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TNO-report

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The Determination of Selected Additives in Consumer Products

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Summary

That hazardous chemicals are present in our environment is confirmed by several studies and is becoming increasingly well documented. Such chemicals are not only found outdoors, but also in ordinary house dust from virtually every home. Among these chemicals are additives that are nowadays used in many consumer goods we buy and use in our home everyday. Following a previous study that focused on textiles, toys, cosmetic and cleaning products, this study focuses on an additional number of consumer products found in many homes, e.g. electronic equipment, sport shoes, mattresses, some food packaging materials and vinyl flooring. Selected products were tested for alkylphenols and alkylphenol ethoxylates, phthalates, brominated flame retardants and organotin compounds.

The results show that with the exception of the vinyl flooring and the electronic equipment, the amount of the listed additives identified in the tested products was limited. With the exception of one of the television sets, all electronic equipment contained high amounts of tetrabromobisphenol-A, in most cases mainly in the polymerised form. It was surprising that in two of the computers tetrabromobisphenol-A was also used as an additive flame retardant, resulting in concentrations up to 20% by weight of tetrabromobisphenol-A monomer in the product. Two of the three sport shoes and the vinyl flooring both contained phthalates. The sport shoes contained up to 3,300 mg/kg DEHP while the total phthalate content of the vinyl flooring was over 40% by weight. The sport shoes also contained nonylphenol ethoxylates and limited amounts of nonylphenol and organotin compounds. The cheese packaging material did contain low amounts of nonylphenol and in one case bisphenol-A. Finally, the mattresses only contained low amounts of phthalates, some nonylphenol ethoxylates and only traces of organotin compounds.

Contents

1. Introduction

The progress of the chemical industry in the past century has supplied the world with a vast amount of chemicals. At present roughly 100,000 chemicals are used and more than 500 new chemicals are introduced annually[1]. From these, several are known to cause adverse effects to man and animal life. The best documented are probably the persistent organic pollutants (POPs), such as the polychlorinated biphenyls (PCB) and the pesticide DDT. Although the use of chemicals as PCBs and DDT is forbidden for some time, it is still possible to measure these compounds in the environment worldwide due to their use in the past. Meanwhile, new chemicals have replaced these compounds, and some of these chemicals, like phthalates, alkylphenols (AP) and alkylphenol ethoxylates (APEO) and flame retardants are produced and used in huge amounts. As a result, these compounds can be found in all environmental compartments and for instance in house dust[2,3]. A recent TNO study showed that phthalates, alkylphenols and alkylphenol ethoxylates and brominated flame retardants were present in precipitation samples[4]. Another study showed that these compounds are also present in typical consumer products like textiles, cosmetic products and toys[5].

Only few people are aware that many of these chemicals are used as additives in consumer goods we buy and use in our home everyday. Of course, these additives are there for a reason, for example, phthalates are added to soften plastics and flame retardants are used in electronic equipment to reduce the risk of fire in the case of overheating of equipment. However, a consequence of their presence in consumer products is that the user is constantly exposed to these chemicals and that they will enter the environment during, or after use of the products. This study focuses on the determination of the presence of a number of additives, alkylphenols and alkylphenol ethoxylates, phthalates and brominated flame retardants and organotin compounds in a number of typical consumer products.

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1 Jackson T. In: Material Concerns. Pollution, profit and quality of life. Routledge, London, ISBN 0-415-13248-7, 40, **1996**.

2 Vethaak A.D., Rijs G.B.J., Schrap S.M., Ruiter H., Gerritsen A., Lahr J. In: Estrogens and xeno-estrogens in the aquatic environment of the Netherlands. RIZA/RIKZ-report no. 2002.001, February **2002**.

3 Santillo D, Labunska I, Davidson H, Johnston P, Strutt M and Knowles O. Consuming Chemicals, Greenpeace Research Laboratories Technical Note 01/2003 (GRL-TN-01-2003), **2003**.

4 Peters R.J.B. Hazardous Chemicals in Precipitation. TNO report R 2003/198, May **2003**.

5 Peters R.J.B. Hazardous Chemicals in Consumer Productrs. TNO report R 2003/370, September **2003**.

2. Study objective and approach

2.1 Objective of the Greenpeace study

A recent TNO study revealed the presence of a number of hazardous chemicals in consumer products[5]. The consumer products tested in that study were mainly textiles, cosmetic and cleaning products. The objective of this study is to determine whether these compounds are also present in other consumer products like electronic equipment and mattresses. Their presence in these products may explain the detection of these compounds in the dust in common homes[3]. This study presents the results for the presence and concentrations of compounds in additional consumer products like computers, television sets, mattresses and sport shoes.

2.2 Chemical parameters

In this study the decision was made to concentrate on compounds similar to those that were analysed in the previous study in precipitation. The following chemical parameters were selected for this study:
- Bisphenol-A
- Alkylphenols and alkylphenol ethoxylates
- Phthalates
- Brominated flame retardants
- Organotin compounds

The individual chemicals are listed in table 1. Some additional information about the use of these compounds can be found in chapter 4.

2.3 Samples

In total 19 samples were received from Greenpeace in The Netherlands. The samples are common consumer products, including television sets, computers, cell phones, sport shoes, mattresses and vinyl flooring. All samples were purchased by Greenpeace in common shops in October 2003 and coded. Table 2 provides an overview of the received samples.

Table 1 Compound groups and specific compounds included in this study.

