Impact Assessment of Potential Restrictions on the Marketing and Use of Certain Organotin Compounds

Final Report

prepared for
European Commission
Directorate-General Enterprise and Industry

RPA

October 2007

DISCLAIMER

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by

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EXECUTIVE SUMMARY

1. Introduction

Organotin compounds (organotins) are substances composed of tin, directly bound to a number of organic groups. They are characterised by the presence of a strong carbon-tin bond and have the general formula: R_x Sn $L_{(4-x)}$, where R denotes an organic alkyl or aryl group and L denotes one or more organic (or sometimes inorganic) ligands, which may or may not be the same. In general, the properties of organotin compounds vary significantly, depending upon their structure. Thus, while the carbon-tin bond is strong, the association with the ligands is less so and has a tendency to undergo dissociation both in use and in the environment (RPA, 2005).

Organotins are not included in the list of priority substances under the Existing Substances Regulation (ESR) (Council Regulation (EEC) No. 793/93). However, due to concerns over potential risks from organotins, the European Commission (DG Enterprise and Industry) undertook a detailed assessment of these risks - which culminated in the September 2005 Risk Assessment Report (RAR) which identified specific unacceptable risks. Following a SCHER opinion on the RAR, the European Commission (DG Enterprise and Industry) commissioned this study to assess the potential impacts of restrictions on the marketing and use of certain organotin compounds used as PVC stabilisers or catalysts in the production of consumer articles.

It should be noted that restrictions have already been introduced at the EU level on certain antifouling applications of organotins by means of amendments to the Marketing and Use Directive (76/769/EEC) (also known as the Limitations Directive). Regulation (EC) No (782/2003) of the European Parliament and the Council also prohibits the use, as from 1 July 2003, of organotin compounds as biocides in anti-fouling systems on EU ships and, as from 1 January 2008, on any ship entering EU waters.

2. Uses, Markets and Economic Profiles

There is a wide range of organotin compounds that can be manufactured and placed on the market and these are used in a variety of industrial applications. Di-substituted organotins (usually in combination with mono-substituted organotins and, to a lesser extent, tri-substituted compounds) are used as stabilisers for PVC and as catalysts for various products. Historically (prior to the introduction of a number of use restrictions), tri-substituted organotins were used as biocides in anti-fouling paints applied to ship hulls, in consumer products, in wood treatments and in pesticides (RPA, 2005). In this study, particular consideration is given to di- and tri-substituted organotins with, respectively, two and three organic groups bound to the tin atom. The Table below provides a summary of the uses of organotin and quantities sold in the EU in 2002 and 2007, where the latter estimates are based on information made available by industry for the purposes of this study while the former are from the RAR.

Table 1: Organotin Uses and Quantities Sold in the EU (2002 and 2007)

Applications	Quantity (tpa) 2002[1]	Quantity (tpa) 2007[2]
PVC stabilisers	15,000	>16,000
Catalysts	1,300 to 1,650	~2,000
- Plasticisers	150 - 350[3]	
- Silicones	50 - 100	
- Electrodeposition coatings	700 - 800	950
- Polyurethanes	400	750
Other uses:		
- Glass coating	760 to 800	Same
- Biocide in anti-fouling paints	1,250	Phased out globally
- Synthesis	< 150	~500
- Biocide (other)[4]	< 100	Reduced
- Pesticide	100	Unknown
- Intermediate in synthesis (tetra-substituted)[5]	N/A	Unknown
All uses	**Approx. 19,000**	**Approx. 21,000**

[1] *RPA, 2005*

[2] *From consultation for this study*

[3] *Derived by subtracting sub-totals for silicones, EDC and polyurethanes from total for 'catalysts'*

[4] *Use of tributyltin compounds for these applications are now prohibited within the EU as they have not been notified under the Biocidal Products Directive*

[5] *ETINSA has advised that the total quantity of tri-substituted tins for use as an intermediate in 2004 was substantially higher than the estimate for 2002. Although not clarified, this could perhaps be because the quantities present in the tetra-substituted tins had been excluded.*

3. Risk Assessment

The RAR identified a significant level of risk (requiring risk reduction measures) for children exposed to organotins from a range of consumer articles (in particular, PVC-printed T-shirts). According to the RAR, the dominant contributor to human uptake is via the environment (close to sources of significant emissions (e.g. timber treatment plants). Other significant source include cookies baked on silicone-coated baking paper (adults and children), food wrapped in PVC film (adults and children), sanitary panty liners (adults) and foot spray (adults). These uses contribute to exposure in the range of 20 – 100% of the tolerable daily intake (TDI) (RPA, 2005).

4. Need for Further Risk Reduction Measures

It is considered that further risk reduction measures are required on the basis of:

- the findings of the risk assessment (RPA, 2005) which show unacceptable risks to children exposed to organotins from fish/fishery products, indoor air/dust and PVC-printed T-shirts;

- the risk of individual members of the general population exceeding the TDI for organotins as a result of the cumulative exposure to organotins from a variety of consumer articles, products and pathways (where some of these contribute to organotin intake in the range 20% to 100% of the TDI); and

- the potential health (and environmental) hazards relating to the PBT, vPvB, CMR and endocrine disrupting properties of certain organotins. On the basis of these properties and under the REACH Regulation which came into force on 1 June 2007, these organotins may be subject to authorisation and included in Annex XIV of the Regulation - or alternatively, measures may be introduced under the restrictions procedure.

The Project Specifications (see Annex I) also state specifically that:

- as highlighted by SCHER, it is the total consumer exposure to organotins that should be used in the RAR, including all the identified pathways, such as those estimated to contribute with less than 20% of the TDI. Therefore, if the total exposure exceeds the TDI, there is a reason for concern and risk reduction measures should be considered, regardless if this exposure comes via one or a large number of pathways;

- for both health and environmental risks, risk estimates of the RPA report may not represent the worst case situations (actual risks may therefore be higher);

- for this study, an attempt should be made to focus on products that either lead to a relatively high level of possible exposure (as concluded in the RAR) or *that are relatively commonplace* so that an average consumer is likely to come into frequent contact with them; and

- appropriate restrictions on the marketing and use of a specific chemical may be proposed under Directive 76/769/EEC, if unacceptable risks from a chemical have been identified and if they cannot be adequately controlled by other measures.

Following from the above, the main type of measure being examined at this time is the introduction at Community level of marketing and use restrictions under Council Directive 76/769/EEC. This option may take several forms; however, for the purposes of this study, the restrictions would cover (individually or in combination):

1. all uses of tri-substituted organotins, in particular TBT and TPT compounds, unless used in chemical synthesis;

2. use of dioctyltin (DOT) and dibutyltin (DBT) compounds as stabilisers in all consumer (PVC) products;

3. use of DOT and DBT compounds in plasticised PVC products; and

4. use of DOT and DBT compounds in specific consumer products, in particular: PVC T-shirts, PVC gloves, PVC sandals, female hygiene products, nappies, dental moulds and 2-part silicone moulds.

5. Assessment of Further Risk Reduction Measures

Option 1: Restrictions on all uses of tri-substituted organotins, in particular TBT and TPT compounds, unless used in chemical synthesis

In theory, this measure should address issues relating to the importation for sale in the EU of consumer articles treated with biocidal organotins outside of the EU, as well as, prevent a substitution of risks, where companies move from known hazardous substances such as TBT to other tri-substituted organotins, whose risks may not be fully known at present. However, the actual extent of the benefits is currently unclear; for instance, if there are no (longer) imports of articles containing tri-substituted organotins, then the restriction would simply serve to ensure that this use does not re-occur in future (which is also a desirable outcome). Overall, the effectiveness, practicality and economic impact of this measure appears to be satisfactory (relative to their objectives), although there may be some minor issues for further clarification at an implementation stage relating to monitorability (i.e. the identification of organotins in articles and imported finished products). No significant impacts are expected on EU trade, competitiveness and employment as a result of this measure.

Use of tri-substituted organotins in plant protection products will be outside the scope of the Limitations Directive. However, this should not constitute a problem as the approvals process under the plant protection products legislation also involves an assessment of the health and environmental impacts of ingredients vis-à-vis their benefits - and as such, is an equally suitable regulatory framework for determining the case for continued use (or non-use) of tri-substituted organotins. Under the REACH Regulation, active substances manufactured or imported for use in plant protection products and biocides and included in their respective legislation are to be regarded as being registered. This measure is, therefore, consistent with the spirit and text of the current EU regulatory framework for chemical risk management.

Option 2: Restrictions on use of dioctyltin (DOT) and dibutyltin (DBT) compounds as stabilisers in consumer (PVC) products

Considering that the major commercial use of organotins is in PVC applications, a total ban on the use of DBT and DOT in PVC products is likely to result in significant reductions in the total concentration of these organotins in the environment and hence, the exposure to humans. In this regard, this measure provides the best possible guarantee of reducing the overall exposure to these groups of organotins (and their contribution to the TDI).

However, considering that there may be genuine difficulties in finding the appropriate alternative for a given product or in retooling a plant or processing system, some companies may have significant difficulties if restrictions were to be put in place immediately. This also takes into account that some companies have not anticipated the need to substitute organotins in unplasticised applications. These problems are likely to be more serious where a significant proportion of a company's portfolio is based on DBT and DOT, as opposed to competitors who also manufacture/use calcium-organic stabilisers and/or methyltin stabilisers.

In order to address this potential imbalance, a time-limited derogation or phase-out period after which all applications should cease use of DOT is likely to be more practical than derogations allowing continued use in specific critical applications (which in any case, industry has provided very little information on). Such a phase-out period would also give industry time to react accordingly to any restrictions while limiting the resulting economic impact on affected businesses.

Option 3: Restrictions on use of DOT and DBT compounds in plasticised PVC products

Overall, this measure wouldill serve to prevent re-occurrence of past uses and restrictions on DBT would also reduce the amount of TBT which will beis available as an impurity - and, therefore, help in achieving the targets of the WFD. Also, because industry has found alternatives to organotins in most plasticised applications, any restriction on the use of organotins can, therefore, be implemented quickly, with the exception of a few cases (coil or steel coating). The overall effectiveness of this measure (as a stand-alone) in reducing the contribution to the overall TDI may, however, be limited, seeing that it only deals with 5 - 7% of the total source of organotin in PVC.

Option 4: Restrictions on use of DOT and DBT compounds in specific consumer products, in particular: PVC T-shirts, PVC gloves, PVC sandals, female hygiene products, nappies, dental moulds and 2-part silicone moulds.

Overall, while this measure has its merits and provides a useful option for addressing the risks from individual applications, in effectiveness terms, it is not considered to be sufficiently robust for effectively reducing consumer exposure or addressing the risk of exceeding the TDI. It may also be necessary to consider some derogations for uses for which suitable alternatives have not been identified.

Very limited information has been provided on the scale of the costs from substitution. It is, however, the case that any costs incurred from restrictions on these uses are likely to be passed on to the consumer.

It is also considered that the health benefits of moving away from DBT outweigh (the costs associated with) the identified hazards/risks (whether on its own as an individual substance or cumulatively with other groups of substances). For DOT, a three-year phase-out period is recommended considered to be suitable to to allow for companies to review their product portfolios and identify suitable alternatives for them and their customers.

6. Recommended Risk Reduction Measure

The following risk reduction measure is recommended:

Recommendation

To consider at Community level, marketing and use restrictions under Council Directive 76/769/EEC (marketing and Use Directive) on all uses of:

- tri-substituted organotins, in particular tributyltin (TBT) and triphenyltin (TPT) compounds (Option 1);
- dibutyltin (DBT) compounds as stabilisers in all consumer (PVC) products (Option 2);
- dioctyltin (DOT) compounds as stabilisers in all consumer (PVC) products with a three-year phase-out period (Option 2);
- dibutyltin (DBT) and dioctyltin (DOT) compounds in plasticised PVC, unless used in steel (or coil) coating (Option 3); and
- dibutyltin (DBT) and dioctyltin (DOT) compounds as silicone catalysts for RTV-2 DIY moulds, baking trays and baking paper coatings and in RTV-1 sealants, with a three-year phase-out period for use of dioctyltin (DOT) compounds in RTV-1 sealants (Option 4).

Uses of organotins in plant protection products, food and food contact materials, biocides, medical devices and applications, and as intermediates in chemical synthesis, are not covered by these recommendations as these uses (apart from intermediates) fall under specific regulatory frameworks (or legislation) which are more appropriate for addressing the identified risks.

7. Summary Justification for Recommended Risk Reduction Measure

The above recommendation is based on the following key considerations (amongst others detailed in the Report):

- **contribution to the TDI**: the SCHER opinion that it is the total consumer exposure to organotins from all identified pathways which should form the basis of the risk assessment, where this includes all the identified pathways, such as those estimated to contribute less than 20% of the TDI. Any risk reduction strategy should, therefore, aim to ensure that the risk of individual members of the general population exceeding the TDI for organotins as a result of the cumulative exposure to organotins from a variety of consumer articles, products and pathways is reduced (regardless if this exposure comes via one or a large number of pathways); and

- **additive effects of the organotins**: the SCHER view that the four groups of organotins (DBT, TBT, DOT and TPT) represent the organotin compounds of most concern and their effects should be viewed as additive both for the target organs (thymus) and for the modes of action (immunotoxicity);

- **hazardous properties of individual organotins**: the potential health (and environmental) hazards relating to the PBT, vPvB, CMR and endocrine disrupting properties of certain organotins have to be taken into account. As noted earlier, in relation to the marine environment, TBT and TPT are likely to be classified as both PBT and vPvB substances, as well as being endocrine disruptors, while DBT is to be classified as a Category 2 reproductive toxin;

- **for tri-substituted organotins, in particular TBT and TPT (Option 1)**: these substances are rarely used without a detailed 'approvals' process (such as under the plant protection products legislation) or for chemical synthesis; however, there may still be importation for sale in the EU of consumer articles treated with biocidal organotins outside of the EU. The restriction is intended to address this issue and also prevent a substitution of risks, where companies move from known hazardous substances such as TBT to other tri-substituted organotins, whose risks may not be fully known at present;

- **for DBT compounds**: these are likely to be included in the 30th/31st ATP of Directive 67/548/EEC as reprotoxic category 2 and a number of companies have indicated that they are currently moving away (or planning to) from this substance (albeit, to other organotins, including DOT). Placing restrictions on DBT would therefore build on the DPD/DSD requirements such that they apply to articles, rather than preparations only. A restriction on DBT would also reduce the amount of TBT which will be available as an impurity - and, therefore, help in achieving the targets of the Water Framework Directive (where it is a priority hazardous substance for which a cessation of emissions, losses and discharges to the aquatic environment is required). In the event of an immediate restriction on DBT, it is considered to be the case that there are alternative compounds which can be used across the vast majority of (if not all) applications. Overall, it is considered that the benefits of moving away from DBT outweigh the costs associated with the identified hazards/risks (whether from DBT compounds themselves or in addition to those from TPT, TBT and DOT);

- **for DOT compounds**: there are current regulatory approvals for use in food packaging (within specific migration limits) and pharmaceutical packaging. Since food and pharmaceutical packaging currently account for around 60% of all organotin use in unplasticised PVC (and have their own regulatory framework for approval), placing restrictions on the remaining 40% of uses (assuming no further derogations on technical grounds are granted) runs the risk of being potentially disproportionate to the actual consumer exposure or the adverse effects that are potentially being avoided (for instance, exposure via food versus exposure via construction products).

There are known alternatives for use in food packaging and non-food contact applications. These are effectively the same for both categories of products and arguments relating to their suitability apply equally to both categories. If the need for risk management is considered to be the same regardless of application (where it is based on the substance itself), and alternatives are available and suitable, then it may be argued that a consistent approach to risk management should be adopted across all uses of DOT (i.e. either restrictions [or limit values] should apply equally to food and non-food applications).

However, the aim is to reduce the risk of individual members of the population exceeding the TDI, therefore, restrictions on non-food packaging applications may be considered to be an appropriate way of achieving this.

Furthermore, the relative safety of using SMLs in food contact materials cannot be directly transposed to other non-food articles, as it does not take into account the wide dispersive uses of DOT (e.g. in construction products), the method of substance loss and subsequent human exposure (wear and tear as opposed to migration into foodstuff) and the long life-spans of these products (10 - 100 years). Taken together, these mean that emissions and exposure could be on-going for a considerable time and will still contribute to the total exposure of the individual, as noted by SCHER.

In this regard, it appears to be the case that while most companies are aware of the need to act towards substituting organotins in plasticised applications ahead of any regulatory action, some companies have not anticipated the need to substitute in unplasticised applications. As it is possible that there may be genuine difficulties in finding the appropriate alternative for a given product or in retooling a plant or processing system, some companies may have significant difficulties if restrictions were to be put in place immediately. These problems are likely to be more serious where a significant proportion of a company's portfolio is based on DOT and DBT, as opposed to competitors who may also have or use calcium-organic stabilisers and methyltin stabilisers. For these reasons, a three-year phase-out period is considered to be suitable to allow for companies to review their product portfolios and identify suitable alternatives for them and their customers; and

- **for use of organotins in silicones**: uses in baking trays and baking papers represent historical uses and, as such, restrictions are intended (amongst other things) to prevent a re-occurrence of use. For RTV-2 moulding compounds, there are suitable alternatives to organotins and CES members are prepared to accept a regulatory decision to phase out this use of organotins. The three-year phase-out period applies in RTV-1 sealants to allow industry sufficient time to identify suitable alternatives to move to.

Overall, it is considered that restriction on three of the four groups of organotins (whose effects should be viewed as additive, according to SCHER) are sufficient as a short-term measure (i.e. for the three years) for protecting the health of consumers and the environment.

TABLE OF CONTENTS

ACRONYMS

AHP(s)	Absorbent Hygiene Product(s)
BPD	Biocidal Products Directive
CSTEE	Committee on Toxicity, Ecotoxicity and the Environment
DBT	Dibutyltin
DBTC	Dibutyltin Chloride
DBTO	Dibutyltin Oxide
DOT	Dioctyltin
DOTC	Dioctyltin Chloride
DOTO	Dioctyltin Oxide
DPD	Dangerous Preparations Directive
DSD	Dangerous Substances Directive
EDANA	European Disposables and Nonwovens Association
EEA	European Economic Area
ESPA	European Stabiliser Producers Association
ESR	Existing Substances Regulation
ETICA	European Tin Catalysts Association
ETINSA	European Tin Stabilisers Association
EuPC	European Plastic Converters
HWD	Hazardous Waste Directive
IPPC	Integrated Pollution Prevention and Control
MPD	Medicinal Products Directive
PVC	Polyvinyl Chloride
RAR	Risk Assessment Report
RRS	Risk Reduction Strategy
SCHER	Scientific Committee on Health and Environmental Risks
SML(s)	Specific Migration Limit(s)
TBT	Tributyltin
TBTC	Tributyltin Chloride
TBTO	Tributyltin Oxide
TDI	Tolerable Daily Intake
TPTC	Triphenyltin Chloride
TPTH	Triphenyltin Hydroxide
WFD	Water Framework Directive

1. INTRODUCTION

1.1 Introduction to Organotins

Organostannic or organotin compounds (organotins) are substances composed of tin, directly bound to a number of organic groups. They are characterised by the presence of a strong carbon-tin bond and have the general formula: $R_x \text{ Sn } L_{(4-x)}$, where R denotes an organic alkyl or aryl group and L denotes one or more organic (or sometimes inorganic) ligands, which may or may not be the same. In general, the properties of organotin compounds vary significantly, depending upon their structure. Thus, while the carbon-tin bond is strong, the association with the ligands is less so and has a tendency to undergo dissociation both in use and in the environment (RPA, 2005).

In this study, particular consideration is given to di- and tri-substituted organotins with, respectively, two and three organic groups bound to the tin atom[1]. Table 1.1 overleaf summarises the physicochemical properties of eight such organotins (which are broadly representative of the range of available organotins of interest): dibutyltin chloride (DBTC), dibutyltin oxide (DBTO), dioctyltin chloride (DOTC), dioctyltin oxide (DOTO), tributyltin chloride (TBTC), tributyltin oxide (TBTO), triphenyltin chloride (TPTC) and triphenyltin hydroxide (TPTH).

There is a wide range of organotin compounds that can be manufactured and placed on the market and these are used in a variety of industrial applications. Di-substituted organotins (usually in combination with mono-substituted organotins and, to a lesser extent, tri-substituted compounds[2]) are used as stabilisers for PVC and as catalysts for various products. Historically (prior to the introduction of a number of use restrictions), tri-substituted organotins were used as biocides in anti-fouling paints applied to ship hulls, in consumer products, in wood treatments and in pesticides (RPA, 2005).

It is, however, important to note that uses of the tri-substituted organotins and uses of the mono-/di-substituted compounds do not overlap. Thus, for example, mono-/di-substituted compounds are not suitable for use as biocides and tri-substituted compounds are not suitable as PVC stabilisers. Also, because the R (alkyl or aryl) groups in most organotin compounds are the same, tributyltin compounds, for instance, will contain (impurities of) other butyltin compounds (e.g. mono-, di- and tetra- butyltin compounds, as well as tin tetrachloride) but not, for example, octyltin compounds (RPA, 2005).

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[1] *Tetra-substituted* organotins are not used commercially, except in the synthesis of other organic chemicals, and as such, have not been considered further in the Risk Assessment Report (RAR) or this study. *Mono-substituted* organotins tend to be used, in some applications, together with di-substituted compounds. Earlier versions of the RAR (RPA & CEH, 2002 and RPA, 2003) did not identify risks of particular concern resulting from the mono-substituted organotins; however, it is possible that any recommended risk reduction measures affecting the end-use products of di-substituted organotins may affect the production and use of some mono-substituted compounds.

[2] Whilst mono- and di-substituted compounds are used mainly as stabilisers in PVC, due to the chemistry involved in their production, tri-substituted organotins will comprise a small fraction of the total amount.

Table 1.1: Physicochemical Properties of Di- and Tri- Substituted Organotins (Butyltin Compounds, Octyltin Compounds and Phenyltin Compounds)

	Di-substituted Organotins				**Tri-substituted Organotins**			
Property	**DBTC**	**DBTO**	**DOTC**	**DOTO**	**TBTC**	**TBTO**	**TPTC**	**TPTH**
CAS No.	683-18-1	818-08-6	3542-36-7	870-08-6	1461-22-9	56-35-9	639-58-7	76-89-9
EINECS No.	211-670-0	212-449-1	222-583-2	212-791-1	215-958-7	200-268-0	211-358-4	200-990-6
Molecular formula	$(C_4H_9)_2Cl_2Sn$	$(C_4H_9)_2OSn$	$(C_8H_{17})_2Cl_2Sn$	$(C_8H_{17})_2OSn$	$(C_4H_9)_3ClSn$	$(C_4H_9)_6OSn_2$	$(C_6H_5)_3ClSn$	$(C_6H_5)_3OHSn$
Mol. weight (g/mol)	303.8	248.9	416.0	361.1	325.5	596.1	385.5	367.0
% Tin	39.1%	47.7%	28.5%	32.9%	36.5%	19.9%	30.8%	32.3%
Melting point (^oC)	42	105	47	230	-19	-45	106	123
Boiling point (^oC)*	250	250	250	250	250	250	250	250
Vapour pressure (25^oC)(Pa)	0.15	4.2E-06	2.63E-04	9.5E-02	1.00	1.0E-03	2.10E-05	4.7E-03
Water solubility (mg/L)	33	4.0	1.6	0.23	10	35	40	1
Source in RAR (RPA, 2005):	*Parametrix, 2004*	*Parametrix, 2004c*	*Parametrix, 2004a*	*Parametrix, 2004d*	*Parametrix, 2005*	*BUA, 2003*	*CICAD 13 (WHO, 1999)*	*CICAD 13 (WHO, 1999)*

** As most organotins decompose, boiling points of 250^{o}C were assumed in the absence of a 'true' boiling point (at atmospheric pressure).*

1.2 Study Background and Objectives

Organotins are not included in the list of priority substances under the Existing Substances Regulation (ESR) (Council Regulation (EEC) No. 793/93). However, due to concerns over potential risks from organotins, the European Commission (DG Enterprise and Industry) commissioned a study in 2002 to assess possible risks from the application of organotins in areas outside of their use as a biocide in anti-fouling systems, as well as to describe the broad economic profile of the organotins industry. This report (RPA & CEH, 2002) was submitted to the Commission and was considered by the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) which raised some concerns regarding the assessment of risks.

In view of these concerns, a second report was prepared in 2003 which updated the 2002 report and, where possible, addressed the concerns expressed by CSTEE. Concerns were again expressed by CSTEE with regard to the 2003 Report. The European Commission then commissioned RPA to conduct a third study to examine possible risks from the applications of four groups of organotins (DBT, TBT, DOT and TPT) including their use as a biocide in antifouling systems. These four organotin groups were deemed to represent the organotin compounds of most concern and their effects were viewed as additive both for the target organs (thymus) and for the modes of action (immunotoxicity).

The third report (RPA, 2005) - hereafter referred to as the Risk Assessment Report (RAR) - identified a significant level of risk (requiring risk reduction measures) for children exposed to organotins from a range of consumer products[3] (in particular, PVC-printed T-shirts). Because consumers within the EU are likely to be exposed to a range of different products containing organotins, the RAR also identified organotin uses that contributed to exposure in the range of 20 – 100% of the tolerable daily intake (TDI). Such a risk could result from the cumulative exposure to organotins from the following consumer products:

- ***adults***: fish and fishery products, PVC gloves, PVC sandals, PVC-printed T-shirts, female hygiene products, foot spray, insoles, dental moulds, 2-part silicone moulds and PVC food packaging; and

- ***children***: PVC sandals, nappies, and PVC food packaging.

Anyone living near industries that produce or use organotins and who is exposed via the local environment may also be at risk (RPA, 2005).

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[3] According to the first RAR (RPA & CEH, 2002), the term 'consumer products' refers to all the products which are sold or otherwise made available to or used by members of the general public [not professionals or industrial users] to which organostannic materials have been intentionally added at any stage of their production process.

In commenting on the RAR, the opinion of the Scientific Committee on Health and Environmental Risks (SCHER, 2006) - which replaced the CSTEE - was that:

- the total consumer exposure to organotins from all identified pathways should form the basis of the risk assessment. A risk assessment of organotin exposure should therefore include those exposure pathways estimated to contribute to less than 20% of the TDI. If the resulting total exposure exceeds the TDI, then there is a reason for concern and risk reduction measures should be considered, regardless of the number of exposure pathways involved;

- the most important exposure pathways are food, indoor air, household dust and dermal contact with different polymer materials;

- there is a high risk of individual members of the general population (greatly) exceeding the TDI for organotins; and

- the health and environmental risk estimates in the RAR may not represent the worst case situations.

Following this SCHER opinion, the European Commission (DG Enterprise and Industry) commissioned this study (in December 2006) to assess the potential impacts of restrictions on the marketing and use of certain organotin compounds used as PVC stabilisers or catalysts in the production of consumer articles (see Annex 1).

It should be noted that restrictions have already been introduced at the EU level on certain antifouling applications of organotins by means of amendments to the Marketing and Use Directive (76/769/EEC) (also known as the Limitations Directive). Regulation (EC) No (782/2003) of the European Parliament and the Council also prohibits the use, as from 1 July 2003, of organotin compounds as biocides in anti-fouling systems on EU ships and, as from 1 January 2008, on any ship entering EU waters.

As stated in the Project Specifications (see Annex 1), the study is to focus on:

- identifying the potential alternatives to certain organotins and their risks and benefits;
- checking the existing EU and national restrictions for certain uses of organotins; and
- proposing possible options for the management of identified risks at Community level (with a description of the potential health, environmental, and economic impacts for each of the options considered).

1.3 Approach to the Study

A kick-off meeting for this project was held with the Commission in January 2007. This involved identification of key contacts within the organotins industry, as well as known sources of information. It also served to further clarify the intended scope of the study.

At the start of the Project, an approach to the study was agreed that involved a review of the relevant literature and consultation with the relevant industry stakeholders in the EU. As part of the consultation process, in February 2007, manufacturers, suppliers and downstream users of organotins, products containing organotins and their alternatives were asked for their views on (a) the current role and importance of organotins in its various products and applications, and (b) the suitability (in terms of their technical, environmental and health aspects) of various alternatives to organotins in these applications. The questionnaire that was used during consultation did not request information on exposure scenarios and other toxicological aspects relating to organotins (as this is outside the scope of the study); however, industry provided such information, where available, and where such information has been found to be relevant, it has been taken into account in this study.

Questionnaires were sent by email to the stakeholders and responses were invited in either written or electronic form. Based on the responses to the questionnaire, follow-up through direct contact was undertaken with a number of respondents (between March and August 2007). The reasons for such follow-up included the wish to gather information outside the scope of the questionnaire, to obtain clarification of questionnaire responses or to discuss particular aspects in more detail. Consultation with companies for this study has relied mainly on contacts with the relevant industry associations, although in some cases, individual companies were approached directly to seek additional information, further characterise the use of organotins from these users or in cases where the information provided was of a confidential nature.

An interim report was submitted for this project in April 2007. The report was made available by DG Enterprise to Government departments in the Member States and stakeholders with an interest in the study. Comments have been received from a number of these organisations and these have been used in clarifying certain aspects of the study. The options for risk management which were identified in the interim report (and circulated to industry stakeholders and EU Competent Authorities in the last week of May/first week of June) were further refined based on the feedback received.

Meetings were also held with certain representatives of the organotins industry on the 7th and 8th of August 2007 in the UK - including members of European Tin Stabilisers Association (ETINSA) and the European Plastic Converters (EuPC). A previous meeting had also been held with representatives of European Disposables and Nonwovens Association (EDANA). At these meetings, industry provided and discussed information on the various uses and markets for organotins, information on exposure and on the toxicological and ecotoxicological effects of organotins and their alternatives. In addition, Competent Authorities in each of the 27 Member States were approached in order to identify any information they have available that may be relevant for the project.

A list of the organisations contacted with regard to the study is included in Annex II and the information received has been incorporated in the appropriate sections of the Report.

This Final Report presents the findings of the study and the conclusions and recommendations for risk management action at the EU level.

1.4 Organisation of the Report

The remaining sections of this report are organised as follows:

- Section 2 provides information on the **uses, markets and economic profile** for organotins in the EU;
- Section 3 gives an overview of the extent of **consumer exposure and risks from organotins**, highlighting the effects which are of importance to this RRS;
- Section 4 discusses **existing risk reduction measures**, including current controls on the marketing and use of certain organotins;
- Section 5 outlines the existing information on possible **alternatives** to organotins in the relevant applications;
- Section 6 describes a range of **possible further risk reduction measures** and outlines how they could apply to the remaining uses of organotins;
- Section 7 provides an **assessment of the potential risk reduction measures** against the standard decision criteria of their effectiveness, practicality, monitorability and economic impact;
- Section 8 presents the **conclusions** of the study and the **recommendations for risk management action**;
- Section 9 lists the **references** used for this report.

Annex I presents the **Project Specifications** as set out by the European Commission. Annex II provides a **List of Consultees** contacted for the purposes of this study and Annex III sets out the **SCHER Opinion on the 2005 RAR and RPA's comments/responses** to this.

2. USES, MARKETS AND ECONOMIC PROFILE

2.1 Introduction

This Section provides an overview of the production and usage of organotin compounds in the EU, followed by a detailed discussion on the use of organotins:

- in PVC stabilisers (Section 2.3);
- as catalysts in esterification reactions (Section 2.4);
- as catalysts in polyolefin antioxidant manufacture (Section 2.5);
- as catalysts in silicones manufacture (Section 2.6);
- as catalysts for electrodeposition coatings (Section 2.7);
- as catalysts in polyurethane applications (Section 2.8); and
- other applications (Section 2.9).

For each of the above applications, the Report provides:

- an introduction to the reasons for the use of organotin compounds, the types of organotins used and the specific manner in which they are used;

- the quantities used in each application and potential end-uses for the products in which organotins are used;

- information on the downstream markets; and

- a summary of the key points which are of particular relevance for the developing a risk reduction strategy (RRS).

The information in this Section is drawn mainly from that presented in the RAR (RPA, 2005) (as well as the preceding 2002 and 2003 Reports)[4] and consultation undertaken with industry for the purposes of this study. The discussion below, therefore, sets out the Consultant's understanding and assessment of the relevant technologies and/or the markets based on the information to hand.

2.2 Production and Overview of Uses of Organotins

There is a wide range of organotin compounds that can be manufactured and placed on the market:

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[4] Note that in the RAR (and the preceding 2002 and 2003 Reports), the term "EU" refers to the then EU-15 Member States. This RRS is intended to cover the EU-27.

