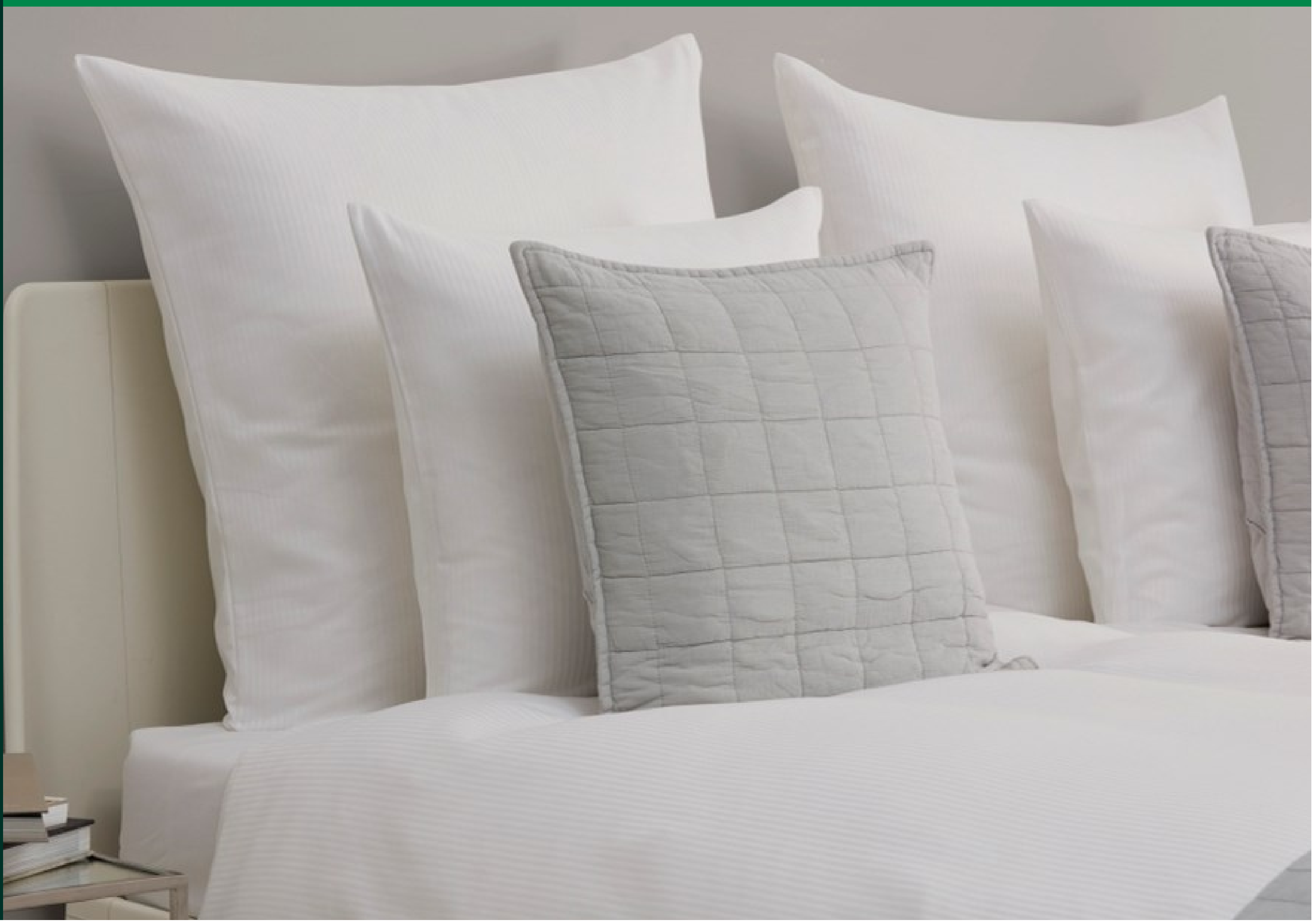
Ministry of Environment and Food of Denmark
Environmental Protection Agency

Substitution of Optical Brightener Agents in Industrial Textiles

MUDP report

October 2018



Publisher: The Danish Environmental Protection Agency

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ISBN: 978-87-93710-91-7

Contents

Foreword

This report describes the purpose of, work in and results of the project *Substitution of Optical Brightener Agents in Industrial Textiles*.

The project *Substitution of Optical Brightener Agents (OBAs) in Industrial Textiles* is an industrial project in the partnership *Kemi i Kredsløb – substitution of harmful chemicals*. The project was granted funding by approval of the Advisory Board for *Kemi i Kredsløb* as well as the Danish Environmental Protection Agency.

This report describes the project aim, methodology used and results achieved. The main purpose is to challenge the use of OBAs by asking the question: *can we reduce the environmental impact of whitened textiles without compromising the whiteness – and, if so, how?*

The project was carried out between October 2017 and June 2018 in collaboration between Beirholms Væverier and two partners from *Kemi i Kredsløb:* Danish Technological Institute and DHI. The project was headed by MSc, PMP Gitte Tang Kristensen, Danish Technological Institute, and significant work was carried out by Yahvi Frimand Paludan-Müller and Tina Hartman Egedal (Beirholms Væverier), Morten Gardum Madsen and Søren Sejer Donau (Danish Technological Institute) and Dorte Rasmussen (DHI). Further, an external partner – a strategic supplier to Beirholms Væverier – contributed with significant work regarding process knowledge and textile processing during the development work.

KEMI i KREDSLØB

1. Introduction

Optical brightening agents are used to obtain white textiles. Due to their environmental properties, the Nordic Ecolabel excludes them from use in detergents and other laundry chemicals in leasing laundries certified with the Nordic Ecolabel to avoid leaching of OBAs to the environments with the washing water. Due to the presence of OBAs in the white textile products treated in the leasing laundries, OBAs are nonetheless present in the washing water. To avoid this, this project aimed to find a way to reduce this leaching of OBA from white textiles by substituting the OBAs used today.

1.1 Background

Optical brightening agents (OBAs), also known as fluorescent whitening agents (FWAs), is a generic term covering a range of compounds, which provide a bluish colour to textiles by fluorescence when exposed to UV light. The bluish colour counteracts the yellow colour that textiles may develop over time (the natural shade for cotton fibres) and, thereby, make the textile appear whiter. Today, OBAs are used in small amounts on the white textiles to obtain the whiteness perceived as the 'right' whiteness for clean and pleasant textiles, e.g. for hospital and hotel linen, towels and cloths.

The OBAs are added to the textiles during production and slowly leached during use by wear and washing. Commonly used OBAs are FWA-1 and FWA-5, which are not readily degradable. A readily primary photodegradation will take place, however FWA-1 will leave some quite persistent but not toxic degradation products. The compounds are not toxic to humans; however, their degradation products are pointed out to be of potential concern in the European Ecolabel Criteria background report.[1].

Many of the most common OBA compounds contain a stilbene moiety as the "core" component (Figure 1-1) and are derivatised by addition of different substituents to attain the desired properties for the respective production process, whiteness enhancement and textile type. In case of the latter, different binding affinities can be achieved with the same "core" component (e.g. stilbene) of the OBA by applying different substituents that enhance the binding properties to specific textile materials. Examples include anionic substituents like sulfonates, which are often used for cotton, whereas nitriles are more common for polyester-based textiles.

[1] http://ec.europa.eu/environment/ecolabel/documents/Laundry%20Detergents%20technical%20report.pdf

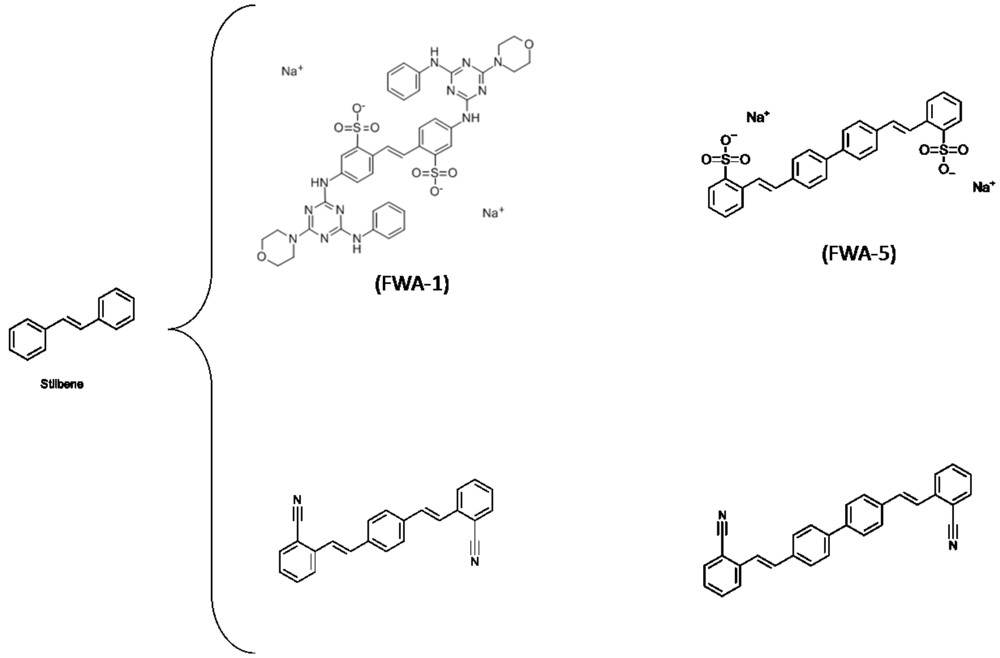

Figure 1-1: Stilbene "core" structure and examples of stilbene-based OBAs. The top row (FWA-1 and FWA-5) are typical sulfonic derivatives used for cotton, while the bottom row is nitrile derivatives typically used for polyester.

Reducing the use and/or leaching of OBAs in e.g. industrial textiles will reduce environmental impact and health discomfort directly. An added benefit is related to the increased lifetime of coloured textiles washed in industrial laundries: to reduce the use of water in industrial laundries, the washing water is reused – and if leached OBAs from whitened textiles are present, coloured textiles will experience colour loss, thereby reducing their product lifetime. Hence, reducing OBA leaching will reduce environmental impact of OBAs from the washing water, increases the lifetime of coloured products and increase the lifetime of the white textiles. This overall contributes to reduced use and waste of materials and benefits the economy of the industry.