Group	Specific compounds	Acronym
Phthalates	dimethyl phthalate	DMP
	diethyl phthalate	DEP
	di-iso-butyl phthalate	DIBP
	di-n-butyl phthalate	DBP
	benzylbutyl phthalate	BBP
	dicyclohexyl phthalate	DCHP
	di-(2-ethylhexyl) phthalate	DEHP
	di-n-octyl phthalate	DOP
	di-iso-nonylphthalate	DINP
	di-iso-decyl phthalate	DIDP
Flame retardants	2,2',4,4'-tetrabromo diphenylether	BDE 47
	2,2',4,4',5-pentabromo diphenylether	BDE 99
	2,2',4,4',6-pentabromo diphenylether	BDE 100
	2,2',4,4',5,5'-hexabromo diphenylether	BDE 153
	2,2',3,4,4',5',6-heptabromo diphenylether	BDE 183
	octabromo diphenylether	BDE octa
	decabromo diphenylether	BDE 209
	hexabromo cyclododecane	HBCD
	tetrabromo bisphenol-A	TBBA
Bisphenol-A	Bisphenol-A	BPA
Alkylphenols and alkylphenol ethoxylates	octylphenol	OP
	nonylphenol	NP
	octylphenol ethoxylates	OPEO
	nonylphenol ethoxylates	NPEO
Organotins	monobutyltin	MBT
	dibutyltin	DBT
	tributyltin	TBT
	tetrabutyltin	TeBT
	monooctyltin	MOT
	dioctyltin	DOT
	triphenyltin	TPT

Table 2 Overview of samples and chemical parameters to be determined.

TNO Code	Greenpeace Code	Product Description	Chemical parameters to be determined				
			BpA	AP/APEO	Phthal	BFR	O-Tin
52003305-001	GP-1	Television: Philips Real Flat: 21PT 5507/01				X	
52003305-002	GP-2	Television: Samsung Plano: CW21A083NXXEC				X	
52003305-003	GP-3	Television: Panasonic TX: 21CK1C				X	
52003305-004	GP-4	Cell phone: Sony/Ericson T610: 35126300-200751-5			X	X	
52003305-005	GP-5	Cell phone: Samsung SGH-A800: 351004/26/634004/8			X	X	
52003305-006	GP-6	Cell phone: Siemens A55: 351855002740670			X	X	
52003305-007	GP-7	Computer: HP Pavilion A250 NL: NLD 33135B4				X	
52003305-008	GP-8	Computer: Dell Optiflex GX240: FJ01G0J				X	
52003305-009	GP-9	Computer: IBM NetVista: 68233KG KBDALYN				X	
52003305-010	GP-10	Shoes: Nike Air Max Plus: 604133 161	X	AP	X		X
52003305-011	GP-11	Shoes: Puma Torceira IT: 100287 05	X	AP	X		X
52003305-012	GP-12	Shoes: Adidas Gammanova 2 IN: 382429	X	AP	X		X
52003305-013	GP-13	Cheese: Unie kaas Goudse belegen ugd 24/12/03	X	X			
52003305-014	GP-14	Cheese: Royal Gouda Jonge kaas 48+ ugd 17/12/03	X	X			
52003305-015	GP-15	Cheese: Frico Kollumer ugd 19/12/03	X	X			
52003305-016	GP-16	Mattasses: Auping Inizio WH Pocket soepel: AB1512	X	X	X	X	X
52003305-017	GP-17	Mattasses: Springfield Ravanna	X	X	X	X	X
52003305-018	GP-18	Mattasses: Ubica Atlanta	X	X	X	X	X
52003305-019	GP-19	Vinyl flooring: Forbo	X	X	X		

3. Methods and materials

3.1 Sample pre-treatment

Samples were stored at room temperature until analysis. All electronic equipment was disassembled and all glass (television tubes), metal parts and electric wiring removed. All plastic materials and printed circuit boards were broken in small pieces. From these and from the other samples proportional sub-samples, with respect to the different parts, were collected. Parts from electronic equipment were grinded into small pieces of <1 mm. Sub-samples of the other samples were cut into pieces smaller than 5 mm with clean scissors or a surgical knife for all other samples. Following homogenisation of each sub-sample, an analytical sample of 1, 2 or 5 grams was collected, depending on the type of analysis.

3.2 Analytical procedures

3.2.1 Sample extraction

3.2.1.1 Bisphenol-A, alkylphenols and ethoxylates

The analytical sample was soxhlet extracted overnight with dichloromethane. The extract was filtered if necessary and brought to a final volume of 100 ml with dichloromethane. A part of this extract was evaporated to dryness under nitrogen. The residue was re-dissolved in a 50/50 mixture of HPLC water and methanol. Finally, the extract was filtered through a 0.45 µm filter and prepared for instrumental analyses.

3.2.1.2 Phthalates

The analytical sample was brought into a soxhlet thimble and extracted overnight with dichloromethane. The extract was filtered if necessary and brought to a final volume of 100 ml with dichloromethane. A part of this extract was concentrated, filtered through 0.45 µm filter and brought to a final volume of 1 ml. Finally, 1,2,3,4-tetrachloronaphthalene was added as an injection standard.

3.2.1.3 Flame retardants

The analytical sample was brought into a soxhlet thimble and extracted overnight with dichloromethane. The extract was filtered if necessary and brought to a final volume of 100 ml with dichloromethane. A part of this extract was concentrated and filtered through 0.45 µm filter. Diazomethane was added for the derivatization of any free tetrabromobisphenol-A in the sample extract. Finally, the extract was concentrated to a volume of 1 ml and 1,2,3,4-tetrachloronaphthalene was added as an injection standard.

For samples from electronic equipment an additional, and different, determination is performed. Many of these materials do contain tetrabromobisphenol-A in a polymerised, non-extractable, form. The presence of tetrabromobisphenol-A is confirmed using the extraction method described above, however, only the residual monomer fraction is determined. The total tetrabromobisphenol-A content, the sum of the monomer and polymer fraction, can only be determined after destruction to bromine. Therefore, a sub-sample of the grinded sample material is collected and digested in a Na/K carbonate melt at 900 ºC. The bromine content of the resulting carbonate mix is determined with ion chromatography. The amount of bromine is recalculated to tetrabromobisphenol-A, which than indicates the maximum amount of tetrabromobisphenol-A in the sample (sum of monomer and polymer).