- *tetra-substituted* organotins: are only used as intermediates in synthesis of other organic chemicals
- *tri-substituted* organotins: are only used as:
  - biocides (including anti-foulants);
  - pesticides; and
  - intermediates in the production of other chemicals
- *mono- and/or di-substituted* organotins: are used as:
  - PVC stabilisers;
  - catalysts; and
  - in glass coating

Information received for this study from a major manufacturer of additives for PVC indicates that mono- and di- alkyltin compounds are not always used as a mixture. For PVC stabiliser applications, mono- and di- alkyltin mercaptides are used as a mixture, whereas dialkyltin carboxylates are used as pure di-compounds. For catalysts, the differentiation is more marked as, in nearly all of the cases, only one species (mono- or di- alkyltin) will work as an efficient catalyst. Often, mono- alkyltin catalysts function in esterification reactions whereas di- alkyltin catalysts are better for trans-esterification reactions. In the case of glass coating, only pure mono- or di- butyltin compounds are used (pers. comm.).

Table 2.1 provides examples of typical organotin compounds that are used in each of the applications under consideration for this study.

Table 2.1: Typical Compounds Used in Applications of Concern for the Study

Applications		**Compounds**
Glass Coating		MBT, DBT
PVC stabilisers		Methyl Butyl (MBT, DBT) Octyl (MOT, DOT) } EHMA Carboxylates
Catalysts	Electrodeposition	DBT, DOT
	Silicones	DBT, DOT
	Esterification	MBT, DBT, MOT, DOT
	Polyurethanes	DBT, DOT

Source: RPA & CEH, 2002; Information provided by organotin manufacturers/suppliers for this study
EHMA = Ethylhexylmercaptoacetate

According to the RAR, organotin compounds are produced at seven sites in the EU and one additional site in the European Economic Area (EEA). This production is carried out by seven companies located in Germany (three), the Netherlands, Italy (two) and Switzerland. In 2001, these production sites used a total of around 12,800 tonnes of inorganic tin (not organotin) in the production of various organotin and inorganic tin compounds (RPA, 2005). However, this tonnage applies only to butyltin and octyltin compounds; industry indicates that methyltin compounds, whilst used in the EU, are only produced outside the EU and are imported. This does not, however, preclude the possibility of these methyltin compounds being produced within the EU in the future.

Table 2.2: Organotin Compounds Produced/Supplied by EU Manufacturers - 2007

Organotin	**Production location**	**No. of Companies**
Methyltin compounds	Essentially non-EU	Two companies
Mono-/di-butyltin compounds	Essentially EU	Five companies
Mono-/di-octyltin compounds	Essentially EU	Five companies
Tributyltin compounds	Essentially EU	One confirmed company[1]
Tetrabutyltin compounds	Essentially EU	Two companies

Source: ETINSA, 2007; RPA, 2005; RPA & CEH (2002)

[1] *As at 2004, only two of the four sites identified in 2001 still produce tri-substituted tins for use in biocidal products. However, the tetra-substituted tins used as an intermediate contain significant amounts of tri-substituted tins and small amounts of tri-substituted tins will still be present as impurities in mono- and di-substituted compounds.*

According to the RAR, in 2002, around 19,000 tonnes of organotins were used in the EU. Information collected during consultation for this project, however, suggests that there may have been some changes in the amount of organotins used in the different applications of interest.

For instance, an aggregation of the tonnages of organotin stabilisers supplied by individual EU manufacturers/suppliers indicates an increase of more than 5% based on the responses from five of the seven companies manufacturing organotins (see Table 2.8). Also, information submitted by the European Stabiliser Producers Association (ESPA) on behalf of the European Tin Catalysts Association (ETICA) suggests that the quantity of tributyltin compounds produced in the EU for synthesis purposes may currently be as high as 500 tonnes per year (ETICA, 2007).

Recent data available from ETICA suggest that that the tonnage of organotins catalysts produced is currently closer to 2,000 tonnes, of which the vast majority (>90%) are the (mono- and di-) butyltin compounds (ETICA, 2007). This information appears to be confirmed by a manufacturer's view of the organotin catalysts market in Western Europe as presented in Table 2.3 below.

When compared with the data for 2002 (as shown in Table 2.4 following), the current situation suggests:

- a large increase in the use of organotins in polyurethanes;
- a steady increase in the use of organotins in electrodeposition coatings; and
- a reduction in the amount of organotins used in plasticisers and other applications (including silicones).

Table 2.3: A Catalyst Manufacturer's View of the Tin Catalysts Market in Western Europe

Segment application	Annual use of tin catalysts (mt/y)	Segment growth	Example of use
Electrodeposition coatings	950	3%	Car paints
Polyurethane foam	750	3%	Building coating, thermal insulation, furniture, flooring
Polyester resins	180	6%	Buttons, appliances, boat structures, paints
Other resins & Miscellaneous	150	5%	Sealants, oil additives, etc.
Total	**2,030**		

Source: Catalyst Manufacturer

Also, the use of tributyltin compounds for biocidal applications is now prohibited within the EU as they have not been notified under the Biocidal Products Directive. According to ETINSA (2007), the production of TBT for this application has strongly decreased (although it is still above 30 tonnes per year for one manufacturer (ETICA, 2007)) and the sales in the EU have stopped and, as such, the tonnages indicated in the RAR are unlikely to be representative of the situation today.

Table 2.4 below provides a summary of the uses of organotin and quantities sold in the EU in 2002 and 2007, where the latter estimates are based on information made available by industry for the purposes of this study while the former are from the RAR.

Table 2.4: Organotin Uses and Quantities Sold in the EU (2002 and 2007)

Applications	Quantity (tpa) 2002[1]	Quantity (tpa) 2007[2]
PVC stabilisers	15,000	>16,000
Catalysts	1,300 to 1,650	~2,000
• Plasticisers	150 - 350[3]	
• Silicones	50 - 100	
• Electrodeposition coatings	700 - 800	950
• Polyurethanes	400	750
Other uses:		
• Glass coating	760 to 800	Same
• Biocide in anti-fouling paints	1,250	Phased out globally
• Synthesis	< 150	~500
• Biocide (other) [4]	< 100	Reduced
• Pesticide	100	Unknown
• Intermediate in synthesis (tetra-substituted) [5]	N/A	Unknown
All uses	**Approx. 19,000**	**Approx. 21,000**

[1] *RPA, 2005* [2] *Estimates based on consultation for this study*

[3] *Derived by subtracting sub-totals for silicones, EDC and polyurethanes from total for 'catalysts'*

[4] *Use of tributyltin compounds for these applications are now prohibited within the EU as they have not been notified under the Biocidal Products Directive*

[5] *ETINSA has advised that the total quantity of tri-substituted tins for use as an intermediate in 2004 was substantially higher than the estimate for 2002. Although not clarified, this could perhaps be because the quantities present in the tetra-substituted tins had been excluded.*

2.3 Use of Organotins in PVC Stabilisers

2.3.1 Introduction to PVC and Stabilisers

Why PVC Requires Stabilisers

Polyvinyl chloride (PVC) is a versatile thermoplastic used in an extensive range of products and applications ranging from car underbody seals and flexible roof membranes to pipes and window profiles. PVC products can generally be tailor-made to suit the needs of any given application; hence, they can be rigid or flexible, opaque, transparent or coloured, insulating or conducting, etc. During production (or compounding), additives are usually added to PVC to influence or determine the mechanical properties, light and thermal stability, colour, clarity and electrical properties of the end-product. These additives include: heat stabilisers, lubricants, plasticisers, fillers, processing aids, impact modifiers and pigments (ECVM, not dated).

Organotins are one of the additives added to PVC during processing. By far, the largest use of organotin compounds is in the stabilisation of PVC (**PVC stabilisers**). Stabilisers are used in all PVC products in order to avoid decomposition whilst being heated during processing and also to reduce deterioration through exposure to ultraviolet light and weathering (RPA, 2005). This is important when considering that, unlike most other thermoplastics, many PVC applications (other than packaging) have a lifetime of between 10 and 100 years and this requires proven durability (ECVM, not dated).

Use of Organotins in the PVC Stabilisation Process

The main (heat) stabilisers (whether organotins or not) in a formulation are usually combined with co-stabilisers which are organic materials such as polyols or epoxidised esters; these provide an additive synergistic effect, and in the case of some forms of heat stabiliser, an enhancement of the overall stabiliser performance (ECVM, not dated)[5].

Stabilisers, along with other additives are dry-mixed with PVC polymer to form a blend which is heated and then processed. The compounding process, during which the additives (including the organotin stabiliser, where this is used) are mixed with other additives and the polymer, can be carried out using three methods:

- in the first method, an intensive high-speed mixer that thoroughly blends all the additives along with the polymer is used. The result is a powder, known as a 'dry blend', which is then fed into the processing equipment. Sometimes the blended PVC may be sold to a separate processor following the compounding (mixing) process;

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[5] To suit the needs of a particular application, a stabiliser "one-pack" is often used. The one-pack often includes a mixture of lubricants (internal and external) and a variety of processing aids (based on industry know-how). Plasticisers, pigments, fillers, impact modifiers and other additives are often used to customise PVC to specific end-uses (ESPA, not dated).

- in a second method, the ingredients are blended in either a low or high-speed mixer and the resulting powder is transferred to a melt compounder. This can either be a compounding extruder, or other special equipment for making PVC compounds. These produce a melt which, when cool, is cut into granules ready for processing; and

- in a specialised process, liquid compounds known as plastisols, are produced as dispersions of very fine PVC polymer particles in liquid organic media (plasticisers).

Chemically, the stabiliser functions by reacting with any chlorine (in radical or hydrochloric acid form) freed during the thermal stress of processing or use. Light-induced degradation is more complex and the protective effect of stabilisers can be reinforced with specific UV-stabilisers.

The typical concentration of organotin stabilisers may be up to 2% of the plastic weight in PVC products (ORTEPA, 1997 in RPA, 2005); the RAR used 1.5% for the environmental exposure assessment. These percentages have been confirmed by information received for this RRS from two PVC processing companies and the European Rigid PVC Film Association (ERPA, 2007).

The PVC compounds are then made into products using a variety of processing methods, e.g. extrusion, injection moulding, blow moulding, calendering, spreading and coating.

Types of Stabilisers Used in PVC Processing

The main types of PVC stabiliser systems are based either on lead, mixed metals (liquid and solid), tin or cadmium, although use of cadmium systems has been phased out in Europe (ESPA, not dated). Approximately 170,000 tonnes of stabilisers were used in Europe in 2000 (EPSA, 2007). At present, the percentage accounted for by the different systems being as follows (ESPA, 2007a):

• lead stabilisers:	56%;
• solid metal (Ca/Zn) stabilisers:	27%;
• liquid mixed metal stabilisers:	9%; and
• organotin stabilisers:	8%.

These figures have been provided by ESPA during consultation for this study and show notable changes compared to figures available on the ESPA Internet site for the year 2000 where lead stabilisers appeared to cover over 70% of all stabilisers used in the EU (with solid mixed metal stabilisers at only 10%) (ESPA (not dated)).

Table 2.5 outlines the key applications for the different types of stabilisers in Europe. In the context of this table, it is important to note that ESPA (not dated) states that "*the mixed metal systems are capable of covering the whole area of PVC applications*".

Table 2.5: Uses of Stabiliser Types in the PVC in Europe

Application		Sn	Pb	Ca/Zn	Ba/Zn	K/Zn*
Unplasticised PVC						
Rigid films and sheets	Sheet	Major use	Minor use	Occasional use		
	Foil	Major use				
Pipes, fittings and profiles	Pipes		Major use	Major use**		
	Fittings	Minor use **	Major use			
	Profiles		Major use	Minor use		
Bottles	Bottles***	Major use		Major use		
Plasticised PVC						
Wires/cables	Cable covering		Minor use	Major use		
Coatings and floorings	Flooring	Minor use			Major use	Major use
	Wall covering	Minor use		Occasional use	Major use	Major use
Steel coating	Steel (coil) coating					
Miscellaneous	Foil and sheet		Minor use	Minor use	Major use	
	Medical use			Major use		
	Tubes and footwear			Minor use	Major use	
	Food packaging film			Major use		
	Fabric coating			Minor use	Major use	Major use

Source: ECVM, not dated
** used as a stabiliser/'kicker' for foamed layers in these products (see more detail below)*
*** used for potable water pipe*
**** bottles are generally not a major use, according to input from ETINSA during consultation*

Types of Organotin Stabilisers Used

Organotin stabilisers are always mono- and/or di-substituted compounds and include methyl, butyl, octyltin and dodecyltin. Only the octyltin and butyltin stabilisers are produced in Europe, with the methyltin stabilisers imported from outside the EU (RPA, 2005; ESPA, 2007). No information has been received on the use of dodectyltin.

According to the RAR, the organotin stabilisers may also be divided into two groups:

- *tin mercaptides* (i.e. stabilisers with tin-sulphur bonds): these stabilisers allow the production of clear, rigid vinyl commodities even under demanding processing conditions, and which also have moderate light stability. The most powerful compounds within the mercaptide class are the mercapto-acetate (thioglycolate) ester derivates and these are the most common tin compounds applied today. The tin mercaptides are usually mixtures of di-alkyl and mono-alkyl tin compounds, of which the ratio can be varied to create stabilisers with the best performance, mainly dependent upon the used PVC type and the end-use application (RPA, 2005); and

- *tin carboxylates* (i.e. stabilisers with tin-oxygen bonds): these are typically used (increasingly) in outdoor applications (such as transparent panels and translucent double-wall panels for greenhouses) as they provide excellent light and weathering stability to PVC products (RPA, 2005). Akcros Chemicals (not dated) also notes butyltin carboxylates may be preferred where the odour of thiotins may present difficulties. Tin carboxylates are usually pure di-compounds (as opposed to mixtures of mono- and di-) and specific stabilisers within this group (e.g. octyltin maleates) are approved for the production of blow moulding films (such as candy wrapping).

Table 2.6 provides details of the estimated quantities of methyl, butyl and octyltin stabilisers used in rigid and flexible PVC applications, as reported in the RAR, as well as some examples of applications in which they are used as indicated by two companies.

It is important to bear in mind that suppliers of finished PVC articles may not be aware of the organotins contained in their products. For instance, a DIY supplier to the Irish market informed his national Competent Authority that they sell PVC paddling pools and PVC floor and wall covering to the general public. While this DIY supplier was able to indicate the organotins found in their flooring ranges, they experienced some difficulty in ascertaining the stabiliser type found in paddling pools as their supplier changes from year to year (Irish HSA, 2007). This situation also applies to a number of organotin manufacturers who when consulted for this RRS were not in possession of various information relating to the end-use processes and/or applications of their products.

Table 2.6: Use of Organotin Stabiliser Types in PVC in Europe (t/pa) according to RAR

Stabiliser	Unplasticised PVC	Plasticised PVC	Total	Example PVC applications
Methyltin compounds	1,090	94	1,184	• Building products (rainwater mouldings, conservatory cappings) • Rigid extrusion (trims) • Rigid mouldings (electrical mouldings) • Calendered sheet (construction, transport, electrical) • Flexible extrusion (doorstrips) • Coatings
Butyltin compounds	3,889	754	4,644	• Building products (cellular profiles, roof sheet, rainwater mouldings, conservatory cappings, skinned profile); • Chlorinated PVC (PVC-C) fittings and tubes
Octyltin compounds	8,922	251	9,173	• Rigid extrusion (integrated circuit carriers, trims, conduit) • Rigid moulding (bottles) • Medical moulding (valves, containers) • Calendered sheet (blister packs) • Flexible extrusion (packaging film) • Coatings
Dodecyltins	N/A	N/A	N/A	N/A
Total	**13,901**	**1,099**	**15,000**	

Source: RPA (2005) - based on data for 2001 and information provided by two companies during consultation for this study

Note: The use of dodecyltins as PVC stabilisers has not been explicitly confirmed by consultees in the course of this study

2.3.2 Applications and End Uses of Organotin Stabilisers

Rigid Films and Sheets[6]

The manufacture of rigid films and sheets is the main use of organotin stabilisers in the EU, accounting for around 50% of the total consumption of organotin stabilisers in the EU (ORTEPA, not-dated). Notably, in the USA, for historical reasons, rigid applications are based on organotin-based stabilisers, while in Europe similar applications are traditionally lead-stabilised (ESPA, 2007).

Clear rigid film is primarily produced by the calendering or flat die extrusion process. The high temperatures and shear forces used in these processes need PVC formulations capable of providing crystal clarity and sparkle, as well as freedom from flow lines. Organotins are able to provide transparency (or clarity) to PVC with almost no discolouration (ORTEPA, not-dated). Careful stabiliser dosing and lubrication is also necessary to optimise melt flow characteristics and anti-sticking properties during processing (ESPA, not dated-a).

Main Applications of Rigid Film

Rigid film is primarily used to make items such like credit cards, food packaging material and blisters (or packaging) for the pharmaceuticals industry. As these three categories of products are often produced at the same factory, producers are very keen on having only one stabiliser suitable for them all (pers. comm.). Information from manufacturers of organotins suggests that organotins (e.g. octyltin mercaptides) are technically important in these applications because:

- for credit cards, in addition to the usual characteristics of organotin stabilisers (good heat stability over a long time and excellent clarity), octyltin compounds are indicated to provide the best performance in terms of printability due to their intrinsic chemistry (surface tension properties);

- regarding food packaging (including food contact plastics produced via moulding), there are specific approvals required prior to any substance being used in food-related applications. Octyltin compounds (and methyltin compounds) have been approved under the relevant food legislation (Directive 2002/72/EC relating to plastic materials and articles intended to come into contact with foodstuffs) within a range of Specific Migration Limits (SMLs) for use as unplasticised PVC film stabilisers for food packaging material. Industry has also highlighted that despite the amendment of Directive 2002/72/EC by Directive 2005/79/EC[7], their products still comply with the pertinent EU legislation. Technically, films for delicate food require special stabilisers to maintain original taste and smell (organoleptic properties), as well as

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[6] 'Sheets' are basically thicker 'films'; the exact specifications when the change from one to the other is made (e.g. > 1 millimetre) varies from company to company.

[7] The SMLs for a series of octyltin compounds were reduced from 0.04 mg/kg (expressed as tin) down to 0.006 mg/kg (expressed as tin).

impart excellent clarity, and organotins are important for this function (ESPA, not dated-a); and

- for medical/pharmaceutical applications (such as in flexible tubes, blood bags and surgical gloves), these are regulated by the European Pharmacopoeia and octyltin mercaptides (and methyltin compounds) are approved for use in these applications. ESPA (not dated-a) notes that all medical applications have to be approved by the relevant national authorities and very often on an individual product-by-product basis.

While the current market share of various stabilisers in the rigid films and sheets market is unknown, ESPA (not dated) notes that traditionally, calcium/zinc stabilisers have been used in food, medical and pharmaceutical packaging applications (where their low toxicity and subsequent regulatory approval in these applications is an advantage).

Other Products/Applications of Rigid Film

Examples of other products and/or applications employing rigid film include:

- office supplies;
- printed films;
- furniture foils and insulation films;
- diskettes and box lids; and
- other non-food packaging.

It has, however, been pointed out that the majority of these products and applications (manufactured via the rigid calendaring process) are produced on the same site as the main applications listed earlier. For manufacturing and cost reasons, all the products manufactured under the rigid calendering process are made to comply with the limits set under the food contact legislation.

Extruded Blown Film

Flexible extrusion products are used in packaging film (mainly octyl) and door strip (mainly methyl) where their main attributes include very clear (glass like) transparency, which is highly desirable in applications such as factory door-strip. In such cases, the safety benefits of highlighting hazards to forklift truck operators and pedestrians at entrances to doorways by providing transparent doorstrips is clearly obvious, whilst the flexible strip also forms an insulative barrier to heat and noise losses from such buildings.

One manufacturer of extruded blown film indicates that butyltin carboxylates are used for technical shrinkable films, while octyltin carboxylates are used for food packaging materials. According to this company, the properties shown by these substances are yet to be matched by any solid calcium/zinc stabilisers.

Rigid Extruded Sheets

Rigid extruded sheets are used in the manufacture of a number of important end products (which may be compact or foamed, pigmented or transparent, flat or corrugated) used mainly in the building industry in panels, sidings, doors, roofing, etc.

Construction sheet, used in flat and corrugated form for roof tiles and panelling, is usually manufactured by flat-die extrusion followed by calender polishing or by pressing calendered sheets. Excellent light stability and weathering properties and colour are necessary for this particular application and UV-light stabilisers are added for maximum performance. Clear indoor sheets or coloured sheets have similar requirements for the stabilisers but do not require UV-light stability (ESPA, not dated-a).

During the production process, the large surface areas involved are rather difficult to process and the formulation of the lubricant system needs special attention to ensure correct melt flow behaviour, good colour control and maximum product clarity. As butyltin compounds feature a higher tin content, they suit technical applications that require optimal heat stability (as thick sheets remain in the die a long time at high temperatures during extrusion) and/or perfect clarity (transparent sheets) and/or good weatherability (e.g. in roofing; in this case butyltin carboxylates are preferred because they display better UV resistance compared to mercaptides).

In calendered clear roof sheeting, it has been indicated by a manufacturer of polymers that the best clarity coupled with good weatherability is achieved through the use of tin based stabiliser systems. This company also notes that the effect of using butyltin stabilisers in exterior coloured profiles is difficult to achieve with any alternative stabiliser system. In addition a number of cellular building products are based on tin stabilisers again for outside applications requiring excellent weathering performance.

Foamed Sheets

As noted in the RAR, PVC foamed sheeting is used in a range of specialist industries (such as aerospace, marine transport and wind energy) due to its rigidity, light weight and moisture resistance. It is also used in more common applications such as notice boards, exhibition boards and indoor panelling. In an increasing number of applications, it serves as a replacement for wood or gypsum providing light weight and minimum maintenance (ESPA, not dated-a).

Stabiliser systems used in the extrusion of foamed PVC are designed to offer control over the foaming process in addition to the standard requirements for sheets. The large surface areas need special attention to ensure correct melt flow behaviour and good colour control. Processing for foamed profiles and sheets require stabilisers which blend well with the used organic and/or inorganic foaming agents. It is necessary to give the foaming process the proper ‘kick’ to obtain an even foam structure without surface deficiencies or mechanical weak points. Furthermore, the achieved overall density has to be low in order to provide lightweight use and economic processing (ESPA, not dated-a).

Summary

In general, it has been highlighted (and appears to be the case, see Table 2.5) that lead-based stabilisers are predominantly used for rigid PVC in building and construction applications (e.g. pipes and profiles, but also in flexible PVC for electrical cable wiring); on the other hand, organotin-based stabilisers are used mainly in rigid PVC film (for food contact plastics and packaging) (where lead is neither used or approved in the EU). Tin-based stabilisers, therefore, do not generally compete with lead in building/construction applications.

Pipes, Fittings and Profiles

PVC pipe applications cover a larger variety of pipes including: high and low-pressure systems, drinking and waste water pipes, smooth large diameter and corrugated drainage pipes. As noted in the RAR, more than half of all pipes (and fittings) are now plastic.

The EU plastic pipe market is of the order of 2,500 kt/yr of which PVC accounts for over 60% (Raynaud, 2004 in RPA, 2005). The most important pipe markets are (ESPA, not dated-a):

- pipes for draining sewage and waste water;
- high-pressure pipes for drinking water;
- gutters and down-pipes for removal of rain water;
- thin-wall, corrugated pipes for land drainage;
- foam core pipes for non-pressure lightweight use; and
- conduit and duct pipes for protecting electrical cables.

The RAR notes that the major use of plastic pipes (which is increasing) is in drainage and sewerage (more than 50%), followed by service applications including gas/water distribution and heating/cooling systems (approaching 30%).

For good processability, particularly where large diameters or high melt temperatures (e.g. corrugated thin pipes) are required, efficient heat stabilisers and lubricants are necessary. Also, due to the expected lifetime of these pipes (up to 100 years of service), the stabiliser systems used have to be tested thoroughly and guarantee long-term performance (ESPA, not dated-a).

As noted in the RAR, although only organotin stabilisers are used for PVC pipes and fittings in North America, the dominant stabiliser throughout the rest of the world is lead which accounts for an estimated 92% of the European stabiliser use in PVC pipes and fittings (Schiller & Fischer, 2004 in RPA, 2005). However, with the declared industry aim of reducing the use of lead stabilisers, there may be a need for replacement stabilisers systems which could include organotins (Vinyl 2010, not-dated). ETINSA advised at the time of undertaking the RAR that, although butyltin stabilisers are used in North America for PVC drinking water pipes, octyltin stabilisers are used in Europe (RPA, 2005).

Furthermore, for special applications such as drinking water pipes, additional restrictions according to national regulations may apply in order to ensure safe drinking water distribution. According to ORTEPA, regulations in France, Germany and the Netherlands approve the use of both thioglycolates and reverse ester products in potable water pipes while in Italy only thioglycolates are allowed (ORTEPA, not dated-a).

Most PVC pipes are connected using injection-moulded fittings. During injection-moulding processes, high temperature and shear occur which require specially formulated stabilisers. These needs are very different compared to pipe extrusion: stabiliser properties have to be optimal and lubrication has to be adjusted to the high shear process in moulding machines. For fittings used for drinking water pipes, national regulations apply to the stabiliser formulations (ESPA, not dated-a).

Case Box 2.1: Use of Organotins in PVC Pipes

Information has been received with regard to the use of organotin stabilisers in chlorinated PVC (PVC-C) applications. According to a global manufacturer of PVC-C, this material is processed into pipes and fittings for hot and cold drinking water, in fire sprinkler systems and pipes and other applications of industrial nature. Owing to the high chlorine content of PVC-C, this material requires more efficient thermal stabilisation compared to unplasticised PVC. The manufacturer has argued that, at present, only organotin compounds may be used as the prime stabiliser while alternative systems do not perform to the required level of effectiveness. The company has also noted that since PVC-C is used for the transportation of water for human consumption, the use of organotin compounds is permitted by national authorities.

Similar to pipes, organotin stabilisers are also used for rigid PVC profiles. Examples of where PVC profiles are used include:

- windows (a major use);
- cable ducts (for protecting electrical cables);
- furniture/furnishings (e.g. venetian blinds);
- cars; and
- electrical appliances.

Information received indicates that the development of solid calcium/zinc stabilisers to replace lead and cadmium in window profiles took over 20 years along with significant research and development (R&D) costs. However, ESPA (2007) notes that, using the mixed metal stabilisers systems, "*for white window frames, excellent colour stability weathering results have been obtained both in long-term testing and from practical experience*". This is also supported by information provided by the Swedish authorities, which states that for both white and coloured flexible PVC, organotin stabilisers have been successfully substituted by calcium-organic stabilisers in Sweden (KemI, 2007). This is particularly true for a specific company which reportedly accounts for about 60% of the EU market for PVC flooring and PVC wall coverings.

ECVM (not dated) also indicates that, as a result of pressures on the continuing use of heat stabilisers based on lead compounds, considerable development work has been carried out on new, improved systems for applications including cable covering, pipe and window profile and many of these are have been in commercial use for several years.

Furthermore, the penetration of the newer forms of the calcium/zinc stabilisers is almost complete in drinking water pipes, well advanced in cables but still limited in some pipes and profiles (ECVM, not dated).

One manufacturer of additives (stabilisers/lubricant systems) for PVC indicates that in Europe, organotin-based stabilisers are not used with the exception of the very small field of crystal clear profiles[8]; lead-based stabilisers were and still are the dominating system and, as indicated earlier, organotin-based stabilisers do not generally compete with lead in building/construction applications. Due to the recent move towards a phase-out of lead use in stabilisers, it has been indicated that there is an on-going process of replacing the lead stabilisers with the calcium/zinc stabiliser systems which represent state-of-the-art as they are a more environmentally friendly alternative system. It has also been suggested that from a production and process adjustment point of view, it is technically easier and more feasible to move from lead-based systems to calcium/zinc systems, as opposed to organotin-based systems. The switch from lead to calcium/zinc is therefore, also more cost effective from a compounder's or processor's viewpoint.

Bottles

Rigid PVC bottles are produced by the (injection) blow moulding process which operates at high speeds and temperatures to ensure economical production and an attractive bottle appearance. Organotin mercaptides are efficient PVC stabilisers in this process due to their very good heat stability and lubricating effect and are, therefore, critical for product quality and process (ORTEPA, not dated).

As well as being transparent, bottles are made in an extensive variety of colours, and the stabilisers have to provide the required colour stability of the bottle as well as long-term storage stability for the products packaged. A large proportion of PVC bottles are used in food packaging (e.g. vegetable oil, juices, wines) for which food-contact approved stabilisers are used (ORTEPA, not dated-a), as well as in non-food packaging (e.g. cosmetics and cleaning materials).

It is currently uncertain if all bottles, regardless of final end use, are produced to the same migration limits for food contact materials. It should, however, be noted that according to ETINSA, the use of organotins in PVC bottles is a minor use (see Table 2.5).

Plasticised PVC

Plasticised PVC is used in a variety of industrial, household and medical applications. In theory, organotins may be present from either the plasticiser component (where the plasticiser serves to increase flexibility, as discussed in detail in Section 2.4) or from the stabiliser component of the PVC. Plasticised PVC can be processed at lower temperatures which results ultimately in lower levels of stabilisers in the final

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[8] While it has been argued that there are currently no technically suitable alternatives for the crystal clear profiles, the requirement for clarity is suggested not to be an issue for window profiles and pipes.

application. In plasticised PVC, the majority of the stabiliser systems used are the liquid mixed metal systems[9] (ESPA, 2007; ESPA, not dated-a).

The main applications of plasticised PVC are in wires/cables, coatings and flooring (including wall covering) and steel coatings.

<u>Wires/Cables</u>

Cables cover a wide range of high and low voltage applications and stabilisers giving high electrical resistance and low energy dissipation are crucial for safe power transmission. Stabiliser formulations can be adopted to suit the requirements of high speed extrusion in production and specific requirements of each wire/cable application, where these include (ESPA, not dated-a):

- in *outer sheathing*: good thermal and mechanical stability (in combination with other formulation additives);
- in *wire insulation*: high thermal stability in the presence of the metallic wire (often copper) and excellent electrical insulation properties balanced with lubrication to satisfy demanding in-service temperatures; and
- in *thin wall sheathing*: high output with good surface finish necessary for telephone cable etc. This requires enhanced performance from the stabiliser.

Additional special requirements from certain large user groups like the automobile industry have to be met as well (e.g. lead-free stabilisers) (ESPA, not dated-a).

In practice, however, it is understood that organotin-based stabilisers are not used in cable insulation; the mixed metal stabilisers appear to be the dominating stabiliser system in these applications.

<u>Coatings and Floorings</u>

Many applications are based on the combination of PVC with other materials to provide excellent durability, hygienic properties, stain resistance and weather resistance, aesthetic appearance. These applications include: tarpaulins, tents, hospital and gym floors and structured wall papers. Stabilisers for these need to provide good clarity, printability and be free of volatile substances (ESPA, not dated-a).

Although industry publications (Akcros Chemicals, not dated) suggest organotin uses for floor and wall coverings, tarpaulins, conveyor belting and artificial leathercloth including automotive low fogging end-use, according to ESPA, the use of tin stabilisers in plastisol (suspension) PVC is highly unusual and these all use the liquid mixed-metal stabiliser systems (ESPA, 2007). With regard to wall coverings and flooring, gloves, PVC-printed

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[9] It is worth noting that due to the flexibility and complexity of PVC formulation, one tin stabiliser can be used for a range of paste polymers whereas different mixed metal stabilisers might be required for different paste polymers (ESPA, 2007).

T-shirts and other plasticised applications identified in the RAR as posing unacceptable risks, ESPA companies are currently working with their customers to change to alternative stabiliser systems with the aim of phasing out this use by the end of 2007. Printed T-shirts are mainly imported from outside the EU but ESPA companies are also looking to ensure that such use ceases in the EU (ESPA, 2007). One such company indicates that these phase-outs will not cause problems for organotin manufacturers or their supply chains.

Information has also been received from the European Resilient Flooring Manufacturers' Institute (ERFMI) which has advised that, with some exceptions, all its members have already stopped using organotin stabilisers some years ago and when the situation was re-assessed in 2006, only a limited number of users were identified or were indicating to plan to phase out the use. These companies have been contacted by the Institute and have indicated that they are not interested in defending the use of this type of stabilisers since the phase-out process is nearly finished (ERFMI, 2007).

Steel (Coil) Coating

One manufacturer of organotins indicates that butyltin mercaptides are used for this plasticised application. They argue that it is very difficult for a customer to switch from organotin stabilisers since coil coatings used in building construction require extensive long term weathering testing for product guarantees. This view is supported by another manufacturer who suggests that restrictions on this use would have a significant impact on product quality due to the high performance required. A third manufacturer, however, indicates that alternative options based on octyltin compounds or solid calcium/zinc or liquid calcium/zinc or barium/zinc are under development and in the future an acceptable compromise on cost-effectiveness is certainly possible

Miscellaneous Consumer Goods

Examples of a wide range of consumer products made from plasticised PVC include (ESPA, not dated-a):

- bath sandals;
- durable walking shoe soles;
- rubber boots;
- gardening hoses;
- car interiors;
- crash-pads;
- meat wrap films;
- refrigerator sealants;
- life vests;
- fishing buoys;
- swimming aids; and
- duct tape.

