2,5-Di-tert-butylhydroquinone.

For paint, lacquer and varnish the conclusion is that 2,5-Di-tert-hydroquinone is almost exclusively used in antifouling paint. The antifouling paints are mainly intended for professional use although some of the products are available to Danish consumers. The products in which the substance is an ingredient are expected to have a content of less than 1 w/w% based on information from the one manufacturer who states to use the substance.

[1] Confidentiality agreements have been signed and no confidential information is included in this report.

The Danish EPA and Danish Technological Institute agreed on six antifouling paint products for analysis of content of 2,5-Di-tert-butylhydroquinone.

The six products were bought from four different manufacturers. Only one of the six tested antifouling paints contains 2,5-Di-tert-butylhydroquinone. The concentration of 2,5-Di-tert-butylhydroquinone in this product is 48 mg/kg (0.0048 w/w%). As expected this content is below 10 g/kg (1 w/w%) as stated during the general survey by the one manufacturer who informed that the substance is used. The other five antifouling paints did not contain 2,5-Di-tert-butylhydroquinone above the detection limit of 1 mg/kg for the analytical method. This was expected for three of the products as the manufacturers of those products stated that they do not use the substance in their production. Also for a single product, for which no information about the product was retrieved beforehand from the manufacturer, the analytical results showed no content of 2,5-Di-tert-butylhydroquinone above the detection limit of the analytical method.

Overall, it can be concluded on the basis of this survey that 2,5-Di-tert-butylhydroquinone is very seldom used in cosmetic products on the Danish market, as only one moisturising creme was identified on the required ingredient declaration on the label.

With respect of use of 2,5-Di-tert-butylhydroquinone in paint and lacquers for the consumer market, only use in antifouling paint was identified as probable in this survey. Analysis of 6 anitfouling paint products showed content in only one of these at a concentration of 0.0048%.

Sammenfatning og konklusion

Stoffet 2,5-di-tert-butylhydroquinon er optaget på Miljøstyrelsens Liste over uønskede stoffer (LOUS) fra 2009. Det tidligere kortlægningsprojekt "Survey of 2,5-Bis(1,1-dimethyl ethyl)-1,4-benzenediol (2,5-Di-tert-butylhydroquinone)", Environmental Project No. 1477, 2013 [DEPA 2013a] angav, at 2,5-di-tert-butylhydroquinon anvendes i kosmetik som en antioxidant. Det blev i projektet ligeledes angivet, at i maling og lak bliver stoffet hovedsageligt anvendt i antifouling maling og muligvis også i UV-metallisk blæk.

Miljøstyrelsen ønskede at gennemføre en kortlægning af anvendelsen af 2,5-di-tert-butyl-hydroquinon i kosmetiske produkter, maling, lak og fernis på det danske forbrugermarked. Miljøstyrelsen udpegede Teknologisk Institut til at udføre kortlægningen.

Den primære metode til kortlægning af 2,5-di-tert-butylhydroquinon i nærværende projekt var kontakt til relevante brancheorganisationer og til producenterne af kosmetik, maling, lak og fernis. Andre anvendte metoder til kortlægningen var søgninger på internettet for relevant information, søgning i litteraturen og søgning i databaser samt i produktsikkerhedsdatablade (MSDS).

I de fleste tilfælde blev brancheforeningerne kontaktet pr. telefon og telefonsamtalerne blev fulgt op af e-mails med detaljerede informationer omkring kortlægningen med vedhæftede spørgeskemaer. De fleste brancheorganisationer tilbød at videresende forespørgslerne til deres medlemmer.

Der blev desuden lavet udtræk for 2,5-di-tert-butylhydroquinon fra databasen "Substances in Preparations in Nordic Countries" (SPIN) sammen med informationer fra det danske produkt-register (PR)[1].

I henhold til SPIN-databasen (med data fra 2000 til 2011) toppede anvendelsen af 2,5-di-tert-butylhydroquinon i Danmark i 2006 med 20,6 tons. Anvendelsen faldt til 0,3 tons i 2011. Data fra SPIN og PR giver dog ikke et komplet billede af udbredelsen af 2,5-di-tert-butylhydroquinon i produkter på det danske marked, da kun produkter til professionelt brug er underlagt krav om registrering.

På baggrund af oplysninger fra brancheorganisationer og industri samt den omfattende søgning i databaser kan det konkluderes, at stoffet ikke er almindeligt anvendt i kosmetik. Der blev kun identificeret et enkelt kosmetisk produkt på det danske marked med indhold af 2,5-di-tert-butylhydroquinon i henhold til indholdsdeklarationen. Det blev i samarbejde med Miljøstyrelsen besluttet ikke at indkøbe kosmetiske produkter til analyse for 2,5-di-tert-butylhydroquinon.