3.2.1.4 Organotin determination

A sub-sample was sonicated for 60 min in a sodium dithiocarbamate solution in ethanol after the addition of tripropyltin chloride (TPrT) as an internal standard. The extracts are left in the dark at room temperature overnight and sonicated a second time for 60 min. Next, the extracts were centrifuged and the sample residue removed. Two more internal standards, mono- and diheptyltin chloride (MHT and DHT) were added to control the extraction and derivatization procedure. After the addition of an acetate buffer (pH 4), HPLC water and a solution of sodium tetraethylborate (the derivatization agent) in ethanol, the mixture was extracted twice with hexane. The combined hexane fraction were dried and concentrated to a small volume. After purification of the extract using column chromatography on alumina, the extract is concentrated to a final volume of 1 ml and 1,2,3,4-tetrachloronaphthalene is added as an injection standard.

3.2.2 Instrumental analysis

Bisphenol-A, alkylphenols and alkylphenol ethoxylates are analysed using liquid chromatography in combination with mass spectrometry (LC/MS). The LC/MS was a Hewlett Packard 1100 LC/ESI/MS system equipped with a guard column and a Waters Symmetry C_{18} analytical column, length 15 cm, 3.9 mm i.d., 5 µm

particle size. For bisphenol-A and alkylphenols negative ionisation was used, for alkylphenol ethoxylates positive ionisation. The mass spectrometer was used in the selected ion monitoring mode and typically three ions were monitored for bisphenol-A and alkylphenols. For alkylphenol ethoxylates fifteen ions (for n=1 to n=15, each separated by 44 mass units) were monitored.

Phthalates, brominated flame retardants and organotin compounds were analysed using gas chromatography in combination with mass spectrometry (GC/MS). The GC/MS was a Hewlett Packard 6890 gas chromatograph equipped with HP-5MS capillary column, length 30 m, 0.25 mm i.d., 0.25 µm film thickness, and interfaced to a Hewlett Packard 5973 mass spectrometer. The mass spectrometer was used in the selected ion monitoring mode and typically two or three ions were monitored for each compound.

3.2.3 Calculation of results

Identification of target compounds was based on retention time and qualifier ion ratios. Quantification was based on external standards analysed within the same series as the sample extracts. The external standards were prepared from commercially available pure substances. The number of ethoxy units in the commercial alkylphenol ethoxylate standards ranged from n=5 to n=15 with a maximum around n=8-9. In all cases peak areas were used for calculations. The recovery of the added extraction standards was calculated but only the organotin results were corrected for this recovery. No correction for blank value was applied.

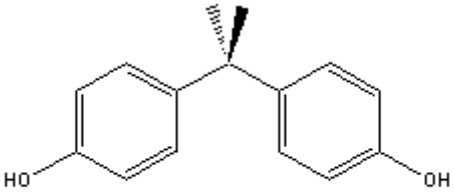
With the exception of the electronic equipment the results are expressed in mg/kg product. For the electronic equipment all glass and metal parts, and all electric wiring was removed prior to sub-sampling. This means that the results are expressed in mg/kg for the sum of all polymer parts of the products and not in mg/kg product.

4. Results

4.1 Bisphenol-A

4.1.1 General information

Bisphenol-A (BPA) is a widely used intermediate in the production of epoxy resins, polycarbonate plastics and flame retardants, e.g. a substance used in an extensive range of products. BPA is the most common monomer for polycarbonates intended for food contact[1]. Not polymerised BPA may be released from the polycarbonate and thus enter the environment or food products. The chemical structure of BPA is given in the figure below.



Bisphenol-A

4.1.2 Results for bisphenol-A in this study

BPA was determined in the samples 52003305-010 to -019, e.g. sport shoes, packaging foil of cheese, mattresses and vinyl flooring. BPA was found in only one of the cheese packaging foils (52003305-015) at a level of 1.2 mg/kg. BPA has been found previously in similar concentrations in the polymer coating of food cans[2]. In two of the three sport shoes traces of bisphenol-A was identified, but these were below the quantification limit of the method used in this study, 0.5 mg/kg.

The results for BPA are presented in table A.1 in the appendix.

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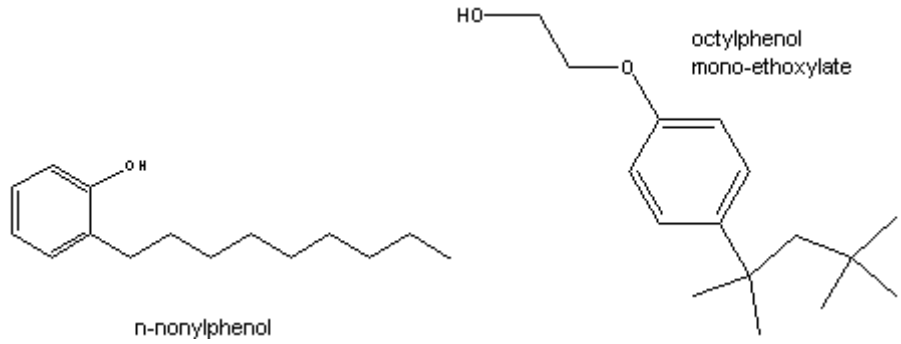
1 Mountfort KA, Kelly J, Jickels SM, Castle L. Food Additives and Contaminations, 56-63, *14*, **1997**.

2 Goodson A, Summerfield W, Cooper I. Food Additives and Contaminants. 1-12, *19*, **2002**.

4.2 Alkylphenol and alkylphenol ethoxylates

4.2.1 General information

Alkylphenols (APs) and alkylphenol ethoxylates (APEOs) are used in plastics as additives and as surface-active ingredients in industrial detergents and emulsifiers. APs commonly used are nonylphenol (NP) and to a lesser extent octylphenol (OP), in both cases pre-dominantly the para-substituted isomers (>90%). APEOs are used as emulsifiers in textile and carpet cleaning products, and as emulsifiers in solvents and agricultural pesticides[1]. As with the APs, nonylphenol ethoxylate (NPEO) is more used than octylphenol ethoxylate (OPEO). The chemical structure of n-nonylphenol and octylphenol-mono-ethoxylate (better known as Triton X-100) are presented below.



4.2.2 Results for alkylphenols and alkylphenol ethoxylates in this study

In total 10 products were analysed for APs and APEOs. These included sport shoes, the packaging foil of cheese, mattresses and vinyl flooring. APs or APEOs, or both were detected in all samples, however in very different amounts. The sport shoes (52003305-010 to -012) mainly contain NPEO and NP in concentrations up to 2100 mg/kg for NPEO and 290 mg/kg for NP. The sample containing the highest amounts NP and NPEO (52003305-010) in addition contained some OPEO, probably as an impurity in the NPEO used in the production of the base materials.