The applied processing procedures cover injection moulding, extrusion, film blowing, calendering and many other processes. The versatility of application of products and processes also require a variety of complex stabiliser systems to fulfil the requirements such as transparency, food approval, weathering resistance, low-fogging, good compatibility, good printability, good adhesion and long term UV-resistance (ESPA, not dated-a).

<u>Toys</u>

Information has been received from the Toys Industries of Europe (TIE) representing 95% of all companies active in the toy sector, including national trade associations as well as toy companies). TIE has advised that most of the industry's suppliers are based in the Far East, typically China; as such, the majority of toys originate in this region. Organotins appear to have a very limited use in the toy industry. They are primarily used for ultra clear applications, especially in packaging (for example, blister cards and blister shells). Calcium/zinc stabilisers are used where they have been demonstrated to be suitable for that particular application. Although TIE members are aware of barium, lead and cadmium based stabilisers, these are not used because of their toxicological or environmental properties (TIE, 2007).

Consumption of Organotin Stabilisers

Information from the RAR

The use of organotins as PVC stabilisers is by far the largest use for organic tin (ESPA, not dated) with about 70% of all produced organotin compounds being used for this purpose. The RAR suggests that over 90% of organotin stabilisers are used in rigid PVC (RPA, 2005) and up to date information from individual manufacturers of organotin stabilisers supports this view. Much of the rigid PVC used in packaging is produced by over 60 large calendering units located at over 20 sites, mainly in Italy and Germany. These large calendaring units each produce of the order of 7,000 tonnes of PVC per year (RPA, 2005).

According to the RAR, the EU market for organotin stabilised PVC is indicated to in the region of 600,000 to 700,000 tonnes per annum (tpa) with the majority being used in rigid PVC packaging. Around 60% of such packaging would be for food contact applications. Focusing upon the consumption of tin stabilisers, in Europe, this is estimated at around 15,000-16,000 tpa, of which about 60% is used for food packaging (as described above) and 40% for technical applications. As noted earlier, contrary to the situation in North America, where tin systems are used for almost all rigid PVC application, the main usage in Europe is for rigid, transparent applications where rigorous processing conditions require a good level of stabilisation.

Up to date Information

ETINSA (2007) suggests that organotin consumption as stabilisers in EU has been almost stable over the last 5 years, with a slight increase in rigid calendering applications, which compensated the decrease in the plasticised ones, where a complete phase out is anticipated in 2007. This, however, does not suggest that there are no changes in the market shares held by individual companies, as shown in Case Box 2.2.

It has been suggested that the aggregated sales of tin stabilisers in the EU by ETINSA members having a production site in the EU has remained fairly stable, with an average growth of about 1.5% each year (average over the last 6 years) (ETINSA, 2007).

However, this could be an underestimate. Table 2.8 presents a comparison on the tonnages used in the 2005 RAR and the aggregates of tonnages supplied by individual EU manufacturers/suppliers of organotin stabilisers. With five out of seven manufacturers/suppliers reporting, the total usage of organotin stabilisers in Europe exceeds 15,000 tonnes. The available data suggest an increase of more than 5% (15,850 compared to 15,000 tpa) across all companies.

Case Box 2.2: Information from a Large PVC Manufacturer on Consumption of Organotins

Information on the use of different organotin stabilisers was provided by a large PVC manufacturer. To prevent the disclosure of commercially sensitive data, 100 has been used as the value for each organotin category consumed in 2004 and the remainder of the table shows the relative increase or decrease for the years 2005, 2006 and 2007 (first six months).

Table 2.7: Consumption of Organotin Stabilisers by a Large EU PVC Manufacturer

Type of organotin stabilisers	Year				Max No. suppliers
	2004	2005	2006	2007 (Jan-Jun)	
All octyltin compounds	100	86	100	31	3
All butyltin compounds	100	419	697	300	6
All methyltin compounds	100	127	90	33	2
All unspecified organotins	100	141	130	67	2
All organotins	**100**	**194**	**280**	**114**	**13**

Source: Consultation

Note: it is possible that the number of suppliers is smaller than 13 as a single supplier may supply more than one type of stabilisers – the available information does not allow for further analysis

In summary, there appears to be a significant growth in the tin based stabiliser systems use from 2004 until 2006, although this has now peaked and on current predictions is likely to remain fairly static. There are several reasons for this growth; however, the main one is the growth in exterior coloured profile stabilised by dibutyltin systems coupled with the fact that the product portfolio of the company does not remain static and in some cases can be hugely influenced by just one major customer. In addition there has been some growth in the medicals business that use octyl based Zn stabiliser.

Finally, the company advises that they are very active in phasing-out lead based stabiliser systems by the end of 2007, and whilst tin stabilisers are not the company's first choice for replacement of lead, for some very demanding applications where lead systems have been used, Ca/Zn alternatives have not been as efficient.

Table 2.8: EU Usage of Organotin Stabilisers in Rigid and Plasticised PVC (2005 and 2007 data)

Application Category	**Applications**	**Data from RAR (2005)**		**Data from consultation (2007)**	
		tpa	**(%)**	**tpa**	**(%)**
Rigid PVC					
Rigid films and sheets	• Food packaging • Pharmaceuticals packaging • Non-food packaging • Credit cards • Rigid construction sheets including foamed sheeting • Other	13,067	87	13,436	85
Pipes, fittings and profiles	• Pipes for draining sewage and waste water • Pipes for drinking water • Conduit and duct pipes for protecting electrical cables • Other pipes • Fittings • Window profiles • Other profiles • Miscellaneous (e.g. rigid toys)	556	4	993	8
Bottles	• Bottles	278	2	243	2
	Totals	**13,901**	**93**	**15,009**	**95**
Plasticised PVC					
Coatings and flooring	• Flooring • Wallcovering • T-shirt stamps	628	4	417	2
Steel (coil) coating	• Coil coatings	314	2	80	1
Miscellaneous	• Bath sandals • Durable walking shoe soles • Rubber boots • Gardening hoses • Car interiors • Crash-pads • Meat wrap films • Refrigerator sealants • Life vests • Fishing buoys • Swimming aids • Duct tape	157	1	343	2
	Totals	**1,099**	**7**	**840**	**5**

Source: RPA (2005) and consultation for this study.

Note: Figures for 2005 are based on percentages (assuming total use of 15,000 tonnes/year) and have been rounded. The figures for 2007 are based on individual responses received from ***5 out of*** *7 EU manufacturers/suppliers of organotin stabilisers*

2.3.3 Downstream Markets

Global demand for PVC exceeds 25 million tonnes per year. According to the RAR, European PVC resin consumption for the EU-25 is in excess of 6.5 million tonnes per year. Production of PVC - including exports - in Western Europe is around 8 million tonnes per year with a market value of around €70 billion (Vinyl 2010, 2007). Table 2.9 outlines the share of the €70 billion Western European market for the different types of PVC applications.

Table 2.9: Overview of the Applications of PVC in Western Europe

Application	Percentage of consumption	Application	Percentage of consumption
Pipes	21.9%	Flexible film/sheet	7.0%
Profiles	18.5%	Other rigid	5.4%
Cables/wires	10.7%	Other flexible	5.2%
Flooring	10.1%	Coatings	5.2%
Rigid film	7.0%	Plastisols	4.9%

Source: Vinyl 2010, 2007

Around 550,000 people work in the European PVC sector, from resin manufacturing to the final product:

- ***resin producers***: the 10 leading Western European firms, all of which are members of ECVM, account for over 98% of total production. They operate about 50 plants on 40 sites and they employ around 10,000 people. One of the four PVC producers in the new EU Member States is also a member of ECVM;

- ***stabiliser producers***: 11 companies - all members of Vinyl 2010 via ESPA - produce more than 98% of the stabilisers sold in Europe. They employ around 5,000 people;

- ***plasticisers producers***: the 11 major European producers employ approximately 6,500 people; and

- ***converters***: the conversion of PVC into final consumer and industrial products involves more than 21,000 companies, mostly small and medium sized enterprises (SMEs). They employ over half a million people.

ESPA estimated in 2002 that there were around 130 major PVC processing plants and a further 250 smaller users, spread fairly evenly across the then EU-15 (RPA, 2005).

2.3.4 Summary – Key Points

- Lead stabilisers are still the most widely used stabiliser systems (accounting for 56% of total stabilisers used today). Mixed metal stabilisers have a much increasing presence in the last few years (having increased from 10% to 27% over the last five to ten years). Tin stabilisers have a fairly stable presence but are used to a lesser extent in comparison to the other two main types. Tin stabilisers are not the first choice for replacement of lead stabilisers (and do not compete directly with lead stabilisers in certain applications (e.g. building and construction) and their presence in plasticised PVC is diminishing in favour of liquid metal stabilisers which have always been the dominant system in plasticised PVC applications for technical reasons.

- The relevant industry association (ETINSA) suggests that organotin consumption as stabilisers in EU has been almost stable over the last 5 years, with a slight increase in rigid calendering application, compensating the on-going decrease in the use in plasticised PVC applications. It has been estimated that 15,000-16,000 tonnes of organotin stabilisers are used each year; however, recent tonnage data from manufacturers/suppliers suggest that the upper limit is an underestimate. Around 60% is used for food packaging and 40% for technical applications while over 90% of the total organotin stabilisers are used in rigid PVC. The main uses of organotin stabilisers in the EU are largely for calendered rigid, transparent sheeting for general packaging, food-contact and pharmaceutical packaging.

- Organotin stabilisers are always mono- and/or di-substituted compounds and include methyl, butyl, octyltin and dodecyltin (the latter not confirmed in the course of this study). Only the octyltin and butyltin stabilisers are produced in Europe, with the methyltin stabilisers imported from outside the EU.

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- Tin mercaptides and tin carboxylates are the key tin compounds used as stabilisers. The former allow the production of clear, rigid vinyl commodities even under demanding processing conditions, and which also have moderate light stability while the latter are typically used in outdoor applications (as they are more resilient to light and weathering or where the odour of thiotins may present difficulties. In PVC stabiliser applications, mono- and di- alkyltin mercaptides are used as a mixture, whereas dialkyltin carboxylates are used as pure di-compounds.

- Mono- and di- alkyltin compounds are not always used as a mixture. For PVC stabiliser applications, mono- and di- alkyltin mercaptides are used as a mixture, whereas dialkyltin carboxylates are used as pure di-compounds. The typical concentration of organotin stabilisers may be up to 2% of the plastic weight in PVC

- Members of ESPA have phased out the supply of organotin stabilisers for the production of plasticised PVC within EU Member States in applications such as wall coverings and flooring. Printed T-shirts are mainly imported from outside the EU but ESPA companies are also looking to ensure that such use ceases in the EU.

- There is some uncertainty associated with the suitability of mixed-metal stabilisers as effective replacements to organotin stabilisers in steel (or coil) coatings; it is, however, noted that these products are not generally made available to the general public and, as such, are not necessarily a consumer use. It has also been suggested that the properties of octyltin and butyltin carboxylates in certain applications have not yet been matched by any solid calcium zinc stabilisers; however, the ESPA (not dated) indicates that mixed metal systems are capable of covering the whole area of PVC applications.

2.4 Use of Organotins as Catalysts in Esterification Reactions

2.4.1 Introduction to Esterification/Transesterification Catalysis

Esterification is the general name for a chemical reaction in which chemicals such as an alcohol and an acid form an ester as the reaction product. Transesterification is the process of exchanging the alkoxy group of an ester by another alcohol. Both these types of reactions are catalysed by substances such as acids (for example, p-toluenesulphonic acid), bases, organotins, organotitanates, etc.

The esterification reactions catalysed by organotin compounds require temperatures above 200°C, which is much higher than those involving strong acid catalysts, such as p-toluenesulphonic acid. However, a number of advantages justify the use of organotin catalysts (Vesta Intracon, 2005):

- the side reactions are minimised so the end products have better colour and odour properties (because fewer by-products are formed); and
- the equipment corrosion is eliminated.

Main disadvantages of organotin catalysts are reported as being (Dupont, not dated):

- their high toxicity;
- their lower reactivity compared with some alternatives (e.g. titanates) which means a longer reaction time); and
- environmental issues relating to catalyst disposal.

Types of Organotin Catalysts Used

According to the RAR, the oxides of MBTO and lesser quantities of DBTO, MOTO and DOTO are used in esterification and transesterification reactions, at a concentration between 0.001% and 0.5% by weight[10] (where the substances may act to reduce the formation of unwanted by-products and to provide the required colour properties) (RPA, 2005). More recent information for this study, however, indicates that, in nearly all of the cases, only one species (mono- or di- alkyltin) will work as an efficient catalyst. Often, mono- alkyltin catalysts function in esterification reactions whereas di- alkyltins are better for trans-esterification reactions.

Following production, the catalyst is retained within the polymer (they are homogeneous catalysts) and hence within the finished product, although in some cases the organotin may be partially degraded by the high temperatures used in the production processes (RPA, 2005). Vesta Intracon (2005) which supplies organotin catalysts presents this as an advantage suggesting that there is no need for refining to remove the catalyst residues, while Dupont (not dated), which markets alternatives, suggests that this is a drawback noting that the complete removal of the organotin catalyst is difficult.

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[10] According to Vesta Intracon (2005), usual levels of tin catalysts are 0.05–0.3 wt % based on the total reactants charged; this is within the concentration limits used in the RAR.

2.4.2 Applications of Organotin Esterification Catalysts

DBT and MBT compounds are used as esterification catalysts for the manufacture of organic esters and/or polyesters, as well as, for transesterification and polycondensation of dimethyl terephthalate into polyethylene terephthalate or manufacturing of high molecular weight copolyester elastomers. The use of these materials is either in packaging applications or engineering plastics (Vesta Intracon, 2005). Use in the production of di-2-ethyl hexyl phthalate (DEHP), diisodecyl phthalate (DINP) and diisononyl phthalate (DIDP) has been noted in the RAR (RPA, 2005).

Organic esters produced using organotins find wide uses as plasticisers, lubricants, and heat-transfer fluids. For instance, according to the RAR, organotin compounds are used in the manufacture of phthalates and adipates (and possibly other substances) which are primarily used as plasticisers – where these are substances which when added to a material, usually a plastic, make it flexible, resilient and easier to handle. About one-third of the PVC used in the EU is plasticised (RPA, 2005).

More recent information received from the European Council for Plasticisers and Intermediates (ECPI) - representing European producers of the whole range of plasticisers (phthalates, adipates, trimellitates, polymeric plasticisers, etc. indicates that organotins are not used as catalysts in the production of PVC plasticisers (ECPI, 2007a). Donnelly (2007) also notes that the use of organotins in the manufacture of plasticisers such as phthalates and adipates is unlikely for technical reasons, since there are far superior catalyst systems for these esters. The catalysts being used in practice, for esterification reactions, range from sulphuric acid to titanates and p-toluenesulphonic acid. It is, however, noted that a catalyst formulator markets monobutyltin oxide catalysts for use in the manufacture of "polymeric plasticisers" (see Table 2.10).

Polyesters produced by the use of organotin compounds are used as binders for formulating coatings for industrial use, or when modified with fatty acids they are used as binders for air-drying coatings for decorative and protective applications. For polyester resins used in industrial powder coatings organotins are used at a concentration of around 0.3%. This use accounts for over 50% of the organotins used in this area. The final coatings consist of the polyester resin, with a curing agent and other additives. They are applied as a dry powder via an electrostatic spray gun and then heating of the coating layer to cause formation of the cured coating. Downstream applications of polyester resin coatings include general metal coating, coil coating and toner, and as alkyd resins in paints (ETICA, 2003 in RPA, 2005).

Other products/applications of esterifications/transesterifications include adhesives and in the manufacture of acrylic resins which may be used in clothing (ETICA in RPA, 2005).

Table 2.10 below provides examples of substances/compounds requiring organotin catalysts as described in the RAR or presented by a catalyst supplier.

Table 2.10: Products of Organotin-catalysed Esterification and Transesterification Reactions

Substances indicated in the RAR	**Substances indicated by a catalyst supplier**	
	Target compounds	**Organotin catalyst**
Polyesters Alkyd resins Fatty acid esters Esters from transesterifications	• Trioctyltrimellitate; • unsaturated polyester; and • saturated polyester	Butyltin chloride dihydroxide (CAS No 13355-96-9)
	• Transesterifications for methacrylate esters used in the water treatment market; • transesterifications for coating resins	Dibutyltin oxide (CAS No 818-08-6)
	• Saturated polyester resins for powder coatings and coil coatings; • Unsaturated polyester resins for gel coat, sheet moulding and casting moulding applications; and • Polymeric plasticisers	Monobutyltin oxide (CAS No 2273-43-0)

Source: RAR, 2005; Vesta Intracon, 2005

2.4.3 Downstream Markets

As a first estimate of the downstream value based on the 2002 RAR, chemicals produced via the esterification reactions (including PVC- and polyolefin-related) are worth €1,000 per tonne (RPA & CEH, 2002). Data were provided for this report which indicate that the combined usage of organotins in all esterification reactions is 250 to 350 tpa. Based upon the range of concentrations for these products (0.001% to 0.5% by weight), the quantities of chemicals produced could be between 50,000 tonnes and 35 million tonnes per annum, with an associated value of between €50 million and €3.5 billion. Assuming a concentration of 0.1% by weight would give perhaps more realistic results: 300,000 tonnes of chemicals/powder coating, worth €300 million per year.

Powder Coatings

Table 2.11 details the *overall* market for powder coatings, as compared to total paints. These data do not separate out the market associated with organotin compounds.

Table 2.11: European Market for Powder Coatings and Total Paints Market in 2003

Parameter	**Percent of tonnage**	**Amount (Mt)**	**Percent of value**	**Value, €bn**	**€/tonne**
Powder coatings	5%	0.27	6 %	0.9	3,300
Total European paints market	100%	5.4	100 %	15.0	2,800

Source: CEPE (2005) in RPA (2005). Data have been rounded.

Typical applications include (ETICA, 2002 in RPA, 2005):

- household appliances (washing machines, refrigerators, etc.);
- office furniture;
- architectural uses (e.g. aluminium window frames);
- automotive components (e.g. trim parts, body primers, wheels);
- lawn and garden equipment; and
- heating and air conditioning systems.

Plasticisers

Plasticisers are organic compounds, with separate polymer chains which allow them to move in relation to one other, thereby improving elasticity. Plasticised PVC can contain up to 60% plasticiser when used as a coating and in very soft products. On average, plasticised PVC contains about 30% plasticiser (PE Europe *et al*, 2004).

There are more than 300 different types of plasticisers, although only between 50 and 100 are in commercial use. The most commonly used plasticisers are phthalates and adipates. In Western Europe, around one million tonnes of phthalates are produced each year, of which approximately 900,000 tonnes (~90%) are used to plasticise PVC. The most common are: DEHP, DIDP and DINP (ECVM, not dated). Table 2.12 outlines the market share for different plasticisers in Europe in 1999 and 2005 and highlights the difference between these two years.

Table 2.12: European Plasticiser Consumption Trends – 1999 & 2005

Plasticiser Type	**1999**	**2005**	**Change 1999-2005**
DEHP	42%	21%	- 50%
DINP/DIDP	35%	60%	+ 70%
Other phthalates	15%	12%	- 20%
Other plasticisers	8%	7%	- 13%

Source: Cadogan, 2006

DEHP was the market leader in 1999 but not so in 2005, after a significant increase in the consumption of DINP/DIDP. Overall, the consumption of phthalate plasticisers has remained unchanged and accounts for more than 90% of the European PVC plasticiser market. Table 2.13 presents the main PVC plasticisers and the key applications of the relevant plasticised PVC.

Table 2.13: List of Main PVC Plasticisers and their Key Product Applications

Plasticiser Type	**Main Use**
Phthalates	Flooring, cable, wire, films and sheets
Adipates	Flooring, cable, cling film
Trimellitates	Products which are exposed to high temperatures, e.g. cables in engine rooms

Source: PE Europe et al, 2004

2.4.4 Summary – Key Points

- The oxides of MBTO with lesser quantities of DBTO, MOTO and DOTO are used in esterification and transesterification reactions. Some of the polymeric products of these reactions are used in packaging applications or engineering plastics. The esters find use in the water treatment market, production of unsaturated polyester resins for gel coat, sheet moulding and casting moulding applications.

- Of particular importance are polyesters used as resins for powder coatings as this use accounts for over 50% of the organotins used in this area. Downstream applications of polyester resin coatings include general metal coating, coil coating and toner, and as alkyd resins in paints.

- Although organotin-catalysed substances/compounds (such as phthalates or adipates) can be used as PVC plasticisers, industry has argued that this use is not relevant.

- The concentration of tin catalysts is between 0.001% and 0.5% of the finished polymer.

2.5 Use of Organotins as Catalysts in Polyolefin Antioxidant Manufacture

2.5.1 Introduction to Polyolefins and their Degradation

Polyolefins are polymers which are produced by polymerising (or bonding) monomeric units of an olefin (usually ethylene and propylene). They exhibit a variety of good chemical and physical properties (e.g. flexibility, lightness, stability, ease of processing, etc) as well as low cost which make them ideal for many uses and applications. Polyethylene and polypropylene are among the most widely used polyolefins in plastics today.

During polymerisation, catalysts are used in closely and carefully controlled processes to produce individual polymer molecules with defined physicochemical properties (e.g. molecular weight (distribution), degree of branching and composition). Once the finished polymers are exposed to certain effects (such as stress, heat, water, mechanical loading, etc), chemical reactions start in the polymer which have the net result of changing the chemical composition (and molecular weight) of the polymer and thereon, the physical and optical properties of the polymer. These changes of the polymer properties relative to the initial, desirable properties are referred to as degradation. In this sense, “degradation” is a generic term for any number of reactions which are possible in a polymer (SpecialChem, 2007).

Two main type of degradation are particularly relevant: *oxidation* (involving the net loss of electrons, which once started, sets off a chain reaction which accelerates degradation) and *photodegradation* (where exposure to sunlight and some artificial lights can have adverse effects (e.g. cracking, chalking, colour changes, etc.) on the physical properties and useful life of plastic products). To combat these effects, effective process and thermal stabilisation is essential in the production of durable plastic products and antioxidants and stabilisers are typically used to interrupt the oxidation and photodegradation cycles respectively.

Antioxidants are molecules that have the ability to slow or prevent the oxidation of other chemicals. As mentioned earlier, oxidation reactions often involve the production of free radicals which can form chain reactions, antioxidants terminate these chain reactions by removing radical intermediates and/or by getting oxidised themselves (similar to reducing agents). Hence, antioxidants are often considered to be process stabilisers and any stabiliser which stops the auto-oxidation cycle is considered an antioxidant. In industry practice, however, antioxidants can also be used to provide protection against oxidation after processing, and in this sense is more referred to as a "long term thermal stabiliser". Long-term thermal stabilisers differ from processing stabilisers in that they must function effectively at temperatures well below the melting point of the polymer (SpecialChem, 2007).

An example of an antioxidant which is commonly used in polyolefin manufacture is the family of hindered phenols. A typical manufacturing process for a hindered phenol antioxidant uses a substituted cresol raw material for the phenolic ring portion of the molecule, and an aldehyde raw material for the bridging or connecting group. The batch reaction takes place in an alcoholic solvent utilising a catalyst (RAPA, 2001).

Open literature suggests organotins are used as catalysts in the production of hindered phenol stabilisers. Mono- and di-substituted organotin-based catalysts, such as dibutyltin oxide (DBTO), have been suggested to be generally used as catalysts in the esterification and trans-esterification reactions for the production of hindered phenol stabilisers (Mayzo, 2002). However, during consultation for this study, ETINSA has argued that synthesis of antoxidants for polyolefins does not utilise organotin chemistry for catalysts (ETINSA, 2007).

RPA (2005) notes that the concentration of the organotin catalyst is between 0.001% and 0.5% of the finished polymer, although the organotin may be partially degraded by the high temperatures used in the production processes. Van Beusichem & Ruberto (not dated) also note that most polyolefins contain one or more antioxidants at levels of 0.05 - 0.10%.

2.5.2 Applications/Uses of Polyolefins based on Organotin Catalysts

Although, organotin compounds have been reported in various consumer products made of various plastics (PVC, polyurethanes, polyethylene, etc.), including gloves, carpets, textiles, PVC beach balls, etc., the 2005 RAR identifies two main products containing polyolefins: nappies and female hygiene products (RPA, 2005). Data from the Women's Environmental Network (as reproduced in RPA, 2005) indicate that butyltin stabilisers have been detected in the non-woven polypropylene top sheet of babies' nappies (diapers). A report by the Dutch National Institute for Public Health and the Environment (RIVM, 2000 in RPA, 2005) noted that dioctyltin has been measured in sanitary panty liners.

RPA (2002) reflects the range of conflicting information which was available in the recent past in relation to the presence of organotin compounds in nappies. Some information indicated that organotins were only present in the securing tapes (in the adhesives); however, further information reported by one of the nappy manufacturers indicated that there were three possible sources of organotin compounds in nappies, these being the elastics, glues (used in securing) and in the non-woven topsheet (PG, 2000 in RPA, 2005). RPA (2005) notes that the organotins could be present as a result of the top sheet being made of silicone-grafted polypropylene or due to use as a catalyst in the production of an antioxidant in polyolefin films. This view has also been echoed by a manufacturer of organotin catalysts in a recent submission by ESPA on behalf of ETICA.

For the purposes of this project, RPA consulted with the European Disposables and Nonwovens Association (EDANA) - which represents the interests of non-woven material manufacturers and users. EDANA advised RPA that organotins are not used intentionally in absorbent hygiene products (AHPs). Historically, the presence of organotins in components of these products was known but not considered an issue of concern. According to EDANA, the release sheet of a nappy or female hygiene product, typically a strip of silicone-coated paper similar to baking paper has been recorded in the past as a major source of organotins in EDANA products. This release sheet is removed before use but was included in the initial organotin human exposure assessment, data from which was used in the 2005 RAR. Following requests made to suppliers, the use of organotins in the production of these release sheets has since been phased out and non-organotin catalysts are now used in their production.

Polyurethane foam in nappy waistbands was also found to contain organotins in the past. This use of polyurethane foam in nappies manufactured by EDANA members has now ceased, but, polyurethane foam, manufactured with alternative catalysts, is still used in adult incontinence products.

An EDANA voluntary agreement sets a limit for TBT contamination of <2 ppb and a limit of <10 ppb for each species of organotins individually; these are indicated to be the current detection limits for the analytical methods adopted. These limits refer to the organotin concentration in the raw materials used and not to the final AHPs and may be occasionally exceeded by suppliers due to contamination.

Historically, there were no standard test methods for measuring organotins in products such as EDANA members'. EDANA, therefore, developed two test protocols which now represent industry standards but have not yet become official ISO standards. The first protocol is based upon ethanol extraction techniques and is used for the measurement of total organotin in a product. The second protocol is based upon extraction with a urine substitute and is used to simulate actual organotin availability and exposure to humans. With the advent of testing for organotins to the ppb, rather than ppm, level, even the use of polythene bags to carry samples for analysis may introduce a measurable level of organotin contamination. Organotins may also still occur at ppb level but this is due to contamination from many sources which may include, for example, PVC flooring[11]. TBT

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[11] As noted elsewhere in this report, the use of organotins in PVC flooring is in decline.

is a sporadic contaminant that has not been accurately traced by suppliers but the suspicion is that the TBT is from contamination of catalysts or polymers via environmental sources, for example, from PVC dust.

According to EDANA, polymeric materials imported into the EU could introduce organotins into products manufactured by EDANA member companies; however, specifications by EDANA members should stop these materials being incorporated.

2.5.3 Summary – Key Points

- Organotins have been reported to be used as catalysts in the production of hindered phenol stabilisers.
- Mono- and di-substituted organotin-based catalysts, such as dibutyltin oxide (DBTO), have been suggested to be generally used.
- The concentration of the organotin catalyst is between 0.001% and 0.5% of the finished polymer, although the organotin may be partially degraded by the high temperatures used in the production processes.
- Baby nappies and female hygiene products have been recorded in the past as containing organotins.
- Currently, the suppliers to EU manufacturers of AHPs (EDANA) do not intentionally use organotins under a voluntary agreement co-ordinated by EDANA which sets a limit for TBT contamination of <2 ppb and a limit of <10 ppb for each species of organotins individually; these are indicated to be the current detection limits for the analytical methods adopted. These may be occasionally exceeded by supplies due to contamination. These limits refer to the organotin concentration in the raw materials used and not to the final AHPs.
- Organotins may still occur at ppb level but this is due to contamination from many sources which may include, for example, PVC flooring.

2.6 Use of Organotins as Catalysts in Silicones Manufacture

2.6.1 Introduction to Silicones and Catalysts

Technically known as ‘polyorganosiloxanes’, silicones are polymeric compounds in which silicon atoms join together with oxygen as chains or networks. The remaining valences of silicon link with organic groups - mainly methyl groups. Silicone elastomers, or rubbers, are made from linear polymers that bear hydroxyl, vinyl or other reactive side chains. The elastomers are rendered flexible by vulcanisation or curing, a process in which the chains are crosslinked in various ways to yield highly elastic, more or less open pored structures (CES, 2003b).

The crosslinking mechanism requires the presence of a catalyst. In the silicone chemistry, two types of catalysts are commonly used: heterogeneous catalysts (in which the catalyst is in a different phase from the reactants and the products) and homogeneous catalysts (in which the catalyst and the reactants are in a homogenous phase, usually liquid). Catalysts, which are commonly used in silicone chemistry are platinum, tin and titanium complexes.

The different silicone elastomers are classified according to the type of vulcanisation (crosslinking agents, temperature) and base-polymer viscosity employed and are broadly distinguished as room-temperature-vulcanising and high-temperature-vulcanising types (CES, 2003b). Organotins are used as catalysts in room temperature vulcanisation (RTV) via a condensation reaction to produce silicone elastomers.

Types of Organotins Used as Catalysts

Table 2.14 presents an overview of the applications of organotin stabilisers in the EU as described by the CES.

Table 2.14: Applications of Organotins used in Silicone Manufacture in the EU

Organotin	**Applications**
Dimethyltin di neo decanoate	Mould making*
Dibutyltin dilaurate (DBTL)	Catalyst for 2-component condensation curing silicone rubber
Dibutyltin diacetate	
Dibutyltin diethyl hexanoate	
Dioctyltin diversatate	
Dioctyltin maleate	
Dioctyltin ethylhexanoate	

Source: CES, 2007

** In mould making, there has been a move away from DBT due to their future classification CMR Cat 2*

According to the RAR (2005), organotin catalysts are typically used at concentrations between 0.01% and 0.1% by weight. On the other hand, CES (2007a) has suggested organotin concentrations of 0.1-1% in cured moulds and 10-30% in the second component of 2-component systems. The shelf-life of the moulds ranges from less than a year (9 months) to 10 years (CES, 2007a).

2.6.2 Applications of Organotin Silicone Catalysts

Current Uses of Organotin Catalysts

RTV One-component Elastomers(RTV-1)

Chemical structure: RTV-1 silicone elastomers are one-component, ready-to-use RTV systems. They comprise polydimethylsiloxanes, crosslinking agents, fillers, and auxiliaries. Crosslinking is triggered by contact with atmospheric moisture and proceeds with the elimination of by-products. It, therefore, starts off at the surface with the formation of a film and gradually extends further and further into the elastomer. The by-product, which is formed in small quantities, varies with the type of crosslinking agent employed and may be an amine, acetic acid or a neutral compound, such as alcohol (CES, 2003b).

Properties: RTV-1 silicone elastomers are the ideal solution to a large number of sealing, bonding and coating problems. According to CES (2007a), sealants are always made of one component-vulcanising materials. They have excellent resistance to weathering and ageing because of their unique chemical properties. Special additives ensure that RTV-1 silicone elastomers can also withstand extremely high and low temperatures (CES, 200b3).

Typical applications: RTV-1 silicone elastomers are effective in nearly all sealing, bonding and coating applications. As a result, they are used extensively in the automotive, construction, electrical, electronics and textile industries (CES, 2003b). Silicone sealants for DIY building work are readily available from DIY supply stores (RPA, 2005).

RTV Two-component Elastomers (RTV-2)

Chemical structure: RTV-2 silicone elastomers are two-component, pourable, spreadable or kneadable compounds that cure highly flexible cured silicone elastomers on addition of the cross-linking agent. Vulcanisation takes place at room temperature by one of two mechanisms, condensation or addition.

