

Survey of Chemical Substances in Consumer Products

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Mapping and liberation of organic tin compounds in mattress pads, top mattresses, and baby/junior duvets

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2 Introduction

May 2002 Eurofins Danmark A/S was requested to carry out a project from the Danish Environmental Protection Agency titled:

- Mapping and liberation of organic tin compounds in mattress pads, top mattresses, and baby/junior duvets

The Danish Environmental Protection Agency had formulated a project (02/05/02, <http://www.mst.dk/kemi/02050112.htm>) that is the basis of the content and scope of the project.

Present project is a follow-up of a former project (performed in 2001 by another sub-contractor than Eurofins Danmark A/S), where the Danish Environmental Protection Agency had purchased and analysed mattress pads and top mattresses for total tin, total antimony, permethrin, and triclosan. As a larger amount of total tin was detected in some of the products the Danish Environmental Protection Agency wanted this new project to investigate if a presence of organic tin compounds could be detected in mattress pads, top mattresses, and baby/junior duvets.

Organic tin is suspected of having long-term effects on the immune response. Furthermore, tributyltin is known for having hormone interfering effects on organisms in the marine environment. Other compounds are suspected of having the same effect. Thus organic tin compounds are unwanted in consumer products.

The producers all have had the report in hearing. From this hearing process it is announced that product no. 3 no longer is no longer on the market

Project leaders for the Danish Environmental Protection Agency were Shima Dobel and Anette Ejersted.

The products included in this project are anonymous in this report

3 Scope

A total of 17 products are included in the investigation consisting of mattress pads, top mattresses, and baby/junior duvets.

Mattress pads are defined as a thin washable protective mattress, and top mattresses are defined as a thicker mattress with a core of PUR (polyurethane)-foam, latex, or the likes.

According to arrangement with the Danish Environmental Protection Agency the project is divided into the following phases:

1. Content analyses of all products
2. Stratification of the products with detected content and products with raised limit of detection due to interference.
3. Migration to synthetic sweat for products with detected content.

4 Mapping

4.1 MAPPING OF THE MARKET FOR TOP MATTRESSES AND BABY/JUNIOR DUVETS

In a former project (see introduction) the largest amount of total tin was detected in top mattresses (120-180 mg/m³ for top mattresses compared to 12 mg/m³ as the highest detected for mattress pads). Thus this project exclusively focuses on top mattresses and baby/junior duvets made from synthetic material as regards mapping and involvement of new products. The original samples (mattress pads and top mattresses) are maintained as products in the project with the exception of one single product that was omitted.

4.2 TOP MATTRESSES

In order to obtain an overview of the top mattress market the following sales chains and mattress producers were contacted:

Idé Møbler
Dunlopillo
IKEA
ILVA
BIVA
Jysk
VM Madrasfabrik
Getama

According to the information from the above mentioned contacts these sales chains and mattress producers cover most of the Danish market. All top mattresses are produced in Denmark or Sweden. The contacts gave no information on mattresses imported from abroad besides Sweden.

Seven products have been chosen in co-operation with the Danish Environmental Protection Agency from the contacts' information on production and sale. According to our information the seven products represent the most sold mattresses, different producers, and different materials.

The products from the former project have equally been included in the investigation.

4.3 BABY/JUNIOR DUVETS

To check the market for baby and junior duvets made from synthetic material the following have been contacted:

BabySam
Baby-Vest
Baby Dan
Jysk

According to information from the above mentioned chains baby and junior duvets from synthetic material are sold in small quantities compared to eiderdown. Duvets from synthetic material are especially sold in case of allergy. The contacts gave no information on mattresses imported from abroad besides Norway and Lithuania.

Two baby duvets were chosen for the project in co-operation with the Danish Environmental Protection Agency.

5 Analytical methods

5.1 SAMPLE PREPARATION FOR THE ENTIRE PRODUCT

Six part samples are cut from each product 12 x 12 cm evenly distributed over the entire mattress or mattress part. Three part samples are accordingly determined for one sample and the remaining three for double determination. Thus the single sample will represent the entire product.

Part samples consisting of layers from the entire product i.e. both core, stuffing, and ticking. Before analysis the part samples are cut into smaller pieces of 2-3 mm.

5.2 SAMPLE PREPARATION FOR LAYERING OF THE PRODUCT

A minimum of 2 part samples of 12 x 12 cm are taken from each product evenly dispersed over the entire mattress or piece of the mattress. The products were divided into three layers corresponding to one ticking layer (textile), one filling layer typically made from cotton batting, and a core of PUR foam or latex. The single layers are described under the section "Results".