For maling, lak og fernis er konklusionen, at 2,5-di-tert-butylhydroquinon næsten udelukkende anvendes i antifouling maling. Antifouling maling er hovedsageligt til industrielt brug, men nogle af produkterne er tilgængelige for de danske forbrugere. Indholdet i produkterne med 2,5-di-tert-butylhydroquinon forventes at være under 1 w/w % baseret på information fra den ene producent, der angiver at anvende stoffet.

Miljøstyrelsen og Teknologisk Institut besluttede at indkøbe seks prøver af antifouling maling til analyse for indhold 2,5-di-tert-butylhydroquinon.

De seks prøver blev indkøbt fra 4 forskellige producenter. Kun et af de testede produkter af antifouling maling viste et indhold af 2,5-di-tert-butylhydroquinon. Koncentrationen af 2,5-di-tert-butylhydroquinon i dette produkt er 48 mg/kg (0,0048 w/w%). Desuden fandtes et oksidationsprodukt fra stoffet.
De øvrige fem produkter indeholder ikke stoffet i mængder over analysemetodens detektionsgrænse på 1 mg/kg. Dette var forventet for tre af produkterne, da producenterne af disse produkter oplyste, at 2,5-di-tert-butylhydroquinon ikke anvendes i deres produktion. Der var ikke nogen præcis information om produktet fra den ene af producenterne, men analyserne viser at indholdet af 2,5-di-tert-butylhydroquinon var under metodens detektionsgrænse.

På basis af denne kortlægning kan det overordnet konkluderes, at 2,5-di-tert-butylhydroquinon er meget sjældent anvendt i kosmetiske produkter på det danske marked, da der kun kunne identificeres en enkelt fugtighedscreme deklareret med indhold af 2,5-di-tert-butylhydroquinon. For malinger og lakker på det danske forbrugermarked kan det konkluderes, at anvendelsen af 2,5-di-tert-butylhydroquinon er begrænset til enkelte antifouling malinger. Analyser af 6 antifouling malinger viste kun indhold i et enkelt af produkterne med en koncentration på 0,0048%.

1. Background and Objectives

The substance 2,5-Di-tert-butylhydroquinone (CAS no. 88-58-4) is included on the Danish Environmental Protection Agency's (Danish EPA)'s List of Undesirable Substances (LOUS), due to the prediction that the substance is toxic to aquatic organisms.

A former survey (Ref: Environmental Project No. 1477, 2013) [DEPA 2013a] showed that the substance might be used in cosmetics[2] and paint.

1.1 Objective of the Survey

The purpose of the survey was to identify consumer products with 2,5-Di-tert-butylhydroquinone as an ingredient on the Danish consumer market within the product groups of cosmetics and paint, lacquer and varnish for the consumer. For the potential identified products the level of concentration of the substance will be clarified.

A starting point will be taken in knowledge from the published survey [DEPA 2013a] from the Danish EPA in which it is stated that the substance is possibly used as an antioxidant in cosmetics and it is expected to be used in antifouling paint and in UV metallic ink.

If relevant, selected products within cosmetics and paint, lacquer and varnish will be purchased for analytical determination of the content of 2,5-Di-tert-butylhydroquinone.

1.2 Description of 2,5-Di-tert-butylhydroquinone

The substance 2,5-Di-tert-butylhydroquinone (with the systematic name 2,5-Bis(2-methyl-2-propanyl)-1,4-benzenediol) with CAS no. 88-58-4 and EC no. 201-841-8 has different synonyms. As the substance is mostly known under the name of 2,5-Di-tert-butylhydroquinone this name will be used for the substance in this report. The INCI[3] name is Di-t-butylhydroquinone.

FIGURE NO 1. STRUCTURAL FORMULA OF 2,5-DI-TERT-BUTYLHYDROQUINONE[4]

[2] Cosmetic products are defined in the Regulation of the European Parliament and the European Council (EU) no. 1223/2009 of 30 November 2009 on Cosmetic products.
[3] INCI: The International Nomenclature of Cosmetic Ingredients
[4] http://www.chemicalbook.com/Search_EN.aspx?keyword=88-58-4

2,5-Di-tert-butylhydroquinone is listed on CosIng (the database of the European Commission on Cosmetic Ingredients) as an antioxidant. This listing does not mean that the substance is necessarily used in cosmetic products or approved for such use.

There are no restrictions for 2,5-Di-tert-butylhydroquinone in the Cosmetics Regulation[5] or in the Cosmetics Directive[6].

Cosmetic products must be declared with the INCI name of the substance. INCI names are mandated on the ingredient statement of every consumer product for personal care.

For paint, lacquer and varnish there is no obligation for declaration of possible content of 2,5-Di-tert-butylhydroquinone.