Typical catalysts for condensation curing are dibutyltin dilaurate and dibutyltin octoate. They catalyse the reaction between a, w-dihydroxypolydimethylsiloxanes and silicic acid esters. Water has a strong accelerating effect on the rate of reaction. The rate of reaction also depends on the crosslinking agent (its functionality, concentration and chemical structure) and on the type of catalyst. Unlike organic latexes and rubbers, no sulphur is used for curing silicone elastomers (CES, 2003b).

Properties: Most RTV-2 cured silicone elastomers retain flexibility up to temperatures as high as 200°C, with some even withstanding brief exposure to 300°C. At the other end of the temperature scale, they are still totally flexible at -50°C, special types withstanding -100°C. Generally, their thermal conductivity allows insulation of electrical equipment without heat accumulation. Their electrical characteristics, especially their insulating resistance, dielectric strength and dissipation factor, are highly advantageous. Not even years of outdoor weathering will significantly impair their properties (CES, 2003b).

Typical applications: Moulds, electronics, mechanical and plant engineering and healthcare devices (CES, 2003b). Silicone elastomer is an ideal material for making moulds of lifecastings and other objects. Example applications include (TAP Plastics, 2007):

- furniture;
- figurines;
- reproduction of statuettes;
- frames, mirrors, paintings;
- buttons;
- souvenirs;
- palaeontology;
- reproduction of old objects;
- various decorative items;
- prototypes;
- leather goods
- shoes;
- interior car trim;
- cornices;
- production of tooling;
- staff;
- master moulds for tiles;
- ceramics;
- porcelain;
- decorative candles;
- artistic metalwork;
- jewellery

The RAR stated that butyltin compounds are present in catalysts in DIY silicone mould kits (RPA, 2005). This final use may expose the consumer to pure DBT catalyst; however, the industry is now moving away from DBT due to its recent (proposed) classification as a CMR category 2.

Dental Silicone Moulds

ETICA identified, in 2003, the use of organotin catalysts in dental moulding (dental impressions)[12] and suggested (in communication to RPA in 2003) a maximum of 5% loading of the silicone elastomer (RPA, 2005). Information from the Federation of the European Dental Industry (FIDE) shows that organotin catalysts are still in use and that the proportion of the actual organotin compounds (DBTO or DBTL) is typically 0.1% w/w (as tin) (FIDE, 2007). FIDE characterised the size of the European market and the consumption of these materials as stable but gave no indication of the size of the market.

FIDE (2007) distinguishes between the use of organotin catalysts in dental moulds:

- as medical devices used by dentists; and
- as technical devices used in the dental lab.

The first is suggested to represent 95% of the EU organotin consumption for dental moulds with the second accounting for the remaining 5% (FIDE, 2007). Products have a shelf-life up to 3 years before use. The impression taking takes approximately 5 minutes and the final impression is stored in the dental lab up to 4 weeks (FIDE, 2007).

Silicone-grafted Polyolefins (Industrial Use)

Organotin catalysts are used condensation in cross-linking of silicone-grafted polyolefins such as polyethylene cable insulation. Consultation with a UK supplier of organotin catalysts suggests that DOTL has a major application in the silane grafted polyethylene market for the production of potable water pipes. DOTL has been suggested as being the only catalyst included in the leachate studies that are integral to the potable water pipe

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[12] Dental impression materials (impression moulds primarily used for crown and bridge reconstruction).

standards used in EU, UK and USA which all derive from an original US standard. No further information is currently available on this use of organotins.

Condensation cross-linking of silicone-grafted polyolefins is a considered by CES to be an industrial use (CES, 2007a).

Historical Uses of Silicone Catalysts

Baking and Cooking Silicone Moulds

Organotin catalysed silicone elastomers may be used to produce baking and cookie moulds (SCHER, 2006). However, CES (the relevant industry association) states that, *"to the best of the knowledge of CES members, which all together represent about 95% of the global market for silicones, no organotins are used or have been used to manufacture baking moulds for consumer use. The baking moulds are manufactured using a thermal curing process which does not require typical room-temperature curing catalysts such as organotins. Such baking moulds, however, are generally produced at elevated curing temperatures not requiring the use of a room temperature vulcanisation (RTV) catalyst such as an organotin"* (CES, 2007a). The same information was recently presented to the UK Advisory Committee of Hazardous Substances, on 6 March 2007, where it was indicated that, in practice, organotin catalysts are not used in baking or cookie mould applications (Donnelly, 2007). This presentation stated that "*according to information received from CES (...), baking moulds sold to consumers are cross-linked at high temperature, typically with platinum or peroxides, but never with organotins*".

Baking Paper Silicone Coatings

Silicone elastomers catalysed by organotins have been used in the production of food contact materials such as coatings for baking papers (RAR, 2005). The use of organotin catalysed silicones for the production of baking paper coatings has ceased in the EU following by voluntary action by industry (CES, 2007a; Donnelly, 2007). But there is evidence to suggest that baking papers with such coatings may well be imported into the EU (DG SANCO, 2005 in RPA, 2005). On the other hand, the key trade association has suggested that the global silicone industry voluntary phase-out of organotin-catalysed baking papers is now effective and that the main catalyst used in current systems is platinum (CES, 2007a).

Applications for Organotin-catalysed Silicones

We have requested information from the Centre Européen Des Silicones (CES) on the consumption of organotins in silicone catalysts and additional detail on use patterns and trends; however, we have been advised that this information is commercially confidential and cannot be disclosed.

According to the RAR, between 50 and 100 tonnes of organotin catalysts were used in production of silicones in 2000.

2.6.3 Downstream Markets and End Applications

It is estimated that the European silicones market is worth €2.5 billion per year and accounts for some 10,000 jobs (RAR, 2005). Furthermore, the downstream uses for silicones represent even greater markets. Silicones that have been produced using organotins represent some fraction of this (although the exact amount is not known).

2.6.4 Summary – Key Points

- Organotin catalysts are used in one-component component sealants (including consumer do-it-yourself products), RTV two-component silicone elastomers (including DIY silicone moulding kits) and condensation cross-linking of silicone-grafted polyolefins such as polyethylene cable insulation. Organotins have also been used as catalysts for baking and cooking moulds and baking paper coatings. Baking and cooking moulding kits and baking paper coatings now appear not to use organotin catalysts. Organotins also find uses as catalysts in RTV two-component dental moulding kits, however this use falls outside the scope of this report.

- Organotin catalysts currently used in the EU include dimethyltin dineodecanoate, dibutyltin dilaurate (DBTL), dibutyltin diacetate, dibutyltin diethylhexanoate, dioctyltin diversatate, dioctyltin maleate, and dioctyltin ethylhexanoate. Dibutyltin dilaurate (mainly) and dibutyltin octoate are key RTV-2 silicone catalysts.

- According to the RAR, organotin catalysts are typically used at between 0.01% and 0.1% by weight. According to industry, the concentrations are 10-30% in the second component and between 0.01% and 0.1% by weight in cured moulds.

- Between 50 and 100 tonnes of organotin catalysts were used in production of silicones in 2000.

2.7 Use of Organotins as Catalysts for Electrodeposition Coatings

2.7.1 Introduction to Electrodeposition Coatings

The metal frame of a car or light truck has an extremely complex shape with many areas hidden from a direct line of sight. It is virtually impossible to coat such a complex shape with conventional spray-applied paint. In order to achieve maximum coverage and therefore maximum corrosion resistance, this first coating layer is applied in a process known as electrodeposition (Dupont, 2007).

In the electrodeposition process, a mixture of resin and binder and a paste containing the pigments are fed into a tank. The vehicle is then lowered into the tank from an overhead conveyor and an electric current applied. This car body becomes the cathode and the tank the anode in an electrocoating reaction that results in a resin polymer being very tightly and evenly bound to the metal surface of the car body (NZIC, 2007). Current practice favours making the vehicle body the cathode as this minimises corrosion for steel, uses less electricity, gives a coating that is more resistant to salt corrosion than either of the other methods, results in good coverage and can be used in conjunction with zinc coated steels (Dupont, 2007, NZIC, 2007).

With regard to the composition of the coating mixture, there are two basic categories of electrodeposition coatings: epoxy and acrylic electrocoats. When the EDC is used as a primer for other top coatings or as a single protective coating for components, epoxy will perform best. Acrylic electrocoating is used mainly as a single coating for products or components that are to be exposed to sunlight for long periods (Electrocoat, 2007).

Catalysts are needed to speed up the curing of EDC; organotins are among the catalysts used in the EDC process.

2.7.2 Applications of Organotin Catalysts for Electrodeposition Coatings

The RAR notes that in 2000, between 700 and 800 tonnes of organotin catalysts were used in EDCs as primers applied for corrosion protection on motor vehicles. However, more recent data (shown in Table 2.4) suggest that the current tonnage is around 950 tonnes per year. Dibutyltin oxide (DBTO) and dioctyltin oxide (DOTO) are the main organotins used as catalysts for the curing of EDCs in Europe. The RAR found that the highest concentration of organotin catalyst in the final EDC coating was 0.5%.

One company manufacturing additives indicates that the modern EDC processes have been designed for the use of DBTO catalysts, for which they are uniquely suited. DBTO has the advantage of a long service time, high catalytic power and selectivity, and fast curing at low temperature on demand. EDC processes are highly efficient, optimised for low energy and material consumption. Emissions from EDC processes and coatings are described as being minimal, while the corrosion protection and lifetime of the finished articles is described as being ‘high’(pers. comm.).

While DOTO can be used in place of DBTO for the production of organotin EDC catalysts, it must be used at higher dosage levels and require changes to the production process and associated equipment. DOTO is produced at a lower production speed than DBTO which will reduce production capacity. In addition, such substitution will necessitate changes to the resulting EDC formulations and will increase the catalyst costs by approximately 50% (pers. comm.).

Bismuth compounds, such as bismuth oxide, as well as lead compounds can be used as alternatives to organotin catalysts. It is, however, noted that the use of bismuth compounds necessitates the use of new formulations and processes. Information on the technical performance, lifetime, corrosion protection and emissions data relating to the use of bismuth and lead compounds is, however, not available (pers. comm.).

An EU automobiles manufacturer provided information on the use of organotin catalysts in EDC coatings; they confirmed that di-substituted organotins are used in EDC by all motor manufacturers[13] but that they prohibit the use of tri-organotins in their products.

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[13] The company also commented on the possibility of organotin stabilisers being used in their materials. It has suggested that, with the advent of the ELV Directive which prohibits the use of lead stabilisers, it is

2.7.3 Downstream Markets and End Applications

Assuming a maximum concentration of organotin catalyst in the final EDC coating of 0.5%, the total quantity of coating produced would be up to 190,000 tonnes (based on a consumption of 950 tonnes of EDC) with a market value of around €200 million (an update on calculations in RPA, 2005 based upon CEPE, 2001).

2.7.4 Summary – Key Points

- DBT and DOT are used as catalysts for the curing of EDCs in Europe. Butyltins appear to be the preferred option for technical and cost reasons.
- The highest concentration of organotin catalyst in the final EDC coating may be as high as 0.5%.
- In 2000, between 700 and 800 tonnes of organotin catalysts were used in EDCs. However, more recent data (shown in Table 2.4) suggest that the current tonnage is around 950 tonnes per year. The main use for EDCs containing DBTO is as a primer applied for corrosion protection on motor vehicles.
- This use is considered to be an industrial use (that an average consumer is unlikely to come into frequent contact) and, as such, is outside the scope of the study.

2.8 Use of Organotins as Catalysts in Polyurethane Applications

2.8.1 Introduction to Polyurethanes

Polyurethanes are formed by reacting a polyol (an alcohol with more than two reactive hydroxyl groups per molecule) with a diisocyanate or a polymeric isocyanate in the presence of suitable catalysts and additives. Polyurethanes exist in a variety of forms including flexible foams, rigid foams, chemical-resistant coatings, specialty adhesives/sealants and elastomers (CPI, 2007; Johnson Matthey, 2002a), as follows:

- ***Flexible polyurethane foams*** can be produced easily in a variety of shapes by cutting or moulding; these are widely used in the furniture and automotive markets as comfortable and durable seating foam and are also popular for mattresses and pillows.
- ***Low-density rigid polyurethane foams*** are highly cross-linked polymers with a closed cell structure - each bubble within the material has unbroken walls so that gas movement is impossible. These materials offer good structural strength in relation to their weight, combined with outstanding thermal insulation properties. They are, therefore, widely used as an insulant in buildings, refrigerators, freezers and refrigerated transport vehicles.

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possible (although the company could not substantiate this with any figures) that this application may have increased since 2003.

- ***Polyurethane coatings*** give the highest wear resistance to surfaces such as floors and the outer skins of aircraft. They are also used in flexible coatings for textiles and adhesives for film and fabric laminates. Polyurethane binders are used to bind waste to produce new materials ranging from construction boards to sports surfaces. Other polyurethane coatings applications include:

  - paints, where they are chosen for their visual aspects in combination with adhesive properties and durability;
  - hard-wearing protection for bridge and car park surfaces; and
  - protective finishes where chemical resistance is key.

- Polyurethane ***sealants*** are tough and typically used to keep liquids from escaping through gaps and crevices, for example, in harsh climatic conditions to protect windows or in the construction sector on concrete expansion joints and as pre-formed gasket seals in piping (Johnson Matthey, 2007a). Polyurethane ***glues*** are generally versatile and can be used to bind together quite different materials such as wood, rubber, carton or glass. Packaging and outside furniture, which need resilience and strength, often rely on polyurethane adhesives as well as construction projects which benefit particularly from these qualities of polyurethanes.

- Most ***polyurethane elastomers*** have excellent resistance to abrasion and attack by oil, petrol and many common solvents. They can be tailored to meet the needs of specific applications, as they may be soft or hard, of high or low resilience, solid or cellular.

2.8.2 Applications of Organotin Catalysts in Polyurethane Manufacture

Organotin catalysts are used in a wide variety of polyurethane applications, aiding formation of the urethane bond and generally functioning as Lewis acid catalysts. As a general rule, organotin catalysts are not selective - they catalyse the reaction of isocyanates with both hydroxyl groups and water and also catalyse the hydrolysis of ester groups (Blank *et al*, 1999).

The key applications or organotin-catalysed polyurethanes include (RPA, 2005):

- urethane modified resins (e.g. alkyd, acrylic and acrylate) for *printing inks*, *adhesives* and surface *coatings*;
- two component polyurethane *elastomers* for a variety of applications; and
- industrial and automotive two-component *coatings*.

The RAR estimates that the polyurethane products in which organotin catalysts are used represent a significant proportion of the total polyurethane market: around 13% of the market by tonnage and of the direct market by value. Exact usage in the individual sectors (coatings, elastomers and automotive) is, however, unknown (RPA, 2005).

Information provided by a major EU polyurethane manufacturer on the use of organotin stabilisers in the EU is summarised in Table 2.15.

Table 2.15: Use of Alkyltin Catalysts in the Production of Polyurethanes in the EU (Estimates Provided by a Major Manufacturer)

Area of application	Market volume	Importance of organotin catalysts	State of substitution
Rigid spray foam for thermal insulation of the roofs and/or walls of buildings	40 – 80 tpa dialkyltin catalysts, supporting a business of 30 – 40,000 tpa of PUR spray systems	On-site foaming needs strong and effective catalysis by dialkyltins	Researched since years, but still not possible. Spray foam business might have to be discontinued without the catalysts
Rigid integral skin foam for car parts, electronics housing, ski cores, etc.	2 – 3 tpa dialkyltin catalysts, supporting a business of 4 – 5,000 tpa of PUR systems	Economic cycle times in production depend on catalysis by dialkyltins	Researched since years, but still not possible. The PUR systems would be difficult and costly to reformulate, because many of them are UL certified and would need re-certification
Shoe soles (polyether PUR)	Approx 6 tpa dialkyl tin catalysts, supporting a business of approx. 20,000 tpa of PUR systems	Economic cycle times in production depend on catalysis by dialkyltins	Researched since years, but still not possible. Reformulated PUR systems would have economic disadvantages for the manufacturers, accelerating the re-location of the industry to Asia and other places outside the EU
Coatings and adhesives	Dialkyltin catalysts may be of particular importance, however, the company could not provide additional information		
Source: Consultation			

Another industry consultee advised that organotin compounds are used in the manufacture of thermoplastic polyurethane (TPU). This may include injection moulding and magnetic media manufacture (videotapes, etc.) as well as breathable fabics (pers. comm.).

Table 2.16 (reproduced from the RAR) provides more detail on the key types of polyurethanes produced using organotin catalysts, the concentrations of the catalysts used and the types of final applications for the products in question.

Table 2.16: Applications for Polyurethane Catalysed with Organotins

Type	Conc.	Applications
Foams	<0.1%	Upholstered furniture, mattress fillings, car seats, car dashboards, insulation panels
Urethane modified resin	0.01% - 0.05%	Printing, surface coating, adhesives
2-component elastomers	0.05% - 0.2%	• Engineering components (gaskets, bearings, oil seals, rollers, etc.); conveyor belts, heavy duty coatings, sealants, sound insulation; • tyre infill elastomers, stacker-truck and skateboard wheels; • electronic component potting compound; • printing rollers and squeegees; • shoes and shoe soles (outer surface); and • mould making

Table 2.16: Applications for Polyurethane Catalysed with Organotins		
Type	**Conc.**	**Applications**
Industrial and automotive 2-component coatings	0.01% - 0.1%	Top coatings for: automobiles, boats, planes, wood varnishes, repair coatings, fabrics, heavy duty flooring in industry and sport grounds
Source: ETICA (2002) and ETICA (2003) in RPA (2005)		

These figures are consistent with the information concentrations implied in the data provided by the EU polyurethane manufacturer and those suggested by another industry consultee pointing to a concentration of 20-100 ppm (without catalysts recovery).

The RAR assumes that the organotin compounds used as polyurethane catalysts include stannous octoate, dibutyltin dilaurate (DBTL) and dioctyltin dilaurates (DOTL). Table 2.17 below outlines the organotin catalysts which are supplied by an EU company for use in different polyurethane applications.

Table 2.17: Examples of Commercially Available Organotin Catalysts for Polyurethane Manufacture		
Catalyst	**Function**	**Areas of application**
Tin-catalyst in dipropylene glycol	Catalyst for polyurethane systems, suitable for use in water-containing rigid foam spray systems	• Insulation
Stannous ethylhexanoate, Stannous octoate	Catalyst for flexible slabstock foam, moulded foam, 2C-paints & coatings and other polyurethane applications	• Furniture and mattresses; • Automotive; and • Coatings, Adhesives, Sealants & Elastomers (CASE) • Magentic media (TPU)
Blend of dibutyltin dilaurate in tertiary amine	Catalyst for rigid foam and especially rigid spray foam	• Insulation
Stannous carboxylate	Processing promoter for polyurethane powder coatings	• Coatings, Adhesives, Sealants & Elastomers (CASE)
Dibutyltin dilaurate	Catalyst for integral skin foam, rigid spray foam, cold curing cast elastomers and other polyurethane applications	• Insulation; and • Coatings, Adhesives, Sealants & Elastomers (CASE) • Breathable fabrics (TPU)
Source: Rhein Chemie, 2007 and pers. comm..		

The RAR assumed that around 400 tonnes of organotins per year were used in polyurethane applications. Recent data collected for the purposes of this study suggest that the current tonnage may have significantly increased and could be around 750 tonnes per year. Taking into consideration the tonnage estimates shown in Table 2.15, it would appear that coatings and sealants/adhesives account for the vast majority of the organotin catalysts consumed by the EU polyurethane industry.

2.8.3 Downstream Markets and End Applications

According to the RAR, 400 tonnes of organotins were used to produce 425 kilotonnes of polyurethane worth €1,316 million with a downstream product market having a total value of €10 billion. Assuming that the current tonnage may be almost double of that in the RAR, the market value of the organotin-catalysed polyurethane may be even greater.

2.8.4 Summary – Key Points

- Dibutyltin compounds, especially dibutyltin and dioctyltin dilaurate, are in widespread use in coatings as catalysts for the isocyanate/hydroxyl reaction.

- Between 400 and 750 tonnes of organotins are used per year as catalysts in the manufacture of polyurethanes. Information suggests catalyst concentration ranging from 0.01% up to 0.25%.

- Applications include urethane-modified resins (e.g. alkyd, acrylic and acrylate) for printing inks, adhesives and surface coatings, two component polyurethane elastomers for a variety of applications (for instance, shoes and shoe soles), industrial and automotive two-component coatings, flexible foams (mattresses, upholstered furniture), rigid spray foam for thermal insulation, and rigid integral skin foams for car parts, electronics housing, ski cores etc.

- Only a few of the uses of organotin catalysts in the polyurethane industry may be considered to be consumer uses. These may include flexible foams used in upholstered furniture and mattress fillings, possibly coatings, adhesives and sealants made available to consumers for DIY applications, shoes and shoe soles (outer surface). The rest may be considered to represent industrial uses and, as such, are outside the scope of the RAR - or any recommendations resulting from this study. Industrial users are considered to use personal protective equipment (PPE) which makes the risks different from those for consumers. They are also covered by the Workers Protection Legislation. The RAR also notes that polyurethane foams are unlikely to present a significant direct risk to consumers (conclusion ii).

2.9 Other Uses of Organotins

2.9.1 Chemical Synthesis

According to the RAR, tetra-substituted organotins are used as an intermediate in the synthesis of other chemicals. They are produced at only two sites in the EU and are limited to use in less than 10 sites in the EU (Donelly, 2007), for the production of mono-/di-substituted organotins through a redistribution reaction to produce organotin chlorides (RPA, 2005).

Since tetra-substituted organotin compounds are not used commercially, except in synthesis of other chemicals (and as, such are intermediates), the RAR did not consider them further and they will not, therefore, be considered further in this study either.

Similarly, the quantity of tri-substituted organotins produced as an intermediate in organic synthesis will not be considered for the purposes of this study. Losses to the environment and exposure of consumers are considered to be negligible.

2.9.2 Glass Coating

Organotin compounds are used in chemical vapour deposition (CVD) operations to deposit tin oxide (SnO_2) coating on glass. These substances carry the tin into contact with the bottle in a pyrolysis process that ends up with just inorganic tin coating and protecting the outside of the bottles (ETINSA, 2007). According to CPIV[14] (2007), these tin oxide-based products are used for solar control and heat loss reduction, and are important components of several types of photovoltaic panels, hence have an indirect positive impact on the environment. Information provided by a specific company on their use of organotins in glass coating is presented in the Box below.

Case Box 2.3: Use of Organotins in Glass Coating

Company A produces MBTC which is used by themselves and their customers for the production of tin oxide precursor formulations to be used for the CVD glass coating of flat and container glass. This market has been progressively increasing by 10% per year for flat glass, with no growth for container glass. Tin oxide coatings allow for the production of glass with increased heat and sun radiation protection and thermal insulation properties, thus enabling material and energy savings during the glass production process and energy savings in transport and use. In electronic applications, indium tin oxide (ITO) coatings allow for the production of glasses which are unique transparent electrical conductors, used for the manufacture of products such as displays, flat screens and solar cells.

Company A are aware that inorganic tin tetra chloride, DMTC, DBTC, DBTF are being used in marketed tin oxide precursor formulations for CVD glass coating. They indicate that while tin tetrachloride is cheaper than MBTC, its use would result in reduced hydrolytic stability, higher maintenance costs, downtime and material failures and higher material waste making it less efficient. On the other hand, DMTC, DBTC, DBT are more expensive in comparison with MBTC; also, they are more difficult to handle and apply and require different (and more expensive) equipment and operating conditions. Company A are also aware of other metal oxides such as titanium oxide being used for CVD glass coating; however, they note that glass coated with other metal oxides have different properties and are not comparable to tin oxide coatings.

Company A also highlights the fact that, while flat and container glass can be produced uncoated, uncoated flat and container glass lacks the specific advantages of coated glass, such as physical stability, thermal insulation and transparent conductivity. Further to this, uncoated glass containers (bottles) require thicker walls and therefore more glass. Uncoated flat glass for buildings has inferior thermal insulation properties resulting in higher energy heating requirements or additional glazing layers for insulation. The use of the extra glass needed to produce thicker bottles and additional glazing layers would result in the production of a corresponding amount of extra glass waste. Uncoated flat glass for electronics has no electrical conductivity therefore a completely new technology would be required for electronics applications currently using tin oxide coated glass.

The RAR estimates that approximately 700 tpa of monobutyltin chloride (MBTC) are used in hot-end coating of glass bottles and a further 60 to 100 tpa are used in coating of flat glass. Such coatings are applied at around 500 sites in the EU and the associated production of glass bottles could be around 130 billion per year (RPA, 2005).

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[14] Standing Committee of the European Glass Industries (CPIV)

Monobutyltin compounds were not considered to pose any risks and were outside the scope of the RAR and, are therefore, not considered further in this study. Information collected for this study suggests no discernible changes in the total tonnage of organotins in this applications, however, the quantity of di-substituted organotins used in glass coating (based on the information provided in Case Box 2.3) is currently unknown.

2.9.3 Antifouling Coatings

Tributyltin (TBT) and triphenyltin (TPT) compounds have been used as a paint additive since the 1970s to prevent the fouling of ship hulls. However, as already indicated, due to effects on marine ecosystems, EC Regulation No 782/2003 now prohibits the use of organotin compounds in all marine anti-fouling paints with effect from 1 July 2003 (although existing (unsealed) coatings may remain in place until 2008). This Regulation applies to the merchant shipping of Member States and to any other ships entering an EU port. ETINSA has advised that the production of TBT for biocides application has strongly decreased and the sales in the EU have stopped (ETINSA, 2007).

2.9.4 Agriculture and Wood Preservation

With regard to use of tri-substituted organotins as pesticides, there are three relevant groups of compounds: triphenyltins, tricyclohexyltins and trineophenyltins. As noted in the RAR, the use of triphenyltin as an active substance in plant protection products is no longer authorised in the EU (following Commission Decisions 2002/478/EC and 2002/479/EC) after evaluation of the toxicological, ecotoxicological and environmental-fate data. Tricyclohexyltin hydroxide, tricyclohexyltin triazole and bis-trineophenyltin oxide are permitted under the Plant Protection Products Directive in the EU and marketed in Europe. The maximum residue levels for these substances have been set by EC Directive 2006/53/EC to ensure that their acute reference dose is not exceeded.

As of 2001, less than 100 tpa of TBT oxide and TBT naphthenate were used as biocides in wood preservatives, primarily in the UK, France and Spain (ORTEPA, 2002 in RPA, 2005). ETINSA has advised that the production of TBT for biocides application has strongly decreased and the sales in the EU have stopped (ETINSA, 2007).

2.9.5 As a Biocide in Other Applications

The RAR notes that in the past, TBT was used as a biocide in a wide range of industrial applications including cooling water, pulp and paper mills, breweries, leather processing and textile mills. In addition, there are a number of products in which tri-substituted organotin compounds are believed to have been used in where these include:

- non-allergenic pillows used in the UK;
- insoles for shoes in the UK;
- use in the padding of cycling shorts in Germany; and
- use in a spray for the treatment of athlete's foot in Germany[15].

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[15] In relation to the historic use of tri-substituted organotin compounds in sprays to treat athlete's foot, it is indicated that the annual market in Germany was around 7.5 tpa (as TBT benzoate). No data are available for the other uses.

These applications are no longer allowed in the EU since TBT has not been notified under the Biocidal Products Directive.; however, it may still be in use outside the EU and, in theory, such articles may indeed find their way into the EU markets (see later discussion in Section 4.5.1). As indicated in the previous section, the production of TBT for biocides application has strongly decreased and the sales in the EU have stopped (ETINSA, 2007).

2.10 Summary of Organotin Uses

Table 2.17 below provides a summary of the types of organotins used in the different applications, the tonnages used and concentrations, the end-products of interest and the possible routes of consumer exposure (which are of key interest from a risk management perspective and for this study).

Table 2.17: Overview of Applications of Organotins for Consumer Uses

	Application area						
	PVC stabilisers	**Esterifications**	**Polyolefin antioxidants**	**Silicones**	**EDC**	**Polyurethanes**	**Biocides**
Types of organotins used	Mono- and/or di-methyl, butyl, octyltin and dodecyltin – the latter not confirmed. Only octyltin compounds and butyltin compounds produced in Europe.	Monobutyltin oxide with lesser amounts of dibutyltin oxide, monooctyltin oxide and dioctyltin oxide Phased out of production of plasticised PVC	Mono- and di-substituted organotin-based catalysts, such as dibutyltin oxide (DBTO)	Dibutyltin dilaurate (mainly) and dibutyltin octoate for RTV-2 silicones. Also, dimethyltin dineodecanoate, dibutyltin diacetate, dibutyltin diethylhexanoate, dioctyltin diversatate, dioctyltin maleate, and dioctyltin ethylhexanoate.	Dibutyltin oxide and dioctyltin oxide	Dibutyltin compounds, especially dibutyltin dilaurate. Stannous ethylhexanoate, stannous octoate, stannous carboxylate	Tri-substituted organotins, e.g. TBT
Tonnage	15,000 (possibly >16,000 according to new data)	150-350		50-100	700-800 (possibly up to 950)	400 (possibly up to 750)	<<100
Concentration	2% wt Possibly up to 3% wt	0.001%-0.5% by wt	0.001%-0.5% by wt of the finished polymer	10-30% by wt in the second component. 0.01%-0. 1% by wt in cured moulds	Up to 0.5% by wt	0.01-0.25% by wt	

Table 2.17: Overview of Applications of Organotins for Consumer Uses

	Application area						
	PVC stabilisers	**Esterifications**	**Polyolefin antioxidants**	**Silicones**	**EDC**	**Polyurethanes**	**Biocides**
Applications	60% is used for food packaging 40% for technical applications Over 90% of organotin stabilisers are used in rigid PVC Small quantities in plasticised PVC where the majority are the liquid mixed metal systems	Manufacture of plasticisers (although industry argues this is no longer valid), lubricants, heat-transfer fluids and adhesives. Polyester resins for powder coatings, general metal coating, coil coating and toner, and as alkyd resins in paints. Acrylic resins in clothing. High molecular weight co-polyester elastomers for packaging applications or engineering plastics. Methacrylate esters for water treatment. unsaturated polyester resins for gel coat, sheet moulding and casting moulding applications	Baby nappies and female hygiene products recorded in the past. Currently, voluntary agreement prevents intentional use in materials used by EU manufacturers of AHPs	One-component consumer (do-it-yourself) sealants (RTV-1). Condensation cross-linking of silicone-grafted polyolefins. DIY silicone moulding kits (RTV-2). Dental moulding kits (RTV-2). Baking and cooking moulds and baking paper coatings. These are now historical uses (global voluntary phase-out)	Primer applied for corrosion protection on motor vehicles	Urethane-modified resins (e.g. alkyd, acrylic and acrylate) for printing inks, adhesives and surface coatings. Two component polyurethane elastomers for a variety of applications (for instance shoes and shoe soles), and industrial and automotive two-component coatings. Furniture and mattresses (foams). Rigid spray foam for thermal insulation, and rigid integral skin foams for car parts, electronics housing, ski cores etc.	Applications are now obsolete due to the effect of the Biocidal Products Directive (no notification of TBT as a biocide means no placing on the market)

Table 2.17: Overview of Applications of Organotins for Consumer Uses

	Application area						
	PVC stabilisers	**Esterifications**	**Polyolefin antioxidants**	**Silicones**	**EDC**	**Polyurethanes**	**Biocides**
Possible consumer exposure routes (not taking into account any recent discontinuation of use)	Food packaging Pharmaceuticals packaging Non-food packaging Construction materials (DIY use of films, sheets, pipes, profiles) PVC sandals and PVC gloves PVC T-shirts PVC squash bottles PVC bags Paddling pools PVC rigid film PVC toys PVC floor and wall coverings Other	Plasticised PVC articles	Baby nappies Female hygiene products	DIY sealants DIY silicone moulding kits Dental moulding kits Baking and cooking moulds Baking paper coatings.	Not relevant	Flexible foams used in upholstered furniture and mattress fillings. Possibly coatings, adhesives and sealants made available to consumers for DIY applications,. Shoes and shoe soles (outer surface)	Non-allergenic pillows Insoles for shoes Padding of cycling shorts Sprays for the treatment of athlete's foot Significantly reduced use of organotins as biocides

3. CONSUMER EXPOSURE AND RISKS FROM ORGANOTINS

3.1 Introduction

This Section considers consumer exposure to organotin compounds and the identified hazards and/or risks which are of relevance, as identified in the Risk Assessment Report (RPA, 2005). The main aim is to describe the nature of the effects of organotins that are of importance in relation to the RRS. It therefore sets out the main results and conclusions of the RAR for organotins (Section 3.2), as well as the other effects of organotins which are of relevance, where these include the persistence, bioaccumulation and toxicity (PBT) characteristics (Section 3.3), endocrine disruption potential (Section 3.4) and carcinogenic, mutagenic and reprotoxic (CMR) effects (Section 3.5).