Prior to analysis the part samples are cut into smaller pieces of 2-3 mm.

5.3 ORGANIC TIN COMPOUNDS

A part sample with known weight and area is taken and extracted with acetic acid in methanol. The extract is shaken in aqueous medium and derived at an extractive derivation with sodium tetraethylborat and pentane. The organic phase is added isooctane, concentrated, and analysed at combined gas chromatography and mass spectrometry (GC/MS) at selective ion monitoring of the substances in question. The content is calculated to relevant standards.

The analysis is performed in duplicate. The limit of detection depends on the single component and is stated below. The unit is μg organotin cation/kg.

Component	Limit of detection
Monobutyltin (MBT)	5
Dibutyltin (DBT)	5
Tributyltin (TBT)	2
Tetrabutyltin	10
Monooctyltin	10
Diocetyltn	10
Tricyclohexyltin	10
Triphenyltin	10

5.4 MIGRATION TEST

Artificial sweat is used as simulant consisting of:

4,5 g	Sodium chloride
0,3 g	Potassium chloride
0,3 g	Sodium sulphate
0,4 g	Ammonium chloride
3,0 g	Lactic acid
0,2 g	Urea
1000 ml	Distilled water

The sample for migration test consisted of two part samples taken two different places on the mattress making it correspond to the content analyses. The sample represented one mattress surface totalling 1 dm² equalling the total surface of the sample 2 x 1 dm² plus the thickness of the mattress. The simulant is added sample the totalling covering the sample and not compressed.

The incubation occurs at 40°C for 48 hours where after the simulant is analysed for organic tin compounds.

The migration test is performed in duplicate.

6 Analytical results

6.1 ORGANIC TIN COMPOUNDS

Undermentioned the results for the organic tin compounds that could be extracted from the products. The limits of detection are stated in the table.

For some of the sample the limits of detection for all tested compounds have been increased due to the determined low recovery of the internal standard. The low recovery may typically be caused by problems either with derivation or extraction from the aqueous liquid phase (e.g. emulsification caused by the sample matrix properties). As the internal standard simulates the tested compounds behaviour during the analytical procedure a low recovery of the internal standard will reflect a corresponding recovery of the tested compounds in the sample in question. This will cause a general lower sensitivity of the method and thus an increase of the limit of detection.

There may be an increase in the limit of detection for single sample for only one or several of the tested compounds. In such cases the reason is that other content compounds in the sample generate (interference with) the chromatographical analysis and prevent detection of a possible content close to the method's normally low limit of detection.

TABLE 1. THE RESULTS FOR THE ANALYSES FOR EXTRACTABLE ORGANIC TIN COMPOUNDS IN MATTRESS PADS, TOP MATTRESSES, AND BABY DUVETS. TWO RESULTS INDICATE DOUBLE IDENTIFICATION. THE RESULTS ARE STATED IN $\mu\text{G}/\text{KG}$.

	LOD	1		2		3		4		5	
Monobutyltin (MBT)	5	-	-	-	-	-	-	-	-	-	-
Dibutyltin (DBT)	5	-	-	-	-	-	-	-	-	-	-
Tributyltin (TBT)	2	-	-	-	-	-	-	-	-	3	3
Tetrabutyltin	10	-	-	-	-	-	-	-	-	-	-
Monooctyltin	10	-	-	-	-	-	-	-	-	-	-
Diocetyltn	10	-	-	-	-	-	-	-	-	-	-
Tricyclohexyltin	10	-	-	-	-	-	-	-	-	-	-
Triphenyltin	10	-	-	-	-	-	-	-	-	-	-

∴ Means less than the limit of detection

LOD: Indicates the limit of detection.

TABLE 1, CONTINUED. THE RESULTS FOR THE ANALYSES FOR EXTRACTABLE ORGANIC TIN COMPOUNDS IN MATTRESS PADS, TOP MATTRESSES, AND BABY DUVETS. TWO RESULTS INDICATE DOUBLE IDENTIFICATION. THE RESULTS ARE STATED IN $\mu\text{G}/\text{KG}$.