2,5-Di-tert-butylhydroquinone does not have a harmonised classification and is therefore not included in Annex VI to the CLP[7] regulation (Regulation (EC) No 1272/2008). Some manufacturers and importers have notified their classifications to ECHA's[8] self-classification list [ECHA 2013a+b].

2,5-Di-tert-butylhydroquinone is not registered under REACH[9].

The substance is shown to be moderately acute toxic following ingestion and has the potential to cause dermal, eye (severe) and respiratory irritation. There are some indications of other effects on humans inclusive of impact on the immune system, skin sensitisation and of mutagenicity/ genotoxicity, but no robust documentation exists on this [DEPA 2013a].

Regarding environmental fate and eco toxicity, QSAR[10] and read-across indicate that the substance is not readily biodegradable and it is toxic to aquatic organisms. The prediction of being toxic to aquatic organisms is the reason why 2,5-Di-tert-butylhydroquinone was listed on LOUS. This assessment is, however, not reflected in the self-classification undertaken by manufacturers and importers [DEPA 2013a] (only one notifier out of 157 has self-classified the substance with hazard class and category code "Aquatic Chronic 2")[11].

1.3 Usage of 2,5-Di-tert-butylhydroquinone

The database of Substances in Preparations in Nordic countries (SPIN) contains non-confidential information on substances from the Product Registers of Norway, Sweden, Finland and Denmark. From these data, a graphical illustration of the total amounts of 2,5-Di-tert-butylhydroquinone used per year in Denmark is generated, see Figure 1. From 2003-2011, the total amount in ton ranges from 20.6 ton in 2006 to 0.3 ton in 2011. The total number of preparations registered per year ranges from 96 to 206. In 2011, it was registered in 151 preparations in only one category: Paint, lacquer and varnish.

5 Cosmetics Regulation" (EC) No 1223/2009
6 Cosmetics Directive" 76/768/EEC
7 Classification, Labelling and Packaging.
8 ECHA: European Chemical Agency
9 Registration, Evaluation, Authorisation and Restriction of Chemical substances. REACH is an EU regulation on chemicals that entered into force on 1st June 2007 (Regulation (EC) No 1907/2006 of the European Parliament and of the council) http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2006:396:0001:0849:EN:PDF
10 Quantitative structure–activity relationship. Mathematical models used to estimate chemical properties by grouping structurally related chemicals into categories and thus fill gaps in e.g. toxicity data needed for assessing the hazard of chemicals.
11 The European Chemical Agency's information on the Classification & Labelling Inventory

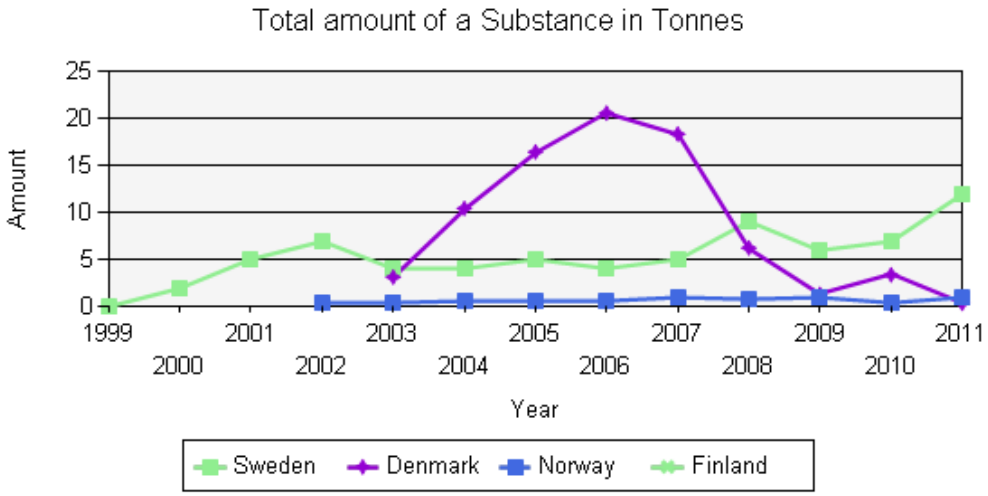

FIGURE 2: TOTAL AMOUNT OF 2,5-DI-TERT-BUTYLHYDROQUINON IN DENMARK AND OTHER NORDIC COUNTRIES FROM 2003 TO 2011.

It should be noted that the Danish Product Registry only applies for the registration of substances and mixtures for occupational use that contain at least one substance classified as dangerous in concentrations of at least 0.1% or 1% (depending on the classification of the substance). As 2,5-Di-tert-butylhydroquinone does not have a harmonised classification, and if it is not self-classified then it would only be registered if the substance is a constituent of products, which are classified as dangerous due to the presence of other constituents. Consequently, the data from SPIN do not provide a complete picture of the presence of 2,5-Di-tert-butylhydroquinone in mixtures on the Danish market.