3.2 Results of the Risk Assessment Report

3.2.1 Approach to Assessment of Consumer Exposure in the RAR

As described in Section 2, organotin compounds in their various forms are used in a wide array of materials which can be utilised in a very large number of different applications, including many consumer products. Consumers within the EU can therefore be expected to be in close proximity to a range of different products containing organotin compounds. However, the presence of a substance in consumer products does not itself provide any indication of possible harm from these substances. Thus, a robust approach was adopted in the RAR in order to estimate the level of consumer exposure to organotin compounds and the likely level of risk.

Firstly, the RAR identified various consumer products in which organotin compounds have been detected and reported – on the basis that the types of products monitored for these organotin substances are those that were studied due to a potential concern. Hence, these products either lead to a relatively high level of possible exposure or are relatively commonplace and, as such, a consumer is likely to come into frequent contact with them. Following this, a number of worst-case exposure scenarios were developed for both adults and children for these consumer products[16].

In addition to the direct exposure to organotin compounds from products, it was also considered that consumers will be exposed to a certain quantity of organotins via the environment. This exposure was estimated based on the environmental exposure assessment using the TGD and the *EUSES2* model.

The actual level of exposure to the organotin compounds from the various sources (i.e. consumer products and via the environment) was then summarised, in order to provide a basis for comparison of the total exposure with the tolerable daily intake (TDI) values used in the assessment and also to allow for comparison of the relative importance of the various sources.

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[16] SCHER opinion is that, for both health and environmental risks, risk estimates of the RPA report may not represent the worst case situations.

The associated degree of risk from organotins was then determined using a 'group' TDI for the four organotins (TBT, DBT, DOT and TPT) in combination. The RAR used a TDI value of 0.1 µg Sn/kg body weight per day[17]; hence, if the organotin intake exceeded the TDI, the RAR concluded that *there was a need for limiting the risks* (i.e. conclusion (iii)).

In explaining the risk conclusions derived, the RAR considered not only the current use pattern of organotins but also the impact of regulatory and market developments relating to organotins which impact on the identified exposure and/or risks.

The RAR also considered the possibility that sources of organotin exposure contributing less than 100% of the TDI may, together, result in the TDI being exceeded. This cumulative risk, associated with exposure to a number of risk sources, could result in a conclusion (iii) being reached. In order to assist in determining which risk sources were likely to be significant contributors to the overall cumulative risk, those risk sources potentially responsible for an organotin intake in the range 20% to 100% of the TDI were thus assigned a conclusion (ii)* (*although there is no need for further information and/or testing and no need for risk reduction measures when considering this risk source in isolation, when considered in combination with other risk sources, it may be desirable to consider limiting the risks (from this risk source)*).

3.2.2 Conclusions of the Risk Assessment Report

Table 3.1 overleaf summarises the results of the RAR (in relation to risks for the consumer) setting out the:

- source of exposure to organotins;
- calculated contribution of the source to the TDI;
- risk characterisation derived in the RAR; and
- any comments to be borne in mind in understanding the risk characterisation.

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[17] The CSTEE proposed that a group TDI value of 0.27µg/kg bw/day for TBT, DBT, DOT and TPT as chloride should be adopted, or 0.1 µg/kg bw/day as Sn.

Table 3.1: Summary of Risk Assessment Findings

Source of Exposure	**Calculated TDI (%)**	**Risk Conclusion**	**Comment in RAR**
Conclusion (iii): there is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.			
Environment (local)	5,092 (child) 1,273 (adult) 1,660 (adult) 415 (adult)	(iii) (iii) (iii) (iii)	High values from use of TBT in wood treatment which is now discontinued This risk derives from production of di-substituted organotins at various sites – although there are uncertainties over leaf-air partition coefficient
Silicone baking paper (cookies)	2,325 (child) 720 (adult)	(iii) (iii)	This risk derives from the use of organotin catalysts which was discontinued in 2005
Fish products	284 (child) 71 (adult)	(iii) (ii)*	This risk derives from the use of organotins in anti-fouling paints (which is now restricted) – child risk is based on an assumed intake per kg bodyweight four times that for adults. The median intake is indicated to be 10 times lower which would result in a conc (ii)* for children and conc (ii) for adults
T-shirts	189 (child) 25 (adult)	(iii) (ii)*	
Indoor air/dust	117 (child) 17 (adult)	(iii) (ii)	This risk derives mainly from use of DBT in PVC wall and floor coverings
Conclusion (ii): although there is no need for further information and/or testing and no need for risk reduction measures when considering this risk source in isolation, when considered in combination with other risk sources, it may be desirable to consider limiting the risks (from this risk source)			
2-part silicone moulds	87 (adult)	(ii)*	
Female hygiene products	62 (adult)	(ii)*	
PVC food packaging	54 (child) 22 (adult)	(ii)* (ii)*	
Foot spray	49 (adult)	(ii)*	See Note
Dental moulding	46 (adult)	(ii)*	
PVC sandals	33 (child) 33 (adult)	(ii)* (ii)*	
PVC gloves	33 (adult)	(ii)*	
Insoles	26 (adult)	(ii)*	See Note
Nappies	21 (child)	(ii)*	
Conclusion (ii): there is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.			
Non-allergenic pillows	19 (child) 2 (adult)	(ii) (ii)	See Note
Cycling shorts (padding)	18 (adult)	(ii)	See Note
PVC Squash Bottles	15 (child)	(ii)	
PVC bags	7 (adult)	(ii)	
Silicone sealant	4 (adult)	(ii)	
Paddling pool	3 (child)	(ii)	
PVC rigid film (used in food and other packaging)	3 (adult)	(ii)	
PVC toys (mouthing)	2 (child)	(ii)	

Source: RPA, 2005

Note: According to the RAR, this risk should be eliminated due to the ban on TBT biocides in consumer products; however, this may not be the case as discussed in Section 4.4.1. Also, as noted by SCHER (2006) products already in use may be there for a considerable time and will still contribute to the total exposure of the individual.

3.2.3 Discussion of Risk Assessment Findings

As can be seen from Table 3.1 above, the RAR identified a significant level of risk (requiring risk reduction measures) for children exposed to organotins from a range of consumer articles (in particular, PVC-printed T-shirts). According to the RAR, the dominant contributor to human uptake is via the environment (close to sources of significant emissions (e.g. timber treatment plants). Other significant sources include cookies baked on silicone baking paper (adults and children), food wrapped in PVC (adults and children), sanitary panty liners (adults) and foot spray (adults). These uses contribute to exposure in the range of 20 – 100% of the tolerable daily intake (TDI) (RPA, 2005).

The RAR also notes that (using a Monte Carlo simulation) for adult consumers, although the overall 'typical' (median) exposure is about 65% of the TDI, about 25% of adult consumers are exposed to more than the TDI. For children, the overall exposure for 70% of young child consumers will exceed the group TDI, while the 'typical' (median) 8kg child consumer is exposed to about 160% of the TDI (RPA, 2005).

In commenting on the RAR findings, the SCHER (2006) opinion was that:

- the total consumer exposure to organotins from all identified pathways – where this includes those exposure pathways estimated to contribute to less than 20% of the TDI - should form the basis of the risk assessment. If the resulting total exposure exceeds the TDI, then there is a reason for concern and risk reduction measures should be considered, regardless of the number of exposure pathways involved;

- the most important exposure pathways are food, indoor air, household dust and dermal contact with different polymer materials;

- there is a high risk of individual members of the general population, especially children, (greatly) exceeding the TDI for organotins; and

- the risks estimates derived in the RAR may not represent realistic worst case situations (due to an underestimate of the exposure for some scenarios).

The SCHER Opinion together with some further comments are presented in Annex III.

3.3 PBT Effects Assessment

In the RAR, an assessment of the PBT (persistence, bioaccumulation and toxicity) and vPvB (very persistent and very bioaccumulating) characteristics of organotins has been undertaken. Overall, the following observations (summarised in Table 3.2) were made:

- ***Persistence***: it is likely that the four (groups of) organotins being considered (TBT, DBT, DOT and TPT) will meet the P and vP criteria.

- ***Bioaccumulation***: the degree to which a substance bioaccumulates is assessed by considering the bioconcentration factor (BCF) associated with that substance. TPT has a BCF of more than 5,000 (in freshwater species) and, as such, is likely to exceed the B and vB criteria for the marine environment. TBT has a BCF value of more than 3,000 and would thus meet the B criterion but not the vB criterion. However, it is important to stress that this is a value obtained for freshwater species. With regard to marine species, much higher BCF values are reported with particular reference to an inverse relationship with concentration (in other words, the lower the concentration the higher the BCF value). Values of 10,000 and upwards have thus been reported. For DBT and DOT, the BCF values are significantly below 2,000. Given the differences in effects in freshwater and marine environments, it is possible that the corresponding BCF values in the marine environment might be somewhat higher but no reliable data were identified.

- ***Toxicity***: TBT and TPT would be classified as T. Furthermore, it is likely that DBT would also be classified as T. However, the situation with DOT is less clear. The freshwater NOEC is above the threshold value and there are insufficient data to demonstrate the use of much lower values in the marine environment.

Table 3.2: Potential PBT/vPvB Classification of Organotins

Criterion	DBT	TBT	DOT	TPT
P	yes	yes	yes	yes
B	possibly	yes	possibly	yes
T	probably*	yes	possibly	yes
PBT	**possibly**	**yes**	**possibly**	**yes**
vP	yes	yes	yes	yes
vB	unlikely	yes	unlikely	yes
vPvB	**unlikely**	**yes**	**unlikely**	**yes**

** SCHER (2006) notes that the classification for DBT as T should be definitely 'yes' as opposed to 'probably'. A careful assessment is, however, required for the B classification.*

Overall, it is concluded (with SCHER agreeing) that, in relation to the marine environment, TBT and TPT are likely to be classified as both **PBT** and **vPvB** substances.

Although DBT and DOT could be classified as PBT substances, they are unlikely to be vPvB substances. It is, however, understood that DOTC is on the European Chemicals Bureau's list for candidate PBT/vPvB substances, subject to further B tests.

3.4 Endocrine Disruption Effects

Endocrine disrupters are defined as a group of chemicals, exposure to which can cause adverse health effects in an intact organism or its offspring or (sub-)population by altering the function of the endocrine system. In wildlife, endocrine disrupters have been shown to cause abnormalities and impaired reproductive performance in some species, and to be associated with changes in immunity, behaviour and skeletal deformities. In humans, endocrine disrupters have been suggested as being responsible for declining sperm counts in some geographical regions, increased incidences in numbers of male children born with genital malformations and increased incidences of certain types of cancer that are known to be sensitive to hormones (EC, 2004).

In December 1999, the Commission adopted a *Community Strategy for Endocrine Disrupters* which set out a number of actions relating to, *inter alia*, identification of endocrine disrupting substances, monitoring, research, international co-ordination and communication to the public. In 2000, a study carried out on behalf of the European Commission by BKH Consulting identified a candidate list of 553 substances for which scientific evidence of endocrine disruption was gathered. Further analysis was undertaken for 146 of these substances (i.e. the high production volume and/or highly persistent ones) and these were grouped into three categories. 66 substances were considered to Category 1 for which there was at least one study providing evidence of endocrine disruption in an intact organism. A further categorisation of the Category 1 substances indicated that 60 of the 66 substances were considered as substances having high exposure concern and evidence of endocrine disruption (BHH, 2000).

A number of tributyltin (TBT) and triphenyltin (TPT) (as well as tripropyltin) compounds are among the list[18] of 60 substances of endocrine disruptors of high concern (or C*ategory I substances: evidence of endocrine disruption in living organism*s) (BKH, 2000).

3.5 Carcinogenic, Mutagenic and Reprotoxic (CMR) Effects

According to the ECB website, the final proposal of the Technical Committee for Classification and Labelling of substances for the 30th Amendment to Technical Progress (ATP) of Directive 67/548/EEC includes a proposal for dibutyltin chloride to be classified as a Category 2 reproductive toxin and Category 3 mutagenic substance[19]. As a category 2 reprotoxic substance, the sale to consumers of preparations containing DBTC will be banned at levels above the limit concentration for exposure as set out in Annex I of Directive 67/548/EEC, relating to the classification, packaging and labelling of dangerous substances.

It is worth noting that a similar classification has been agreed by the Commission Working Group on Classification and Labelling for dibutyltin oxide (DBTO); however, this is not listed in the 30th ATP. It is also understood that there is a German proposal (similar to an earlier Swedish proposal) to extend the ECB classification decision for DBTC to a group entry in Annex I for salts of DBT in due course (Rohm & Haas, 2005).

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[18] The listings produced are not final and chemicals may be added or removed in response to either developments in scientific knowledge or changes in chemical usage patterns.

[19] Category 2 refers to substances that should be regarded as having C/M/R properties. Category 3 refers to substances suspected of having C/M/R properties, but the available data are insufficient either to classify the substance in category 1 or 2 or to conclude that no classification is needed.

However, in relation to human health risks, it is important to bear in mind that the ‘safe’ level of exposure for the four groups of organotins (DBT, TBT, DOT and TPT) being considered in this study is determined by other types of effects. Specifically, the opinion of SCHER is that the human health effects for these four groups of organotins are additive both for the target organ (thymus) and for the mode of action (immunotoxicity).

4. EXISTING RISK REDUCTION MEASURES

4.1 Overview

The following sections provide an overview of the various risk management measures that are currently in place, or are expected to be implemented, to control the emissions and exposure to organotins. An assessment of these existing controls will aim at determining whether existing risk reduction measures are sufficient for addressing the identified risks and, if not, what additional controls (or tightening of existing controls) may be required.

In this Section, an overview of the existing EU-wide legislative controls is provided, sub-divided into those controls/measures addressing risks from organotins to humans:

- via the environment (Section 4.2);
- from the organotins themselves or in consumer products (Section 4.3); and
- from biocides and food products (which are subject to their own regulatory framework) (Section 4.4).

This is followed by a consideration of legislative controls in specific Member States (Section 4.5) and other international and national initiatives which are of relevance (Section 4.6). Finally, there is a consideration of (voluntary) risk management measures implemented by industry (Section 4.7).

4.2 Measures Addressing Risks to Humans via the Environment

4.2.1 Integrated Pollution Prevention and Control (IPPC) Directive (96/61/EC)

At the Community level, the main existing legislation of direct relevance to controlling the risks from industrial point sources of organotins is the IPPC Directive (96/61/EC). The IPPC Directive lays down measures designed to prevent or, where that is not practicable, to reduce emissions to air, water and land from the activities mentioned in Annex I to the Directive, including measures concerning waste. It also makes reference to, or is referred to by, the main pieces of legislation for the three environmental compartments (e.g. the Waste Directives, Water Framework Directive, etc.).

All installations covered by Annex I of the Directive - mainly medium-sized and large scale industrial installations but also waste management installations - are required to obtain an authorisation (permit) from the authorities in the various EU countries[20]. Installations/sites should be operated (and permits granted) according to the 'best available techniques' (BAT) which are set out for the various process types covered in BAT Reference (BREF) Documents. The BREF Documents are only intended to assist

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[20] New installations listed in Annex I require a permit from the competent authority before being put into operation. Existing installations will have to operate in accordance with the Directive by 30th October 2007 at the latest.

the licensing authorities as the final decision on emission limits and process conditions for individual sites is established by the Member States' competent authorities[21].

Under IPPC, a permit application must include a description of the nature and quantities of foreseeable emissions from the installation into each medium as well as identification of significant effects of the emissions on the environment. Emission limit values (ELVs) may be set in the permit for all pollutants likely to be released in significant quantities. Permits issued by the authorities must also contain suitable release monitoring requirements, specifying measurement methodology and frequency, and the operator must provide monitoring data to enable compliance assessment.

IPPC does not impose any specific restrictions on the release of organotins to the environment. However, organotin compounds are included in the list of pollutants to be reported if a threshold value is exceeded (as presented in Annex A1 to Commission Decision 2000/479/EC on the implementation of a European Pollutant Emission Register (EPER))[22]. For organotins, the reporting threshold for emissions to water is 50 kg/per annum.

4.2.2 Water Framework Directive (WFD) (2000/60/EC)

On 17 July 2006, the Commission adopted a proposal for a Parliament and Council Directive on environmental quality standards (EQS) in the field of water policy. This Directive is intended to implement Article 16 of the Water Framework Directive (2000/60/EC) (WFD) which requires the Commission to come forward with EQS in surface waters for priority substances. It aims to ensure a high level of protection against risks to or via the aquatic environment attributable to 33 priority substances (PS) and certain other pollutants which are potentially harmful by setting EQS which should not be exceeded in the aquatic environment. Member States are also required to take measures to aim to achieve the WFD objective of 'good status' for water bodies by 2015.

Tributyltin compounds have been included in the list of priority hazardous substances (PHS) in the Directive. Article 16(6) of the WFD requires the cessation or phase-out of discharges, emissions and losses of PHS within 20 years of adopting measures for that purpose. The proposed EQS for organotins is 0.0002 μg/L as an annual average value for all surface waters.

In considering the relevance of the WFD to organotins, it should be borne in mind that the introduction of actual controls and measures under the WFD is occurring over time, and the Directive provides a timetable for the identification of measures as part of River Basin Management Plans. The consequence of the classification of organotins as a PHS is that adequate combinations of process and product control measures should be taken for the progressive reduction (and eventual cessation) of discharges, emissions and

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[21] Article 9 of the Directive states that authorities must take into account (a) the technical characteristics of the installation, (b) its geographical location and (c) the local environmental conditions.

[22] Note that E-PRTR is the European Pollutant Release and Transfer Register, which will succeed the EPER. It is based on Regulation (EC) No 166/2006 and is intended to fully implement the obligations of the UN-ECE PRTR Protocol, which was signed in May 2003 by 36 countries and the European Community.

losses. The impact assessment carried out by the Commission prior to the adoption of the proposal showed that it would be more cost-effective, flexible and proportionate to leave the introduction of additional control measures, including ELVs, to Member States. Should Member States provide sufficient evidence that additional measures are needed at Community level, there would be various mechanisms under existing and upcoming instruments to allow them to put this to the Commission as a basis for discussion.

4.2.3 Hazardous Waste Directive (91/689/EEC)

Council Directive 91/689/EEC (Hazardous Waste Directive (HWD) of 12 December 1991 on hazardous waste (as amended) was introduced in the general framework of Directive 2006/12/EC[23] on waste and its aim is to approximate the laws of the Member States on the controlled management of hazardous waste. It provides a common definition of 'hazardous waste', lists wastes that can be classified as hazardous (including their constituents and properties) and prohibits the mixing of hazardous waste with other types of waste except where it is a necessary part of the disposal operation.

Central to the application of the HWD is the revised European Waste Catalogue (EWC) which defines and categorises all wastes, hazardous and non-hazardous, according to the generic industry or process from which the waste originates, or by the generic waste type. The entries in the EWC are differentiated into three waste types: absolute hazardous waste, mirror waste and non-hazardous waste. Absolute hazardous waste and non-hazardous waste are identified from their source and no further assessment is necessary. Mirror waste, however, is considered as hazardous depending upon the dangerous substances within it, where these "dangerous substances" refer to those substances classed as dangerous under the Dangerous Substances Directive and Dangerous Preparations Directive. These dangerous substances are assigned one or more hazard properties, which relate directly to the hazard classification allocated to them under the DSD. Certain organotins are, therefore, likely to be considered as mirror waste based on their classification and labelling (as well as concentrations) as discussed in Section 4.3.1.

The HWD also requires that the national competent authorities publish a hazardous waste management plan. Such a plan can be published as part of the general waste management plan drawn up under the Framework Directive on Waste, or it can be published as a separate document.

4.3 Measures Addressing Direct Risks to Humans

4.3.1 Classification, Packaging and Labelling of Dangerous Substances and Preparations (Directives 67/548/EEC and 1999/45/EC) and the Proposed GHS

Council Directive 67/548/EEC (also known as the Dangerous Substances Directive (DSD)) sets out harmonised EU rules regarding the classification, packaging and labelling of dangerous chemical substances. Directive 1999/45/EC (also known as the Dangerous Preparations Directive (DPD)) extends these rules to dangerous preparations.

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[23] This Directive consolidates and replaces Directive 75/442/EEC as subsequently amended.

Together, these Directives are aimed at improving awareness of the 'proper' use, handling and disposal of a substance or preparation. To this end, the packaging of all classified substances must be labelled to show, inter alia:

- symbols indicating the danger involved in using the substance;
- symbols indicating the specific risks arising from use of the substance; and
- symbols relating to safe use of the substance.

The DPD describes the methodology for assessing the safety properties of finished products – based on the safety properties of individual substances as determined under the DSD. It should be borne in mind that the classification and labelling Directives are focussed on the assessment of the intrinsic hazards of chemicals, rather than the actual risks from use, as they do not take exposure into account.

Table 4.1 overleaf provides the current classification and labelling requirements for the organotins. As can be seen, the table includes a proposal for dibutyltin chloride and dibutyltin oxide to be classified as Category 2 reproductive toxins and Category 3 mutagenic substances. As indicated earlier, there were proposals for the classification of DBTC to be extended to a group entry in Annex I (of DSD) for salts of DBT (Rohm & Haas, 2005). This is pertinent to the control of organotins because classification as Category 2 reprotoxic substances, automatically triggers marketing and use restrictions under the framework of Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations. Preparations containing such substances may not be placed on the market for sale to the general public in concentration equal to or greater than those set out in Annex I to Directive 67/548/EEC (shown in Table 4.1). If no limit concentration is set out in Annex I of Directive 67/548/EEC, a generic concentration limit is set from Table VI of Annex I to Directive 1999/45/EEC (0.1% w/w).

It is, however, important to note that no indication has been found of plans to classify DOTC (or any other DOT) as reprotoxic. According to the ECB website, the final proposal of the Technical Committee for classification and labelling of substances for the 30th Amendment to Technical Progress of the DSD was forwarded to the European Commission DG Environment in March 2007. It is understood that the 30th and 31st ATPs will not be published as such but included in the Globally Harmonised System (GHS) of Classification and Labelling.

On 27 June, 2007, the European Commission adopted the *Proposal for a Regulation on classification, labelling and packaging of substances and mixtures* (EC, 2006) which amends (and will eventually supersede) the existing DSD and the DPD with the aim of ensuring a high level of protection of human health and the environment as well as the free circulation of substances on the internal market while enhancing competitiveness and innovation. The implications for organotins (in tandem with the REACH Regulation which it complements) are currently unclear.

Table 4.1: Classification and Labelling of Organotins

Substance	Classification	Labelling	Concentration
Classification and Labelling Currently in Annex 1 of Directive 67/548/EEC			
Tributyltin compounds	T; R25-48/23/25 Xn; R21 Xi; R36/38 N; R50-53	T; N; R: 21-25-36/38-48/23/25-50/53 S: (1/2-)35-36/37/39-45-60-61	**C ≥ 25%**: T, N; R21-25-36/38-48/23/25-50/53 **2.5% ≤ C < 25%**: T, N; R21-25-36/38-48/23/25-51/53 **1% ≤ C < 2.5%**: T; R21-25-36/38-48/23/25-52/53 **0.25% ≤ C < 1%**: Xn; R22-48/20/22-52/53
Triphenyltin compounds	T; R23/24/25 N; R50-53	T; N; R: 23/24/25-50/53 S: (1/2-)26-27-28-45-60-61	**C ≥ 25%**: T, N; R23/24/25-50/53 **2.5% ≤ C < 25%**: T, N; R23/24/25-51/53 **1% ≤ C < 2.5%**: T; R23/24/25-52/53 **0.25% ≤ C < 1%**: Xn; R20/21/22-52/53
Triphenyltin hydroxide	Carc. Cat. 3; R40 Repr. Cat. 3; R63 T+; R26 T; R24/25-48/23 Xi; R37/38-41 N; R50-53	T+; N; R: 24/25-26-37/38-40-41-48/23-50/53-63 S: (1/2)-26-28-36/37/39-45-60-61	
Trioctyltin compounds	Xi; R36/37/38, R53	Xi; R: 36/37/38-53 S: (2-)61	**C ≥ 25%**: Xi; R36/37/38-53 **1% ≤ C < 25%**: Xi; R36/37/38
Tin tetrachloride	C; R34, R52/53	C; R: 34-52/53 S: (1/2-)7/8-26-45-61	**C ≥ 25%**: C; R34-52/53 **10% ≤ C < 25%**: C; R34 **5% ≤ C < 10%**: Xi; R36/37/38
Classifications Discussed by the Commission Working Group on Classification and Labelling and Yet to be Published in Annex 1			
Dibutyltin oxide	Repr. Cat. 2; R60-61 Muta. Cat. 3; R68 T; R25-48/25 Xi; R41 N; R51/53	R: 60-61-25-41-48/25-68-51/53 S: 53-45	

Table 4.1: Classification and Labelling of Organotins

Substance	**Classification**	**Labelling**	**Concentration**
Dibutyltin chloride	Repr. Cat. 2; R60-61 Muta. Cat. 3; R68 T+; R26, R25-48/25 C; R34 Xn; R21 N; R50-53	R: 60-61-21-25-26-34-48/25-68-50/53 S: 53-45-60-61	**C ≥ 25%**: T+, C, N; R60-61-21-25-26-34-48/25-68-50/53 **10% ≤ C < 25%**: T+, C, N; R60-61-22-26-34-48/25-68-50/53 **7% ≤ C < 10%**: T+, N; R60-61-22-26-36/38-48/22-68-50/53 **3% ≤ C < 7%**: T, N; R60-61-22-23-36/38-48/22-68-50/53 **2.5% ≤ C < 3%**: T, N; R60-61-23-36/38-48/22-68-50/53 **1% ≤ C < 2.5%**: T, N; R60-61-23-36/38-48/22-68-51/53 **0.5% ≤ C < 1%**: T, N; R60-61-20-36/38-51/53 **0.25% ≤ C < 0.5%**: Xn, N; R20-36/38-51/53 **0.1% ≤ C < 0.25%**: Xn; R20-36/38-52/53 **0.025% ≤ C < 0.1%**: Xi; R36/38-52/53 **0.01% ≤ C < 0.025%**: Xi; R36/38
Dioctyltin chloride	T; R23-48/25, R53	R: 23-48/25-53 S: (1/2)-38-45-61	

Key:
C = Corrosive; **T** = Toxic; **T+** = Very Toxic; **N** = Dangerous to the Environment; **Xi** = Irritating; **Xn** = Harmful; **Muta** = Mutagenic; **Repr** = Reprotoxic

R21 = Harmful in contact with skin. **R23/24/25** = Toxic by inhalation, in contact with skin and if swallowed. **R26** = Very toxic by inhalation. **R34** = Causes burns. **R36/37/38** = Irritating to eyes, respiratory system and skin.
R40 = Possible risks of irreversible effects. **R41** = Risk of serious damage to eyes. **R48/23/25** = Toxic: danger of serious damage to health by prolonged exposure through inhalation and if swallowed. **R50** = Very toxic to aquatic organisms. **R51** = Toxic to aquatic organisms. **R52** = Harmful to aquatic organisms. **R53** = May cause long-term adverse effects in the aquatic environment. **R60** = May impair fertility. **R61** = May cause harm to the unborn child. **R63** = Possible risk of harm to the unborn child. **R68** = Possible risk of irreversible effects.

S1/2 = Keep locked up and out of reach of the children. **S7/8** = Keep container tightly closed and dry. **S24** = Avoid contact with the skin. **S25** = Avoid contact with eyes. **S26** = In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. **S28** = After contact with skin, wash immediately with plenty of ... (to be specified by the manufacturer). **S35** = This material and its container must be disposed of in a safe way. **S36** = Wear suitable protective clothing. **S37** = Wear suitable gloves. **S38** = In case of insufficient ventilation, wear suitable respiratory equipment. **S39** = Wear eye/face protection. **S45** = In case of accident or if you feel unwell, seek medical advice immediately. **S60** = This material and its container must be disposed of as hazardous waste. **S61** = Avoid release to the environment.

4.3.2 Marketing and Use Restrictions Directive (76/769/EEC)

Marketing and use restrictions are used to either restrict or prevent the marketing of specific substances or products (that contain dangerous chemicals) which may adversely affect public health or the environment. Directive 76/769/EEC (also known as the Limitations Directive) is the main regulatory instrument for restricting or prohibiting the use and placing on the market of such dangerous chemicals. One potential application of this Directive of relevance to organotins has been described above within the discussion of Directives 67/548/EEC and 1999/45/EC relating to the classification, packaging and labelling of dangerous substances

Further restrictions, via amendments to Directive 76/769/EEC, which are of relevance to organotins include:

- Directive 89/677/EEC which places restrictions on the marketing and use of organostannic compounds which may no longer be used for the protection of the hulls of boats or of any totally or partially submerged appliances or equipment;

- Further adaptations to technical progress (e.g. Directive 1999/51/EC and 2002/62/EC) state that organostannic compounds:
    - may not be placed on the market for use as substances and constituents of preparations when acting as biocides in free association paint;
    - may not be placed on the market or used as substances and constituents of preparations which act as biocides to prevent the fouling by microorganisms, plants or animals of: (a) all craft irrespective of their length intended for use in marine, coastal, estuarine and inland waterways and lakes; (b) cages, floats, nets and any other appliances or equipment used for fish or shellfish farming; (c) any totally or partly submerged appliance or equipment; and
    - may not be used as substances and constituents of preparations intended for use in the treatment of industrial waters;

- Regulation No 782/2003 which prohibits the use of organotin compounds in anti-fouling systems on EU registered ships from 1 July 2003, and from 1 January 2008, on any ship entering the EU waters; and

- indirectly limiting the use of organotins as plasticisers, Directive 2005/84/EC relating to restrictions on the marketing and use of phthalates in toys and childcare articles. This Directive prohibits the use of certain phthalates in toys and childcare products intended to be placed in the mouth by children under three years of age and the marketing of products containing certain phthalates. It also imposes an obligation to affix a warning notice to soft PVC toys intended for children under three years of age and likely to be placed in the mouth.

4.3.3 REACH Regulations

The main objectives of the REACH Regulation (EC) No 1907/2006 which entered into force on 1 June 2007, are to (a) improve the protection of human health and the environment while (b) maintaining the competitiveness and enhancing the innovative capability of the EU chemicals industry.

Under REACH, responsibility for the management of the risks of chemical substances should lie with the enterprises that manufacture, import, place on the market or use these substances. Manufacturers and importers will be required to generate data on the substances they manufacture or import, use these data to assess the risks related to these substances and develop and recommend appropriate risk management measures. Where the recommended risk management measures are considered to be insufficient to control risks at the Community level, measures may be introduced under the Restrictions procedure.

The Restrictions procedure enables the introduction of Community-wide conditions for the manufacture, placing on the market or use of dangerous substances or the prohibition of any of these activities, if necessary. Any substance on its own, in a preparation or in an article may be subject to Community-wide restrictions, if it is demonstrated that risks are not adequately controlled. Thus, the Restrictions procedure will act as a safety net that will replace the current system of risk reduction based on the preparation of risk reduction strategies for existing chemicals in accordance with the Existing Substances Regulation and the Limitations Directive.

Proposals for restrictions are to be prepared by Member States or by the European Chemicals Agency on behalf of the Commission in the form of a structured dossier. This dossier (also known as an Annex XV dossier) is required to demonstrate that there is a risk to human health or the environment that needs to be addressed at Community level and to identify the most appropriate set of options for risk management.

In the meantime, the REACH Regulation notes that "*in order to take full advantage of the work performed under Directive 76/769/EEC and to avoid such work being lost, the Commission is empowered during the start-up period to initiate restrictions based on that work without following the full restrictions procedure laid down in this Regulation. All those elements should be used, as soon as this Regulation enters into force, to support risk reduction measures* (Recital 126, REACH Regulation preamble)". This study may, therefore, be considered in this context.

On the other hand, because the organotins in question may exhibit PBT, vPvB, CMR and endocrine disrupting effects (as appropriate for each individual group), they may be subject to authorisation under REACH[24]. The authorisation process is intended to address substances of very high concern where these include substances having *serious*

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[24] Note that according to Recital 75 of the REACH Regulation preamble, restrictions on the placing on the market and the use of substances which are carcinogenic, mutagenic or toxic to reproduction, category 1 or 2, for their use by consumers on their own or in preparations should continue to be introduced.

and irreversible effects to human health and the environment. Such substances will be prioritised by the Chemicals Agency and may be included in Annex XIV of the REACH Regulation. Substances included in Annex XIV shall not be used or placed on the market, unless the use is authorised by the Commission in accordance with a regulatory committee procedure. Authorisations may be granted for (specific) uses for which the applicant shows that the risks posed by a substance are adequately controlled or where the socio-economic benefits for those uses outweigh the risks and there are no alternative substances or technologies. Decisions on authorisation will take into account the opinions of the Agency Committees on risk assessment and socio-economic analysis.