1.2 Objective

The project objective was to reduce the environmental impact of OBAs used as whiteners in industrial textiles. Success criteria included a whitening technology with a significantly better environmental profile than currently used OBAs, while the product is market fit, i.e. product performance, such as whiteness, is preserved and the price is cost competitive.

1.3 Structure of the report

To achieve the objective, commercially available technologies and possible new innovative solutions that may substitute currently used OBAs to obtain desired whiteness were approached and evaluated based on the maturity of the technologies and the possible effects (environmental, health and technical) to be achieved as well as with consideration to the resources available in the project. This screening of possibilities and definition of scope is described in Chapter 2 and states the reasoning behind the choice of development strategy chosen in the project.

In Chapter 3, technical baseline information is outlined, i.e. data on the current textiles and OBAs are analysed and described to be able to evaluate how alternatives perform. Methods for the used analyses are described in this chapter.

In Chapter 4, health and environmental profiles of the OBAs used today and their possible alternatives chosen are evaluated followed by a description of the overall development, test and assessment of a potential alternative to current OBAs. This includes outlines of methods for and results of experimental work with prototype production of textiles with alternative OBAs, evaluations of their technical performance as well as leaching of OBAs during washing.

A summary and concluding remarks as well as perspectives of the challenges related to OBAs and whitened textiles are given in Chapter 5.

Due to confidential manufacturing processes and recipes, some compounds and processes described in the text are referred to by code names.

2. Definition of project scope

In this chapter, an outline of the preliminary considerations of the work and aim is described. First task included of a substitution process includes defining the substitution criteria, which are related to process, product, health and environment as well as cost. Based on the criteria, three strategies were outlined and evaluated in relation to potential impact, risk and timeframe. Substitution of current OBAs with better-performing alternative OBAs was chosen as the main strategy and supplemented by development of an analysis to efficiently screen and compare potential alternative candidates.

2.1 Criteria for a suitable substitute

In the process of finding a new alternative to current OBAs, a list containing the ideal product criteria was created for which the perfect solution should comply.

- Same whiteness as the current product
  - Bluish tint
  - Colour values of 200 – 220 GG[2]
- Must not be on the Candidate List of substances of very high concern for authorisation under REACH[3]
- Must meet the criteria set by the Nordic and EU Ecolabel
- Good or better environmental profile (biodegradation, binding affinity etc.)
- Cost price of the treated textile should be on the current level or not significantly higher
- Extensive range of stability with respect to washing processes
  - Has strong binding affinity to the textiles
  - Good temperature resistance
  - Good chemical resistance
- No cross-contamination of other textiles during washing procedures.

2.2 Criteria for OBAs in textiles set by the Nordic Ecolabel

Currently, Beirholms Væverier is certified with the EU Ecolabel, meaning the products are beyond compliance with regard to legal requirements to e.g. chemicals in the products. In some areas, the Nordic Ecolabel even have more strict criteria than the EU Ecolabel; thus, for this project, the criteria set by the Nordic Ecolabel is used as point of reference to aim high.

If textile products fulfil the criteria outlined for colouring agents in general by the Nordic and EU Ecolabel, there is no restrictions to the use of OBAs in textile production. In contrast, textile services certified with the Nordic Ecolabel cannot use laundry chemicals containing OBA, and similar regulation applies to produce sanitary products.

By studying the definition of OBAs, it was found, that the definition is not fully aligned between different criteria; however, a popular definition of OBA in criteria for labelling strategies was

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[2] GG: Measure of the colour – here whiteness; see description in Section 4.3.4.1.

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

found to be: *all compounds that contribute to an optical illusion of whiteness*.[4] This definition excludes any type of OBA, regardless of its environmental and health profile. If the regulation of OBA for Nordic or EU Eco-labelled companies or products becomes stricter, in line with the presented definition, an extra level of complexity is added to the project. Consequently, possible directions of the project were assessed, and three distinct project strategies are described in the next section.

2.3 Project strategies

While the current criteria for the Nordic and EU Ecolabel do not restrict the use of OBA in textile production, the broad definition and possible future exclusion of all fluorescence-based whitening agents allows three distinct project strategies:

S1 Replacing the current OBA with new and better OBA products

S2 Developing an analysis method capable of detecting OBA in washing water

S3 Finding non-fluorescent alternatives to OBA

The strategies are outlined below.

2.3.1 Description of possible project strategies

S1. Replace current OBA with new improved OBA

The first strategy, S1, involves substitution of the current OBA by new types of OBA products, which have improved environmental, health and 'product enhancing' properties – or that as a minimum ensure that the final product has these features compared to the current textile product. The new type of OBA should comply with the current requirements from the Nordic and EU Ecolabel.

Strategy S1 provides Beirholms Væverier with an improved textile product with respect to its general properties and to reduced OBA leaching and cross-contamination of laundry. At the same time, strategy S1 ensures that the product meet the criteria set by the Nordic and EU Ecolabel. According to manufacturers of OBAs, new and better OBA products have been developed, and these are stated to have enhanced properties in relation to fabric "adhesion", health and environment. Replacing the current OBA by another property-enhanced OBA will provide Beirholms Væverier with an improved product, even if the Nordic and EU Ecolabel restrictions of the use of OBAs extend to textile production. Also, the higher binding affinity of the new OBA results in less cross-contamination of other non-OBA-treated textiles (thereby extending the lifetime of the coloured textiles handled in laundries) and an indirect improvement in relation to the environmental profile, as the enhanced binding properties reduce OBA leaching to the environment. Additionally, since the threshold values for hazard labelling of compounds is dynamic, the better an environmental or health profile a substance has, the less is the risk of being hazard labelled and excluded from use in production of products with the Nordic or EU Ecolabel.

S2. Development of analysis method

The second strategy, S2, concerns the development of an analysis method for identification and quantification of OBA compounds in e.g. laundry washing water. The method will be of value to S1 to evaluate the leaching of OBAs from textile during laundry, i.e. to assess improvement by substitution of current OBAs to alternatives.

To focus the effort of the project, verification of the most leaching OBA is developed. Currently, Beirholms Væverier uses two different types of OBA; one for the cotton fibres and one for

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[4] Cf. email correspondence Ecolabelling Denmark 08-11-2017

polyester. Thus, an analysis method capable of distinguishing between the two types of OBA provides valuable information by enabling focus of the efforts towards the most leaching OBA. While cross-contamination of other textiles can be observed visually and quantified using standard colour measurements, an analysis method is valuable to evaluate leaching of alternative OBAs from textiles by comparing and screening the level (quantitative or semi-quantitative) of leaching. The S2 strategy is a prerequisite for continuous development in S1, and price vs. applicability/performance of the method for the specific use is optimised.

S3. New non-fluorescent OBA alternative

Screening for any technique that has the potential to be a future alternative to OBA; that is, alternatives that do not relay on "*the illusion of white by means of fluorescence*".

This strategy provides alternative methods capable of replacing OBA with "*non-fluorescent*" alternatives, which, therefore, provide Beirholms Væverier with a competitive edge in relation to regulations of OBA. However, the risk that the timeframe of the project restricts results by either identifying no good alternatives **or** identifying numerous possible alternatives. In case of the latter, the process of reducing the number of candidates will only be initiated, leaving Beirholms Væverier with a lot of untested/unqualified alternatives at the end of the project due to the confined project resources.

2.3.2 Evaluation and choice

The project partners from Danish Technological Institute (DTI) and Beirholms Væverier agreed that the project direction S1 provides the most value for Beirholms Væverier, when taking the timeframe of the project into consideration. As S2 is a prerequisite for the best possible outcome of S1, this strategy was also included to efficiently assess potential candidates with the aim of refining the method to the most appropriate balance between performance (adequate information to evaluate alternatives) and analysis cost.

A preliminary search for non-fluorescent alternatives only provided early-stage development and plausible ideas. Further development of these early-stage alternatives was evaluated to be non-viable during the timeframe of this project. So, while S3 is highly interesting from a scientific and developing point of view, the risk and risk impact are high.

2.3.3 Summary

In summary, the criteria set by the Nordic Ecolabel currently do not contain any restrictions concerning the use of OBA in textile productions. However, future iterations of the criteria may result in an exclusion of OBAs in the production of Nordic Ecolabel textiles. Three project strategies were identified and evaluated. It was decided to continue with strategy S1 and S2 to allow the potential improvements from using alternative OBAs in near future despite the possibility of losing the Nordic Ecolabel certification due to a very general and broad definition of OBAs.

3. Establishing the baseline of the current OBAs

An important part of the chosen strategy, S1, is to establish a baseline of the current products from Beirholms Væverier with respect to the OBAs used today. The baseline constitutes a point of reference to evaluate the performance of alternatives in textiles.

3.1 Basic baseline measures

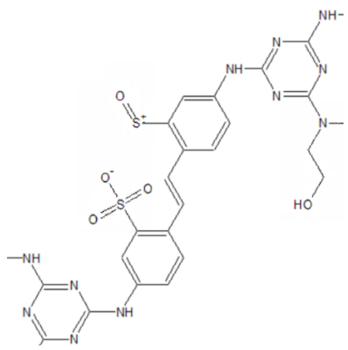
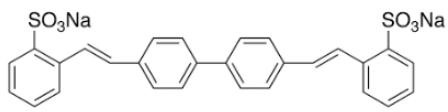
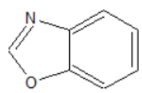
This baseline consists of identifying the extent of the challenges caused by the current OBAs and to investigate, if the challenges are related to one or both types of OBAs, i.e. OBA used for cotton and/or OBA used for polyester.

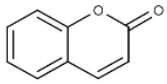
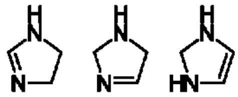
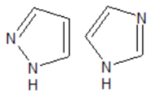
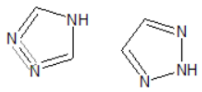
Further, the leasing laundries often call attention to increased colour loss of coloured textiles due to transfer of OBAs to non-OBA-containing textiles. To examine the extent of this challenge, the cross-contamination of textiles was tested in addition to measuring the amount of OBA present in the washing water and identification of the most leaching OBA. Combined with an initial health and environmental evaluation based on the typical OBA structures, the results of these tests and analyses were used as the beforementioned baseline for the development.

3.2 Primary chemical structures of OBAs

OBAs may be classified according to their chemical structure. Basic classes of chemicals used in OBAs include several structures as given in TABLE 1.

TABLE 1. Typical OBA structures and their type (anionic, neutral or cationic).