2. Data Collection

2.1 Methodology

The survey was carried out from mid-September till the beginning of December 2013.

Several different strategies were used to obtain the most accurate information about the products and the level of concentrations of the substances, e.g.:

- Internet search for background information, literature, MSDS and patents.
- Internet search on databases.
- Contact to the sector specific associations for cosmetics both in Denmark and abroad.
- Contact to the sector specific associations for paint, lacquer and varnish both in Denmark and abroad.
- Contact to manufacturers of cosmetics.
- Contact to manufacturers of paint, lacquer and varnish.
- Contact to building markets / do-it-yourself (DIY) centres.
- Visit at a building market / DIY centre.
- Visit at a maritime shop.
- Contact to relevant information centres/interest groups.
- Information from SPIN and the "Danish Product Register" (PR)[1].

The contacts were identified via internet pages and through our general knowledge about the relevant players on the market. See list of contacts attached in appendix 1.

The contacts were contacted by telephone and/or e-mail. The telephone calls were in most cases followed up by an informative e-mail with or without a questionnaire attached prepared in Danish and/or English. The questionnaires gave information about the survey and contained a table to be filled in with potential products with a content of 2,5-Di-tert-butylhydroquinone.

The main sources of information for the survey were the contact to relevant sector specific associations and manufactures of cosmetics, paint, lacquer and varnish. For cosmetics, database searches were also relevant.
The procedure for direct contact is described below.

2.1.1 Enquiries to Sector Specific Associations

Sector-specific associations were contacted by telephone and/or by e-mail.

Enquiries regarding cosmetics were directed to four sector specific associations. As The Danish Association of Cosmetic and Detergent Industries (SPT) already had been contacted in the former survey, COLIPA[12], Personal Care Products Council (USA) and CCTFA (Canadian Cosmetic, Toiletry and Fragrance Association) were contacted as well. The purpose of the contact abroad was to discover the general prevalence of the substance in cosmetics for potential import of products to the Danish market.

[12] Cosmetic Europe. The Personal Care Association

In relation to paint, lacquer and varnish, the Confederation of Danish Industry (DI) was contacted, specifically The Danish Coatings and Adhesives Association (Foreningen for Danmarks Farve- og Limindustri, DFL). The members of DFL account for around 90% of the Danish market within paints, adhesives, varnishes, sealants and wood impregnation.

Enquiries were made to European associations such as the European Council of producers and importers of paint, printing inks and artists' colours (CEPE)[13], the Association of the European Adhesive and Sealant Industry (FEICA) and the European Federation for Construction Chemicals (EFCC). In addition, Danboat, the Danish Water Sports Trade Association (Søsportens Branche-forening) was contacted due to the potential use of antifouling paint among private consumers (owners of boats/yachts).

A number of these associations kindly forwarded our enquiries and/or our questionnaires to their members in order to help identify products containing 2,5-Di-tert-butylhydroquinone that might be used by private consumers.

See appendix 1: List of contacts.

2.1.2 Enquiries to Manufacturers/Importers/Retailers

In addition to the enquiries sent to the above-mentioned associations, there was also a direct approach to a number of manufacturers, importers and retailers of paint, lacquer and varnish. Some of them might also have been contacted via a sector specific association. The retailers contacted were mainly Building markets/DIY centres. Regarding cosmetics one manufacturer was contacted.

See appendix 1: List of contacts.

2.1.3 Enquiries to Knowledge Centres/Interest Groups

Knowledge centres/interest groups in Denmark with focus on health and the environment were contacted in order to obtain any information that they might have regarding 2,5-Di-tert-butylhydroquinone and its possible content in consumer products.

See appendix 1: List of contacts.

2.1.4 Other Approaches of the Survey

Other approaches of the survey were internet searches for relevant information, databases, literature, patents and more.

A thorough search for cosmetic products with a possible content of 2,5-Di-tert-butylhydroquinone was executed. The homepage of the Scientific Committee on Consumer Safety (SCCS)[14] was examined for an opinion on the substance.

Different databases were applied as for example: SPIN2000[15], CosIng[16], Innovadex[17] and Kemilex[18] (search engine of Asthma-Allergy Denmark), EWG's cosmetics database, Skin Deep Cosmetics

[13] Members from the European Union, Norway and Switzerland
[14] Scientific Committee on Consumer Safety
[15] http://www.SPIN2000.com
[16] http://ec.europa.eu/consumers/cosmetics/cosing
[17] http://www.innovadex.com. Innovadex
[18] http://www.astma-allergi.dk/kemilex

Database[19] (American database with about 80.000 products), GoodGuide (Best Personal Care Product Ratings)[20], SpecialChem4cosmetics[21] and a German database, codecheck[22] (a German database for cosmetics and other consumer products).