Some of the organotin groups considered in this report generally meet the criteria for inclusion in Annex XIV of the REACH Regulation in accordance with Article 57 (substances of very high concern). DBT is toxic for reproduction category 2, TBT may be identified as PBT and vPvB and TPT may also be identified as PBT and vPvB. Furthermore, TBT and TPT display endocrine disruption properties. DOT, could possibly be identified as having PBT properties, as detailed in Section 3.3, and thus may be identified as being of equivalent concern as other substances listed in Annex XIV; however this is less likely than for the other organotin groups in question. Arguably, such identification may find support from the use of a group TDI in the RAR for these organotin groups.

An issue of note relates to the presence of organotins in articles. Under REACH, producers and importers of articles are responsible for their articles. In the case of substances of very high concern which are present in articles above 1 tonne, where exposure to the substance cannot be excluded and where the substance has not been registered by any person for this use, the Agency should be notified. The Agency is also empowered to request that a registration be submitted if it has grounds for suspecting that the release of a substance from the article may present a risk to human health or the environment and the substance is present in those articles in quantities totalling over 1 tonne per producer or importer per year[25]. The Agency may also consider the need for a proposal for a restriction where it considers that the use of such substances in articles poses a risk to human health or the environment that is not adequately controlled (Recital 29, REACH Regulation preamble). It can be argued that in the light of the currently available information on the risks from the organotin groups in question being present in consumer articles, the Agency would be likely to consider a proposal for a restriction targeting the organotin groups in question.

4.3.4 General Product Safety Directive (2001/95/EC)

The purpose of the General Product Safety Directive (2001/95/EC) (GPSD) is to ensure that all products intended for, or likely to be used by, consumers, under normal or reasonably foreseeable conditions, are safe. ‘Products’ within the meaning of the legislation can best be described as all goods that are (or could be) placed on the market,

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[25] Nevertheless, with particular reference to the organotin groups in question, registration of these substances is expected to be undertaken anyway irrespective of the provisions of the REACH Regulation on substances in articles.

or supplied or made available (including in the course of providing a service) to consumers for their private use. Therefore, the provisions of the Directive are generally applicable to many of the uses identified in Section 2.

The GPSD provides a generic definition of a 'safe' product and obliges producers to place only such products on the market. A 'safe product' means a product which, under normal or reasonably foreseeable conditions of use, does not present any risk or only the minimum risks considered to be acceptable and consistent with a high level of protection for the safety and health of persons. Producers must take measures to ensure that they are informed of the risks posed by their products and take appropriate measures to prevent the risks; consumers must also be informed of the risks associated with the products they use. Under the GPSD, if a manufacturer identifies a safety risk in a product already on the market, he will need to inform its distributors and also immediately inform the relevant authority, both of the risks and the actions taken to protect consumers.

4.4 Measures Addressing Risks to Humans via Biocides and Food Products

4.4.1 Biocidal Products Directive (98/8/EC)

The Biocidal Products Directive (BPD) (98/8/EC) aims to harmonise the European market for biocidal products and their active substances while also providing a high level of protection for humans, animals and the environment. The implementation of the BPD requires that only biocidal active substances that have been placed on a positive list, after evaluation and approval by the European Commission, may be used in biocidal products.

Under the BPD, producers and formulators of biocides were required to identify or notify all existing active substances to the European Chemicals Bureau before 31 January 2003. Manufacturers or importers are then required to apply for the active substance(s) to be included in the BPD Annex(es) by submitting a dossier, containing information on the substance properties, its uses and resulting exposures and risks[26]. These active substances will be assessed at the Community level over a 10-year transition period ending in 2010.

For those substances for which industry did not intend to apply for listing in an Annex, the BPD allowed for such substances to remain on the market, but must be withdrawn by 1 September 2006. Member States could, however, apply to the Commission for an extension of the 1 September 2006 deadline for the removal from the market of undefended substances, where they consider that such a substance is essential for them for reasons of health, safety, protection of cultural heritage or is critical for the functioning of society, and where there are no available technically and economically

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[26] Similar to biocides, active ingredients used in plant protection products are subject to a human health and environmental risk assessment before approval is granted for their use. Toxicological and ecotoxicological data must be supplied in relation to the whole product (not just the active ingredient) and approval is normally granted only in relation to individual products and only for specified uses, and remain subject to immediate revocation, suspension or amendment at any time if safety considerations so demand.

feasible alternatives or substitutes that are acceptable from the standpoint of environment and health.

With regard to organotins (of which, as noted earlier, only tri-substituted organotins are used as biocides), it is understood that five TBT compounds were originally identified by industry, with two others notified for use in wood preservatives; however, these notifications were formally withdrawn. On this basis, all TBT compounds should have been removed from the EU marker from 1 September 2006 (and no dossiers will be required). TBT compounds which were being used as biocides but were neither identified nor notified were required to have been removed from the market in December 2003. There is also no indication that any Member State has applied for an extension of the 1 September 2006 deadline for any TBT compounds.

Borderline Products and Other Regulatory Issues Arising

The term 'borderline products' refers to those products that at first sight might be difficult to classify into one or another product category, either in the same country or in different countries. Within the context of biocides, borderline products may refer to those products which are defined as biocides but which have certain properties, effects and/or claims associated with products defined by other legislation. Differences in regulatory frameworks can be particularly significant for so-called borderline products. Within the context of this study, there appear to be some borderline issues between the Biocidal Products and Medicinal Products Directives for certain products.

Under the BPD, biocidal products are defined as:

> *'Active <u>substances and preparations</u> containing one or more active substances, put up in the form in which they are supplied to the user, intended to destroy, deter, render harmless, prevent the actions of, or otherwise exert a controlling influence on any harmful organism, by chemical or biological means'.*

Directive 2004/27/EC defines a medicinal product as:

> *'(a) Any substance or combination of substances presented as having properties for treating or preventing disease in human beings; or*
> *(b) Any substance or combination of substances which may be used in or administered to human beings with a view to restoring, correcting or modifying physiological functions by exerting a pharmacological, immunological or metabolic action, or to making a medical diagnosis .*

Under this definition, a product can be defined as a medicinal product according to either its composition or presentation. Under definition (a) a product could be considered to be a medicinal product if it is presented for treating and preventing disease, even if it does not in fact have such an effect. In practice, though, case law (see Case C-112/89) has stated that only products that 'significantly affect the metabolism' should be categorised as medicinal products. Similarly, the fact that a product is presented simply as helping to protect against certain diseases does not qualify it as a medicinal product in most Member States (RPA, 2004).

Initially, the BPD was not intended to apply to products covered by other Community legislation, including the Medicinal Products Directive (MPD). However, the 2004 amendment to the MPD clearly states that "*where a product comes clearly under the definition of other product categories, in particular food, food supplements, medical devices, biocides or cosmetics, this Directive should not apply.*"

Thus, while it would appear to be the case that the biocidal uses of organotins within cycling shorts and shoe insoles (as identified in the RAR) should be addressed as product type 1 (human hygiene products) under the BPD (and such use is therefore restricted in the EU); in practice, the BPD does not apply to substances in articles (rather preparations and substances, as shown in the relevant definition). Also, it has been suggested that under the BPD, products (such as textiles) containing TBT can still be imported into the EU, provided they are not making biocidal claims.

On the other hand, foot sprays and non-allergenic pillows fulfil the definition of a medicinal product under the Medicinal Products Directive and do not appear to readily fall within any of the product types to be assessed under the BPD; however, this does not exclude them from falling under the BPD (based on their mode of action).

Overall, it is not clear whether the marketing and use of these compounds in cycling shorts, shoe insoles, foot sprays and non-allergenic pillows are currently banned under the BPD or controlled under the Medical Products Directive. This raises the possibility that consumer products containing TBT may still be marketed and used within some EU Member States but not within others. This position seems to be confirmed from the information received from a number of Member State Competent Authorities. For instance, the Dutch Food and Consumer Product Safety Authority indicates that all of the consumer biocidal applications of interest to this study are already banned under the BPD (VWA, 2007). Information received from the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, however, states that a TBT containing foot spray is currently being imported into, and sold in Germany (BMU, 2007).

It is, however, understood that the European Commission is aware of some of these issues and in fact, there is a study for the European Commission (DG Environment) on the impacts of possible measures to manage articles or materials treated with biocides with particular emphasis on imported articles (Milieu Ltd and DHI, 2006).

4.4.2 Food Products

There are various pieces of legislation concerning food safety and these are under the remit of DG SANCO (Health and Consumer Protection). Of particular relevance to this study is Regulation (EC) No 1935/2004 on materials and articles intended to come into contact with food. Under this regulation, food contact materials should be safe and should not transfer their components into food (a process known as migration).

Two types of migration limit have been established for plastic materials:

- an overall migration limit (OML) of 60 mg (of substance)/kg (of food stuff) and this applies to all substances that can migrate from food contact materials to foodstuff; and
- a specific migration limit (SML) which applies to individual authorised substances and is established based on the acceptable or tolerable daily intake (ADI/TDI) as set by the Scientific Committee.

Commission Directive 2002/72/EC, relating to plastic materials and articles intended to come into contact with food stuffs (and its amendments), sets specific SMLs for certain organotin compounds which may be found in food contact materials as shown in the Table below. Industry notes that the amendment of Directive 2002/72/EC by Directive 2005/79/EC resulted in the SMLs for octyltin compounds being reduced from 0.04 mg/kg down to 0.006 mg/kg (expressed as tin). Notably, there are no approvals for dibutyltin compounds.

Table 4.2: Specific Migration Limits for Organotins

Description	**CAS Number/s**	**Specific Migration Limit**
Methyltin compounds	-	0.18 mg (Sn)/kg*
Mono-n-octyltin compounds	-	1.2 mg (Sn)/kg*
Di-n-octyltin compounds	-	0.04 mg (Sn)/kg*
Di-n-dodecyltin bis(isooctyl mercaptoacetate)	84030-61-5	12 mg/kg
Mono-n-dodecyltin tris(isooctyl mercaptoacetate)	67649-65-4	24 mg/kg
Bis(2-carbobutoxyethyl)tin-bis(isooctyl mercaptoacetate)	63397-60-4	18 mg/kg

**Total migration limit for all such compounds*

Within the context of this study, it is considered that the regulatory framework for food contact materials is more relevant for addressing the risks from organotins in food-related applications and, as such, they have been excluded from the scope of the study or further detailed analysis.

4.4.3 Medical Products

The use of organotin catalysts in dental moulding kits has been confirmed as being a medical use which is better regulated under the Medical Devices Directive. As a result, this use falls outside the scope of this study and any potential risks from this use of organotins will not be addressed by the recommendations of this Report.

4.5 Measures Addressing Risks at Member State Level

4.5.1 Introduction

A number of European countries have put in place national measures to control the marketing, use and exposure to organotins. These are described below; however, it is important to note that these measures are likely to have been superseded by more recent EU legislation (in particular, the BPD).

4.5.2 Austria

Since 2001, Austria has prohibited ‘quality assured floor coverings’ from containing TBT as a biocidal finishing product (TRIS-2001/200/A, 2001).

4.5.3 Denmark

From 1999 onwards, the biocidal use of (tri-substituted) organotin compounds for the treatment of wood was being phased out by a voluntary agreement; this use is, however, now banned across the EU under the BPD (DEPA, 2007).

DBT, DOT, TBT and TPT are also on the Danish Environmental Protection Agency’s (DEPA) list of unwanted substances, i.e. substances whose use the DEPA would like to see phased out (DEPA, 2007). However, inclusion on this list does not have any direct consequences upon the use of these organotin compounds, or of any other unwanted substances, within Denmark.

4.5.4 France

Under the framework of Act 2006-1172 of 30 December 2006, which transposes the BPD into French law, reporting obligations on those wishing to place biocidal products on the French market are proposed in addition to those contained in 98/8/EC, as is an inventory to be prepared ahead of that set out under 98/8/EC (TRIS-2004/398/D, 2005). Under the Technical Standards Directive (98/34/EC) the French authorities cannot proceed with these additional measures until after a consultation period which was expected to end on 21st May 2007[27].

4.5.5 Germany

From 2005, Germany’s Biocidal Products Register placed a reporting obligation on those wishing to place biocidal products on the German market over and above EU reporting obligations (TRIS-2004/398/D, 2005).

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[27] This period may be extended and it is not certain that the proposed additions to the Biocidal Products Directive 98/8/EC will enter into French law.

The German Federal Ministry of the Environment, Nature Conservation and Nuclear Safety also states that there are non-binding recommendations regarding the use of organotin stabilisers and catalysts within materials intended for food contact (BMU, 2007). These recommendations provide concentration limits for dioctyltin compounds within unplasticised PVC intended for food contact materials (BfR, 2006). With regards to plasticised PVC for use in food contact materials or toys, the recommendations above state that "*organic tin stabilisers (e.g. dioctyltin compounds, butylthiostannoic acid) must under no circumstances be added*" (BfR, 2006).

Finally, with regard to the use of organotin compounds as catalysts in silicones, DOT may be used so long as it constitutes no more than 1.5% of the final product (BfR, 2005).

Case Box 4.1: Maximum Concentrations of Production Aids in the Final Silicone Elastomer of Products intended for Food Contact

A publication by the German Federal Institute for Risk Assessment (BfR, 2005) outlined the recommended maximum concentrations of production aids in the final silicone elastomer of products intended for food contact. This, among others, refers to hardeners or catalysts and their conversion products and identifies the following components:

- *di-n-octyl-tin-dimaleinate* <u>*plus*</u> *di-n-octyl-tin-dilaurate* <u>*plus*</u> *esters of titanic acid with isobutyl alcohol, n-butanol based on and the enolate of acetoacetic ester finished product* <u>*plus*</u> *amides of aliphatic carboxylic acids,* C_8-C_{22}*: a maximum concentration of 1.5% of the finished product;*
- *coordination compounds of platinum,: max. 50 mg platinum per kg of finished product.*

The following substances may be used as inhibitors for these coordination compounds:

- *1-ethinyl-cyclohexanol and 2-methylbutine-3-ol-2, with a total maximum concentration of 0.1%.*

To the extent that the silicone elastomers are intended for coating paper or plastic films, the concentration of platinum could be as high as 120 mg platinum per kg of finished product.

4.5.6 Netherlands

Under framework of the Decree on the Prevention of Pollution by Ships, the Netherlands has imposed restrictions on the use of organotin biocides on ocean going vessels authorised under Dutch law to fly the Dutch flag, in addition to those contained under the BPD and provides for an environmental certification scheme for these vessels.

4.5.7 Other

For special applications such as drinking water pipes, additional restrictions according to national regulations may apply in order to ensure safe drinking water distribution. According to ORTEPA, regulations in France, Germany and the Netherlands approve the use of both thioglycolates and reverse ester products in potable water pipes while in Italy only thioglycolates are allowed (ORTEPA, not dated-a).

4.6 Measures Addressing Risks at an International Level

At a ministerial meeting of the Contracting Parties to the OSPAR Convention in Sintra in 1998, it was agreed that man-made hazardous substances should not occur in the marine environment and that naturally occurring hazardous substances should not exceed natural background concentrations. To this end, it was agreed to make every endeavour to cease all discharges, emissions and losses of hazardous substances that could reach the marine environment by the year 2020 (OSPAR, 1998).

As a consequence of the hazardous properties of organotins, a variety of activities have been initiated in an attempt to control releases of organotins to the marine environment. For example, organotins have been included on the OSPAR List of Chemicals for Priority Action and an OSPAR background document on organotins was published in 2000 (with the Netherlands as the lead country). TBT and DBT are also part of the annual OSPAR reporting on dumping of wastes at sea. The management of dredged materials containing hazardous substances, such as organotins, is regulated under OSPAR guidelines on the management of dredged materials.

The International Maritime Organisation (IMO) Assembly Resolution A.895 (21) has also agreed a global phase out of TBT in shipping. Organotins have also been proposed for addition to the list of persistent organic pollutants (POPs) under the Stockholm Convention. Two PARCOM Recommendations (87/1 on the *use of tributyltin compounds* and 88/1 on *reducing emissions from organotins via docking activities*) are also applicable to tributyltin compounds.

4.7 Voluntary Initiatives to Address Risks

4.7.1 Use of Stabilisers in PVC

In 2000, the European PVC industry started a 10-year plan to enhance the sustainability of its products and production over the full lifecycle. The programme is based on the 'Voluntary Commitment' signed by four industry associations: ESPA, ECVM, ECPI and EuPC. The main commitments of this voluntary initiative, known as Vinyl 2010, are:

- compliance with ECVM Charters on PVC production standards;
- a plan for full replacement of lead stabilisers by 2015, in addition to the replacement of cadmium stabilisers that was achieved in March 2001;
- the recycling by end 2010 of 200,000 tonnes/year of post-consumer PVC waste;
- the recycling of 50% of the collectable available PVC waste for windows profiles, pipes, fittings and roofing membranes in 2005, and flooring in 2008;
- a research and development programme on new recycling and recovery technologies, including feedstock recycling and solvent-based technology; and
- the implementation of a social charter signed with the European Mine, Chemical and Energy Worker's Federation (EMCEF) to develop social dialogue, training, health, safety and environmental standards, including transfer to EU accession countries.

The programme provided for a mid-term revision of targets in 2005 and the definition of new objectives in 2010 to take into account, technical progress and EU enlargement. The progress of Vinyl 2010 is monitored by a committee comprising industry representatives, representatives of the European Commission (both Directorates General Enterprise and Industry and Environment) and Parliament. Annual reports, which are subject to independent verification, are produced detailing the progress of the initiative.

It should, however, be noted that none of the measures currently relates specifically to organotins; however, measures aimed at a phase-out of lead stabilisers may have implications for the use of organotin-based stabilisers.

4.7.2 Use of Organotins in Absorbent Hygiene Products

Members of the European Nonwovens & Disposables Association (EDANA) have voluntarily agreed to ensure that from 2000, raw materials that come into contact with the user contain less than 2 ppb of TBT and <10 ppb for each species of organotins individually (EDANA, 2007). These limits refer to the organotin concentration in the raw materials used and not to the final AHPs and both are indicated to be the current detection limit for the analytical methods adopted.

It is, however, important to note that TBT is a contaminant in these products and not an intentional input. While it has been traced by manufacturers/suppliers of AHPs, the suspicion remains that organotins are mainly introduced from contamination (e.g. PVC dust in production sites).

4.7.3 Use of Organotins in Silicone Baking Paper

As noted in the RAR, members of the Centre Européen des Siliconés (CES), as part of an informal voluntary agreement among their members, have phased out the use of organotins for the production of silicone coated baking paper since 2002 (RPA, 2005). While the RAR noted that sampling undertaken in 2003 indicated that silicone coated baking papers containing organotins were being imported from outside of the EU (RPA, 2005), CES has confirmed for the purposes of this report that the global silicone industry has now voluntarily phased out this use of organotins (CES, 2007a).

4.8 Assessment of Effectiveness of Measures

A summary assessment of the effectiveness of current risk reduction measures for addressing the risks from organotin compounds, as well as the need for further risk reduction measures is provided in Table 4.3.

Table 4.3: Existing Risk Reduction Measures and Relevance for RRS

Source of Exposure and Risk	**Identified Route of Exposure**	**Existing Risk Reduction Measure**	**Need for Further Risk Reduction Measures**
Risk to humans via the environment	Environment (local)	WFD: TBT compounds are priority hazardous substances for which a cessation of emissions, losses and discharges to the aquatic environment is required IPPC: The requirements (including the reporting threshold for emissions to the environment) may be useful (in tandem with the WFD) in addressing local risks from production and processing of di-substituted organotins at various sites. REACH: The REACH regulations when introduced may place restrictions or use requirements on organotins on the basis of their PBT, vPvB, endocrine disrupting and/or reprotoxic effects. These measures would cover the use of organotins in articles if they are subject to authorisation. Other: Use of organotins in wood treatment has been discontinued.	The introduction of further risk reduction measures are unlikely to deliver significant benefits beyond those expected under WFD and the IPPC requirements. While placing restrictions may influence the timing and costs of such benefits in relation to the risks, it is considered that Directive 76/769/EC is not best suited for addressing local risks. These would be best managed by local authorities as part of their obligations and the requirements under the IPPC and WFD. It is, however, recognised that placing restrictions on specific organotins may impact on production processes and quantities, and thereon, the local risks. For indoor air/dust, specific measures may, however, be required to address the identified sources (e.g. flooring).
	Indoor air/dust*		
Risk to humans via food and food contact materials	Silicone baking paper (cookies)	Food Contact Materials Legislation: The relevant legislation for addressing these risks is under the food contact materials legislation and the remit of DG SANCO. Marketing and Use Directive: Use of organotins in anti-fouling paints is now restricted. Other: Use of organotins in organotin catalysts in baking paper has been discontinued.	The introduction of further measures will be undertaken under the food contact materials regulations and, as such, is outside the scope of this study or Directive 76/769/EC.
	Fish products		
	PVC food packaging		
	PVC rigid film (food packaging)		

Table 4.3: Existing Risk Reduction Measures and Relevance for RRS

Source of Exposure and Risk	Identified Route of Exposure	Existing Risk Reduction Measure	Need for Further Risk Reduction Measures
Risk to humans via consumer products	T-shirts	Classification and Labelling: Classification of dibutyltin as CMR Cat 2 may impact on use in some consumer articles; some industry sectors are already moving away from DBT. Impact of GHS is less certain. REACH: If, in the future, organotins go to Authorisation (as would be likely based on their properties), this will require their use in consumer products, including imported articles, to be authorised. Benefits may, therefore, accrue from early action. Other: EDANA voluntary commitment limiting the organotin content of raw materials used in AHPs that come into contact with the user to less than 2 ppb of TBT and <10 ppb for each species of organotins individually may have some impact in reducing risks. However, contamination issue may need to be addressed.	No EU legislation of relevance is currently is in place for specifically addressing the risks from these products. Impact of classification and labelling, or REACH, regulations may be felt in future; however, these cannot be guaranteed and early action may bring benefits to human health. Further measures are, therefore, required as these products contribute to the TDI.
	Female hygiene products		
	Nappies		
	2-part silicone moulds		
	PVC sandals		
	PVC gloves		
	Foot spray	BPD or MPD: Uncertainties relating to whether these products are currently restricted under the BPD or controlled under the MPD still exist which means that these products may still be placed on the EU market, thereby, posing risks to consumers.	Further measures are required to clarify borderline issues and close loopholes. The MPD may be a more appropriate framework for such measures.
	Dental moulding		
	Shoe insoles		
Other non-risk sources of exposure	Non-allergenic pillows		
	Cycling shorts (padding)		
	PVC toys (mouthing)	REACH: If in future, the relevant organotins are prioritised under the Authorisation process (as would be likely based on their properties), this would mean that authorisations will only be granted for specific uses where the risks are adequately controlled, socio-economic benefits outweigh the risks, or there are no alternatives. There may be some benefits of early action.	Taking into account the view of SCHER that it is the total consumer exposure to organotins that should be used in the RAR, including all the identified pathways, such as those estimated to contribute with less than 20% of the TDI, further measures are required to address these uses. These measures may, however, take into account the risks, availability and suitability of alternatives and socio-economic benefits.
	Silicone sealant		
	Paddling pool		
	PVC bags		
	Other		

** May also qualify as risk via consumer goods (due to PVC floor and wall coverings)*

5. ALTERNATIVES TO ORGANOTINS IN PVC AND CATALYSTS

5.1 Introduction to the Assessment of Alternatives

In developing any strategy for reducing the risks relating to a given substance, it is important to consider the availability of alternatives for the applications of concern, where this includes alternative substances, systems and/or techniques. Such considerations are important since any proposed restrictions may instigate a shift to such alternatives.

For instance, in the event that the marketing and use of certain organotins is restricted, it would be necessary for companies using these substance(s) to adopt a substitute chemical or an alternative method in order to achieve the various standards, performance and/or properties required either by legislation, customers or applications. In this regard, the replacement of organotins by another chemical or an alternative system would need to take into account the:

- **availability** and **technical suitability** of a substitute or alternative system (including the capability of the substitute or alternative system to meet the required performance or safety standards/requirements);

- **cost** of the substitute or alternative system and any **wider economic and social implications** arising from the use (or lack) of alternative substances/techniques; and

- **environmental and human health effects** of the substitute or alternative system. The use of alternatives should not result in greater or equal risks to humans and the environment.

The following Sections present the information obtained from a literature review and consultation with various stakeholders on potential alternatives to organotins in PVC and catalyst applications.

5.2 Alternatives to Organotin-based Stabilisers in PVC

5.2.1 Introduction

Five main types of alternative stabiliser systems have been identified, as follows:

- lead-based stabilisers;
- cadmium-based stabilisers;
- calcium-organic stabilisers;
- liquid mixed metal stabilisers; and
- other organotins (in particular, methyltins).

These are discussed in detail below.

5.2.2 Availability of Alternatives

Introduction

In discussing the technical suitability of any stabiliser system, it is important to bear in mind that because of the complexity of processes, uses and applications of PVC, the selection of the appropriate stabiliser system requires considerable knowledge and expertise of process equipment, polymer choice, final application, regulatory approval requirements and cost (ESPA, not dated; ECVM, not dated). Also, depending on the stabiliser selected, it is possible to obtain a selection of properties including good clarity, good weatherability, good colour hold, good long-term stability, suitability for white pigmented applications, low migration, low odour and low volatility. Some products are specifically designed to meet just a few of these criteria but others can achieve a good compromise of all the above features (ECVM, not dated).

The discussion below recognises that the decision on what constitutes a technically suitable stabiliser depends on the knowledge and experience of the formulator or PVC converter and the application type, as much as on the stabiliser itself. This is the reason why the stabiliser industry offers a lot of technical service to customers and why there are many stabiliser blends devised for specific customer applications; the requirement for some formulation properties can also limit exactly what stabilisers are appropriate (ESPA & ERPA, 2007).

Lead-based Stabilisers

Lead-based stabilisers are the most common form of stabiliser used for PVC in Europe. Although, their use has been decreasing, they still account for over 50% of total stabilisers used in PVC (ECVM, not dated). Table 5.1 below sets out the main chemical compounds on which lead stabiliser systems are based (note that different lead compounds can be used in PVC formulations to provide optimum performance in a particular application).

Table 5.1: Lead Compounds Used as PVC Stabilisers

Product Compound	Key Attribute	Lead content
Tri- or tetra-basic lead sulphate	Strong heat stabiliser	82% or 85%
Di-basic lead phosphite	Heat and light stabiliser	82%
Di-basic lead phthalate	Strong heat stabiliser	75%
Poly-basic lead fumarate	Very strong heat stabiliser	
Di-basic or normal lead stearate	Stabiliser/lubricant	51% or 28%

Source: ESPA, not dated; ECVM, not dated

The key characteristics of lead-stabilised PVC include (ECVM, not dated):

- excellent heat and light stability;
- good electrical properties;
- excellent short and long-term mechanical properties;

- low water absorption;
- wide processing range; and
- good cost/performance ratio.

In the manufacturing environment, lead stabilised formulations, due to their high heat stability, reduce wear on processing equipment and allow recycling of scrap to be carried out (ESPA, not dated).

According to industry, for historical reasons (relating to how the industry developed), most rigid PVC in the USA is organotin-stabilised whereas, in Europe, most rigid PVC is lead-stabilised. This does not, however, indicate that lead-based stabilisers would be technically suitable as an alternative to organotin-based stabilisers because:

- in clear rigid calendering films where organotin-based stabilisers are largely used, lead is not used as it produces opaque films that technically do not meet the clarity requirements;

- traditionally, lead-based stabilisers are predominantly used for rigid PVC in building and construction applications (e.g. pipes and profiles, but also in flexible PVC for electrical cable wiring) (ESPA, not dated); organotin-based stabilisers are, however, used mainly in rigid PVC film (for food contact plastics and packaging). Organotin-based stabilisers are approved for use in food-contact plastics and pharmaceutical packaging, but lead-based stabilisers do not currently have such approvals. The two types of stabilisers do not, therefore, compete directly in these applications; and

- in practice, lead-based stabilisers in Europe are currently being phased out according to the Vinyl 2010 agreement and are being substituted by calcium-organic systems, rather than organotin-based stabilisers (as can be seen by the tonnages reported by industry under the Vinyl 2010 agreement).

Cadmium-based Stabilisers

Cadmium-based stabilisers have been available for many years, exhibiting excellent performance qualities. Typically, in stabilising PVC, cadmium was used in the form of a stearate or laurate and often combined with a similar barium ester and lead stabiliser (ECVM, not dated). The barium/cadmium stabilisers impart good heat stability and weatherability to PVC compounds and were used in semi-rigid and flexible foil for products such as roofing membranes and in rigid applications for outdoor use such as window profiles.

However, the use of cadmium PVC stabilisers was completely phased out voluntarily by the PVC industry in the EU by 2001 as part of the Vinyl 2010 voluntary agreement (and restrictions placed on the use of cadmium under the EU Marketing and Use Directive)[28].

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[28] Directive 91/338/EEC relating to restrictions on the marketing and use of cadmium prohibits the use of cadmium and its compounds in pigments, stabilisers and surface treatment. It provides for a general exemption clause where justification exists on the grounds of safety or reliability and where the use of cadmium is unavoidable.

The Directive would still allow the use of cadmium stabilisers in window profile and roofing membranes but the Vinyl 2010 voluntary agreement (signed in 2000) resulted in the discontinuation of use of cadmium stabilisers as described above (ECVM, not dated).

The use of cadmium-based stabilisers in foils has also been replaced by barium/zinc (also known as 'liquid mixed metal') stabilisers. No stabiliser containing cadmium has ever been used for food contact applications or toys (ECVM, not dated). Industry notes that, in any case, even at a theoretical level, cadmium-based stabilisers could not act as a complete replacement for organotin stabilisers, as they are mainly specific to plasticised PVC applications while organotin stabilisers are used mainly in rigid applications; there is therefore, no direct competition between these two types of stabilisers. It has, however, been highlighted that some imported articles can still contain cadmium, provided this is in compliance with EU legislation, and that cadmium stabilisers have some limited use in other regions.

Calcium-organic Stabilisers

Introduction

Calcium-organic stabilisers were originally known as calcium/zinc systems; however, during the development of alternatives to cadmium- and lead-based systems, the newer stabilisers sometimes required less or no zinc component, and hence the new name that replaces the word 'zinc' with 'organic'. For the purposes of this report, we shall consider that calcium-organic stabilisers include (traditional) calcium/zinc stabilisers and those stabilisers which, on occasion, are called organic based stabilisers (OBS)[29].

Calcium-organic stabilisers belong to the wider family of mixed metal stabilisers, which traditionally tended to be complex mixtures of metal soaps with a variety of non-metallic co-stabilisers and antioxidants. The stabilisers come in liquid or solid forms, where the latter is preferred in applications that are extremely sensitive to volatile emissions or to odour (and reductions of both are required)[30]. With the mixed metal stabilisers, wide variation in composition is possible and this results in significant differences in performance and other important characteristics. This versatility is, however, one of the primary reasons that these stabilisers are extensively used in the processing of PVC.

Calcium/Zinc Stabilisers

Calcium/zinc stabiliser systems are generally based on (or used in the form of) metal carboxylates and will sometimes incorporate other elements to boost performance such as aluminium or magnesium. Organic co-stabilisers (such as polyols, epoxidised soya bean

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[29] It should, however, be noted that calcium salts are used in nearly all stabiliser formulations as a co-stabiliser to make $CaCl_2$, a safe end-point for the chloride anion. Barium has this same role in the Ba/Zn mix.

[30] Solid calcium/zinc systems are usually based on stearic and lauric acids whereas the liquid mixed metal stabiliser systems are based on shorter chain fatty acids. The component acids for the liquid mixed metal salts tend to be 2-ethylhexanoic acid, versatic acid and other shorted chain acids plus aromatic acids such as benzoic acid and tert-butylbenzoic acid (ESPA & ERPA, 2007).

oil, antioxidants and organic phosphates) and phenolic antioxidants may also be added to enhance the heat stability in some applications and provide a more balanced stabiliser system - with the stabilisers frequently provided as pastes (ECVM, not dated; ESPA & ERPA, 2007).

In providing input to this study, ESPA and ERPA (2007) indicate that traditional uses of these calcium/zinc solid stabiliser systems were for plasticised PVC applications for food-contact and also medical applications, but some were also used in rigid PVC for applications such as toys. The ECVM and ESPA Internet sites, however, suggest a much wider use. According to ECVM, calcium/zinc stabilisers have been used for over 25 years in many plasticised and rigid PVC applications ranging from toys, healthcare products (such as blood bags and disposable PVC gloves[31]), semi-rigid and flexible foil for food packaging to water bottles and potable water pipes (ECVM, not dated). The ESPA Internet site (ESPA, not dated) also notes that the properties of calcium/zinc systems mean that they have been used essentially as a lead stabiliser replacement in demanding applications (such as food, medical and pharmaceutical packaging) where their low toxicity and subsequent regulatory approval in these applications is an advantage). Other applications identified include (ESPA, not dated):

- white window profiles;
- technical profiles;
- flooring;
- roof sheeting; and
- cables.