	LOD	6		7		8		9		10	
Monobutyltin (MBT)	5	-	-	-	-	-	-	< 20*	< 20*	< 10*	< 10*
Dibutyltin (DBT)	5	-	-	-	-	-	-	< 20*	< 20*	< 10*	< 10*
Tributyltin (TBT)	2	-	-	15	19	-	-	< 10*	< 10*	< 5*	< 5*
Tetrabutyltin	10	-	-	-	-	-	-	< 50*	< 50*	< 20*	< 20*
Monooctyltin	10	-	-	-	-	-	-	< 50*	< 50*	< 20*	< 20*
Diocetyl tin	10	-	-	-	-	-	-	< 50*	< 50*	< 20*	< 20*
Tricyclohexyltin	10	-	-	-	-	-	-	< 50*	< 50*	< 20*	< 20*
Triphenyltin	10	-	-	-	-	-	-	< 50*	< 50*	< 20*	< 20*

-: Means less than the limit of detection

LOD: Indicates the limit of detection.

* Indicates increased limit of detection due to interference from the sample.

Table 1, continued. The results for the analyses for extractable organic tin compounds in mattress pads, top mattresses, and baby duvets. Two results indicate double identification. The results are stated in $\mu\text{G}/\text{kg}$.

	LOD	11		12		13		14		15	
Monobutyltin (MBT)	5	-	-	< 10*	< 10*	-	-	5	5	-	-
Dibutyltin (DBT)	5	-	-	< 10*	< 10*	-	-	-	-	-	-
Tributyltin (TBT)	2	-	-	< 5*	< 5*	-	-	-	-	-	-
Tetrabutyltin	10	-	-	< 20*	< 20*	-	-	-	-	-	-
Monooctyltin	10	-	-	< 20*	< 20*	-	-	-	-	-	-
Diocetyl tin	10	-	-	< 20*	< 20*	-	-	-	-	-	-
Tricyclohexyltin	10	-	-	< 20*	< 20*	-	-	-	-	-	-
Triphenyltin	10	-	-	< 20*	< 20*	-	-	-	-	-	-

-: Means less than the limit of detection

LOD: Indicates the limit of detection.

* Indicates increased limit of detection due to interference from the sample.

Table 1, continued. The results for the analyses for extractable organic tin compounds in mattress pads, top mattresses, and baby duvets. Two results indicate double identification. The results are stated in µg/kg.

	LOD	16		17	
Monobutyltin (MBT)	5	-	-	-	-
Dibutyltin (DBT)	5	-	-	-	-
Tributyltin (TBT)	2	-	-	-	-
Tetrabutyltin	10	-	-	-	-
Monooctyltin	10	-	-	-	-
Diocetyl tin	10	-	-	-	-
Tricyclohexyltin	10	-	-	-	-
Triphenyltin	10	-	-	-	-

-: Means less than the limit of detection

LOD: Indicates the limit of detection.

* Indicates increased limit of detection due to interference from the sample.

6.2 STRATIFICATION OF PRODUCTS

The Danish Environmental Protection Agency wanted to stratify the products where a content of one or more organic tin compounds were detected in order to determine whether the compounds were present in all layers or exclusively originated from one layer. Furthermore, the Danish Environmental Protection Agency wants to include the products with increased limit of detection due to interference. The products with detected content were 5, 7, and 14 and the products with increased limit of detection were 9, 10, and 12.

Undermentioned the results for the organic tin compounds that could be extracted from the single layer in the products. The limits of detection are stated in the table.

TABLE 2. RESULTS FOR ANALYSES FOR EXTRACTABLE ORGANIC TIN COMPOUNDS IN THE SINGLE LAYER FROM THE SELECTED PRODUCTS. TWO RESULTS INDICATE DOUBLE IDENTIFICATION. THE RESULTS ARE STATED IN µG/KG.

	LOD	5					
		Ticking		Felt layer		Heat layer	
Monobutyltin (MBT)	5	-	-	-	-	6	6
Dibutyltin (DBT)	5	-	-	-	-	-	-
Tributyltin (TBT)	2	-	-	2	2	-	-
Tetrabutyltin	10	-	-	-	-	< 50*	< 50*
Monooctyltin	10	-	-	-	-	-	-
Diocetyl tin	10	-	-	-	-	-	-
Tricyclohexyltin	10	-	-	-	-	< 50*	< 50*
Triphenyltin	10	-	-	-	-	-	-

-: Means less than the limit of detection

LOD: Indicates the limit of detection.

* Indicates increased limit of detection due to interference from the sample.