OBA-type	Structure	Type (anionic, neutral or cationic)
Triazine-stilbenes (di-, tetra- or hexa-sulfonated)		Anionic
Biphenyl-stilbenes		Anionic
Benzoxazolines		Neutral

Coumarins		Neutral
Imidazolines		Cationic
Diazoles		Neutral
Triazoles		Neutral

Generally, anionic OBAs exhaust on cotton, wool and silk, cationic OBAs exhaust on acrylic and certain polyesters, and nonionic OBAs are exhaust on all synthetics.

Nearly 80 % of all OBAs produced are derived from stilbene derivatives[5]. Different substituents – depending on the type of fibre on which it is applied and which promote the affinity – are used. For example, brighteners suitable for cotton are more or less derivatives of triazine stilbene-(diamino-stilbene) disulphonic acid. A total of 18 stilbene derivatives used in textiles have been registered under REACH and most of these are triazine-stilbene derivatives (at least 12 out of the 18).

Eight benzoxazoline-based substances used in textiles have been registered under REACH, and one of these were registered for use as OBA.

Two coumarin-based substances used in textiles have been registered under REACH, but none of these are likely to be OBA (one of these gives a yellow colour and the other is used as a fragrance and is not reported to be used as an OBA). Consequently, these are not considered relevant for the present assessment.

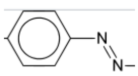
No imidazoline-based substances used in textiles registered under REACH were found.

A total of 11 diazol-based substances used in textiles are registered under REACH; however, only three of these are considered relevant for the present. They give a blue colour, whereas the others give yellow/red/orange colours. However, the three diazol-based substances giving the right colour do all include the aryl-azo structure[6], which can be degraded down to aryl amines – of which some of them is judged to be carcinogenic and under restrictions for use. Therefore, it is not recommendable to use any of these substances for the current substitution.

A total of six triazol-based substances used in textiles are registered under REACH; however, they are either aryl-azo-based substances and/or they do not have the right colour.

A preliminarily conclusion is that only stilbene-based and benzoxazoline-based substances appear relevant for the current substitution project.

[5] Pratima Bajp (2015): Pulp and Paper Industry: Chemicals. Elsevier Inc..

[6]Aryl-azo: 

3.3 Transfer of OBA to other textiles

According to the textile services, OBAs are transferred from white textiles to other textiles during washing procedures. To test this, Beirholms Væverier evaluated cross-contamination by washing OBA-treated textiles together with coloured non-OBA treated textiles and subsequently measure the colour and presence of OBA in the latter. In total, the white OBA-containing textiles were washed 11 times, with coloured textiles in the first, second and eleventh washing cycle. The coloured textiles were new in each of the three tested washing cycles. The results are summarised in TABLE 2.

TABLE 2. Results of colour evaluation of non-OBA textiles after wash with OBA-containing textile. The OBA textile had been exposed to 0 to 10 washing cycles prior to the washing cycle with the new non-OBA textiles. Evaluation of the non-OBA textiles is measured by comparing the change in colour to a grey-scale, when the textiles are exposed to UV light.
An evaluation of 5 means no colour change, and an evaluation of 3 and below is not acceptable.

Sample type	Washing cycle count of the OBA textile	Evaluation of non-OBA textile
Pillow case	1	3
	2	3
	11	4
Napkin 1	1	2/3
	2	3
	11	3/4
Napkin 2	1	2
	2	2/3
	11	3/4
Towel	1	4/5
	2	4/5
	11	4
Bed sheet	1	2
	2	2/3
	11	3

The transfer of OBA to other textiles can be detected even after 11 washing cycles, and a colour evaluation conducted by Beirholms Væverier showed that in some cases the coloured textiles would not hold up to their quality criteria after having been washed with OBA-containing textiles – even not after previous 10 washing cycles of the white textile. This poses a problem in relation to textile services, as re-use of washing water is an essential part of modern laundry service procedures, and new OBA-containing textiles would smudge other textiles in the washing sequence even after several washing cycles.

The presence of OBA in non-OBA textiles after the washing procedure was visualised by exposure to UV light as shown in Figure 3-1.

Figure 3-1: Example of visualisation of OBA in non-OBA textile after wash with OBA textiles when exposed to UV light. OBA is detectable by the bluish glow of the textiles.

3.4 Identification of OBA by fluorescence spectroscopy

While several methods for detection of OBA were considered, time consumption and price of the analysis was evaluated as essential for current and future usability of the technique. Also, the lower detection limit of the methods was discussed as an important parameter. Since these compounds exhibit strong fluorescence, fluorescence seemed a logic choice for measuring the concentration of OBA, as this probably would provide a sufficiently low detection limit and introduce less interference from other substances in the washing water, eliminating the need for pre-purification of the samples. Also, when compared to other types of more advanced analysis techniques, measurements of fluorescence are much less expensive.

In the manufacturing process of textiles from Beirholms Væverier, two OBAs are used; one for cotton (OBA-C1) and one for polyester (OBA-P1). To determine the OBA concentration in washing water by fluorescence, it was essential to identify, which OBA product (cotton or polyester types) is most predominant in the laundry washing water.

Two methods, both relying on the fluorescence of OBA, were utilised to distinguish between cotton- and polyester-intended OBA: thin layer chromatography (TLC) and fluorescence profile. Identification of the most abundant OBA in the washing water also added the benefit of focusing the effort towards substitution of the most leaching OBA.

3.4.1 General methodology

3.4.1.1 Fluorescence measurements

Samples of laundry washing water were extracted as two samples of water taken from a washing procedure performed according the standard, ISO 6330 N9 1A, at different water discharges during a single washing cycle. Water samples were provided by Beirholms Væverier. Samples of OBA-C1 (yellow-greenish powder) and OBA-P1 (yellow-greenish liquid) were provided by the strategic partner of Beirholms Væverier.

Fluorescence measurements were performed on a Thermo Scientific Varioskan LUX Multimode Microplate Reader, using a LAT module. The samples were loaded into an opaque black 96-well microplate. Analysis was performed *top-down*, so that only emitted fluorescence was measured.

To identify the wavelength of UV light of maximum fluorescence, excitation scans (343 nm to 401 nm) were performed for all samples.

3.4.1.2 Thin-layer chromatography

TLC was performed on a silica gel matrix on aluminium foil support, (Sigma-Aldrich, Germany) and eluated with dichloromethane. Both reference compounds (OBA-C1 and OBA-P1) as well as the washing water was spotted in the TLC. A co.-spot consisting of both reference compounds was likewise spotted on the TLC. The result was visualised using UV light.

3.4.2 Identification of most abundant OBA in washing water

3.4.2.1 Identification of cotton- and/or polyester-intended OBAs in washing water

The excitation wavelength giving maximum fluorescence emission for the washing water was found to be 363 nm. The results of the fluorescence measurements of OBA-C1, OBA-P1 and the first washing water sample are summarised in Figure 3-2.

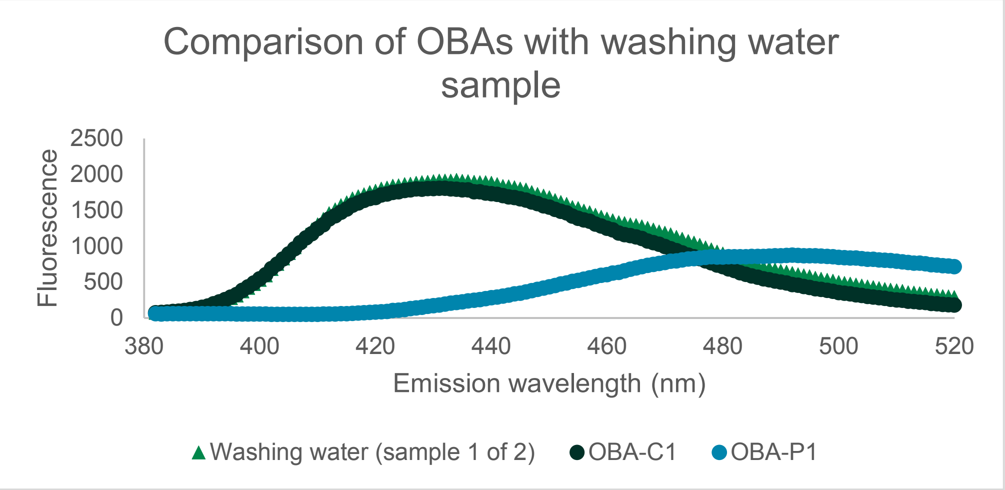


Figure 3-2: Comparison of OBAs with washing water sample.

Maximum emissions for OBA-C1, OBA-P1 and washing water were observed at 431 nm, 462 nm and 431 nm respectively (cf. Figure 3-2). As illustrated in Figure 3-2, the fluorescence emission curve of the washing water closely resembles the graph for the OBA-C1 reference, indicating that the washing water contains OBA-C1. This is supported by the TLC results (Figure 3-3).

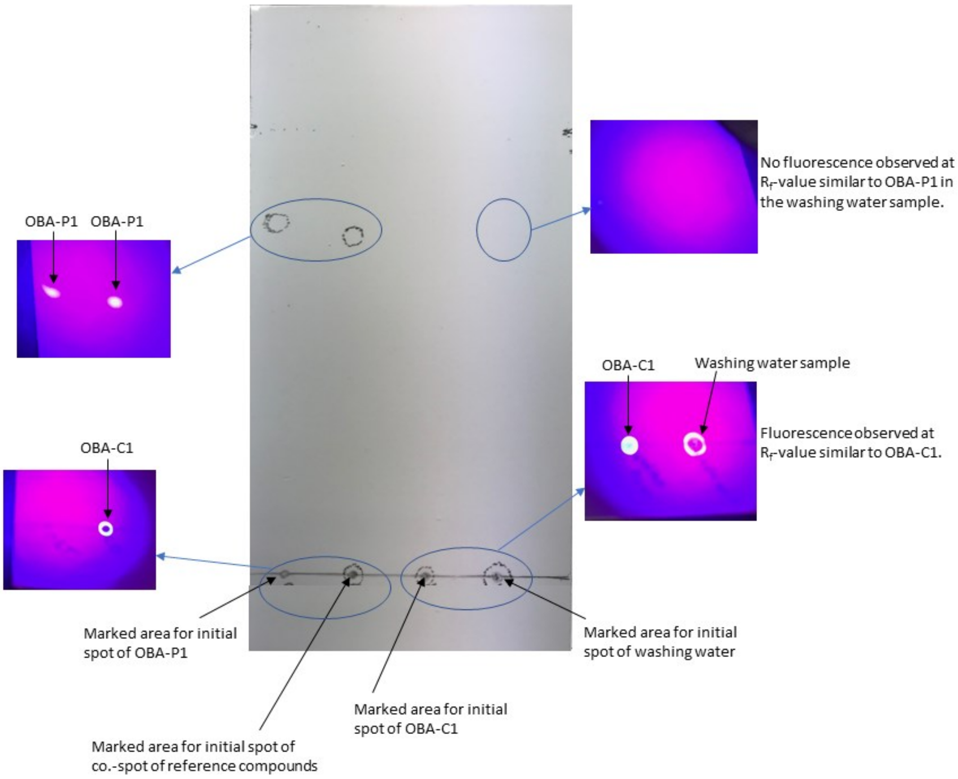


Figure 3-3: Illustration of the TLC for the OBA reference compounds and the washing water. The area exhibiting fluorescence when exposed to UV ligth after eluation is indicated by dashed gray markings. The black arrows mark the spotting area prior to eluation. The blue marking and arrows indicate the area given in photos while exposed to UV ligth to illustrate the fluorescense (or absence thereoff) in the indicated areas.