Regarding their technical characteristics, calcium/zinc stabilising systems are reported to give products which have a high degree of clarity, good mechanical and electrical properties, excellent organoleptic properties and good outdoor weatherability (ECVM, not dated). In fact, ESPA (not dated) notes that "*the mixed metal systems* (with calcium/zinc stabilisers forming part thereof) *are capable of covering the whole area of PVC applications. In some cases such as window frames, excellent colour stability weathering results have been obtained both in long-term testing and from practical experience*". As indicated earlier in this report, the suitability of calcium-organic stabilisers for both white and coloured flexible PVC products has been indicated by the Swedish authorities (KemI, 2007).

<u>Organic-based Stabilisers (OBS)</u>

According to Manolis Sherman (2005), OBS were introduced around six years ago to help European pipe makers replace lead. Since then, they have made inroads in rigid injection moulding, indoor profiles, sheet and as a replacement for barium and zinc in plasticised PVC (Manolis Sherman, 2005). ECVM (not dated) confirms that these new improved calcium/zinc systems (or in this context, OBS) are the result of considerable development work which has been undertaken, as a result of pressures on the continuing

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[31] According to Akcros Chemicals (not dated), manufacturers of disposable PVC gloves, particularly for medical use, favour the use of low toxic or non-toxic calcium/zinc stabilisers.

use of heat stabilisers based on lead compounds, for applications including cable covering, pipe and window profile where they have now been in commercial use for several years. It also goes on to indicate that OBS are potential technical alternatives to most other stabilising systems, including lead and barium/zinc (which is the main stabiliser in flexible foils) (ECVM, not dated).

These newer forms of calcium-organic stabilisers are in general more complex and expensive than the traditional soaps mainly because of the specialised co-stabilisers required to meet the specific requirements of these applications. . According to ECVM (not dated), the penetration of calcium-organic stabilisers is almost complete in drinking water pipes, well advanced in cables but still limited in other pipes and profiles. Originally developed for rigid PVC, the new stabilisers reportedly have been effective in plasticised applications as well (in flexible foils, the substitution of barium/zinc stabilisers with OBS is reportedly currently on-going).

Regarding the technical characteristics of OBS stabilisers, Manolis Sherman (2005) suggests that they can display lubrication of vinyls similar to formulations with organotins or traditional mixed metal systems. Compared with standard stabilisers, the manufacturer indicates that OBS are priced competitively and provide some improvements in performance. Other benefits include low migration, low odour, low VOC emissions, good initial colour and excellent transparency, especially in plasticised PVC. OBS compounds are also reportedly suitable for recycling; there are no interactions (such as cross-staining) with other stabilisers and only a minor decrease in thermal stability after reprocessing five times (Manolis Sherman, 2005).

Liquid Mixed Metal Stabilisers

Liquid mixed metal stabilisers include barium/zinc systems, potassium/zinc systems, or less commonly calcium/zinc stabilisers. Important features of liquid mixed metal stabilisers are (Akcros Chemicals, not dated):

- good air release properties from the PVC plastisol;
- good heat stability during processing;
- good clarity in the finished product;
- reduced PVC resin sensitivity;
- good long-term, low temperature ageing properties;
- low volatile emissions during processing; and
- low volatile emissions from the finished product.

Originally barium/cadmium and barium/cadmium/zinc systems dominated this market but since the early 1990's, there has been a move to barium/zinc systems (as cadmium and zinc act in the same manner in exchanging anions with barium).

These liquid mixed-metal stabilisers are used only in plasticised PVC whether the process involved relates to technology using paste PVC (dip coating, rotational moulding, spread coating etc.) or to suspension PVC (calendering, extrusion or injection moulding). Typical metal contents, for the liquid mixed metal stabilisers are:

- barium/zinc systems: Ba (7-12%) / Zn (1-3%); and
- calcium/zinc systems: Ca (1-2%) / Zn (1-2%).

Barium/zinc stabilisers are the most commonly used stabiliser in flexible foils (for membranes, stationery and automotive applications), flooring, wall covering, roofing, tarpaulins, flexible tubing and footwear and coil coating formulations where they have proven performance. In these applications, 'traditional' calcium/zinc systems are reported not to be as effective as barium/zinc systems because they are more difficult to formulate to give the same ability to stabilise the PVC during processing (ESPA, not dated). This argument is believed to refer to liquid calcium/zinc stabilisers and needs to be considered in the light of the earlier discussion on solid calcium-organic stabilisers which suggests that (modern) calcium-organic stabilisers are replacing barium/zinc stabilisers in plasticised PVC applications. In contrast to the solid calcium/zinc systems, these liquid mixed-metal stabilisers use organophosphites as the main co-stabiliser (ESPA, not dated).

A group of specialised liquid soap stabilisers allied to barium/zinc soaps are zinc or potassium/zinc soaps. These are generally laurates or octoates and are used as PVC stabilisers and as activators (or 'kickers') for the blowing agent used in making the foamed layer in a number of plastisol applications (ECVM, not dated). The foaming of PVC plastisol by a chemical means is a technique which is used widely in the production of flooring, wall coverings and a variety of supported and unsupported sheeting. It is achieved by the incorporation of a suitable blowing agent such as azodicarbonamide together with a suitable *'kicker'* in the formulation. Kicker stabilisers promote the decomposition of the blowing agent at a temperature below the paste gelation temperature (Akcros Chemicals, not dated). The potassium/zinc stabilisers are widely used in cushion flooring, foamed wallpaper and in foamed fabric coating - where they allow PVC cushion flooring in particular to have raised patterns as part of their design.

Methyltin Stabilisers

It is important to note that methyltins may also be suitable as alternatives to butyltin and octyltin stabilisers. The use of methyltins as stabilisers in PVC (rigid sheet) may perhaps be more relevant in non-EU countries, as confirmed in a recent Australian publication (Scheirs, 2003) as well as by a company supplying the EU market which notes that methyltin stabilisers are sold for rigid packaging films, profiles and pipes, although its non-EU sales are more important than EU sales.

Other Stabilisers

A type of stabiliser based on an aminocrotonic acid ester may also be used for rigid and plasticised PVC processing (Crompton Corporation, not dated). Especially in emulsion PVC, this stabiliser has reportedly proven to give good results:

- in rigid PVC, it reduces the melt viscosity and therefore facilitates processing on calenders, extruders and injection moulding machines; and

- in plasticised PVC formulations, it confers good compatibility. The combination with calcium and zinc stearate is useful as they do not only improve the heat stability, but also have an external lubricating action.

Its recommended concentration is reported as 1.0-2.0 phr (parts per hundred of resin) and is reportedly approved in many countries for the stabilisation of rigid and plasticised PVC packaging materials (Crompton Corporation, not dated).

5.2.3 Technical Suitability of Alternatives by Application Type

Rigid Film and Sheet

The following points describe the issues that could be considered to be for or against the technical suitability of alternatives (effectively calcium-organic stabilisers) in specific PVC applications.

Food Packaging Applications

For: calcium/zinc stabilisers are currently approved for use in food contact materials. On this basis, they are considered to be safe and technically suitable and the existing approvals process for food contact materials is indeed more relevant for addressing the suitability of different materials for food-related applications.

Against: some consultees suggest that there are issues relating to their suitability for manufacturing crystal clear films.

Pharmaceutical Applications

Similar to food packaging, there is a range of European and national legislation (as well as the European Pharmacopoeia) which are more relevant for addressing the suitability of different materials for medicinal products packaging. The time required for obtaining approvals for pharmaceutical and food-related (applications) would also need to be taken into account.

Credit Cards

For: the criticality of organotin-based stabilisers for this application has not been fully substantiated.

Against: industry indicates that, compared with other stabilisers, in credit cards, octyltins provide the best performance in terms of printability due to their intrinsic chemistry. According to one stabiliser manufacturer, organotin-based stabilisers have a far better processing window and better transparency and, as such, are essential for credit cards. Information received for this study also indicates that there is scope for making further improvements in losses of organotins during the production process (although it is not clear whether and how industry intends to implement these emission reduction measures). It has also been noted that credit cards, food and pharmaceutical packaging are often produced at the same factory and producers are very keen on having only one stabiliser suitable for all of these uses.

Construction Sheets (including Foamed Sheeting)

For: a major manufacturer of organotins indicates that in rigid extruded sheets, butyltin mercaptides can be substituted by octyltin mercaptides for the compact (pigmented and transparent) sheets and possibly with calcium/zinc, especially in the foamed formulations.

Against: the same company however, believes that it would be more difficult to substitute butyltin carboxylates in roofing as there are currently no technically suitable alternatives in their view. This view is echoed by another company which notes that in calendered clear roof sheeting, the best clarity coupled with good weatherability is achieved through the use of organotin-based stabiliser systems.

Other Rigid Films and Sheets

It has been indicated that all rigid films and sheets (including the non-food contact applications) currently comply with the migration limits set under the food contact legislation. While such compliance is mainly for production/process reasons, this may have implications in terms of the risk management strategy.

Pipes, Fittings and Profiles

Information was received from a number of companies on the use of organotin stabilisers in profiles and pipes. The key points are as follows:

Points in Favour of Substitution

According to one manufacturer, in pipes and pipe fitting, tin-stabilised PVC is used to a very small extent in PVC in Europe (less than 2%) - traditionally in France and Belgium. In pressure pipe fittings (which account for around 0.4% of total PVC consumption), organotin-based stabilisers are used for the heavy and complicated fittings. Again, lead-based stabilisers are still the dominating system and the process of replacing these with calcium/zinc and OBS systems is on-going and it is suggested that a few countries have been lead free since 2001. Calcium-organic stabiliser systems "*represent state-of-the-art*" as they are a more environmentally friendly alternative. It has been indicated that the use of lead stabilisers for potable water piping has been voluntarily discontinued as of the end 2005 by the pipe producers who are members of the European Plastic Pipes and Fittings Association (TEPPFA), which is a partner of Vinyl 2010 (ECVM, not dated).

While the development of solid calcium-organic stabilisers to replace lead and cadmium in window profiles took over 20 years along with significant research and development (R&D) costs, according to ESPA, using the mixed metal stabilisers systems, "*for white window frames, excellent colour stability weathering results have been obtained both in long-term testing and from practical experience*". A stabiliser manufacturer also notes that they currently sell other methyltin stabilisers that can be used in rigid applications, such as profiles and pipes - although this company has a much larger business outside of the EU for these applications, compared with intra-EU sales.

Points against Substitution

There are still concerns on the suitability of alternative stabilisers for crystal clear profiles. This has been suggested by the company which noted the limited use of tin stabilisers in pipes and pipe fittings in France and Belgium (see above). Another company suggests that the use of butyltin stabilisers in exterior coloured profiles and other cellular building products is difficult to achieve with any alternative stabiliser system.

Another organotin manufacturer provided a chart (see Figure 5.1 below and Table 5.2) comparing the heat stability of PVC made with tin, lead and calcium/zinc stabilisers. In general, it is indicated that PVC made with organotin stabiliser is whiter and stays whiter over longer period of time under processing conditions, as shown in Figure 5.1 below. (Lead A also performs well in this test).

The manufacturer (which provided this chart) indicates that calcium/zinc underperforms based on heat stability, processing window, output rate and cost. They indicate that since rigid calendering uses more rigorous process conditions than pipes, the differences seen below would be even more pronounced and economics and performance might not allow calcium/zinc stabilisers to be used.

Figure 5.1: Heat stability - 2-roll mill @ 200°C - 1 min. intervals

Table 5.2: PVC Heat Stabilisers for Pipes			
Parameter	**Pb**	**Ca/Zn**	**Sn**
Heat stability	+	-	++
Physical properties	+	+	+
Processing window	++	-	+
Output rate	+	-/=	+
Cost	+	--	+/-
Performance history	+	?	+
(+) good (-) bad (=) equivalent (?) unknown *Source: Consultation*			

Bottles

A large proportion of PVC bottles are used in food packaging (e.g. vegetable oil, juices, wines) for which food-contact approved stabilisers are used (ORTEPA, not dated), as well as in non-food packaging (e.g. cosmetics and cleaning materials). It is currently unknown if all bottles, regardless of final end use, are produced to the same migration limits for food contact materials, although this could be preferable in terms of practicality and manufacturing/process efficiency.

Plasticised PVC

The following points describe the issues that could be considered to be for or against the technical suitability of alternatives.

For: only small quantities of tin stabilisers are used in plasticised PVC where the main stabiliser systems used are the liquid mixed metal systems. As shown in Table 2.8, recent information from consultation with industry shows that only 5% of organotin stabilisers are used in plasticised PVC. As noted by one tin stabiliser manufacturer, the move away from tin stabilisers in the plasticised applications would represent probably <5% of the tin stabiliser market and would only increase the use of liquid mixed-metal stabilisers also by about 5%.

In a number of applications where organotin-based stabilisers are used, they are currently being phased out. With regard to wall coverings and flooring, ESPA companies are currently working with their customers to change to alternative stabiliser systems with the aim of phasing out this use by the end of 2007. Printed T-shirts are mainly imported from outside the EU but ESPA companies are also looking to ensure that such use ceases in the EU (ESPA, 2007).

Against: There have been mixed views on the criticality of organotin stabilisers in steel (coil) coatings. One organotin stabiliser manufacturer argues that alternative options based on octyltins or solid calcium/zinc or liquid calcium/zinc or barium/zinc are under development and, in the future, an acceptable compromise on cost-effectiveness is certainly possible. Another organotin stabiliser manufacturer suggests that restrictions on this use would have a significant impact due to the high performance required. They, however, note that it is very difficult for a customer to switch from organotin stabilisers since they will need extensive testing since coil coatings used in building construction require extensive long term weathering testing for product guarantees.

Summary on Alternative Stabilisers

In summary, each stabiliser system has unique advantages and disadvantages which may vary by application or end-product and the decision on which is most appropriate requires an overall assessment of advantages and disadvantages specific to the product, application or company.

Overall, it is accepted that in nearly all cases, calcium-organic stabilisers would be the preferred alternative, except perhaps in crystal clear applications where organotin-based stabilisers are claimed to offer the best clarity. There may also be issues relating to heat stability and processability for certain applications. The time required for obtaining approvals for pharmaceutical and food-related (and possibly construction-related applications) would also need to be taken into account.

While a number of respondents have indicated that calcium-organic stabilisers are currently unproven in certain applications, it appears to be the case that, for these companies, a significant proportion of research and development has been concentrated on phasing out cadmium and lead stabilisers. Also, as noted in Section 2, there seems to be a general move away from butyltins as a result of its classification as CMR category 2; however, this move appears to be towards octyltins (and possibly other organotins).

It is also important to note that, owing to pressures on the continuing use of stabilisers based on lead compounds (and the phasing out of cadmium stabilisers), sales of formulated calcium-organic stabilisers in Western Europe and Turkey, including calcium/zinc, have increased from 18 kilotonnes in 2000 to 42 kilotonnes in 2005. Further growth is expected as a result of the progressive phasing out of lead-based systems which were traditionally used in many parts of the world to stabilise rigid PVC for the construction industry use and in flexible PVC for electrical wire and cable applications (ESPA, not dated).

Alternative Materials

It should be noted that apart from the aforementioned alternative components, there are materials which could be use in the place of PVC, as identified in PE Europe *et al* (2004). The following bulletpoints show the availability of alternative materials to PVC packaging applications for which industry has argued on the importance of using PVC with specific technical characteristics (clarity, transparency, etc.). The same report provides (on page 45) an extensive list of alternatives in other application areas such as construction and consumer goods.

- in *bottles* (where the market share of PVC is suggested as “small”), alternatives include PET, glass, polyolefins and ceramics;

- in *food packs* (where the market share of PVC is suggested as “medium”), alternatives include PET, aluminium, paper, polystyrene, polyolefin and polyamide;

- in *shrink foils* (where the market share of PVC is suggested as “small”), alternatives include polyolefins; and

- in *blister packs* (where the market share of PVC is suggested as “medium”, alternatives include cyclic olefin copolymer, PP/cyclic olefin copolymer/PP-layer-compound, polyethylene/polyvinylidene chloride and paper.

Materials readily available to consumers can reasonably be expected to meet the requirements of the market (for instance, PET clear packaging for food which is already widely used). Nevertheless, a full comparison of materials cannot be provided here as this could entail a full lifecycle assessment for these.

5.2.4 Cost and Socio-economic Considerations

Cost Comparisons between Organotin Stabilisers and Alternatives

Based on the discussion earlier, the assessment of costs will focus on (solid) calcium-organic stabilisers (calcium/zinc stabilisers and OBS) and tin stabilisers. This is on the basis that:

- lead stabilisers are being phased out by 2015 and will not replace or be replaced by organotin-based stabilisers;
- cadmium based stabilisers have been phased out; and
- liquid mixed metal stabilisers are in the process of replacing organotin stabilisers in plasticised PVC where a gradual phase out of organotin stabilisers is pursued by the EU PVC industry.

With regard to methyltins and possibly other organotins which may act as alternatives (in the event of the introduction of a restriction on the four organotin groups in question), all information collected in the course of the study has been provided in this report; unfortunately, the potential costs of such a move to other organotin stabilisers are not known at present.

In general, calcium/zinc stabilisers are indicated to be slightly more expensive than the organotin-based stabilisers. The newer forms of calcium-organic stabilisers (OBS) are more complex and expensive than the traditional soaps mainly because of the specialised co-stabilisers required to meet the specific requirements of these applications. This means that the rate of introduction of such stabilising systems is also slowed down by the extensive evaluation work required and the need for acceptance by the specifier.

Somewhat conflicting views on the relative cost of calcium/zinc stabilisers and OBS compared to organotin stabilisers – it is possible that this may have to do with the varying requirements of different PVC applications. We can identify two approaches:

- ***calcium-organic stabilisers are more costly than organotin stabilisers***: a company manufacturing organotin stabilisers has argued that, in rigid PVC films and other applications where clarity and long-term stability are important, alternative stabiliser systems require high loading levels and use of expensive co-stabilisers to achieve acceptable performance.

  In rigid moulding applications, one company indicates that a calcium/zinc formulation is 3 - 6% more expensive than an organotin-based stabiliser. As tin stabilisers are natural bactericides, in some applications, a more potent chemical may be required to achieve the same level of protection in a calcium/zinc formulation and this would add to the cost as an additional formulation ingredient may be required in certain applications (e.g. roof sheet and doorstrips, as well as medical mouldings etc.). The same company also notes that higher addition rates would be required using alternatives such that the unit cost of the compound may be higher, although the stabiliser would have similar costs.

Regarding co-stabilisers, it is indicated that an epoxy typically acts as a synergistic stabiliser with a mixed metal stabiliser and it has been part of standard formulation practice for flexible PVC for over 35 years. Industry suggests that 1 part per hundred of resin would be a typical stabiliser load for tin-stabilised PVC; this might have to be substituted 2.5 parts per hundred of resin mixed metal and 3 parts per hundred of resin of epoxy.

- ***calcium-organic stabilisers are less costly than organotin stabilisers***: on the other hand, another company indicates that while the cost per tonne of the tin stabilisers is higher than the mixed metal stabilisers but the dosage rate of the latter is higher. The total cost of the stabiliser package is dependant on the stability required but is very slightly higher. In terms of process changes, and associated costs, that were necessary for a move from organotin stabilised PVC, this company indicates that, because of the increased quantity used and the extra material, extra storage tanks and dosing equipment are required.

Tables 5.3 and 5.4 overleaf outline the costs of replacement of organotins in pipes by calcium/zinc stabilisers and OBS. It illustrates the relationship between addition rates and unit costs typically experienced and indicates that the costs between organotins and the other two stabiliser systems are not significant overall.

Although as noted before, the cost comparison between organotin stabilisers and liquid mixed metal stabilisers for plasticised PVC applications is not of primary importance, however, information has been collected during consultation and this is presented in Table 5.5. It appears that the alternatives may be up to 50% more costly compared to organotins.

Table 5.5: Direct Cost Comparison of Alternative Stabilisers

Alternative	Relevant application	Price*
Liquid Ca/Zn	Plasticised PVC	+ 50% expensive
Liquid Ba/Zn (1)	Plasticised PVC, including flooring	Similar
Liquid Ba/Zn (2)	Plasticised PVC	+ 50% expensive
Ba/Ca-Zn stabilisers	Plasticised PVC, including flooring	20% more

** price comparison is relative to organotins*
Source: Consultation

Table 5.3: Calculation of Raw Material Costs for Three Stabilisation Systems in PVC Brown Sewage Pipes									
Component	**Organotin**			**Calcium/Zinc**			**OBS**		
	Dosage in phr	**Costs in €/kg**	**Total costs in €**	**Dosage in phr**	**Costs in €/kg**	**Total costs in €**	**Dosage in phr**	**Costs in €/kg**	**Total costs in €**
sPVC K66/68	100.00	0.92	92.00	100.00	0.92	92.00	100.00	0.92	92.00
Filler	10.00	0.25	2.50	10.00	0.25	2.50	10.00	0.25	2.50
Stabiliser/Lubricant									
One pack based on									
Sn	2.20	2.72	5.98						
Ca/Zn				2.60	1.78	4.63			
OBS							2.40	1.925	4.62
	112.20		**100.48**	112.60		**99.13**	112.40		**99.12**
Dry blend costs in €/kg	**0.896**			**0.880**			**0.882**		
Source: Consultation									

Table 5.4: Calculation of Raw Material Costs for Three Stabilisation Systems in PVC Grey Sewage Pipes									
Component	**Organotin**			**Calcium/Zinc**			**OBS**		
	Dosage in phr	**Costs in €/kg**	**Total costs in €**	**Dosage in phr**	**Costs in €/kg**	**Total costs in €**	**Dosage in phr**	**Costs in €/kg**	**Total costs in €**
sPVC K66/68	100.00	0.92	92.00	100.00	0.92	92.00	100.00	0.92	92.00
Filler	10.00	0.25	2.50	10.00	0.25	2.50	10.00	0.25	2.50
Stabiliser/Lubricant									
One pack based on									
Sn	2.20	2.72	5.98						
Ca/Zn				2.60	1.78	4.63			
OBS							2.40	2.20	5.28
	112.20		**100.48**	112.60		**99.13**	112.40		**99.78**
Dry blend costs in €/kg	**0.896**			**0.880**			**0.888**		
Source: Consultation									

Other Socio-economic Issues

Development of New Alternatives

For products where there currently no suitable alternatives (according to industry), new products would need to be developed to attain similar performance to that of today. Development costs would be high both at the compounder level and the stabiliser manufacturer level. Once a feasible product had been established, industry estimates that it could take five years for approvals to be established for roof sheet such that adequate guarantees could be given on performance (manufacturers of such articles would be expected to provide certified guarantees that the products would not fail in service over a reasonable time period). Approvals for medical compounds (world-wide) would also be costly and time consuming. Again gaining regulatory approvals such as listings on EU Directives can also be costly to the raw material supplier.

Cost of Re-tooling

For profile applications where extruders would require tool tuning would be required, a cost of €7,000 has been identified per company affected.

Potential for Migration of PVC Industry to non-EU Territories

Certain industry consultees have argued that organotin stabilisers provide excellent clarity for PVC while also providing excellent processing rates and cost performance, and that this balance of performance has not been matched by any other stabiliser system until now. In addition, it is suggested that the packaging market is extremely competitive in terms of performance (clarity) and cost. As a result, some consultees have argued that a more expensive stabiliser system that does not deliver the clarity will make PVC significantly less competitive in the packaging market. Furthermore, the desirability for PVC as a packaging material may lead manufacturers to import PVC packaging material from outside the EU; manufacturing will move outside the EU and the relevant articles will simply be imported from outside the EU. It has also been suggested that if octyltins are no longer available to rigid calenderers, calenders can be physically moved overseas to the USA or Asia (there are more than 50 calendering plants in Europe). It has been speculated that the few large companies will move production to their other non-European plants, while several smaller ones will close down).

5.2.5 Environmental and Health Effects

An assessment of the environmental and health effects of alternative stabilisers would focus mainly on the calcium-organic stabilisers (calcium/zinc stabilisers) and other tin stabilisers on the basis that:

- lead stabilisers are being phased out by 2015 and will not replace or be replaced by organotin-based stabilisers; and
- cadmium based stabilisers have been phased out.

Calcium-organic Stabilisers

For the calcium-organic stabilisers, a review of various MSDS sheets provided by manufacturers and available in the open literature does not indicate any major concerns relating to any human and environmental effects; there is, however, the possibility that other substances used in these stabilisers may have some undesirable effects. For instance, one MSDS sheet refers to their calcium-organic stabiliser as a "*solid blend based on Ca and Zn metal soaps, inorganic complexes based on Na, Mg, Ca and Al, phenolic antioxidants, beta-diketones and polyols*".

The European Plastics Converters (EuPC) provided RPA with a study they commissioned to investigate the human health and environmental hazards of calcium/zinc stabiliser systems. This study considered seven major ingredients of a commercially available calcium/zinc stabiliser system (which for reasons of commercial confidentiality could not be named). The study concluded the following (Eurotoxis, 2007):

- ***for human health***: using a database of variable detail for each component, the hazard from these to systemic toxicity was considered to be generally low, on the basis of available information. No specific hazard due to systemic toxicity was identified from the ingredients; however, data gaps would be identified under REACH for three of these. Further, the structure of the ingredients suggests that the probability of untoward findings is low but cannot be excluded. The insoluble ingredients however may pose a risk by inhalation when formulating the stabiliser mixture or adding the stabiliser to the PVC; and

- ***for environment***: again, using a database of variable detail, several data gaps were identified and for two of the ingredients the hazard to the environment could not be sufficiently evaluated due to the lack of data. One of the components might be considered as posing a hazard to the environment linked to its persistence in the environment while another component showed aquatic toxicity with possible acute and long-term effects not excluded.

Alternative Organotins

With regard to other organotins used as alternative stabilisers, the discussion below provides an overview of some of the hazards and human health effects of methyltin compounds, which may be used as alternative stabilisers. For the purposes of this overview the chloride salts of the alternative organotins have been examined with the 2002 RAR being the main source of information.

Physico-chemical Properties and Classification and Labelling

Table 5.6 summarises the key physicochemical properties for organotins other than those under consideration as possible alternatives in the stabilisation of PVC. The table provides an overview of the TDIs and environmental (water) PNECs expressed as Sn or alkyltin chloride as well as the current classification and labelling for the two substances, MMTC and DMTC. A search on the ClassLab database of the European Chemicals

Bureau did not reveal an existing classification for the four aforementioned organotins. However, entries exist for MMTC and DMTC on the working database which are summarised below.

Table 5.6: Physico-Chemical Properties and Classification and Labelling (on the ECB Working Database) of two Methyltins

Parameter	**Alkyl Tin Chloride (ATC)**	
	MMTC	**DMTC**
CAS No.	993-16-8	753-73-1
EINECS No.	213-608-8	212-03902
Chemical Formula	CH3Cl3Sn	C2H6Cl2Sn
Molcular Weight	240.8	219.7
%Tin	49.3%	54.0%
Physical state (ambient)	Solid	Solid
PNEC (water) mcgSn/l	0.5	0.6
TDI (oral) mcgSn/kg bw/day	0.6	0.6
PNEC (water) mcgATC/l	1.014	1.110
TDI (oral) mcgATC/kg bw/day	1.217	1.110
ClassLab Tracking		
Health tracking	TC C& L EH 09/07: concluded reprotox	TC C&L EH 10/06: concluded
Environment tracking	Did not appear on agenda for Jan07 No ATP proposal	Did not appear on agenda for Jan07 No ATP proposal
Classification and Labelling		
Classification	Muta. Cat. 3; R68 Repr. Cat. 3; R63 Xn; R22 [N; R50-53]	Repr. Cat. 3; R63 T+; R26 T; R25 Xn; R21 T; R48/25 C; R34 [R52-53]
Risk phrases	22 - 63 - 68 - [50/53]	21 - 25 - 26 - 34 - 48/25 - 63 - [52/53]
Safety phrases	2 - 36/37	26 - 28 - 36/37/39 - 45 - [61]
Indications of danger	Xn	T+
Seveso Data		
Seveso substance	No data	Yes
Seveso categories	No data	Main category: 1 Other categories: 2-2

Source: RPA & CEH, 2002

Human Health Risk Assessment

In relation to human health effects, a wide range of data was used to form a basis for values for tolerable daily intake (TDI), which are shown in Table 5.6. Using the above TDIs and a series of calculations of exposure, the 2002 RAR performed a risk characterisation for consumer exposure to these four organotins from use in a number of relevant (at the time) applications. This is summarised below for both adults and children.

Table 5.7: Worst-case Consumer Risk Characterisation - Percentages of TDI by Source for Alternative Alklytin Compounds

Application	MMT	DMT
Food wrapped in PVC [a]	15% to 58% (adult & children)	15% to 58% (adult & children)
Via env. (worst local)	0.31% (adult & children)	0.47% (adult & children)
Via env. (regional)	0.003% (adult & children)	0.006% (adult & children)

Source: RPA & CEH, 2002
Notes:
a Lower values represent exposure calculated using fat consumption reduction factors and are likely to be more representative of actual exposure (though still realistic worst-case)

It should be noted that the above percentages are given as background information only as they may not directly relate to the risk reduction measures considered in this report.

Environmental Risk Characterisation

PBT/vPvB Assessment

The 2002 RAR also assessed the PBT and vPvB properties of several organotins. On the basis of available data, it was found that MMTC and DMTC would not come anywhere close to fulfilling the PBT/vPvB criteria, since the BCF values for these substances are significantly below 2,000.

Regional Risk Characterisation

All of the regional PEC values are well below the PNEC values, indicating no concern for the aquatic environment for these substances from the uses considered at the regional level. At the local level, the risk characterisation ratios for the various uses are detailed in Table 5.8.

Table 5.8: PEC/PNEC Ratios at a Regional Level for the Aquatic Environment for two Methyltins

Parameter	MMTC	DMTC
Regional PEC	1.1	1.7
PNEC	1,014	1,110
PEC/PNEC	0.001	0.002

Source: RPA & CEH, 2002
Note: PEC and PNEC values in ng/l

Local Environmental Risk Characterisation

Table 5.9 summarises the results of the local risk characterisation for the two alternative organotins. There is only one application area of relevance and this is the processing of PVC using organotin stabilisers. In the worked examples used in the 2002 RAR - a large calendering plant and a small spread coating plant - the RCR values for MMTC and

DMTC were predicted to be slightly above unity. However, there were areas where the input data used were subject to some uncertainty, including physicochemical parameters, environmental fate and behaviour and the validity of the emission scenarios adopted.

Table 5.9: PEC/PNEC Ratios at a Local Level (for the Aquatic Compartment) for Alternative Alkyltin Compounds

Activity	MMTC	DMTC
Organotin Production		
No production in the EU	-	-
PVC Processing Sites (using Stabilisers)		
- Large Calendering Plant (using TGD)	**2.10**	**2.35**
- Small Spread Coating Plant (using TGD)	**1.27**	**1.42**
- Generic Plant (EUSES)	0.001	0.002

Source: RPA &CEH, 2002

For the areas where a PEC/PNEC ratio above unity has been calculated, a targeted sensitivity testing was undertaken on the input parameters, on the basis that further information might later be made available by industry (or others). For MMTC and DMTC in relation to the risk characterisation ratios calculated using the TGD equations and emission estimates from the emission scenario document, the RCR values were reduced to significantly below unity. The conclusion of the 2002 RAR was that, given that the calculated PEC/PNEC ratios were not significantly above unity for even the worst-case exposure estimates (using the TGD equations), there is not sufficient concern for the use of organotin stabilisers in PVC processing to warrant the implementation of any further risk reduction measures at the time.

In summary, the 2002 RAR findings suggest that the two methyltins do not pose unacceptable risks to the environment and have a less hazardous profile compared to the four organotins of concern with regard to human health. However, the above discussion reflects the assessment of risks for uses and tonnages identified in the 2002 RAR; also, while no classification and labelling entries are to be found at present in Annex I of Directive 67/548/EEC, the ECB working database suggests a potential classification as reprotoxic category 3 for both methyltins and as mutagen category 3 for MMTC.

5.2.6 Summary

The key alternative to organotin stabilisers is calcium-organic stabilisers for rigid PVC applications. In plasticised PVC applications, organotins find continuously decreasing use and where they are currently used, industry intends to soon replace them by liquid mixed metal (barium/zinc) stabilisers which already dominate the plasticised PVC market.

Concerns have been raised in respect to the clarity/transparency of PVC articles stabilised with calcium-organic stabilisers as well as the processability of these products as opposed to organotin-stabilised PVC. However, several sources (including the ESPA and ECVM Internet sites) suggest that desired clarity can be achieved with calcium-organic stabilisers. Evidently, the requirement for clarity is not an issue for window profiles and pipes, as compared with rigid films and sheets.