The cheese packaging foil samples all contained low amounts of NP, ranging from 1.3 to 3.4 mg/kg. This is in agreement with the results from another presently conducted study where similar concentrations of NP are found in wrapping foils for food packaging.
All mattresses contained NPEO in concentrations ranging from 25 to 190 mg/kg. The sample with the highest concentration of NPEO in addition contained low con-

[1] Maguire R.J. Water Qual. Res. J. Canada 34, 37-78, **1999**.

centrations of NP and OPEO, again probably as an impurity in the NPEO used in the production of the base materials.
The vinyl flooring sample contained NPEO in a concentration of 460 mg/kg. As in the mattresses samples NP and OPEO were identified also, however, in much lower concentrations.

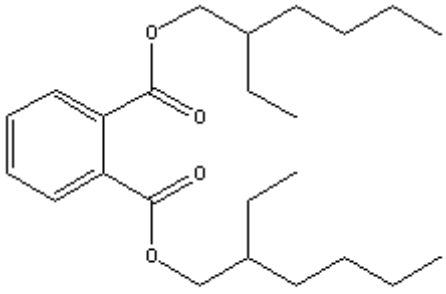
The complete results for AP and APEO are presented in table A.1 in the appendix.

4.3 Phthalates

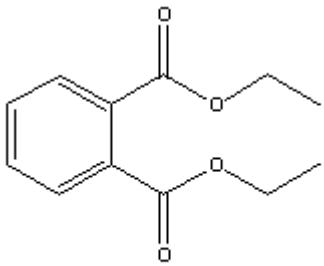
4.3.1 General information

Phthalates are commonly found in soft plastics, cosmetic and personal care products. In general phthalates are used as plasticizers to increase the flexibility of high molecular weight polymers. In some soft plastics phthalates may comprise up to 50% of the total weight. Major phthalates used are di-(2-ethylhexyl) phthalate (DEHP) and di-iso-nonyl phthalate (DINP). In food packaging materials a similar type of compound, di-iso-octyl adipate, the di-iso-octyl ester of hexanedioic acid, is often used instead of phthalates.

Due to the presence of phthalates in common household products, cosmetics and toys, the potential for human exposure is very high. The EU has imposed an emergency restriction for 6 phthalates (DBP, BBP, DEHP, DOP, DINP and DIDP) in articles for children in the age of 0-3 years[1]. The chemical structure of DEHP and DEP is presented below.



di-(2-ethylhexyl phthalate (DEHP)



diethyl phthalate (DEP)

[1] Rastogi SC, Worsoe IM. Danisch National Environmental Research Institute. NERI Technical Report No. 373, **2001**.

4.3.2 Results for phthalates in this study

In total 10 products were analysed for phthalates. These include cell phones, sport shoes, mattresses and the vinyl flooring material. Only low concentrations of phthalates were found in the cell phones and the mattresses, the highest concentration being 120 mg/kg DEHP in one of the cell phones. This indicates that these phthalates are probably not true additions, but more likely residues resulting from the raw production materials or otherwise. In two of the sport shoes higher concentrations of DIBP, sample 52003305-010 concentration 1700 mg/kg, and DEHP, sample 52003305-011 concentration 3300 mg/kg were found. The third type of sport shoe showed only low concentrations of phthalates up to 35 mg/kg for DEHP. In the mattresses only low amounts of various phthalates were found that were probably residues resulting from the raw production materials. As expected the vinyl flooring material contained the highest concentrations of phthalates, especially BBP and another phthalate that was identified as di-iso-heptyl phthalate. The concentration of BBP was 150,000 mg/kg while the concentration of di-iso-heptyl phthalate (based on the response factor of BBP) was estimated to be 270,000 mg/kg. This means that the total phthalate content of this material is over 40% by weight.

The complete results of the phthalate analysis are presented in table A.2 in the appendix.

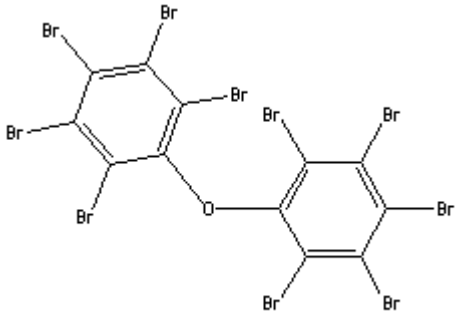
4.4 Brominated flame retardants

4.4.1 General information

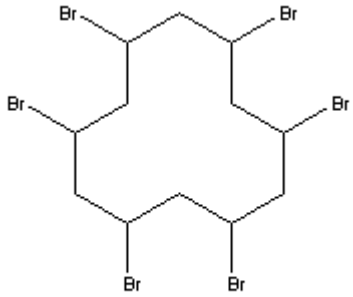
Flame retardants are added to polymers used in a wide range of materials such as electric and electronic equipment, paint, textiles and in carts and aircraft to prevent them from catching fire. Within the group of the brominated flame retardants two types of flame retardants can be distinguished.
Polybrominated diphenyl ethers (PBDE) are so-called additive flame retardants. PBDEs are used as commercial mixtures such as Bromkal, with different degrees of bromination. Typically, PBDEs may comprise up to 5% to 20% of the total weight of a product to which they are added. Since these chemicals are not chemically bound they may “leak” from the polymer product, thus entering the environment. Hexabromocyclododecane (HBCD) is a cyclo-aliphatic brominated chemical meant to partially replace PBDEs because of their known toxicity. HBCD is also an additive flame retardant and can enter the environment in much the same way.