A search for paint, lacquer and varnish was carried out on the homepages of the manufacturers, through relevant web shops and via Google, including a search for a possible content of 2,5-Di-tert-butylhydroquinone in consumer products.

Chemspider[23] was mainly a search for patents including 2,5-Di-tert-butylhydroquinone.

Data from PR were applied in cooperation with the Danish EPA and were handled strictly in compliance with the precept for confidential data from the PR[1].

[19] http://www.ewg.org/skindeep
[20] GoodGuide has assembled a team of scientific and technology experts to take on the challenge of organizing the world's product information.
[21] http://www.specialchem4cosmetics.com/services/formulation.aspx?id=1000
[22] http://www.codecheck.info.
[23] http://www.chemspider.com

3. Results of the Data Collection

3.1 Result of Enquiries to Interest Groups/Knowledge Centres

The contacted interest groups/knowledge centres working within health and the environment, Asthma-Allergy Denmark (Astma-Allergi Danmark) and the Information Centre for Environment and Health (Informationscenter for Miljø og Sundhed) could not provide information regarding consumer products containing 2,5-Di-tert-butylhydroquinone or other relevant information pertaining to the substance.

3.2 Results for Cosmetics

Among the four contacted associations for cosmetics on the list in appendix 1, we only got feedback from the Danish association, The Danish Association of Cosmetic and Detergent Industries (SPT) [SPT 2013a].

The Danish SPT responded that none of their 79 members within the cosmetic line of business use 2,5-Di-tert-butylhydroquinone as an ingredient [SPT 2013b]. That was confirmed by a product developer at one of the SPT members who has years of experience within formulations for cosmetic products.

CosIng, which is the database of the European Commission with information on cosmetic substances and ingredients, stated that the substance is not regulated in the Cosmetics Regulation or the Cosmetics Directive. CosIng stated that 2,5-Di-tert-butylhydroquinone functions as an antioxidant. There was no other reporting on the substance.

The homepage of the Scientific Committee on Consumer Safety (SCCS) was investigated. The Committee provides opinions on health and safety risks (chemical, biological, mechanical and other physical risks) of non-food consumer products (e.g., cosmetic products and their ingredients, toys, textiles, clothing, personal care and household products) and services (e.g., tattooing, artificial sun tanning).
There were no SCCS opinions on 2,5-Di-tert-butylhydroquinone.

The search engine “Innovadex”[24] for product innovators was utilised, and there was no results for 2,5-Di-tert-butylhydroquinone as an ingredient or as part of a formula for products in the category “Personal Care & Cosmetics”.

The thorough searching in other databases: Kemilex, EWG’s cosmetics database, Skin Deep Cosmetics Database (American database with about 80.000 products), GoodGuide for personal care, SpecialChem4cosmetics and the German database codecheck did not identify any cosmetic products with 2,5-Di-tert-butylhydroqinone as an ingredient.
During the general search on the internet only one single product with a content of 2,5-Di-tert-butylhydroqinone was identified. The product is a moisturising cream to be used for sensitive skin.

[24] Innovadex members represent over 60,000 professional and consumer product companies operating in North America, Latin America, Europe (EMEA) and Asia Pacific. Innovadex provides results for technical product information in those markets.

In the advertisement, the cream has a healing character for damaged skin. The same product can be bought in different shops on the internet.

Conclusion for Cosmetics

All feedback and the above-mentioned results are strong indicators that the substance is rarely used in cosmetics in Denmark. However, one skin moisturising creme sold on the internet was found to contain 2,5-Di-tert-butylhydroquinone, based on information on the label

3.3 Results for Paint, Lacquer and Varnish

14 manufacturers/importers/retailers of paint, lacquer and varnish were contacted. All 14 contacts gave feedback. Only one manufacturer out of the 14 contacted manufacturers/importers/retailers replied that 2,5-Di-tert-butylhydroquinone is an ingredient in their DIY products available for Danish consumers. The products with the substance as an ingredient are all antifouling paints for boats including yachts.

CEPE [CEPE 2013a] contributed with response from 16 members. Among the responses from the 16 CEPE members only one member (a manufacturer) replied that they use 2,5-Di-tert-butylhydroquinone in a few DIY products. The manufacturer stated that the actual products with 2,5-Di-tert-butylhydroquinone as an ingredient are yacht antifouling paints and varnishes and a single filler from their product range. The manufacturer also informed that the content in all products with 2,5-Di-tert-butylhydroquionone is less than 1 w/w%.
CEPE brings together approximately 85% of the European industry in its membership and the responses obtained were judged by one of the directors of the organization to be representative of the CEPE market [CEPE 2013b]. The members of CEPE are 25 national associations, 6 suppliers plus a number of companies that also are members of one of the national associations affiliated with CEPE.