As illustrated by the co-spot in Figure 3-3 (second spot from the left), the two types of OBA were clearly separated, even when mixed, making it easy to distinguish them by TLC. This was expected based on the different functionality used for cotton and polyester OBAs (generally sulfonates and nitriles as previously described). OBA-P1 exhibited a retardation factor (R_f) of 0.7, whereas OBA-C1 exhibited an R_f of 0. The washing water did not show any signs of OBA-P1, whereas strong fluorescence was observed at the initial spotting area, i.e. an R_f value of 0, similar to that of OBA-C1. Since no other OBAs are used in the production of these textiles, besides the two reference compounds provided by Beirholms Væverier, and since no other OBAs were added in the washing cycles (e.g. by the laundry chemicals), OBA-C1 was the only identified OBA in the laundry water. Hence, the OBA used for cotton fibres, OBA-C1, is the most relevant OBA to substitute.

Additionally, these findings support that OBAs for cotton have been believed to adhere less strongly to the fibres compared to OBAs for polyester.

To obtain detailed information on the fluorescence measurements of the OBA compound in washing water, a three-dimensional fluorescence profile was constructed as displayed in Figure 3-4.

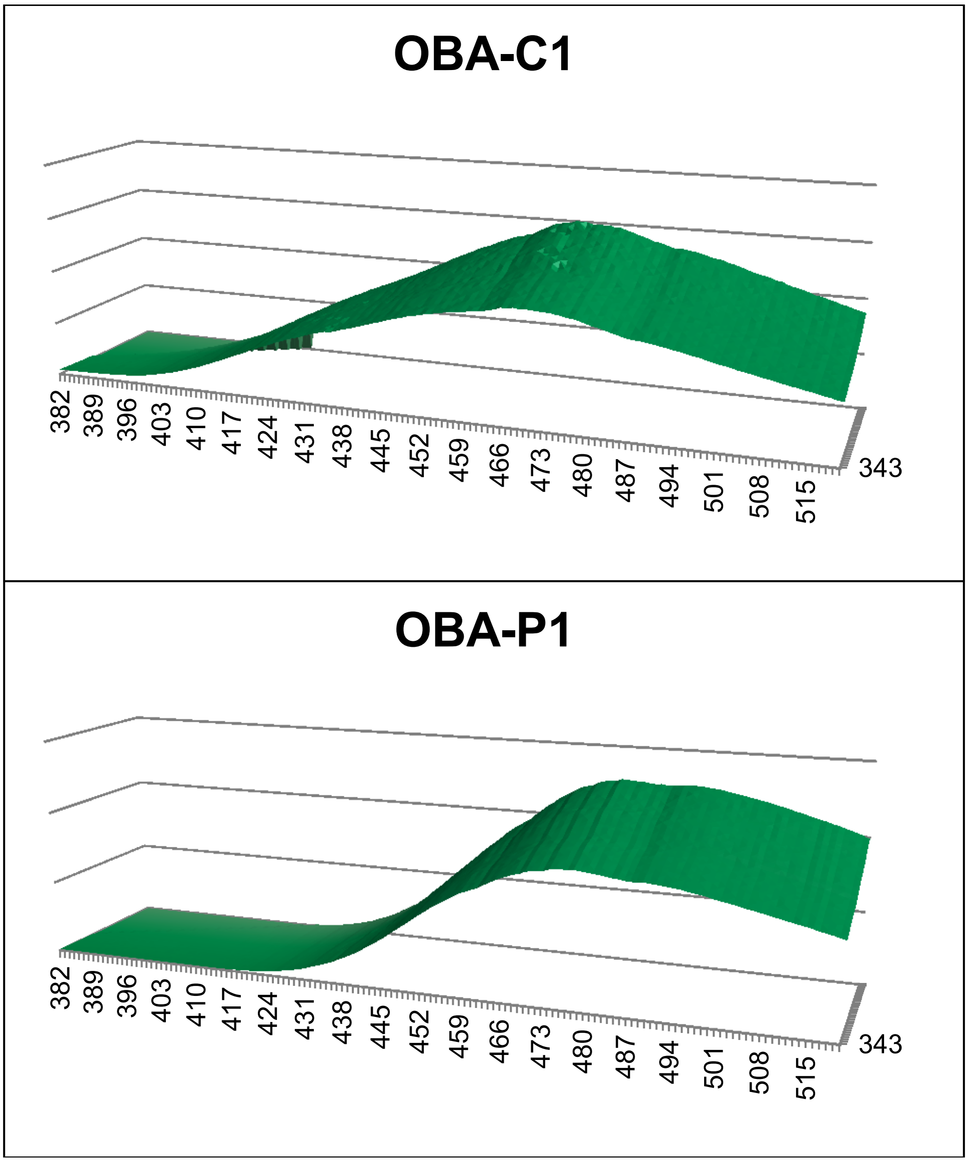


Figure 3-4: Three-dimensional fluorescence profile of OBA-C1 (upper graph) and OBA-P1 (lower graph).

While the results of the three-dimensional fluorescence profile, summarised in Figure 3-4, did not enhance the identification beyond what was achieved by single wavelength excitation (Figure 3-2) and TLC (Figure 3-3), it did provide important information regarding the development of the identification and quantification method using fluorescence measurements: i) a loss of fluorescence is possibly observed as a result of continuous exposure to UV light and ii) a strong concentration-dependent redshift (observed by the maximum emission at a longer wavelength at the higher concentration compared to the standard measurements (Figure 3-2), which was at lower concentration).

The decrease in fluorescence intensity while performing continuous measurements is indicated by the slightly downfacing curve in the depth-plane of Figure 3-4. While the depth-plane is the wavelength of excitation, the innermost measurement is also the first measurement in a series of measurements of the same sample; thus, each subsequent measurement has already been exposed to the UV excitation of all previous measurements. The slightly downfacing curve in the depth-plane can therefore be due both to loss of fluorescence from exposure to UV light as well as lower fluorescence at the increasing excitation wavelengths. The fact that the samples do exhibit a loss in fluorescence intensity at repetitive measurements on the same sample was demonstrated through a series of measurements on the same sample at a fixed excitation wavelength, where a decrease in fluorescence in the resulting emission spectrums was observed as the number of repetitively measurements grew (data not shown). This phenomenon could be caused by stereochemical interconversion from the (*E*)-isomer of the molecule to the (*Z*)-isomer. Due to steric hindrance of the (*Z*)-isomer, the aromatic moieties on both sides of the stilbene are forced out of plane, consequently breaking the conjugation of the molecule over the double bond, which in turn results in a significant loss of fluorescence. When developing a method for identification and especially for quantification, this is important, as neither samples nor reference compounds should be exposed to UV light prior to the measurement, and, likewise, each of the prepared samples should only be measured once.

The redshift causes another problem, both in relation to identification and in relation to quantification. For identification purposes, the concentration-dependent redshift means that the reference compounds should be prepared so that concentration of OBA is close to that of the washing water samples. This could possibly mean that several samples of various concentration for each reference compound need to be prepared. However, the use of TLC eliminates this problem, as redshift is not of concern for the TLC identification. For quantification, the concentration-dependent redshift introduces the necessity of constructing a standard curve with concentrations positioned relatively close to the concentration of the washing water sample, thus a general (reusable) standard curve extending over a larger concentration area is not feasible.

3.5 Determination of concentration of OBA in washing water

After determining the type of OBA in the washing water, the concentration of OBA-C1 was determined based on fluorescence. A standard curve was constructed from the dilution of a stock solution of 1 g/L. The standard curve was measured using an excitation wavelength of 363 nm and fluorescence values at an emission wavelength of 431 nm.

The resulting standard curve was used to determine the concentration of OBA-C1 in the two washing water samples.

TABLE 3. Fluorescence and concentration results of OBA-C1 in washing water samples from the first washing cycle of textiles. Two samples were taken during the washing cycle.

Sample	$\text{Fluorescence}_{431\ \text{nm}}$	Concentration of OBA-C1 [mg/L]
Washing water, 1st sample	1906	34
Washing water, 2nd sample	106.4	2

As expected, the first discharge of laundry water from the washing cycle of the fabric contains the most OBA.

3.5.1 Summary and conclusions

Transfer to, or cross-contamination of, non-OBA textiles was tested through several washing cycles. It was found that even after 11 washing cycles, OBA-treated textiles still transferred OBA to non-OBA treated textiles during washing procedures, significantly lowering the colour quality of the coloured products.

By a combination of fluorescence spectrometry and thin layer chromatography, OBA-C1, the OBA for cotton fibres, was identified in the washing water. In contrast, no sign of OBA-P1 was observed. OBA-C1 was thereby identified as the most important component for substitution in order to reduce leaching of OBA.

An initial method capable of determining the concentration of two specific OBAs was developed. It is expected that the method will also be capable of determining the concentration of other OBAs. Two samples of washing water were extracted, and it was determined that they both contained OBA-C1 in concentrations of 34 mg/L and 2 mg/L, respectively. Using the developed method, it is possible to evaluate the fastness of new OBAs, or whether new manufacturing processes influence the fastness of current OBAs.