Tetrabromobisphenol-A (TBBA) can be used as both a reactive and an additive flame retardant. In its more common reactive use, it is added to materials as a co-polymer, which means that it is chemically bound to, and part of, the polymer ma-

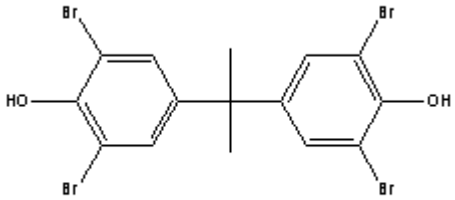
terial itself. TBBA is used in this way in epoxy polymers such as printed circuit boards in electronic equipment like computers and television sets. Even when used in this manner, small amounts of the TBBA monomer will not be polymerized and can "leak" into the environment. In other cases, mostly in ABS plastics, TBBA is used as an additive flame retardant in concentrations up to 16% by weight[1,2]. Its use in this additive mode can result in proportionately much higher losses to the environment from products during use than when used reactively.
The chemical structure of decabromodiphenylether (BDE-209), HBCD and TBBA are presented below.



decabromo diphenylether (BDE 209)



hexabromo cyclododecane (HBCD)



tetrabromo bisphenol-A (TBBA)

4.4.2 Results for brominated flame retardants in this study

A number of relevant PBDE, HBCD and TBBA were determined in the electronic equipment samples in this study, e.g. television sets, computers and cell phones, and in mattresses. For the interpretation of the data, especially those of the electronic equipment, it is necessary to understand how the final sample is prepared. For the electronic equipment all metal parts and glass parts, e.g. the television tube itself, and all electrical wiring were removed. From all remaining parts that could

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1 Luijk R. PhD dissertation "Formation of polyhalogenated dibenzo-p-dioxins and benzofurans during thermal degradation processes" University of Amsterdam, may **1993**.

2 Danish Environmental Protection Agency, Environmental Project no. 494 1999, "Brominated Flame Retardants", www.mst.dk/udgiv/Publications/1999/87-7909-416-3/html/default_eng.htm. **1999**.

be differentiated visually, proportional sub-samples were collected. No differentiation has been made between printed circuit boards and other polymers. The amounts of these sub-samples were based on the estimated total amount of that particular part or material in the product. This means that only small sub-samples are collected from small parts while large sub-samples are collected from, for instance, the outside material of the product.

The results for the brominated flame retardants are presented in table A.3 in the appendix. In general, only small amounts of PBDE were found in three of the samples, one cell phone (52003305-004) and two computers (52003305-007 and 52003305-009). In the mattresses no brominated flame retardants were found at all. The relative amounts of the PBDE found in one of the computers clearly show the signature of the commercially available Octa-mix that consists mainly of hexa-, hepta- and octa-BDE. HBCD was identified in one of the computers (52003305-009) in a concentration of 70 mg/kg. The low concentrations of these brominated flame retardants indicate that these are not a true addition if they originate from a main polymer part of the product. More likely, they originate from a smaller sub-sample, e.g. from a small polymer part in the computer or cell phone.

For TBBA two different determinations, a specific extraction and destruction to bromine, are performed. As pointed out earlier TBBA is often used as a copolymer in the epoxy material of printed circuit boards. An extraction of the sample will only reveal the amount of monomer TBBA still present in the sample (column “TBBA-monomer” in table A.3). The polymerised TBBA can only be determined by destruction to bromine and recalculation of the bromine content to TBBA. Note that such a determination will produce a result that represents the maximum TBBA amount in the product (column “TBBA-maximum” in table A.3). The TBBA amount may even be overestimated if other bromine sources are present in the sample.

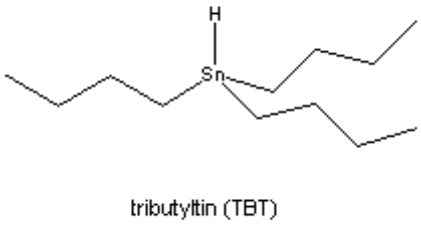
The results in table A.3 show that all electronic equipment contains TBBA in monomer or polymer form. Taking into account that only non-polymerised TBBA is available for extraction, and that the printed circuit board generally is not the major part of the polymer material in these products, only low or medium TBBA-monomer concentrations up to 100 mg/kg are expected to result from the printed circuit boards. This means that with the exception of samples 52003305-002, -007 and -009, TBBA results most likely from the printed circuit boards or minor parts of the electronic product. For the computers with TNO codes 52003305-007 and -009 the maximum- and monomer-TBBA concentrations are of the same order of magnitude, indicating that in these products TBBA is also used as an additive flame retardant. Sample 52003305-007 contains TBBA in its monomer form up to 20% by weight, probably originating from the computer monitor since the casing of the computer itself is mainly made of metal.

The complete results of the brominated flame retardants are presented in table A.3 in the appendix.

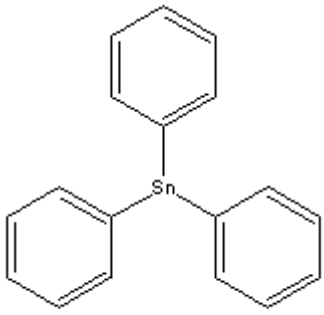
4.5 Organotin compounds

4.5.1 General information

There are three major applications for organotin compounds. First, the use of tributyltin (TBT) in anti-fouling paints for ships, secondly, the use of triphenyltin (TPT) as a pesticide, and third, the use of butyl- and octyltin compounds as stabilisers in polymers. Therefore, many textile products containing polymer parts, like T-shirts with prints, sanitary bandages, plasters and diapers, can contain organotin compounds[1]. In some occasions organotin compounds are used as fungicides on textiles that are exposed to extreme whether conditions, such as canvas. The structures of TBT and TPT are presented below.



tributyltin (TBT)



triphenyltin (TPT)

Until a few years ago mainly TBT and its degradation products dibutyltin (DBT) and monobutyltin (MBT) were found. Nowadays, it is more often di-octyltin (DOT) and mono-octyltin (MOT) that are found, always in the polymer parts (foam, plastic or adhesives) used in these of products[2]. Concentrations range from 0.01 mg/kg up to more than 2 mg/kg for textile products, and up to more than 50 mg/kg for polymer parts of products.