TABLE 2, CONTINUED. RESULTS FOR ANALYSES FOR EXTRACTABLE ORGANIC TIN COMPOUNDS IN THE SINGLE LAYER FROM THE SELECTED PRODUCTS. TWO RESULTS INDICATE DOUBLE IDENTIFICATION. THE RESULTS ARE STATED IN $\mu\text{G}/\text{KG}$.

	LOD	7					
		Ticking		Felt layer		Core	
Monobutyltin (MBT)	5	< 10*	< 10*	13	12	-	-
Dibutyltin (DBT)	5	< 10*	< 10*	5	5	5	7
Tributyltin (TBT)	2	< 5*	< 5*	45	29	9	11
Tetrabutyltin	10	< 20*	< 20*	-	-	-	-
Monooctyltin	10	< 20*	< 20*	-	-	-	-
Diocetyl tin	10	< 20*	< 20*	-	-	-	-
Tricyclohexyltin	10	< 20*	< 20*	-	-	-	-
Triphenyltin	10	< 20*	< 20*	-	-	-	-

:- Means less than the limit of detection

LOD: Indicates the limit of detection.

* Indicates increased limit of detection due to interference from the sample.

TABLE 2, CONTINUED. RESULTS FOR ANALYSES FOR EXTRACTABLE ORGANIC TIN COMPOUNDS IN THE SINGLE LAYER FROM THE SELECTED PRODUCTS. TWO RESULTS INDICATE DOUBLE IDENTIFICATION. THE RESULTS ARE STATED IN $\mu\text{G}/\text{KG}$.

	LOD	9					
		Ticking		Felt layer		Core	
Monobutyltin (MBT)	5	7	5	-	-	-	-
Dibutyltin (DBT)	5	-	-	-	-	-	-
Tributyltin (TBT)	2	-	-	-	-	-	-
Tetrabutyltin	10	-	-	-	-	-	-
Monooctyltin	10	-	-	-	-	-	-
Diocetyl tin	10	-	-	-	-	-	-
Tricyclohexyltin	10	-	-	-	-	-	-
Triphenyltin	10	-	-	-	-	-	-

:- Means less than the limit of detection

LOD: Indicates the limit of detection.

TABLE 2, CONTINUED. RESULTS FOR ANALYSES FOR EXTRACTABLE ORGANIC TIN COMPOUNDS IN THE SINGLE LAYER FROM THE SELECTED PRODUCTS. TWO RESULTS INDICATE DOUBLE IDENTIFICATION. THE RESULTS ARE STATED IN $\mu\text{G}/\text{KG}$.

	LOD	10					
		Ticking		Felt layer		Core	
Monobutyltin (MBT)	5	-	-	-	-	< 20*	< 20*
Dibutyltin (DBT)	5	-	-	-	-	< 20*	< 20*
Tributyltin (TBT)	2	2	2	-	-	< 10*	< 10*
Tetrabutyltin	10	-	-	-	-	< 40*	< 40*
Monooctyltin	10	-	-	-	-	< 40*	< 40*
Dioctyltin	10	-	-	-	-	< 40*	< 40*
Tricyclohexyltin	10	-	-	-	-	< 40*	< 40*
Triphenyltin	10	-	-	-	-	< 40*	< 40*

-: Means less than the limit of detection

LOD: Indicates the limit of detection.

* Indicates increased limit of detection due to interference from the sample.

TABLE 2, CONTINUED. RESULTS FOR ANALYSES FOR EXTRACTABLE ORGANIC TIN COMPOUNDS IN THE SINGLE LAYER FROM THE SELECTED PRODUCTS. TWO RESULTS INDICATE DOUBLE IDENTIFICATION. THE RESULTS ARE STATED IN $\mu\text{G}/\text{KG}$.

	LOD	12					
		Ticking		Felt layer		Core	
Monobutyltin (MBT)	5	-	-	-	-	-	-
Dibutyltin (DBT)	5	-	-	-	-	14	15
Tributyltin (TBT)	2	-	-	-	-	-	-
Tetrabutyltin	10	-	-	-	-	< 50*	< 50*
Monooctyltin	10	-	-	-	-	-	-
Dioctyltin	10	-	-	-	-	-	-
Tricyclohexyltin	10	-	-	-	-	< 50*	< 50*
Triphenyltin	10	-	-	-	-	-	-

-: Means less than the limit of detection

LOD: Indicates the limit of detection.

* Indicates increased limit of detection due to interference from the sample.