4. Evaluation of OBA alternatives

A new OBA was proposed by the current OBA supplier as having a higher affinity for the cotton fibre; i.e., the compound should theoretically bind stronger to the cotton fibre and be less prone to leaching to washing water. An environmental and human health evaluation of OBA-C1 and OBA-C2 was prepared, and OBA-C2 was tested to confirm or disprove leaching performance.

4.1 Identification of potential OBA alternatives

Through extensive research and dialog with chemical suppliers, several potential cotton OBA alternatives were identified. The identified substances were ranked based on their affinity properties and environmental profiles as informed by the suppliers. The strategic partner for Beirholms Væverier selected the OBA alternative ranked best based on the above parameters. This OBA is referred to as OBA-C2. The new OBA-C2 and the currently used OBA-C1 are both provided by the same chemical supplier.

4.2 Health and environmental evaluation of alternative OBAs

Mainly stilbene-based substances are used for OBAs, and to gain information of their health and environmental profiles, a human health and environmental screening of several stilbene-based OBAs was prepared.

4.2.1 Human health and environmental hazard assessment

Today, Beirholms Væverier use OBA-C1, which may be substituted with OBA-C2. Information on the exact active ingredient in each of the two products was provided by the supplier. These two active ingredients were included in the human health and environmental hazard assessments.

A screening of a number of benzoxazole- and stilbene-based substances was performed. The screening relates solely to the environmental and health properties of the substances.
The starting point for the screening is the criteria formulated in the EU Eco Label Criteria Document for Textile Products[7]. It should be noted that the criteria for environmental classification have been slightly lowered in the criteria document if the optical brighteners are used only in the following cases:

- When printing with white colours
- To achieve brighter colours in uniforms and workwear
- Use as additives to produce polyamide and polyester with recovered contents.

[7] COMMISSION DECISION of 5 June 2014 establishing environmental criteria for the award of the Community eco-label to textile products (notified under document number C (2014) 3677) (Text with EEA relevance) (2014/350 / EU)

The screening was based on available data in REACH registration dossiers and QSAR calculations; either drawn from the Danish Environmental Protection Agency's QSAR database (http://qsardb.food.dtu.dk/db/index.html) or made using EpiSuite[8].

The results of the screenings are given in a separate document, but the drawn main conclusions of the screening are described below.

4.2.1.1 Physical-chemical data

Generally, the benzoxazole-based substances have a very high logP_{ow}[9] and correspondingly a very low water solubility (which may be beneficial for fabrics to be incorporated in textiles). Thus, if the benzoxazole-based substances are strongly bound to the fabric, the release upon washing must be low. Conversely, stilbene-based substances have a relatively low logP_{ow}[9] and a moderate to high water solubility.

Neither benzoxazole-based nor stilbene-based substances have a high vapor pressure or high Henry's constant, meaning they are not volatile, either in pure form or dissolved in water.

4.2.1.2 Environmental fate and toxicity

Neither benzoxazole- nor stilbene-based substances are readily biodegradable and most likely not inherently biodegradable.

No information has been found on the degradation and degradation pathways of the benzoxazole-based substances in the environment. However, as the substance is an OBA, some degree of photolytic activity and degradation are expected.

Some studies have been conducted on degradation in the environment for some of the stilbene-based substances (FWA-1 and FWA-5). It is found[12,13] that a rapid photolytic degradation occurs (half-lives below 1 day), where the double bond in the stilbene is degraded and replaced with aldehyde compounds. The aldehyde compounds formed by the photolytic degradation of FWA-5 and FWA-1 are likely to be readily biodegradable (validated by EpiSuite calculations), while the melamine[10] compounds also formed by the degradation of FWA-1 are known to be not readily biodegradable and non-toxic[11]. Thus, generalisation of this knowledge for other stilbene-based compounds indicates that stilbene-based OBA substances that do not contain melamine-like groups will rapidly degrade in the environment, whereas part of the stilbene-based OBAs that contain melamine-like groups will not be rapidly degraded in the environment - but also that the formed degradation products are not environmentally toxic.

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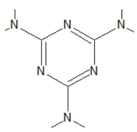
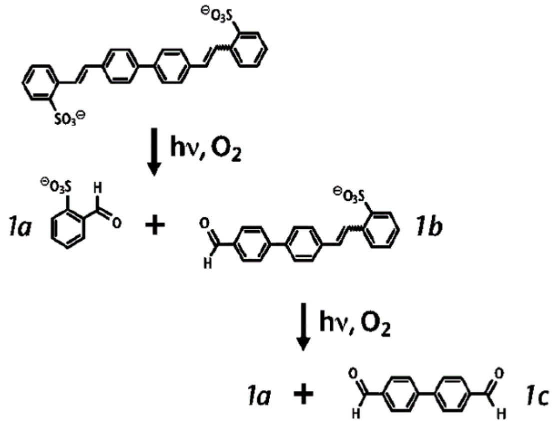
[8] Epi Suite is a programme which can be used to estimate physical-chemical and fate properties of chemicals on the basis of their structure. The programme can freely be downloaded from https://www.epa.gov/tsca-screening-tools/download-epi-suitetm-estimation-program-interface-v411.

[9] P_{ow}: **o**ctanol-**w**ater **p**artition coefficient

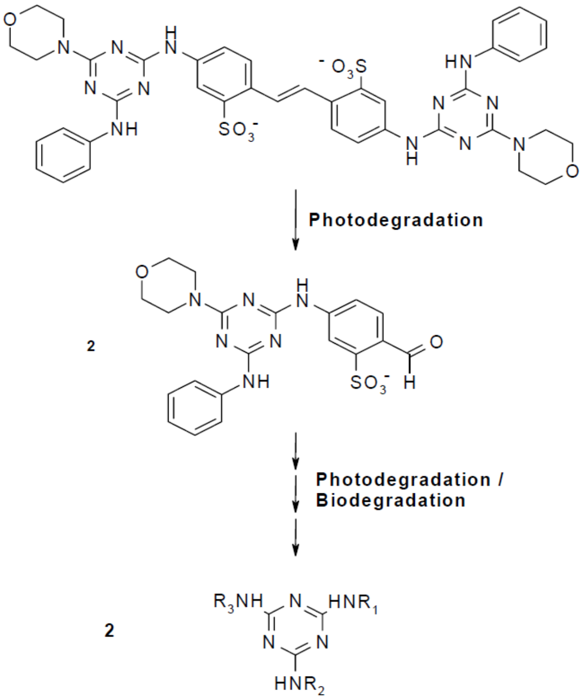
[10] The OBA compounds that have the following structure included will most likely form melamine-like (triazine) compounds by photolytic degradation and biodegradation



[11] Melamine (CAS No.108-78-1): Not readily biodegradable; Acute toxicity (E(L)C50): Fish: 3 g / L; Daphnia: 200 mg/L; Algae: 325 mg/L; Chronic toxicity (NOEC / EC10): Fish:> 5.1 mg/L; Daphnia: 11-18 mg/L; Algae: 98 mg/L



Photolytic degradation of FWA-5[12]



Photolytic degradation of FWA-1[13]

Figure 4-1: Degradation pathways for FWA-5 (left) and FWA-1 (right).

The benzoxazole-based substances are not acute toxic below and at their water solubility. Furthermore, 2,5-bis(5-tert-butyl-benzoxazol-2-yl) thiophene shows no chronic toxicity (daphnia and algae) at and below the water solubility. It is therefore generally concluded that the investigated benzoxazole-based substances are neither chronic nor acute toxic at concentrations at or below their water solubility.

A single substance based on both stilbene and benzoxazole (4,4'-bis (2-benzoxazolyl) stilbene) is identified. Its environmental data remind largely of the environmental data for the other benzoxazole-based substances investigated.

The acute toxicity E(L)C50 for some of the studied stilbene-based substances is > 100 mg/L (including the active ingredients in OBA-C1 and OBA-C2), while some of the studied stilbene-based substances have an acute toxicity E(L)C50 between 10 mg/L and 100 mg/L (including the known FWA-1 and FWA-5). Chronic data (NOEC / EC10) is available for only four of the studied stilbene-based substances, namely for FWA-1, FWA-5 and the active substances in OBA-C1 and OBA-C2. FWA-1 and FWA-4 show a higher chronic toxicity to algae (NOEC/EC10 ~1-10 mg/L) than the active ingredients in OBA C-1 and OBA C-2 (NOEC/EC10 >100 mg/L). The chronic toxicity to daphnia is on the same level for the FWA-1, FWA-5 and the active ingredients in OBA C-1 and OBA C-2 (NOEC/EC10 ~1-10 mg/L).

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[12] From HERA (2003): Human & Environmental Risk Assessment on ingredients of European household cleaning products. Substance: Fluorescent Brightener FWA-5 (CAS 27344-41-8). DRAFT. Version November 2003

[13] From HERA (2004): Human & Environmental Risk Assessment on ingredients of European household cleaning products. Substance: Fluorescent Brightener FWA-1 (CAS 16090-02-1). Draft - Version October 2004

4.2.1.3 Human health

In general, only very few measurement data describing the possible effects on human health is available for the benzoxazole-based substances.

The most tested benzoxazole-based substance is 2,5-bis(5-tert-butyl-benzoxazol-2-yl) thiophene. The substance is not classified. However, it should be noted that data for acute dermal toxicity, sensitisation by inhalation and toxicity to breast-fed children are missing. QSAR calculations for the substance suggest that the substance is not sensitising by inhalation.

QSAR calculations give a slight indication that the benzoxazole-based substances can be carcinogenic, but experimental data for 2,5-bis(5-tert-butyl-benzoxazol-2-yl) thiophene demonstrate that the substance should not be classified as carcinogenic – therefore it is indicated that the QSAR method probably is too conservative for this group of substances. Furthermore, QSAR calculations suggest that the benzoxazole-based substances may be sensitising by skin contact, but experimental data for 2,5-bis(5-tert-butyl-benzoxazol-2-yl) thiophene demonstrate that the substance is not sensitising by skin contact - it is therefore assessed that the QSAR method is probably too conservative for this group of substances.

In general, it is therefore concluded that the investigated benzoxazole-based substances are not CMR-substances and that they are not sensitising by inhalation and skin contact.

The stilbene-based OBA substances appear not to be acute toxic, sensitizers by skin contact and does not have CMR-properties (based on information for a limited number of stilbene-based compounds). It should be remarked that some of the QSAR calculations suggest possible CMR properties, but the test data do not support the results of these calculations. It cannot be excluded that the substances are sensitising by inhalation - however, no measurement data have been found confirming/excluding this.