4.5.2 Results for organotin compounds in this study

In this study six samples, sport shoes and mattresses were analysed for seven individual organotin compounds. The organotin compounds MBT, DBT, MOT and DOT where found in the sport shoes in concentrations ranging from 0.05 to 2.0

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1 Gaikema F.J., Alberts P.J. Gaschromatografische bepaling van residuen van organotinverbindingen in textielproducten. De Ware(n)-Chemicus 1999, 23-33.

2 Observations of over four years of organotin determinations in materials by TNO

mg/kg product for the individual compounds. Since all parts of the shoes were sub-sampled it is not clear from which part the organotin compounds originate.
In the mattresses only low amounts of the organotin compounds DBT, TeBT and DOT were found with a maximum concentration of 0.07 mg/kg. These concentrations may be impurities in one of the base materials of the mattresses, but it is more likely that one of the base materials, present as a minor part of the entire sample, contains these organotins.

4.6 Quality control measurements

4.6.1 Method validation parameters

All methods applied were already used in earlier studies and were validated in according to research and development protocols. The linearity of the instrumental analysis is known but in this case the linearity of the complete method is not a very useful parameter since the concentrations in the products can be so far apart that extracts have to be concentrated or diluted for the result to fall in the linear range of the instrumental analysis.

The repeatability for each of the methods is determined by replicate analyses of the same sample. For homogenous samples, like the cheese packaging material, the repeatability is better than 15%. For non homogenous samples, like television sets, the repeatability within the collected sub-sample is comparable with the previous one, but the repeatability for the complete method, e.g. analysis including all sample pre-treatment, sub-sampling and analysis, is estimated to be no better than 50%.

The quantification limits are given in the result tables in the appendix and generally vary between 0.01 mg/kg and 1 mg/kg, depending on the type of analyses and expected result.

4.6.2 Recovery of extraction standard

Internal (extraction) standards were added for the determination of the organotin compounds. In all cases the recovery was above 70% and the results for the organotin compounds are corrected for this recovery. For the other compounds the addition of an extraction standard to a solid product sample, finely cut or grinded to small pieces, does not say much about the quality of the extraction. For the phthalates and flame retardants the quality of the extraction was tested additionally by extracting the same sample three times. Analyses showed that 100% of the analytes were found in the first extract.

4.6.3 Blank samples

With each series blank samples were included. These blank consisted of a complete analysis in the same series as the samples, however, without the addition of sample material. With the exception of the phthalate DEHP no blank values were observed.

5. Conclusions

In this study 19 consumer products have been tested for the presence various additives. A selected number of these 19 products were analysed for bisphenol-A, alkylphenols and ethoxylates, phthalates, flame retardants and organotin compounds.

- From the electronic equipment tested in this study, two of the computers contained high amounts of TBBA used as an additive flame retardant, in one sample up to 20% by weight. Six out of nine samples contained high amounts of polymerised TBBA probably originating from the printed circuit boards. Only traces of PBDEs and HBCD were found in the samples, mainly in the computers. In addition the cell phones were tested for the presence of phthalates. These were found, however, only in low concentrations.

- Two of the three sport shoes did contain phthalates, DIBP in a concentration of 1,700 mg/kg and DEHP in a concentration of 3,300 mg/kg. In addition all shoes contained NPEO with a maximum concentration of 2,100 mg/kg. In that latter sample NP was also found in a concentration of 290 mg/kg. Finally all sport shoes were found to contain organotin compounds. The total amounts organotin ranged from 1.5 to 2.8 mg/kg, mainly DBT and DOT.

- The foil packaging of the cheese products were tested for BPA, APs and APEOs. Only one of them did contain low amounts of BPA while all contained NP in concentrations up to 3.4 mg/kg.

- The mattresses were analysed for all chemicals that were part of this study. In general they only contained traces of APs, APEOs, phthalates and organotin compounds. Brominated flame retardants were not identified in these samples. The most prominent compound identified was NPEO in concentrations ranging from 25 to 190 mg/kg.

- As expected by the nature of the product, the vinyl flooring material contained high amounts of phthalates, in total up to 40% by weight. Apart from the phthalates originally involved in this study, di-iso-heptyl phthalate was identified as the major phthalate in this material. In addition the vinyl material contained NPEO in a concentration of 460 mg/kg and low amounts of OPEO and NP.

6. QA/QC statement

The analytical determinations in this study are performed in compliance with NEN-EN-ISO/IEC 17025 and RvA accreditation no. 54, “The development and application of methods for the determination of organic contaminants in environmental matrices, wastes and materials”. TNO Environment, Energy and Process Innovation is listed in the RvA register under no. L 026. The Dutch Council for Accreditation (RvA) and is a member of the European co-operation for Accreditation (EA) and the International Laboratory Accreditation Co-operation (ILAC). TNO Environment, Energy and Process Innovation operates in compliance with the Quality System standard ISO 9001 (certificate no. 00680-97-AQ-ROT-RvA).

7. Authentication

Name and address of the principal:
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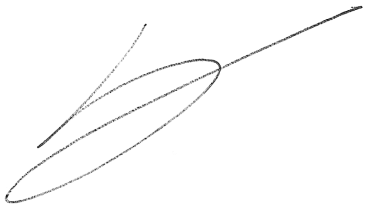
Names and functions of the cooperators:

Dr. R.J.B. Peters	Project Leader
Ing. R. Geenen	Technician
Drs. R.J. van Delft	Technician
Ing. H. Beeltje	Technician

Date upon which, or period in which, the research took place:
November 2003 – December 2003

Signature:



R.J.B. Peters
Project leader MA

Approved by:

Dr. M.P. Keuken
Head of Department MA

Appendix Full results of all product analysis

In the result tables the following acronyms are being used:

Group	Specific compounds	Acronym
Phthalates	dimethyl phthalate	DMP
	diethyl phthalate	DEP
	di-iso-butyl phthalate	DIBP
	di-n-butyl phthalate	DBP
	benzylbutyl phthalate	BBP
	dicyclohexyl phthalate	DCHP
	di-(2-ethylhexyl) phthalate	DEHP
	di-n-octyl phthalate	DOP
	di-iso-nonylphthalate	DINP
	di-iso-decyl phthalate	DIDP
Flame retardants	2,2',4,4'-tetrabromo diphenylether	BDE 47
	2,2',4,4',5-pentabromo diphenylether	BDE 99
	2,2',4,4',6-pentabromo diphenylether	BDE 100
	2,2',4,4',5,5'-hexabromo diphenylether	BDE 153
	2,2',3,4,4',5',6-heptabromo diphenylether	BDE 183
	octabromo diphenylether	BDE octa
	decabromo diphenylether	BDE 209
	hexabromo cyclododecane	HBCD
	tetrabromo bisphenol-A	TBBA
Bisphenol-A	Bisphenol-A	BPA
Alkylphenols and alkylphenol ethoxylates	octylphenol	OP
	nonylphenol	NP
	octylphenol ethoxylates	OPEO
	nonylphenol ethoxylates	NPEO
Organotins	monobutyltin	MBT
	dibutyltin	DBT
	tributyltin	TBT
	tetrabutyltin	TeBT
	monooctyltin	MOT
	dioctyltin	DOT
	triphenyltin	TPT

Note: With the exception of the electronic equipment the results are expressed in mg/kg product. For the electronic equipment all glass and metal parts, and all electric wiring was removed prior to sub-sampling. This means that the results are expressed in mg/kg for the sum of all polymer parts of the products and not in mg/kg product.

Table A.1 Concentrations of bisphenol-A, alkylphenols and ethoxylates in consumer products

TNO Code	Greenpeace Code	Product Description	Bisphenol-A, alkylphenols and alkylphenol ethoxylates				
			BpA mg/kg	OP mg/kg	NP mg/kg	OPEO mg/kg	NPEO mg/kg
52003305-010	GP-10	Sport shoes: Nike Air Max Plus: 604133 161	<0.5	<0.5	290	11	2100
52003305-011	GP-11	Sport shoes: Puma Torceira IT: 100287 05	<0.5	<0.5	21	<0.5	200
52003305-012	GP-12	Sport shoes: Adidas Gammanova 2 IN: 382429	<0.5	<0.5	34	<0.5	480
52003305-013	GP-13	Cheese: Unie kaas Goudse belegen ugd 24/12/03	<0.5	<0.5	3.4	<0.5	<0.5
52003305-014	GP-14	Cheese: Royal Gouda Jonge kaas 48+ ugd 17/12/03	<0.5	<0.5	2.3	<0.5	<0.5
52003305-015	GP-15	Cheese: Frico Kollumer ugd 19/12/03	1.2	<0.5	1.3	<0.5	<0.5
52003305-016	GP-16	Mattrasses: Auping Inizio WH Pocket soepel: AB1512	<0.5	<0.5	<0.5	<0.5	73
52003305-017	GP-17	Mattrasses: Springfield Ravanna	<0.5	<0.5	1.4	1.1	190
52003305-018	GP-18	Mattrasses: Ubica Atlanta	<0.5	<0.5	<0.5	<0.5	25
52003305-019	GP-19	Vinyl flooring: Forbo	<0.5	<0.5	10	3.1	460

Table A.2 Concentrations of phthalates in consumer products

TNO Code	Greenpeace Code	Product Description	Phthalates				
			DMP mg/kg	DEP mg/kg	DIBP mg/kg	DBP mg/kg	BBP mg/kg
52003305-004	GP-4	Cell phone: Sony/Ericson T610: 35126300-200751-5	1.6	1.7	13	35	63
52003305-005	GP-5	Cell phone: Samsung SGH-A800: 351004/26/634004/8	1.5	1.0	13	37	<0.1
52003305-006	GP-6	Cell phone: Siemens A55: 351855002740670	0.2	0.4	16	<0.1	0.2
52003305-010	GP-10	Sport shoes: Nike Air Max Plus: 604133 161	0.2	140	1700	4.6	2.8
52003305-011	GP-11	Sport shoes: Puma Torceira IT: 100287 05	<0.1	23	23	5.5	0.6
52003305-012	GP-12	Sport shoes: Adidas Gammanova 2 IN: 382429	0.2	19	7.4	3.3	5.0
52003305-016	GP-16	Mattrasses: Auping Inizio WH Pocket soepel: AB1512	<1	0.7	11	2.8	0.8
52003305-017	GP-17	Mattrasses: Springfield Ravanna	0.2	1.9	15	4.0	0.7
52003305-018	GP-18	Mattrasses: Ubica Atlanta	<0.1	0.7	14	3.8	9.7
52003305-019	GP-19	Vinyl flooring: Forbo*	0.1	13	24	130	150000

TNO Code	Greenpeace Code	Product Description	Phthalates				
			DCHP mg/kg	DEHP mg/kg	DOP mg/kg	DINP mg/kg	DIDP mg/kg
52003305-004	GP-4	Cell phone: Sony/Ericson T610: 35126300-200751-5	<0.1	<0.1	<0.1	<1	<1
52003305-005	GP-5	Cell phone: Samsung SGH-A800: 351004/26/634004/8	<0.1	<0.1	0.3	<1	<1
52003305-006	GP-6	Cell phone: Siemens A55: 351855002740670	0.2	120	<0.1	<1	<1
52003305-010	GP-10	Sport shoes: Nike Air Max Plus: 604133 161	<0.1	14	11	<1	<1
52003305-011	GP-11	Sport shoes: Puma Torceira IT: 100287 05	<0.1	3300	<0.1	<1	<1
52003305-012	GP-12	Sport shoes: Adidas Gammanova 2 IN: 382429	<0.1	35	<0.1	<1	<1
52003305-016	GP-16	Mattrasses: Auping Inizio WH Pocket soepel: AB1512	<0.1	3.1	<0.1	<1	<1
52003305-017	GP-17	Mattrasses: Springfield Ravanna	0.2	30	<0.1	<1	<1
52003305-018	GP-18	Mattrasses: Ubica Atlanta	0.1	8.5	<0.1	<1	<1
52003305-019	GP-19	Vinyl flooring: Forbo*	<1	620	<1	<1	<1