The Danish Water Sports Trade Association, Danboat [Danboat 2013a] with 59 members did not provide specific information on the use of 2,5-Di-tert-butylhydroqinone in maritime products for the private consumer, but kindly informed about the major manufacturers and Danish importers of maritime products [Danboat 2013b].

The Association of the European Adhesive and Sealant Industry (FEICA) and the European Federation for Construction Chemicals (EFCC) did not respond to our enquiry.

The member association The Danish Coatings and Adhesives Association (DFL) informed that 2,5-Di-tert-butylhydroquinone is not used in coatings or inks for metal packaging [DFL 2013a]. DFL stated that 2,5-Di-tert-butylhydroqinone can be utilised as antioxidant in antifouling paints. The members of DFL account for around 90% of the Danish market within paints, adhesives, varnishes, sealants and wood impregnation [DFL 2013b].

The general search on the internet did not discover other paints, lacquers or vanish beyond the antifouling paints with 2,5-Di-tert-butylhydroqinone as an ingredient.

According to a visit in a maritime shop, 96% of the market for antifouling paint is covered by two main manufacturers in the ratio of 60% and 40%. There are only very few other operators on the Danish market for antifouling paints, and their products are not as easily accessible as for the main operators. This information was supported by the antifouling products available on the more than 10 visited internet shops.

Conclusion for Paint, Lacquer and Varnish

For paint, lacquer and varnish the conclusion is that 2,5-Di-tert-hydroquinone is almost exclusively used in antifouling paint. The antifouling paints are mainly intended for professional use although some of the products are available to Danish consumers. The products in which the substance is an ingredient are expected to have a content of less than 1 w/w% based on information from one manufacturer who uses the substance.

4. Products for Analyses

4.1 Cosmetics

In consultation with the Danish EPA it was decided that no cosmetic products would be included for analyses of 2,5-Di-tert-butylhydroquinone due to the very limited number of cosmetic products identified to contain the substance is an ingredient. That decision was based on the results of the survey with statements from SPT that the substance is not used by their members as an ingredient, and on the thorough search in databases covering a very large number of cosmetics with no declaration of 2,5-Di-tert-butylhydroquinone. Only one single product with a content of 2,5-Di-tert-butylhydroqinone was identified on the general comprehensive search on the internet.

4.2 Antifouling Paint

In consultation with the Danish EPA it was decided to analyse six antifouling paints. The selection of the products was based on the following criteria:

- Products from the manufacturer using the substance
- The mostly sold products
- One product from an less known brand on the Danish market

To cover the products mainly used by the Danish consumers, the most sold products (according to a major maritime shop) were chosen for analysis plus a single product from a small operator to cover a less used product on the market. The samples for analysis originate from four different manufacturers.
Information on the 6 purchased products appears from Table 4.1.

TABLE 4.1
OUTLINE OF CONSUMER PRODUCTS PURCHASED FOR DETERMINATION OF CONTENT OF 2,5-DI-TERT-BUTYLHYDROQUINON BY CHEMICAL ANALYSIS

Product no	Manufacturer (Nationality)	Product description	Application area/Use
1	A (Danish)	Antifouling paint, self-polishing	For cruising and sailing boats of glass fibre, wood, plywood, steel and ferro-cement.
2	A (Danish)	Antifouling paint, self-polishing	For cruising and sailing boats of glass fibre, wood, plywood, steel and ferro-cement.
3	B (Danish)	Antifouling paint, hard	For aluminium and high speed boats
4	B (Danish)	Antifouling paint, self-polishing	For cruising and sailing boats of glass fibre, wood, steel and aluminium

Product no	Manufacturer (Nationality)	Product description	Application area/Use
5	C (Swedish)	Antifouling paint, water-based	For sailing and motor boats
6	D (Danish)	Antifouling paint, hard	For high speed boats

5. Chemical Analyses

Six antifouling paints were chosen for analysis.

5.1 Description of Analytical Method

The content of 2,5-Di-tert-butylhydroquinone in the antifouling paints was determined as analyses in duplicate for each sample by gas chromatography with a mass selective detector (GC-MS).
To the sub-samples amounts internal standards of bromobenzene and o-terphenyle were added, then the sub-samples were extracted with solvent and the analysis was performed by GC-MS.

TABLE 5.1 GC-MS CONDITIONS

Equipment	Agilent GC (7890A) with MSD (5975C)
Column	Zebron ZB-1 MS 20 m x 0.18 mm x 0.18 µm
Injector	Split 50:1, 250 °C
Oven settings	35-210 °C, 20 °C per min.
Mass spectrometer	Scan mode

5.2 Validation of the Quantitative Method

A validation of the applied method for quantification was carried out.

A reference standard was analysed for 2,5-Di-tert-butylhydroquinone in order to carry out identification by retention time and mass spectra in addition to comparison of the mass spectrum with the MS library of NIST[25]. The reference standard was prepared on the basis of a chemical purchased from Sigma-Aldrich.