4.2.2 Comparison of OBA-C-1 and OBA-C-2

Data have been found for the active substances in OBA-C-1 and OBA-C-2. Both active substances are stilbene-based and contain melamine-like groups. Thus, the quite persistent melamine is likely to be formed in the environment from the active ingredients in both OBA-C-1 and OBA-C-2. The data also show that the substances are not readily biodegradable. They have a specified chronic NOEC (daphnia, reproduction) of 1 mg/L, so it may be argued that it should be environmentally classified with H411 (the substances are currently not environmentally classified).

In comparison with the reference substances FWA-1 and FWA-5, the active substances OBA-C-1 and OBA-C-2 are generally less environmentally toxic than FWA-1 and FWA-5. The active substances in OBA-C-1 and OBA-C-2 have almost identical human health and environmental profiles. The Derived No Effect Level (DNEL[14]) for dermal exposure – expressed as mg substance per kg bodyweight and per day - is the same for the two alternatives. In addition, the Predicted No Effect Concentration (PNEC[15]) expressed as mg substance per volume water is the same for the two alternatives. OBA-C-2 is informed to have a higher dosage than OBA-C-1 – being 20-25% higher than the dosage of OBA C-1, then the risk to human health and the environment maybe slightly higher for OBA-C-2 than for OBA-C-1.

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[14] DNEL is a value used in a risk (or safety) assessment and can be expressed as a threshold value. If the dermal exposure exceeds DNEL, then it cannot be excluded that the substance may cause effects on human health

[15] PNEC is the highest concentration in the environment where no effects on the organisms are expected. If the concentration exceeds the PNEC, then it cannot be excluded that the substance may cause effects on the environment.

Due to the similar human health and environmental profiles and due to the higher dosage of OBA C-2, then the real advantage of substituting OBA-C-1 with OBA-C-2 appears not obvious.

4.2.2.1 Conclusions to health and environmental evaluations

A screening of a range of stilbene-based and single benzoxazole-based OBA substances has been performed.

No significant evidence has been found indicating that the investigated OBA substances are harmful to health; however, data that can definitively confirm that the substances are not sensitising by inhalation, are not acutely toxic by dermal contact and are not toxic to breast-fed children are missing. The investigated OBA substances are not readily biodegradable. Stilbene-based OBAs, which do not contain melamine-like groups, are expected to be rapidly reacted in the environment, while the stilbene-based OBA substances containing melamine-like groups will be converted into the rather persistent, but also non-environmentally toxic, melamine-like substances. The environmental toxicity of the investigated substances is moderate, with an acute toxicity E(L)C50 of between 10 mg/L and above 100 mg/L and a chronic toxicity above 1 mg/L The active substances in OBA-C-1 and OBA-C-2 have almost identical human health and environmental profiles – so from this perspective and knowing that the dosage of OBA-C-2 is higher than the dosage of OBA-C-1 – then, there is no real advantage of substituting OBA-C-1 with OBA-C-2.

4.3 Performance evaluation of alternative cotton OBAs

4.3.1 Performance aim

As established above, the suggested alternative, OBA-C2, is not exhibiting better performance in the health and environmental evaluation.. Due to the low biodegradability of these OBAs, leaching to the washing water (waste water) should therefore be minimized to avoid accumulation in the environment. The claimed higher affinity for cotton fibres of this alternative OBA is therefore essential for the compound to remain in the material during washing procedures and not leaching to the environment with the washing water. The tests aim to confirm, if a substitution of OBA-C1 with OBA-C2 does reduce leaching of OBA from the textiles during washing.

4.3.2 Experimental design

To test the leaching, an experimental setup was planned and included three steps:

1) Pilot production of textiles with the new OBA (OBA-C2)
2) Washing of the fabrics up to ten times while collecting water samples.
3) Analyses:
    a. Measurements of textile whiteness
    b. Measurement of OBA concentration in the washing water to benchmark leaching performance.

4.3.3 Materials and methods

4.3.3.1 Production of textiles with new OBA

In textile production, there are two main types of processing flow: processing flow A and processing flow B. The strategic partner's processing unit is configurated according to processing flow A, and the currently used OBA-C1 is designed to be applied in this flow. The alternative OBA-C2 is, however, designed for application in processing flow B. To be able to apply the OBA-C2 in processing flow A conditions, the strategic partner for Beirholms Væverier refined the procedure through laboratory trials.

After the initial trials, the OBA-C2 was tested in the actual application conditions in the processing flow A production unit. To make this trail possible, their production unit, with the capacity of 110,000 meters pr. day, was closed for 24 hours. All machines were cleaned to prepare the pilot production, and the trials were conducted processing greige fabric[16] with the OBA-C2.

A total of seven fabric lots were processed, consisting of three textile qualities. In the below overview, detailed information about the lots is listed (TABLE 4).

TABLE 4. Overview of processed lots (textile options).

Option	Composition	Gram per square meter (GSM)	Applied OBA
Option A	50% Polyester 50% Cotton	145 GSM	OBA-C2
Option B	50% Polyester 50% Cotton	145 GSM	OBA-P1
Option C	50% Polyester 50% Cotton	145 GSM	OBA-C2 OBA-P1
Option D	20% Polyester 80% Cotton	115 GSM	OBA-C2
Option E	20% Polyester 80% Cotton	115 GSM	OBA-P1
Option F	20% Polyester 80% Cotton	115 GSM	OBA-C2 OBA-P1
Option G	100% Cotton	115 GSM	OBA-C2

After processing, the seven lots were forwarded to the stitching unit and made into quilt covers and sheets. Each lot was stitched with coloured sewing thread in red, green etc. to secure identification according to the options from A to G. After stitching, the goods were dispatched to Beirholms Væverier's laboratory facilities in Denmark, where washing tests were conducted in the laboratory.

4.3.3.2 Washing procedure

Washing tests were performed to examine whether OBA-C2 leaches from the textiles into the washing water during a mechanical washing process, to the same or a lower degree than the currently used OBA-C1. The seven options were weighed upon receival at Beirholms Væveri-er, and 10 kg. of each were taken out for washing test. Depending on the gram per square meter (GSM) and the article size, between 10.8 and 17.9 articles amounting up to a total of 10 kg. were included in each washing test. For option E, there was a shortage in the delivery and due to this only 9.21 kg were washed.

The wash was performed according to ISO standard 6330 N9 A1. The mechanical washing process has a duration of 66 minutes, and washing water was taken from two rinses for each of the performed washes: the first after 45 minutes and the second after 60 minutes. The water samples were taken from both rinses for each of the performed washes. The washing water samples were collected in a clean metal jug directly from the drain tube through a sealed hose with an open/close nozzle attached. The metal was used to better control the water coming out from the machine and was cleaned between the two rinses. The water from the jug was trans-ferred to small glass containers with plastic top. The glass containers were placed in a dark cabinet to protect the water from daylight, and they were marked according to option details and whether the sample was from the first or second rinse. In between the washes of each option, a rinsing program of 16 minutes was conducted to avoid the risk of contamination of water from one lot to the next.

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[16] Greige fabric: fabric that has been woven and which is still in natural/ un-bleached and un-dyed shade.

A reference lot was included in the test. The reference lot consisted of quilt covers from running production of 50% Polyester/ 50% Cotton, 145 GSM, treated with OBA-C1. The reference lot was the same quality and design as the testing options A, B and C with the alternative OBA-C2 option.

TABLE 5. Overview of textiles options and the number of washes.

Option	Number of washes	Composition	Gram per square meter (GSM)	Applied OBA
Option A	1. wash 2. wash	50% Polyester 50% Cotton	145 GSM	OBA-C2
Option B	1. wash	50% Polyester 50% Cotton	145 GSM	OBA-P1
Option C	1. wash 2. wash 10. wash	50% Polyester 50% Cotton	145 GSM	OBA-C2 OBA-P1
Option D	1. wash 2. wash	20% Polyester 80% Cotton	115 GSM	OBA-C2
Option E	1. wash	20% Polyester 80% Cotton	115 GSM	OBA-P1
Option F	1. wash 2. wash	20% Polyester 80% Cotton	115 GSM	OBA-C2 OBA-P1
Option G	1. wash 2. wash 10. wash	100% Cotton	115 GSM	OBA-C2
Reference	1. wash 2. wash 10. wash	50% Polyester 50% Cotton	145 GSM	OBA-C1 OBA-P1

All textile options were washed and two water samples taken from the first washing cycle. Textile option D, F and G went through a second washing cycle with samples taken of the washing water. Textile option A, C and the reference went through a total of 10 washing cycles with samples of the washing water taken at the 2nd and 10th cycle (TABLE 5).

4.3.3.3 Washing water analysis

A 3D spectrum was recorded as described in chapter 3.4.1. The concentration of OBA was determined in accordance with the method described in chapter 3.5, but with an excitation wavelength of 369 nm and emission wavelength of 434 nm (determined from the recorded 3D fluorescence spectrum).

4.3.3.4 Whiteness measurements

Whiteness was measured on DataColor for textile option A to G and the reference textile before wash, after 2 washes and after 10 washes for the relevant samples. No whiteness measurement was performed for Option E due to shortage in delivery and due to this, no unwashed fabric being available.

Colour and whiteness were measured at Beirholms Væverier using a DataColor spectrophotometer, which allows calculation of the metameric value and the exact dye concentration in the textile.

4.3.4 Results and discussion

4.3.4.1 Whiteness

The product must meet the strict quality requirements set by Beirholms Væverier to proceed from the test and become a final product. The whiteness of the textiles is, therefore, of the outmost importance for the evaluation of the alternative OBA.

In the Ganz Griesser formula, different weighting can be given to quantitative standards for all possible hue preferences for fluorescent whites. The GG whiteness index consists of Ganz Griesser whiteness (GG) and tint-CIE whiteness (Tint). The GG value for a specific sample is generated through calibration against a selected standard shade. Hence, the obtained value is a variable parameter and it must be analysed based on the standard shade, which has been applied. On the contrary, the CIE formula is based on fixed parameters and is not dependent on the use of standards. Moreover, the tint value indicates the bluish tone of a sample, while the GG value indicates the general nature of the whiteness shade. At Beirholms Væverier it is found that using both measures gives a good insight into the whiteness shade of a product.