* An additional phthalate in this sample was di-iso-heptyl phthalate with an estimated concentration of 270,000 mg/kg

Table A.3 Concentrations of brominated flame retardants in consumer products

TNO Code	Greenpeace Code	Product Description	Brominated flame retardants				
			BDE 47 mg/kg	BDE 99 mg/kg	BDE 100 mg/kg	BDE 153 mg/kg	BDE 183 mg/kg
52003305-001	GP-1	Television: Philips Real Flat: 21PT 5507/01	<0.1	<0.1	<0.1	<0.1	<0.1
52003305-002	GP-2	Television: Samsung Plano: CW21A083NXXEC	<0.1	<0.1	<0.1	<0.1	<0.1
52003305-003	GP-3	Television: Panasonic TX: 21CK1C	<0.1	<0.1	<0.1	<0.1	<0.1
52003305-004	GP-4	Cell phone: Sony/Ericson T610: 35126300-200751-5	<0.1	0.2	<0.1	<0.1	<0.1
52003305-005	GP-5	Cell phone: Samsung SGH-A800: 351004/26/634004/8	<0.1	<0.1	<0.1	<0.1	<0.1
52003305-006	GP-6	Cell phone: Siemens A55: 351855002740670	<0.1	<0.1	<0.1	<0.1	<0.1
52003305-007	GP-7	Computer: HP Pavilion A250 NL: NLD 33135B4	<0.1	<0.1	<0.1	0.4	1.6
52003305-008	GP-8	Computer: Dell Optiflex GX240: FJ01G0J	<0.1	<0.1	<0.1	<0.1	<0.1
52003305-009	GP-9	Computer: IBM NetVista: 68233KG KBDALYN	<0.1	<0.1	<0.1	<0.1	0.4
52003305-016	GP-16	Mattrasses: Auping Inizio WH Pocket soepel: AB1512	<0.1	<0.1	<0.1	<0.1	<0.1
52003305-017	GP-17	Mattrasses: Springfield Ravanna	<0.1	<0.1	<0.1	<0.1	<0.1
52003305-018	GP-18	Mattrasses: Ubica Atlanta	<0.1	<0.1	<0.1	<0.1	<0.1

TNO Code	Greenpeace Code	Product Description	Brominated flame retardants				
			BDE octa	BDE 209	HBCD	TBBA[1] monomer	TBBA[2] sum monomer and polymer
52003305-001	GP-1	Television: Philips Real Flat: 21PT 5507/01	<0.1	<0.1	<0.1	2.1	130
52003305-002	GP-2	Television: Samsung Plano: CW21A083NXXEC	<0.1	<0.1	<0.1	210	34000
52003305-003	GP-3	Television: Panasonic TX: 21CK1C	<0.1	<0.1	<0.1	5	8300
52003305-004	GP-4	Cell phone: Sony/Ericson T610: 35126300-200751-5	<0.1	<0.1	<0.1	<0.1	6500
52003305-005	GP-5	Cell phone: Samsung SGH-A800: 351004/26/634004/8	<0.1	<0.1	<0.1	<0.1	12000
52003305-006	GP-6	Cell phone: Siemens A55: 351855002740670	<0.1	<0.1	<0.1	0.6	14000
52003305-007	GP-7	Computer: HP Pavilion A250 NL: NLD 33135B4	1.0	<0.1	<0.1	200000	190000
52003305-008	GP-8	Computer: Dell Optiflex GX240: FJ01G0J	<0.1	<0.1	<0.1	31	15000
52003305-009	GP-9	Computer: IBM NetVista: 68233KG KBDALYN	<0.1	<0.1	70	21000	57000
52003305-016	GP-16	Mattrasses: Auping Inizio WH Pocket soepel: AB1512	<0.1	<0.1	<0.1	<0.1	<100
52003305-017	GP-17	Mattrasses: Springfield Ravanna	<0.1	<0.1	<0.1	<0.1	<100
52003305-018	GP-18	Mattrasses: Ubica Atlanta	<0.1	<0.1	<0.1	<0.1	<100

[1]: TBBA monomer is free extractable TBBA content, determined specifically as TBBA

[2]: TBBA is an estimate of the sum of monomer and polymer TBBA, determined by a very different method than TBBA monomer (see section 3.2.1.3)

Table A.4 Concentrations of organotin compounds in consumer products

TNO Code	Greenpeace Code	Product Description	Organotin compounds			
			MBT mg/kg	DBT mg/kg	TBT mg/kg	TeBT mg/kg
52003305-010	GP-10	Sport shoes: Nike Air Max Plus: 604133 161	0.05	0.82	<0.01	<0.01
52003305-011	GP-11	Sport shoes: Puma Torceira IT: 100287 05	0.20	2.0	<0.01	<0.01
52003305-012	GP-12	Sport shoes: Adidas Gammanova 2 IN: 382429	0.13	1.7	<0.01	<0.01
52003305-016	GP-16	Mattrasses: Auping Inizio WH Pocket soepel: AB1512	<0.01	0.03	<0.01	0.03
52003305-017	GP-17	Mattrasses: Springfield Ravanna	<0.01	<0.01	<0.01	<0.01
52003305-018	GP-18	Mattrasses: Ubica Atlanta	<0.01	<0.01	<0.01	<0.01

TNO Code	Greenpeace Code	Product Description	Organotin compounds		
			MOT mg/kg	DOT mg/kg	TPT mg/kg
52003305-010	GP-10	Sport shoes: Nike Air Max Plus: 604133 161	0.16	0.47	<0.01
52003305-011	GP-11	Sport shoes: Puma Torceira IT: 100287 05	<0.01	0.10	<0.01
52003305-012	GP-12	Sport shoes: Adidas Gammanova 2 IN: 382429	0.19	0.81	<0.01
52003305-016	GP-16	Mattrasses: Auping Inizio WH Pocket soepel: AB1512	<0.01	<0.01	<0.01
52003305-017	GP-17	Mattrasses: Springfield Ravanna	<0.01	0.07	<0.01
52003305-018	GP-18	Mattrasses: Ubica Atlanta	<0.01	<0.01	<0.01