Bromobenzene and o-terphenyl were added as internal standards to compensate for possible variations in the GC-MS analysis.

The accuracy of the analysis was determined with six repeated measurements of a control sample.

Linearity of the measurement range was investigated by analysing the reference standard on two different days at 5 different concentration levels.
The linearity of the reference standard on both days was acceptable as $R^2>0.99$. R is the correlation factor. The closer R^2 is to 1 the better the quality of the predictions made through the calibration.

The uncertainty of the method was calculated to be 15% (RSD, relative standard deviation) based on the determination of the accuracy and the standard deviation of the recovery investigation.

A recovery investigation was carried out by spiking a sample with 2,5-Di-tert-butylhydroquinone. The average recovery was calculated to 111% which is acceptable as the uncertainty of the method was determined to be 15% (RSD).

[25] National Institute of Standards and Technology

Blank specimens were included in all analyses and no interference with 2,5-Di-tert-butyl-hydroquinone was detected.

The detection limit was calculated to 1 mg/kg.

5.3 Results of Chemical Analyses

All samples were analysed in duplicate. The results of duplicate analyses, the average of the determinations and the standard deviations are reported.

The analytical results of the six samples are stated in the table below.

TABLE 5.2 RESULTS OF CHEMICAL ANALYSES

Sample	Total content 2,5-Di-tert-butylhydroquinone		
	mg/kg	mg/kg mean	Standard deviation
1	<1	-	-
	<1		
2	49.4*	47.7*	2.4*
	46.0*		
3	<1	-	-
	<1		
4	<1	-	-
	<1		
5	<1	-	-
	<1		
6	<1	-	-
	<1		

< : Means less than the limit of detection

- : Not relevant

* The analysis revealed a content of an oxidation product of 2,5-Di-tert-butylhydroquinone in the product.

5.4 Conclusion of the Chemical Analyses

Only one of the 6 tested antifouling paints had a content of 2,5-Di-tert-butylhydroquinone. The concentration of 2,5-Di-tert-butylhydroquinone in this product is 48 mg/kg (0.0048 w/w%). In addition analysis revealed that a larger proportion of the 2,5-Di-tert-butylhydroquinone component had oxidised. The 5 antifouling paints from 3 other manufacturers showed contents less than the detection limit of 1 mg/kg.

6. Conclusion

The results of the survey for cosmetic products including feedback from The Danish Association of Cosmetic and Detergent Industries (SPT) and the search in databases as for example: SPIN2000, CosIng, Innovadex and Kemilex (search engine of Asthma-Allergy Denmark), EWG's cosmetics database, Skin Deep Cosmetics Database (American database with about 80.000 products), GoodGuide (Best Personal Care Products Ratings) and codecheck (a German database for cosmetics and other consumer products) covering a huge amount of cosmetic products gave a very good indication that the substance 2,5-Di-tert-butylhydroquinone is very rarely used in cosmetics.

In our thorough search on the internet, we only found one cosmetic product on the Danish consumer market with a content of 2,5-Di-tert-hydroquinone. The product is a moisturising cream for sensitive skin. The same product can be bought in different shops on the internet.

The conclusion is therefore that the use of 2,5-Di-tert-butylhydroquinone is close to none in cosmetics on the Danish consumer market.

In consultation with the Danish EPA it was decided not to analyse cosmetic products for 2,5-Di-tert-butylhydroquinone because of the very limited number of identified cosmetic products with the substance as an ingredient.

For paint, lacquer and varnish the survey indicated that 2,5-Di-tert-hydroquinone is almost exclusively used in antifouling paint. The antifouling paints are mainly intended for professional use although some of these antifouling paints can be accessed by the general public. The products in which the substance is an ingredient are expected to have a content of less than 1 w/w% based on information from the only manufacturer who stated that the substance is used.

According to the SPIN database (with data from 2000 to 2011) the use of 2,5-Di-tert-butylhydroquinone in paint, lacquer and varnish peaked in Denmark in 2006 with 20.6 tonnes. That amount decreased to 0.3 tonnes in 2011.

The Danish EPA and Danish Technological Institute agreed on six antifouling paints for analysis of content of 2,5-Di-tert-butylhydroquinone from four different manufacturers. The choice of products was based on the following criteria:

- Products from the manufacturer using the substance
- The mostly sold products
- One product from an less known brand on the Danish market

Only one of the 6 tested antifouling paints from the 4 different manufacturers contains 2,5-Di-tert-butylhydroquinone. The concentration of 2,5-Di-tert-butylhydroquinone in this product is 48 mg/kg (0.0048 w/w%). In addition, analysis revealed that a larger proportion of the 2,5-Di-tert-butylhydroquinone component had oxidised.
The other five antifouling paints did not contain 2,5-Di-tert-butylhydroquinone above the detection limit of 1 mg/kg for the analytical method. This was expected for three of the products as the manufacturers of those products stated that they do not use the substance in their production.