Comparing the results for Option C and for the reference lot it can be concluded, that GG value before wash is at the same level, but that Options C is falling in GG value after two washes compared to the reference lot. After 10 washes, the level has again reached the same level. This result indicates that more OBA has leached from Option C than from the reference lot in the first two washes; however, this difference in Ganz Griesser whiteness has been neutralised after 10 washes. The expected GG value before wash is 210 and the allowed tolerance is between 200 and 220 GG. Tint values are found to be low for all measures, both for the reference and the new options. The expected value is 1.5, and the allowed tolerance is between 0 and 3.

TABLE 6. Results of textile whiteness. NA denotes when data have not been measured.

Option	Number of washes	Composition	Applied OBA	Whiteness before wash	Whiteness After 2 x wash	Whiteness After 10 x wash
Option A	1. wash 2. wash	50% Polyester 50% Cotton	OBA-C2	GG 190.79 Tint 0.47	GG 170.13 Tint 0.59	NA
Option B	1. wash	50% Polyester 50% Cotton	OBA-P1	GG 171.25 Tint -0.12	NA	NA
Option C	1. wash 2. wash 10. wash	50% Polyester 50% Cotton	OBA-C2 OBA-P1	GG 208.16 Tint 0.27	GG 196.09 Tint 0.42	GG 196.05 Tint 0.44
Option D	1. wash 2. wash	20% Polyester 80% Cotton	OBA-C2	GG 212.57 Tint 0.23	GG 192.35 Tint 0.54	NA
Option E	1. wash	20% Polyester 80% Cotton	OBA-P1	NA	NA	NA
Option F	1. wash 2. wash	20% Polyester 80% Cotton	OBA-C2 OBA-P1	GG 220.90 Tint 0.33	GG 206.26 Tint 0.31	NA
Option G	1. wash 2. wash 10. wash	100% Cotton	OBA-C2	GG 204.84 Tint -0.38	GG 210.38 Tint -0.03	GG 202.00 Tint -0.0
Reference	1. wash 2. wash 10. wash	50% Polyester 50% Cotton	OBA-C1 OBA-P1	GG 208.69 Tint -0.53	GG 206.52 Tint 0.20	GG 197.19 Tint 0.15

4.3.4.2 Reflections of the method for determination of OBA concentration

The method used for analysis of washing water and concentration determination of OBA in washing water was developed and continuously refined to serve as an efficient tool for comparison and evaluation of alternatives. Refinement of the method was continuous throughout the project as new discoveries lead to improvements and overall better performance of the method. The method was, however, not perfected during the project, and a few points of possible further improvement were observed during the final analyses:

- Dilution of initial washing samples: the concentration of OBA in the washing water samples was higher than expected, and in a few cases the concentration exceeded what can be accurately determined as the standard curve becomes non-linear above this concentration. Some of the impracticalities involved in the analysis of samples with high OBA concentration is related to the redshift described in Chapter 3. This can, however, easily be overcome by dilution of the samples prior to performing the measurements. For this project, dilution and more accurate values would, however, not change the overall conclusion or improve on the validity of the result, thus such experiment was not performed.
- The exact values of the upper and lower limits of detection as well as the precision and the accuracy of the method for each OBA were not determined due to time constraints and the value of these were evaluated to be of lesser value to the project as it, likewise, would not improve on the validity of the overall result or change the final conclusion. Instead the upper concentration limit was estimated from the standard curves to be about 35 mg/L for both cotton OBAs.
- The washing water (especially for the first washing cycle) contains remains of textiles fibres/lint. OBAs in these textile remains increase the subsample variation when performing repetitive analyses of the washing water (see Figure 4-3). Introduction of filtering or extraction methods is under evaluation.

Due to the assessment that these improvements do not add sufficient news to the project and taking the time used on these improvement into consideration, neither of these possible improvements were validated or implemented. Instead, they are considered in future iterations of the method for more detailed evaluations in other developments. Conclusively, the method developed for screening and evaluating the alternative OBA provided data of adequate quality to conclude on the performance based on a benchmark approach.

4.3.4.3 Concentration of OBA in washing water

OBA-C2 does not seems to be as prone to repetitive exposures to UV light as it was observed for OBA-C1 and OBA-P1 (Figure 3-4). This is indicated by the increase in fluorescence to a maximum over the repeated emission scans with different excitation wavelengths. The maximum fluorescence was found to be at an emission wavelength of 434 nm at an excitation of 369 nm.

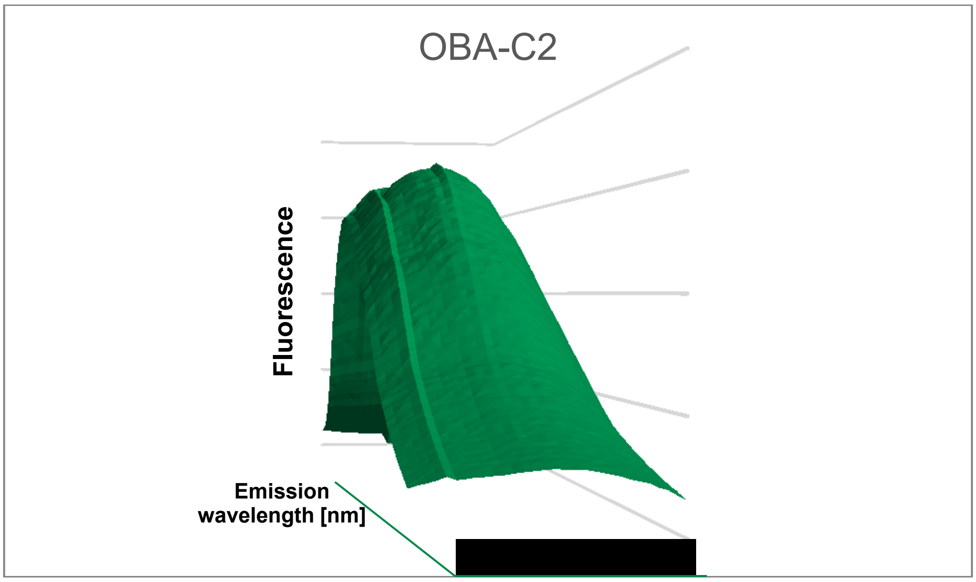

Figure 4-2. Three-dimensional fluorescence profile (varying excitation wavelength and resulting emission intensities as different wavelengths) of OBA-C2.

Option B (50 % Polyester/ 50 % Cotton) and Option E (20 % Polyester/ 80 % Cotton) do not contain the cotton OBA, OBA-C2, and, therefore, it was not expected to identify any significant concentrations of OBA in these samples, since OBA-P1 was not found in the washing water during the initial experiments (see chapter 3.4). Nevertheless, these textiles were tested as points of reference (eventually, higher concentrations of OBA-P1 would show up at excitation and emission wavelengths of 369 nm and 434 nm respectively, cf. Figure 3-4). While the small concentrations found in the washing water (Figure 4-3), potentially could be “misinterpreted” fluorescence from OBA-P1, the initial measurements and TLC results (chapter 3.4) did not show any indications of OBA-P1 leaching to the washing water. Consequently, these small concentrations of OBA in the washing water of option B and option E are believed to be small remains of OBA-C2 from previous textile options, which results in cross-contaminating the samples.[17]

[17] In a post-project study, small amounts of OBA were identified in washing water from laundry not containing OBAs (even after pre-rinsing the machine), supporting the hypothesis of cross-contamination of option B and E.

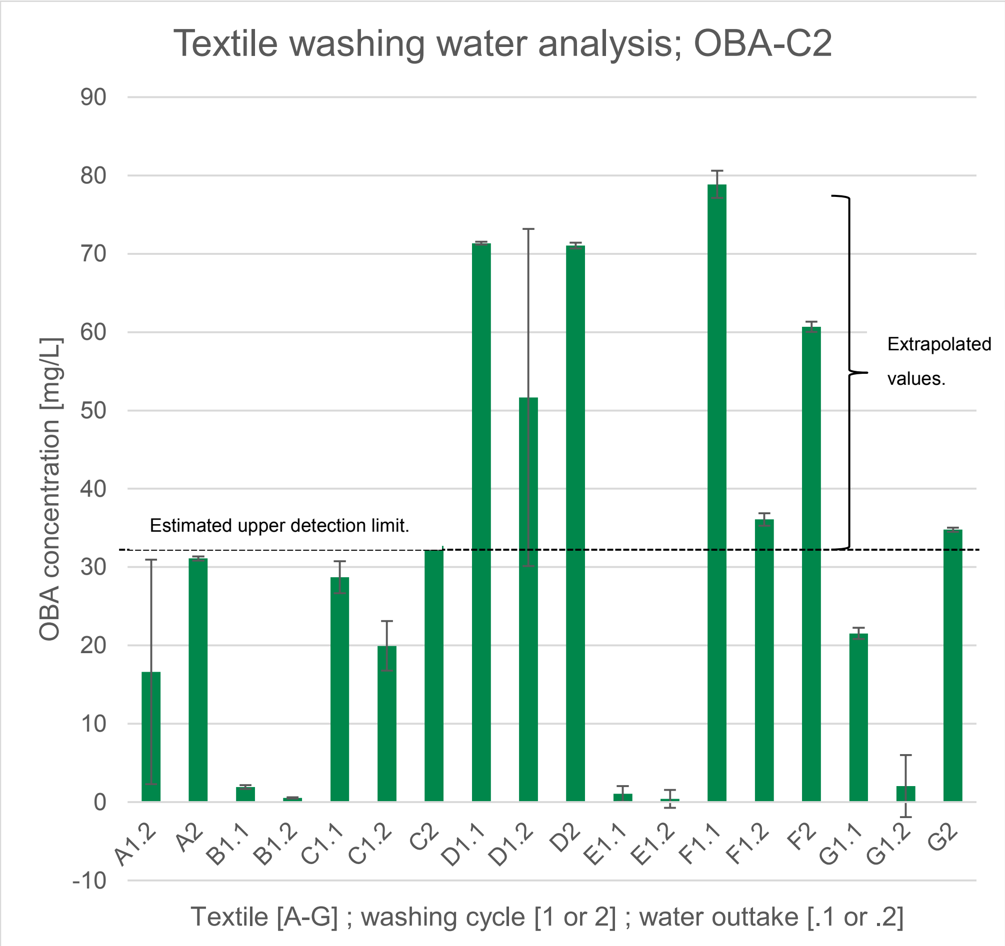

Figure 4-3. Concentration of OBA measured for each of the textiles options (A to G). The first number after the option depicts the washing cycle [1 or 2], and the number after the punctuation denotes if the sample was taken from the first [.1] or second [.2] flush during the respective washing cycles. The estimated upper detection limit (35 mg/L) is marked with a horizontal line. Values above the estimated upper detection limit are extrapolated; thus, the values of these cannot be regarded as exact.