TABLE 2, CONTINUED. RESULTS FOR ANALYSES FOR EXTRACTABLE ORGANIC TIN COMPOUNDS IN THE SINGLE LAYER FROM THE SELECTED PRODUCTS. TWO RESULTS INDICATE DOUBLE IDENTIFICATION. THE RESULTS ARE STATED IN $\mu\text{G}/\text{KG}$.

	D.G.	14					
		Bolster		Filtlag		Core	
Monobutyltin (MBT)	5	-	-	12	18	-	-
Dibutyltin (DBT)	5	-	-	-	-	-	-
Tributyltin (TBT)	2	-	-	-	-	-	-
Tetrabutyltin	10	-	-	-	-	-	-
Monooctyltin	10	-	-	-	-	-	-
Diocyltin	10	-	-	-	-	-	-
Tricyclohexyltin	10	-	-	-	-	-	-
Triphenyltin	10	-	-	-	-	-	-

∴ Means less than the limit of detection

LOD: Indicates the limit of detection.

In the sample with increased limits of detection (9, 10, and 12) the interference could be concretised to one single layer (the core in sample 10) or limited to single components in the single layer (tetrabutyltin and tricyclohexyltin in the core of sample 12). For all three samples (9, 10, and 12) the stratification lowered the limit of detection where there was no interference that resulted in minor amounts of organic tin compounds being detected in the single layer.

For samples with detected amount (sample 5, 7, and 14) new components could likewise be detected at stratification. In sample 5 MBT could be determined in the heat layer (a woollen layer) and TBT in the felt layer. Both values are just above the limit of detection.

For sample 7 the stratification resulted in the appearance of new components. MBT, DBT, and TBT were all detected in the felt layer and DBT and TBT were detected in the core. For sample 14 no “new” components were detected at the stratification with an increase of the value for MBT and a localisation of the felt layer.

Generally the stratification of the products resulted in a lowering of the limits of detection thus causing new detections. Thus the stratification gave new information compared to the original analyses.

6.3 MIGRATION TEST

As requested by the Danish Environmental Protection Agency a migration test was performed on the three products that contained organic tin compounds. The simulant was artificial sweat and the test was performed at 40°C for 48 hours. The result of the test is given in table 3.

TABLE 3. RESULT FOR EXTRACTABLE ORGANIC TIN COMPOUNDS IN THE SIMULANT. TWO RESULTS INDICATE DOUBLE IDENTIFICATION. THE RESULTS ARE STATED IN µG/KG.

	LOD	5		7		14	
Monobutyltin (MBT)	0.2	-	-	-	-	-	-
Dibutyltin (DBT)	0.1	-	-	-	-	-	-
Tributyltin (TBT)	0.05	-	-	-	-	-	-
Tetrabutyltin	0.1	-	-	-	-	-	-
Monooctyltin	0.1	-	-	-	-	-	-
Diocyltin	0.1	-	-	-	-	-	-
Tricyclohexyltin	0.1	-	-	-	-	-	-
Triphenyltin	0.1	-	-	-	-	-	-

∴ Means less than the limit of detection

LOD: Indicates the limit of detection.

Provided that the limit of detection is converted it corresponds to 0.7 – 6.0 µg/kg mattress or 0.01 – 0.05 µg/dm².

The migration test results in no detected liberation of organic tin compounds at simulated use of the products.

7 Summary and conclusions

7.1 CONTENT ANALYSES

Tributyltin (TBT) was detected in two products and monobutyltin (MBT) in one product at the content analyses. Furthermore, there was an increased limit of detection for three of the products due to interference from the samples.

7.2 STRATIFICATION OF THE PRODUCTS

The Danish Environmental Protection Agency wanted determined where the organic tin compounds occurred in the products. Therefore the three products with determined content and the three products with increased limit of detection were stratified and analysed.

For samples 5, 9, and 10 the results are close to the limit of detection. Due to the stratification the interference from the samples could be concretised to one layer or specific compounds in one single layer.

No general tendency could be determined as regards the occurrence of organic tin in specific materials as the components could be detected in all layers – however, not in the same product.

Generally the stratification of the products resulted in a lowering of all limits of detection for which reason new detections occurred.

7.3 MIGRATION TEST

The migration test was performed with artificial sweat as simulant and incubated at 40°C for 48 hours. No organic tin compounds were detected in the simulant following the migration test for which reason no exposure of the consumer could be determined at simulated used of the products under the given conditions.