There was no exact information about the product from one of the manufacturers, but the analytical results shows no content of 2,5-Di-tert-butylhydroquinone in this product.

Overall, it can be concluded on the basis of this survey that 2,5-Di-tert-butylhydroquinone is very seldom used in cosmetic products on the Danish market, as only one moisturising creme was identified on the required ingredient declaration on the label.

With respect of use of 2,5-Di-tert-butylhydroquinone in paint and lacquers for the consumer market, only use in antifouling paint was identified as probable in this survey. Analysis of 6 anitfouling paint products showed content in only one of these at a concentration of 0.0048%.

Abbreviations and Acronyms

CAS	Chemical Abstracts Service
CEPE	The European Council of producers and importers of paints, printing inks and artists' colours
C&L	Classification & Labelling
CCTFA	Canadian Cosmetic, Toiletry and Fragrance Association
CLP	Classification, Labelling and Packaging
COLIPA	Cosmetics Europe
DFL	Foreningen for Danmarks Farve- og Limindustri (The Danish Coatings and Adhesives Association)
DI	Dansk Industri (Danish Industry)
DIY	Do-it-yourself
ECHA	European Chemicals Agency
EFCC	European Federation for Construction Chemicals
EPA	Environmental Protection Agency
FEICA	Association of the European Adhesive and Sealant Industry
INCI	The International Nomenclature of Cosmetic Ingredients
LOUS	List of Undesirable Substances
MSDS	Material Safety Data Sheet
PR	Product Register
QSAR	Quantitative Structure–Activity Relationship
REACH	Registration, Evaluation, Authorisation and Restriction of Chemical Substances
SPIN	Substances in Preparations in Nordic Countries
SPT	The Danish Association of Cosmetic and Detergent Industries

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EWG's cosmetics skin deep: http://www.ewg.org/skindeep

GoodGuide (Best Personal Care Products Ratings): http://www.goodguide.com

INCI: The International Nomenclature of Cosmetic Ingredients.

Innovadex: http://www.innovadex.com/PersonalCare

Kemilex: www.astma-allergi.dk/kemilex

REACH: Registration, Evaluation, Authorisation and Restriction of Chemical substances:
http://ec.europa.eu/enterprise/sectors/chemicals/reach/index_en.htm

SCCS : Scientific Committee on Consumer Safety:
http://ec.europa.eu/health/scientific_committees/consumer_safety/index_en.htm

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Appendix 1: List of Contacts

Sector Specific Associations:

- SPT (The Danish Association of Cosmetic and Detergent Industries)
- COLIPA (Cosmetics Europe)
- Personal Care Products Council, USA
- CCTFA (Canadian Cosmetic, Toiletry and Fragrance Association)

- European Council of producers and importers of paints, printing inks and artists' colours (CEPE)
- Association of the European Adhesive and Sealant Industry (FEICA)
- European Federation for Construction Chemicals (EFCC)
- Danish Coatings and Adhesives Association (Foreningen for Danmarks Farve- og Limindustri, DFL)
- Danboat, the Danish Water Sports Trade Association (Søsportens Brancheforening).

Manufacturers/Importers/Retailers:

- Members of the above listed sector specific associations.
- Urtekram

- Henkel
- Hempel
- Akzo Nobel DECO
- Akzo Nobel Performance Coatings
- Jotun
- jem & fix
- Silvan
- Bygma
- Bauhaus
- Flügger
- Biltema
- HF Marine
- Meripol Glasfiberservice
- Watski

Knowledge Centres/Interest Groups

- Asthma-Allergy Denmark (Astma-Allergi Danmark)
- The Information Centre for Environment and Health (Informationscenter for Miljø og Sundhed)

Survey of 2,5-Di-tert-butylhydroquinone in Cosmetics, Paint, Lacquer and Varnish for the Consumer

This project is a survey of the occurrence of 2,5-Di-tert-butylhydroquinone (DTBHQ) specifically in cosmetics and in paint, lacquer and varnish on the Danish consumer market. The project is part of the Danish EPA's LOUS project 2012-2015. The aim of the project is to clarify the possible use of the substance in cosmetics and in paint, lacquer and varnish intended for the consumers identified in the initial survey under the Danish EPA's LOUS-review (Environmental Project no. 1477).

Based on literature search, contact to producers, importers and branches, the use of 2,5-Di-tert-butylhydroquinone in these product categories evaluated to be scarce, with only one cosmetic product identified to contain the substance, and identification of possible use of 2,5-Di-tert-butylhydroquinone in antifouling paint. Analysis of 5 antifouling paints revealed a very low concentration in one of the products.

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