With the exceptions of options B, E and G1.2, all measurements revealed high concentrations of OBA, many of which are close to or above the estimated upper detection limit. The upper detection limit was estimated based on the linearity of the standard curve.

Cotton content having an influence on the OBA concentration in the washing water was not unexpected; however, the 20/80 textiles seemed to exhibit the largest leaching of cotton OBA, whereas the 50/50 and 100% cotton leached similar amounts of OBA. Though, it is important to emphasise that the concentrations of OBA in the 20/80 samples were above the concentration for accurate values to be determined, and the results are, therefore, constructed by extrapolation of the standard curve, resulting in much less precise values from the 20/80 types of textiles. While the exact values of 20/80 textiles may not be accurate, the leaching from this textile is unambiguously higher than for 50/50 or 100% cotton types of textiles.

The lower GSM of the 20/80 types textiles compared to the 50/50, results in an increase of about 26% additional square meters of textile in the 10 kg used for the test, possibly causing an increase in leaching of OBA per mass of textile versus the 50/50 textiles. Still, this does not explain why the 100% cotton (which has a GSM similar to the 20/80 textile), does not exhibit higher leaching of OBA. The reason for this was later identified as being an overdosage of the OBA during the fabrication of the textiles. We found that the strategic partner had fo-

cused on the 100% cotton (option G) and based the amount of OBA-C2 on this option, not accounting for the difference in textile composition. The amount of OBA-C2 applied to all 50/50 and 20/80 textiles is, therefore, highly overdosed compared to the cotton content of the textiles.
This also explains why the 50/50 textiles (A and C) does not seem to result in a lower concentration of OBA-C2 compared to the 100% cotton type (G), despite it being partly polyester (thus containing OBA-P1 instead of OBA-C2).

The results for the 50% Cotton/ 50% Polyester with both OBA-P1 and OBA-C1/OBA-C2 applied (Option C and the reference textile) are summarised in TABLE 7 for 1, 2 and 10 washing cycles. Comparing the measured concentrations in the washing water, there is no indication of a vast difference between OBA leaching from the textiles treated with the original OBA-C1 and the alternative OBA-C2. At the current state of the analysis method development, the differences are too small to provide any clear conclusion if one is performing slightly better than the other.

TABLE 7. Concentrations of OBA-C1 and OBA-C1 in the washing water after 1, 2 and 10 washing cycles.

Washing cycle 1		
Textile type	OBA-C1	OBA-C2
50/50	>35	29
Washing cycle 2		
Textile type	OBA-C1	OBA-C2
50/50	28	33
Washing cycle 10		
Textile type	OBA-C1	OBA-C2
50/50	2	4

However, as previously described, the amounts of OBA-C2 was found to have been overdosed, and, thus, a direct comparison of OBA-C1 and OBA-C2 were not possible. Nevertheless, the very similar performance of OBA-C2, despite the overdosage, indicates that better performance might be achieved by optimizing the recipe, which will be pursued after completion of the project.

4.3.5 Conclusion on technical performance

The analysis method developed during the project provided a strong tool for screening alternative types of OBA and provides valuable information about the leaching to the washing water. However, in order to achieve a higher precision and accuracy, the method could be continuously perfected. At the current state, the method does provide the accuracy for doing screening, but Danish Technological Institute are looking into further development of the method to provide even better data with higher precision and reproducibility.

Results indicated overdosage of OBA-C2 on the 20/80 and 50/50 textiles, which was confirmed by detailed discussions of the processing with the strategic partner. The overdosage of OBA-C2 overshadowed conclusive performance differences. However, similar performance, i.e. similar leaching values, of OBA-C1 and OBA-C2 despite the overdosage indicates a potential for reducing the leaching by optimization of the OBA dosage. This hypothesis stands for further testing, and no further conclusions could be drawn from the data.

5. Summary, conclusion and perspectives

With a main purpose of challenging the use of OBAs by asking the question: *can we reduce the environmental impact of whitened textiles without comprising the whiteness – and, if so, how?* – this project started by considering the current regulation (voluntary and mandatory) in different industries with regards to the use of OBAs. Having realised that in many other industries, OBAs are not allowed in products labelled by the EU and Nordic Ecolabel, the project partners considered different strategies for answering the question. Since the current "non-fluorescent" alternatives were evaluated to be far from market, focus was directed to replacing current OBA(s) with better alternatives in the sense that they e.g. possess a better environmental and health profile and/or higher affinity to the textiles, thus lowering leaching of the OBAs to the washing water.

For textiles with currently used OBAs, cross-contamination from OBA-treated textiles to non-OBA-treated textiles was found to cause a problem. Even after 11 washing cycles, the cross-contamination from OBA-treated textiles was still measurable. This finding emphasised the need for alternative OBAs with reduced leaching.

White textiles with a composition of mixed fibres require different types of OBA, depending on the fibres; i.e. one type of OBA for cotton and another for polyester. Cotton OBA (OBA-C1) was identified as the main leaching OBA in current textiles, while no leached polyester OBA (OBA-P1) was observed in the washing water. Consequently, the project focused on finding an alternative OBA suitable for replacement of the current cotton OBA-C1.

Based on communication with OBA suppliers, a list containing relevant specifications of different commercial available OBAs was constructed. From an evaluation of the candidate list focusing on enhanced cotton affinity, the most promising OBA (OBA-C2) was selected as a candidate for substitution of OBA-C1.

The environmental and health profile of several general OBA structures, including the specific structures of OBA-C1 and OBA-C2, were evaluated. The active substances in OBA-C1 and OBA-C2 have almost identical human health and environmental profiles, so from this perspective and knowing that the dosage of OBA-C2 is higher than the dosage of OBA-C1, there is no real advantage of substituting OBA-C1 with OBA-C2 with respect to environment and human health.

With health and environmental profiles being almost indistinguishable, the increased cotton affinity and possibly significantly lower OBA leaching from textiles became even more important for verifying the potential of OBA-C2. By producing and testing a range of textiles with OBA-C2, the performance of the compound was analysed with respect to whiteness and leaching. While textiles with whiteness levels meeting the quality criteria set by Beirholms Væverier, concentrations of leached OBA to washing water was found very similar to that of OBA-C1. The results indicated that process parameters during textile production may influence the leaching of OBA to the washing water highly. When carefully inspecting the production parameters of the textiles containing OBA-C2, the project group learned that the amount of OBA for these textile samples were dosed based on the 100% cotton textile, meaning that a large excess of OBA was applied to the 20/80 and 50/50 textiles. Consequently, no definitive conclusion on the leaching performance could be taken; however, a possible potential for optimisation of the OBA dosage was revealed by surprisingly low leaching values – given the significant overdosage – were obtained, and this will be further explored.

The overall results thereby demonstrated no clear benefits of using OBA-C2 over OBA-C1 based on neither health and environmental profiles nor technical performance, and combining these outcomes with the fact that the dosage as well as price of OBA-C2 was higher (also for the 100% cotton), this study found that OBA-C2 does not necessarily meet the objectives of development work by reducing OBA leaching and/or provide an improved health/environmental profile of the textile product. Indications have been found that leaching, while not eliminated, possibly can be reduced to some extent by optimisation of the process parameters during the fabrication of the textiles. After concluding the project, additional work will be performed to illuminate if lower dosage of OBA-C2 (and eventually OBA-C1) and/or other process parameters can be optimized and implemented in the textile production, while not compromising the whiteness, and eventually improve on the leaching of the compounds.

OBA-C1 and OBA-C2 are both stilbene-based compounds and contain melamine moieties. The finding of very similar human health profiles, environmental profiles as well as similar levels of leaching indicates that these possibly very similar molecules are not sufficiently different to exhibit vast differences in performance. Instead, it could be interesting to test and compare the stilbene-based compounds with a benzoxazole-based compound identified in this project. The evaluation of benzoxazole-based compounds indicated that these molecules do not exhibit acute toxicity or chronic toxicity, and due to their low aqueous solubility, a decreased leaching from the textiles may be achievable. However, the lack of knowledge of these types of compounds, especially in relation to degradation, should be studied before considering textile applications. Additionally, the compounds should be compatible with the processes needed for the textile production, and last, but not least; the compound should be compatible with the cotton fibres and provide sufficient product performance to pass the quality criteria.

Another subject of interest would be to approach the current OBA challenges by developing chemically modified OBAs specifically designed to form chemical bonds with cotton during production of the cotton strand. By chemical attachment of the OBA to the fibres, a very significant reduction in leaching of OBA during washing procedures would be achieved and, hence, result in significant reduction of both environmental impact and cross-contamination of other textiles. While a very interesting approach, many other factors beside the compound and its chemistry must be evaluated for such an approach to be successful. For one, the financial viability; the final textile should be at a reasonable cost price compared to the traditional OBA-containing textiles. The level of a “reasonable cost price” depends on the product performance, expected product life environmental effects and market acceptance: how much are customers willing to pay for the improved product? Secondly, the chemical treatment of the fibres should be developed and optimised to safeguard similar or better health and environmental profiles of the processing of fibres and textiles.

Substitution of OBAs in Industrial Textiles
Can we reduce the environmental impact of whitened textiles without comprising the whiteness – and, if so, how?

Setting out to find an answer to this question, the partners in the present project have evaluated several strategies to reduce the leaching of OBAs from whitened textiles. The chosen strategy of work focused on commercially available OBAs by studying chemical structures and building blocks for OBA to establish knowledge on their chemical nature, building blocks, performance as well as health and environmental effects, and a method for comparative evaluation of the leaching of OBAs was developed to assess alternatives in a product development setting.

A list of OBAs was assessed based on supplier information, knowledge of OBAs and their building blocks as well as a health and environmental screening to select and deselect potential alternatives. One alternative was chosen for detailed studies with respect to properties such as affinity, leaching and smudging in addition to financial evaluations.

The studies revealed no definitive conclusions with respect to leaching; however, optimization of the OBA dosage has a potential to reduce leaching of the alternative OBA to values lower than the values achieved in the studies and, as hypothesized, lower than the leaching of current OBAs.

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