So far, the penetration of calcium/zinc stabilisers in cable covering, pipe and window is almost complete and many of these are been in commercial use for several years. The use in profiles, in drinking water pipes and cables is well advanced but still limited in other pipes and profiles (ECVM, not dated). In flexible foils where the main stabiliser used is barium/zinc soap, substitution by calcium/zinc materials is also taking place although, there are technical issues which need to be overcome (ECVM, not dated). As ECVM notes, the performance of more recent developments in calcium/zinc stabilisers makes them potential technical alternatives to most other stabilising systems (ECVM, not dated).

Moreover, it appears that most stabiliser manufacturers will be able to supply calcium-organic stabilisers (as they already do) and this would offset partly or wholly any losses resulting from a restriction on the marketing and use of organotin stabilisers. Moreover, the available information suggests that the manufacture and marketing of mono-substituted or methyltin alternatives is possible, therefore, in the event that DOT and DBT are restricted, these companies would still be able to supply their customers with organotin stabilisers.

It is appreciated that the introduction of a new stabiliser system may involve certain evaluation work and the need for acceptance by the specifier. Also, processability may be an issue and re-tooling costs may accompany any such change to a different system. With regard to processing characteristics, careful stabiliser dosing and lubrication is necessary to optimise melt flow characteristics and anti-sticking properties during processing (ESPA, not dated-a). For extruded applications, there could be significant costs involved in the replacement of manufacturing equipment to accommodate the different processing requirements for different stabilisers systems - which could potentially result affect a number of PVC processing operations (it has been argued that such costs could be high enough to threaten businesses with closure).

On the other hand, the comments made by ESPA and ECVM on their website as well as by, Manolis Sherman (2005) (OBS can display lubrication of vinyls similar to formulations with organotins or traditional mixed metal systems) suggest that modern calcium-organic stabilisers may not have immense processability differences compared to organotin-based systems. However, the recycling of calcium-organic stabilised PVC may be an issue at present. Manolis Sherman suggests that OBS compounds are suitable for recycling; there are no interactions (such as cross-staining) with other stabilisers and only a minor decrease in thermal stability after reprocessing five times (Manolis Sherman, 2005). Scheirs (2003) also quoted industry consultees suggesting that the mechanical recycling capability of calcium/zinc stabilised PVC is poor – this of course may not necessarily apply to recently developed OBS.

5.3 Alternatives to Organotin-based Catalysts in Esterification Reactions

The information received in the course of this study (as set out in Section 2) indicates that organotins are not currently used as catalysts in esterification reactions for the manufacture of PVC plasticisers. As a result, a discussion of alternatives that may be used following a restriction on the use of organotins in the manufacture of plasticisers would be of limited use and is not provided here.

Also, as noted in Section 2.1, for catalysts, in nearly all of the cases, only one species (mono- or di- alkyltin) will work as an efficient catalyst. Often, mono- alkyltin catalysts function in esterification reactions whereas di- alkyltins are better for trans-esterification reactions.

It is, however, noted that titanate catalysts are used in the manufacture of plasticisers.

5.4 Alternatives to Organotin-based Catalysts in Polyolefin Antioxidant Manufacture

5.4.1 Alternative Catalysts in Manufacture of Phenol Hindered Antioxidants

Introduction

In assessing alternative catalysts, it is important to note that catalyst recipes are one of the most important ‘secrets’ in the plastics and chemical industry. As one source put it, “*catalysts are the difference between one company producing 100,000 tons per year and another producing 150,000 tons per year at the same costs*” and as such, most companies are reluctant to release this information.

It is important to note that organotins are no longer used in absorbent hygien products (AHPs) manufactured by members of EDANA; there are suitable alternatives as identified by EDANA and, as such, the information below is provided as a background only.

Lithium Compounds

A US manufacturer of hindered phenols indicates that non-tin containing catalysts based on lithium compounds can be used for their manufacture, instead of organotin-based catalysts. These compounds are functionally identical to those stabilisers made using the organotin catalysts and at prices that are competitive with that of the organotin-based materials, although some larger additive companies charge a higher price for their organotin-free versions (Mayzo, 2002).

The company notes that “*while there is no proof that organotin residues in personal care products lead to adverse health effects… there is also a compelling case for the removal of any source of organotin, especially since this can be done at no added cost to the companies that use stabilisers in their products*”. They also note that apart from the avoidance of potential consumer exposure, “*the use of these organotin-free stabilisers* *would also eliminate any health concern for plant workers who might come in contact with the pure stabilisers during additive handling and masterbatching at resin manufacturing and compounding facilities*" (Mayzo, 2002).

The company argues that "*there is no performance or functional difference between the organotin-free stabilisers, and those made using the organotin catalysts that are currently in use. The end-use company can therefore simply make a specification change for the additives that they use in their products, with no need for any manufacturing changes on their part*" (Mayzo, 2002).

Metallocene Catalysts

Metallocene catalysts have been highly publicised in the olefin polymerisation catalyst area for the last twenty years and have become increasingly popular in the plastics industry.

Metallocenes are made of a positively charged metal ion 'sandwiched' between two negatively charged cyclopentadienyl anions (or simply, a single metal atom held between two carbon rings). Cyclopentadienide ions have a charge of -1, so when combining with a cation such as Fe^{2+}, the two anions will form an iron sandwich which is called ferrocene. Sometimes a metal with a higher charge is involved, like zirconium with a +4 charge. To balance the charge, the zirconium will bond to two chloride ions, -1 charge on each (in addition to the two cyclopentadienide ions), to give a neutral compound. Metallocene catalysts are homogenous single-site systems, implying that there is a single, uniform type of catalyst present in the system.

Titanate Catalysts

Titanate catalysts are widely used to produce plasticisers such as phthalates and hindered phenol antioxidants (pers. comm). Organic titanates, such as tetraisopropyl titanate, $Ti(OC_3H_7)_4$, readily undergo transesterification when mixed with higher alcohols (Johnson Matthey, 2002). The demand for titanates for this application has grown steadily since their introduction in the 1950s and now accounts for a significant proportion of the total market for these compounds. The biggest use is in the large tonnage plasticiser industry for producing such esters as dioctyl phthalate from phthalic anhydride (Johnson Matthey, 2002).

5.4.2 Alternative Antioxidants in Polyolefin Manufacture

There are two key categories of antioxidants:

- ***primary antioxidants***: which are free radical scavengers, typically with reactive OH or NH groups, which inhibit oxidation via chain termination reactions; and

- ***secondary antioxidants***: which decompose hydroperoxides into non-radical, non-reactive, and thus thermally stable products.

Four principal antioxidant types are considered in this Report:

- hindered phenols;
- secondary aromatic amines;
- lactones; and
- organophosphorus compounds.

The first three are primary antioxidants (or hydrogen donors/radical scavengers) while the last is a secondary antioxidant (or hydroperoxide decomposer).

Hindered Phenols

Phenolic stabilisers are primary antioxidants and are the most widely used stabilisers of this type (SpecialChem, 2007). They are often used in combination with secondary antioxidants and are effective during both processing and long term thermal aging. For instance, acrylated bisphenols (or acrylate functionalised hindered phenols) are very effective in preventing styrene copolymers from crosslinking or degrading during processing, particularly under oxygen deficient conditions. They are usually used in conjunction with other stabilisation chemistries (SpecialChem, 2007). Hindered phenol antioxidants, which contain the 2,6-di-tert-butylphenol functional group, are also very effective primary antioxidants for polyolefins (Dong Ryun *et al*, 2001).

Secondary Aromatic Amines

Secondary aromatic amines act as primary antioxidants and are excellent hydrogen donors. Also available in an extensive range of molecular weights and product forms, aromatic amines are often more active than hindered phenols, because of less steric hindrance. Aromatic amines, however, are more discolouring than hindered phenols, especially on exposure to light or combustion gases (gas fade).

For instance, hydroxylamines may act as both primary and secondary antioxidants, providing processing stability, comparable to phenol/phosphite systems. In addition, they provide excellent light stability when used in combination with hindered amines and are resistant to gas-fade discoloration (SpecialChem, 2007).

Hindered amine stabilisers can also offer very high performance as long-term thermal stabilisers. Hindered amine stabilisers are extremely efficient stabilisers against light-induced degradation of most polymers. They do not absorb UV radiation, but act to inhibit degradation of the polymer. Significant levels of stabilisation are achieved at relatively low concentrations. Their high efficiency and longevity are due to a cyclic process wherein the stabilisers are regenerated rather than consumed during the stabilisation process. Because of the regenerative nature of this process, as well as the typically high molecular weights of the stabilisers, hindered amine stabilisers are capable of providing extreme long-term thermal and light stability (SpecialChem, 2007).

Lactones

Carbon centred radical scavengers, such as lactones and acrylated bisphenols, are extremely effective in oxygen deficient environments. Lactones (benzofuranone derivatives) are powerful radical scavengers. Even when added in small amounts, they help control melt stability during polymer processing. Substituted benzofuranone are mainly used in combination with phenolic compounds and phosphite to provide materials the desired performance even at low concentrations (SpecialChem, 2007).

Organophosphorus Compounds

Hydroperoxide decomposers are secondary antioxidants (used in combination with primary antioxidants to yield synergistic stabilisation effects) that prevent the split of hydroperoxides into extremely reactive alkoxy and hydroxy radicals. Organophosphorus compounds are widely used hydroperoxide decomposers. Trivalent phosphorus compounds are excellent hydroperoxide decomposers; generally, phosphites (or phosphonites) are used. Some of these compounds are sensitive to water and can hydrolyse, leading to formation of acidic species. While addition of acid scavenger can minimise the effect in polyolefins, industry has generally converted to hydrolysis-resistant compounds (SpecialChem, 2007). Some examples of phosphite antioxidants are (Great Lakes, 2004):

- tris(2,4-di-t-butylphenyl) phosphate (CAS No 31570-04-4);
- bis(2,4-di-t-butylphenyl)pentaerythritol diphosphite (CAS No 26741-53-7); and
- bis(2,4-di-t-butylphenyl)pentaerythritol diphosphite (CAS No 264741-53-7, 11097-59-9).

Table 5.10 outlines the suitability of the different antioxidants for long-term and melt processing stabilisation of polyolefins. It appears that hindered phenols are the only group of substances that currently offers both types of stabilisation. This explains their leading role in the antioxidants market.

Table 5.10: Effective Temperatures for Polyolefin Antioxidants

Stabiliser	Low temperature effectiveness (long-term thermal stability)	High temperature effectiveness (melt processing stability)
Hindered phenols	Yes	Yes
Hindered amine	Yes	No
Phosphite	No	Yes
Hydroxylamine	No	Yes
Lactone	No	Yes

Source: King, 2001

Other

Multi-functional antioxidants have only recently become available. Due to their special molecular design, they optimally combine primary and secondary antioxidant functions in one compound (an example is 4,6-bis (octylthiomethyl)-o-cresol – CAS No 110553-27-0). Having several stabilising functions combined in the same molecule, multi-functional antioxidants eliminate the need for co-stabilisers, such as phosphites and thioethers. This not only simplifies the formulation, but it also simplifies the storage, handling, and use of the stabiliser (SpecialChem, 2007).

Dong Ryun *et al* (2001) suggest that low molecular weight antioxidants are easily lost from the polymers by physical loss such as migration, evaporation, and extraction. Physical loss of antioxidants, therefore, constitutes a major concern in the environmental issues and safety regulation, as well as in long-term use of polymers. The researchers suggest that, thus far, polymeric antioxidants have gained much interest to overcome the physical loss of antioxidants and to enhance the thermal stability. The copolymerisation or homopolymerisation of the monomeric antioxidants is a conventional methodology for preparing polymeric antioxidants.

5.5 Alternatives to Organotin-based Catalysts in Silicones Manufacture

5.5.1 Introduction

As discussed in Section 2.6, organotins are used as catalysts in the following silicone-related applications:

- one-component component consumer (do-it-yourself) sealants;
- condensation cross-linking of silicone-grafted polyolefins such as polyethylene cable insulation and polyethylene potable water pipes;
- two-component do-it-yourself silicone mould kits;
- two-component dental silicone moulds;
- baking and cooking silicone moulds; and
- baking paper silicone coatings.

Of the above, silicone-grafted polyolefins are considered to be industrial uses and will not be considered further in this Section. Furthermore, industry suggests that baking and cooking silicone moulds sold to consumers are cross-linked at high temperature, typically with platinum or peroxides, but never with organotins; as a result, a discussion on alternatives is not provided here[32]. Finally, the key trade association (CES) has suggested that the global silicone industry voluntary phase-out of organotin-catalysed baking papers is now effective and that the main catalyst used in current systems is platinum; again, no further discussion on alternatives to organotins in silicone-coated baking paper is provided here.

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[32] It is of note that a recent patent published in a scientific publication suggests that an addition-crosslinked silicone elastomer (1) is formed in the presence of at least one Rh or Ir hydrosilylation catalyst, such as $Rh_2(C_8H_{15}O_2)_4$ or $[IrCl(olefin)_2]_2$, or a mixture. (1) can be made transparent and colourless, is flexible and is suitable for use as food and baking moulds in the food industry. The catalysed addition crosslinkable components reportedly display excellent pot life and good high-temperature cure (Platinum Metals Review, 2007).

The main applications of relevance are therefore:

- one-component component consumer (do-it-yourself) sealants (RTV-1);
- do-it-yourself silicone mould kits (RTV-2); and

For dental silicone moulds (RTV-2), a discussion on potential alternatives is provided in Section 5.5.4 for completeness.

5.5.2 Alternative Catalysts Used in One-component Silicone Sealants

Alternative Sealants

Applications for silicone sealants are extremely broad. Markets include construction, automotive, assembly, maintenance, electrical/electronic, aerospace, and consumer products. Silicone sealants often compete with other materials such as polyurethanes, polysulfides, and acrylics; however, in applications requiring long-term durability to harsh environments, silicones are generally specified (Petrie, 2005).

Alternative Silicone Catalysts

The available information suggests that the most common catalyst for RTV-1 silicone sealants are dialkyltin compounds, e.g. dibutyltin dilaurate or diacetate. Alternatives include titanium compounds, such as tetrabutyl or tetraisopropyl titanate or titanium chelates or zirconates. It is reportedly also possible to use catalyst mixtures.

Titanates and zirconates appear to be important additives in moisture curing RTV-1 silicone sealants where a,w-dihydroxy polydimethyl siloxanes are crosslinked by three functional alkyl or vinyl silanes. The titanates/zirconates act as (Dupont, not dated):

- catalyst for the crosslinking reaction of the silane with the silicone (sometimes in combination with tin compounds);

- drying agent: the titanate consumes the water in the formulation and thus prevents the pre-crosslinking of the sealant; and

- crosslinker: epending on the sealant system titanates/zirconates are efficient crosslinkers with and without silanes as bridging agent.

  The main substances used are reported to be the following (Dupont, not dated):

- ethylacetoacetate titanium chelates – best choice for stability and reactivity;
- tetra n-butyl titanate or n-butyl titanate polymer - with higher reactivity; and
- titanium acetylacetonates with reduced reactivity.

Specific titanate catalysts from the above groups that may be used in the manufacture of silicone sealants include (Dupont, 2001):

- tetra iso-propyl titanate (CAS No: 546-68-9);
- tetra n-butyl titanate (CAS No: 5593-70-4);
- n-butyl titanate polymer (CAS No: 9022-96-2);
- titanium acetyl acetonate (IPA/EtOH) (CAS No: 68586-02-7);
- titanium diisopropoxide bis(ethylacetoacetate) (CAS No: 27858-32-8);
- ethyl acetoacetic ester titanate (butyl in BuOH) (CAS No: 20753-28-0);
- ethyl acetoacetic ester titanate (CAS No: 83877-91-2);
- titanium ethylacetoacetate/silane chelates; and
- n-butyl zirconate (CAS No: 1071-76-7).

Another manufacturer further indicates the following titanates as suitable for catalysis of alkoxy and oxime neutral cure RTV (Gelest, 2004):

- titanium di-n-butoxide (bis-2,4-pentanedionate) ($C_{18}H_{32}O_6Ti$; CAS No: 16902-59-3);
- titanium diisopropoxide(bis-2,4-pentanedionate) ($C_{16}H_{28}O_6Ti$;CAS No: 17927-72-9);
- titanium 2-ethylhexoxide tetraoctyltitanate ($C_{32}H_{68}O_4Ti$; CAS No: 3061-42-5); and
- titanium trimethylsiloxide tetrakis(trimethylsiloxy)titanium ($C_{12}H_{36}O_4Si_4Ti$; CAS No: 15990-66-6).

On the other hand, CES (2007a) has argued that there are no technically suitable alternatives to organotins in RTV-1 sealants. It has suggested that RTV-1 sealants are very crucial in many construction industry applications such as double-glazing.

Technical Characteristics of Alternative Catalysts

Titanates may cause yellowing of the sealant with time. Zirconates do not show this tendency. The titanate is normally added before or sometimes together with the crosslinker. The amount is in the range of 1-10 % with respect to the siloxane. Other typical components of RTV-1 silicone sealant formulations are extenders or reinforcing fillers ($CaCO_3$, pigments, quartz, fumed silica, etc), wetting agents, and other additives (Dupont, not dated).

Relative Cost of Alternative Catalysts

In terms of cost, according to one company, titanium and zirconium are more expensive compared with tin; titanium catalysts are approximately 5 times the cost of equivalent tin catalysts. Technically high and approximately equivalent, loading levels are used for both tin and titanium catalysts for these applications. The high catalyst loading makes the cost of the catalyst a major contributor to overall formulation costs. Titanium catalysts are competitive products in this market with a significant market share. They tend to produce coloured silicones while tin can produce colourless products. Titanium catalysed silicones therefore require pigmentation but this is often the case, regardless of the catalyst used. Some but not all, customers have reported that titanium catalysts have a slightly shorter shelf life than tin catalysts. This can be improved via reformulation and some companies are understood to be currently developing titanium and zirconium catalysts with longer shelf lives. Zirconium catalysts are still under development and not yet commercially available but these have produced colourless silicones (pers. comm.).

5.5.3 Alternative Catalysts Used in Two-component Silicone Moulding Kits

Identities of Alternative Catalysts

Apart from tin octoate or dibutyl tin dilaurate, several alternatives have been suggested such as platinum, rhodium and palladium (see information from CES below) as well as carboxylic salts of lead, zinc, zirconium, and antimony may also be used (Petrie, 2005). According to CES (2007a), platinum catalysts may indeed be used in RTV-2 silicone formulations instead of organotin catalysts. Other catalysts that have been mentioned include rhodium and palladium, however, CES has suggested that rhodium and palladium are alternatives to platinum, not organotins, and users of the latter would probably move to platinum, if necessary, rather than to the other two metals.

With regard to platinum, it is understood that platinum complexes containing nitrogen are used for effecting addition curing at elevated temperatures (e.g. Pt-complexes with pyridine, benzonitrile or benzotriazole). Curing will, however, take place at room temperature if platinum-olefin complexes are used (CES, 2003a). Table 5.11 shows examples of platinum complexes with an olefin ending[33] used in silicone addition curing (as opposed to condensation curing that takes place with organotins) supplied by a US company[34]. It appears that the concentration of platinum ranges between 1 and 10%. However, concentrations as low as 0.5% have been identified in a search of the electronic literature available from an EU supplier (Hanse Chemie, 2004).

Table 5.11: Examples of RTV-2 Silicone Addition Curing Platinum Catalysts

Platinum catalyst complex	**Silicone parameters**	**Conc.**
Platinum divinyl complex (platinum concentration in xylene) Example substance: *Platinum, 1,3-dierhyenyl-1,1,3,3-tetramethyldisiloxane complexes* CAS Number: *68478-92-2*	Highest reactivity, for room temperature addition cure and where for applications where cured silicones require high transparency	1-3% Pt
Platinum divinyl complex (platinum in octamethylcyclotetrasiloxane)	Colourless, low viscosity solvent, high reactivity	2% Pt
Platinum divinyl complexes (platinum in vinyl terminated polydimethylsiloxane) Example substance: *Platinum divinyl complex 1.0 - 1.5%* CAS Number: *68478-92-2*	Intermediate reactivity, useful for slow room temperature cures and moderate (30-100°C) higher temperature cures	1-5% Pt
	Intermediate reactivity, lower viscosity vinyl fluid carrier and higher platinum content allow more facile additions of small quantities of catalyst to formulation batches	10% Pt

Source: UCT, not dated

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[33] An example of such hydrosilylation catalysts comprising Pt(0) complexes containing vinyl-siloxane ligands is Karstedt's catalyst, formed by the reaction of divinyltetramethyldisiloxane with chloroplatinic acid, H_2PtCl_6 (Lewis *et al*, 1997).

[34] These are also presented in Gelest, 2004. Both sources indicate other platinum complexes as suitable for silicone curing in elevated temperatures (indicative CAS Nos: 68412-56-6, 68585-32-0, 73018-55-0) as well as rhodium catalysts (CAS No: 55425-73-5)

Technical Characteristics of Alternative Catalysts

Differences between Condensation and Addition Curing of RTV-2 Elastomers

Table 5.12 summarises the key differences between condensation and addition curing in RTV-2 elastomers.

Table 5.12: Key Differences between Condensation and Addition Curing in RTV-2 Elastomers

Condensation curing	**Addition curing**
Blending ratio of silicone elastomer and catalyst variable within limits	Blending ratio of the two components is fixed
Crosslinker agent and catalyst are both contained in the catalyst	Cross linking agent (H-siloxane) in elastomer component 1, catalyst (platinum complex) in elastomer component 2
Curing impaired only by lack of water	Curing impaired by various substances: sulphur compounds (mercaptans, sulphates, sulphides, sulphites, thiols and rubbers vulcanised with sulphur), nitrogen compounds (amides, amines, imides, nitriles) and tin compounds (condensation-cure silicones, stabilised PVC). This makes them unsuitable for certain clays, which contain sulfur or latex gloves.
Curing rate largely independent of temperature	Curing rate heavily dependent on temperature
Chemical shrinkage due to release of alcohol (0.8 - 1.2%)	Practically no shrinkage (0.05 - 0.2%)
Release products (alcohol) may cause reversion from 80 °C and above	No reversion possible
Long pot life and hence long curing times	Where pot life is long, curing can be accelerated by exposure to elevated temperatures
Less expensive	More expensive
Easier to use	Less easy to use
Typically of low viscosity (easier to pour)	Higher viscosity
Often used for low-volume plaster casting	Used for more specialised resin or epoxy casting (especially in high volumes)
Tin-based silicone cannot be used against the skin	Certain platinum-based silicones are deemed skin safe.
Silicone moulds may be used for casting polyester, epoxy, polyurethane, masonry, gypsum and candle wax	Silicone moulds may be used for casting epoxies, low melting-point metals and polyurethanes

Source: TAP Plastics, 2007; Gelest, 2004; CES, 2003a; McCormick, not dated; Silicones Inc, not dated

Relative Costs of Platinum Catalysts

The platinum catalysts are more expensive than the organotins on a functional basis and the increase in cost will have to be eventually borne by the downstream user (McCormick, not dated).

The financial impact of regulatory actions taken on RTV-2 DIY silicone moulding organotin compounds will not significantly affect CES member companies as opposed to dental moulds, as discussed further below (CES, 2007a). CES members are prepared to accept a regulatory decision to phase out the use of organotins in RTV-2 moulding compounds for the DIY market although it is noted that there are hundreds of applications for RTV-2 systems and a response would have to be developed on a case-by-case basis (CES, 2007a).

5.5.4 Alternative Catalysts Used in Two-component Silicone Dental Mould Kits

Alternatives to organotin catalysts that have been suggested in the course of this study include titanates and platinum compounds. FIDE (2007) has suggested that titanium complexes are condensation curing catalysts that may be given consideration as alternatives, however, there is limited scope for such a replacement to take place in dental moulds since they require a considerably longer time before curing is complete (therefore the treatment of patients would be considerably longer). FIDE (2007) also emphasised the greater sensitivity of platinum catalysts with respect to setting problems due to other materials used by dentists (methacrylates, some dental cements, materials for retraction cords). A replacement of organotin catalysts with platinum catalysts would require a different application technique for dental impression materials and a greater cost (due to the increased cost of raw materials and manufacturing processes).

It is important to note that different stakeholders may have somewhat differing views on the criticality of use of organotin catalysts in dental mould kits. For instance, while FIDE argues that organotins are currently in use by European dentists and they reportedly perform better than the alternatives, the European association representing the manufacturers of silicones (CES) has suggested during consultation "*the silicone industry is prepared to supply an alternative system not using dibutyltin compounds*" (CES, 2007b). It is unclear whether industry implies that another organotin group could replace dibutyltin compounds.

We have not received any indication of the costs that would be associated with the replacement of organotin catalysts by alternatives. FIDE (2007) notes that the comparatively slow speed at which other condensation catalysts such as titanates act renders them effectively unsuitable, therefore no realistic assumption on the costs of substitution may be made. CES has also advised that developing new dental mould formulations would have a significant financial impact on formulators since these are classified as medical devices and require a proportionally high cost due to extensive testing and registration dossier development and submission (CES, 2007a).

5.5.5 Environmental and Health Effects

Titanium Catalysts

There is generally limited information readily available on the human health and environmental effects of alternative catalysts such as titanates and platinum compounds. Information identified for a limited number of substances mentioned earlier in this Section is provided below in tabular form. Although it appears evident that these substances have a less hazardous profile than the organotins of concern, there are considerable gaps in the available information.

Table 5.13: Human Health and Environmental Effects of Titanium Tetraisopropanolate		
General Information		***Reference***
EINECS Name	Titanium tetraisopropanolate	IUCLID Dataset, 2000
EINECS No.	208-909-6	IUCLID Dataset, 2000
CAS No.	546-68-9	IUCLID Dataset, 2000
Synonyms	Tetra iso-propyl titanate, 2-propanol, titanium(4+) salt, Isopropyl orthotitanate, Isopropyl titanate(IV), Tetraisopropoxide titanium, Tetraisopropoxytitanium, Titanium isopropylate	Sigma Aldrich, 2007; IUCLID Dataset, 2000
Formula	Ti[OCH(CH3)2]4	IUCLID Dataset, 2000
Classification	None official identified (ClassLab database) ***Symbol of Danger***: Xi ***Indication of Danger***: Irritant ***R phrases***: 10 (flammable), 36 (Irritating to eyes) ***S phrases***: 16 (Keep away from sources of ignition - no smoking), 26 (In case of contact with eyes, rinse immediately with plenty of water and seek medical advice), 36/37/39 (Wear suitable protective clothing, gloves, and eye/face protection)	Sigma Aldrich, 2007
Ambient State	Liquid	IUCLID Dataset, 2000
Health Endpoints		***Reference***
Skin Irritation	Slightly irritating (rabbit) (GLP: no data)	IUCLID dataset, 2000
Eye Irritation	Slightly irritating (rabbit) (GLP: no data)	IUCLID dataset, 2000
Skin Sensitisation	No data identified	
Acute Toxicity	***Oral***: LD50 rat = 7,460 mg/kg bw (GLP: no data) ***Inhalation***: LCO rat (4 hours) = no data (4 hours was reported to be the maximum time at which rats exposed to concentrated vapour resulted in no deaths) (GLP: no data) ***Dermal***: LD50 rabbit > 16 mg/kg bw (GLP: no data)	IUCLID dataset, 2000
Mutagenicity/Carcinogenicity	No data identified	
Repeated Dose Toxicity	No data identified	
Reproductive Toxicity	No data identified	
Environmental Endpoints		***Reference***
Persistence and Degradation	No data identified	
Bioconcentration	No data identified	
Toxicity	On contact with moist air or water tetra-iso-propyl titanate hydrolyses to eventually form titanium dioxide and iso-propanol. Consequently the aquatic toxicity of this substance will be that of titanium dioxide (13463-67-7) and iso-propanol (67-63-0)	IUCLID Dataset, 2000

Table 5.14: Human Health and Environmental Effects of Tetrabutyl Orthotitanate

General Information		***Reference***
EINECS Name	Tetrabutyl Orthotitanate	Oxford University, 2005
EINECS No.	227-006-8	Oxford University, 2005
CAS No.	5593-70-4	Oxford University, 2005
Synonyms	Titanium (IV) butoxide, Tetrabutyl titanatate, n-tetrabutyl titanate, Tetra-n-butyl titanate, n-tetrabutyl orthotitanate, Butyl titanate, n-butyl titanate, Titanium butoxide, 1-butanol titanium (4+) salt	Oxford University, 2005
Formula	C16H36O4Ti	Oxford University, 2005
Classification	None official identified (ClassLab database) ***R phrases***: 10 (flammable), 20/21/22 (Harmful by inhalation, in contact with skin and if swallowed), 37 (Irritating to respiratory system), 41 (Risk of serious damage to eyes) ***S phrases***: 16 (Keep away from sources of ignition - no smoking), 26 (In case of contact with eyes, rinse immediately with plenty of water and seek medical advice), 39 (Wear eye/face protection)	Oxford University, 2005 Sigma Aldrich, 2005
Ambient State	Liquid	Oxford University, 2005
Health Endpoints		***Reference***
Skin Irritation	Causes skin irritation - May be harmful if absorbed through the skin	Sigma Aldrich, 2005
Eye Irritation	Causes eye irritation	Sigma Aldrich, 2005
Skin Sensitisation	No data identified	
Acute Toxicity	***Oral***: LD50 rat = 3,122 mg/kg	Oxford University, 2005
Mutagenicity/Carcinogenicity	No data identified	
Repeated Dose Toxicity	May cause damage to the following organs: central nervous system (CNS) (lung irritant)	ScienceLab, 2005
Reproductive Toxicity	No data identified	
Environmental Endpoints		***Reference***
Persistence and Degradation	No data identified	
Bioconcentration	No data identified	
Toxicity	No data identified	

Table 5.15: Human Health and Environmental Effects of Titanium(IV) butoxide, polymer		
General Information		***Reference***
EINECS Name	Titanium(IV) butoxide, polymer	Sigma Aldrich, not dated
CAS No.	9022-96-2	Sigma Aldrich, not dated
Synonyms	n-butyl polytianate	Super Urecoat Industries, not dated
Formula		
Classification	None official identified (ClassLab database) ***Symbol of Danger***: Xn ***R phrases***: 10 (flammable), 22 (Harmful if swallowed), 37/38 (Irritating to respiratory system and skin), 41 (Risk of serious damage to eyes), 67 (Vapours may cause drowsiness and dizziness) ***S phrases***: 16 (Keep away from sources of ignition - no smoking), 26 (In case of contact with eyes, rinse immediately with plenty of water and seek medical advice), 36/39 (Wear suitable protective clothing and eye/face protection)	Sigma Aldrich, not dated
Ambient State	Liquid	Sigma Aldrich, not dated
Health Endpoints		***Reference***
Skin Irritation	Irritant	Sigma Aldrich, not dated
Eye Irritation	No data identified	
Skin Sensitisation	No data identified	
Acute Toxicity	No data identified	
Mutagenicity/Carcinogenicity	No data identified	
Repeated Dose Toxicity	No data identified	
Reproductive Toxicity	No data identified	
Environmental Endpoints		***Reference***
Persistence and Degradation	No data identified	
Bioconcentration	No data identified	
Toxicity	No data identified	

Platinum Catalysts

According to CES (2007a), there are no known health or environmental effects related to the use of platinum catalysts in silicones. There have been several publications looking at their safety. The consensus is that platinum catalysts used in silicones are very safe, as the oxidation state of the platinum is zero, as in the metal (CES, 2007a). Safety datasheets (Oxford University, 2005a; Johneson Matthey, 2000) suggest that any classification and labelling of solutions of platinum compounds in organic solvents (such as propan-2-ol or xylene) are likely to relate to the solvent rather than the platinum compound.

5.5.6 Summary

There is a mixed picture with regard to the availability of suitable alternatives for organotin catalysts in the field of silicone chemistry. ETICA has argued that it is generally hard to replace organotins in catalyst applications, for selectivity and efficiency, with few exceptions (ETICA, 2007). On the other hand, according to CES, the industry is moving away from DBT as a result of classification as CMR Cat. 2.

The available information – which may not be considered to be complete – suggests:

- for RTV-1 silicone sealants, there appear to be commercially available alternatives such as titanates and zirconates although organotins are the established catalysts of choice. Issues have been raised with regard to the increased costs of alternatives, the colour of the produced sealant and the expected shelf-life of alternatives, however these technical issues may be overcome as more research is put into the development of these alternatives. As noted further above, titanium catalysts are competitive products in this market with a significant market share. On the other hand, CES has argued in favour of the criticality of construction applications of organotin catalysts in this area; however, with the exception of the increased cost, the case for the criticality of these applications has not been adequately made. It is also important to note that not all construction applications are consumer applications, however, RTV-1 silicone sealants may generally be available in DIY stores to both consumers and professional users alike;

- for RTV-2 DIY silicone moulds, addition curing catalysts such as platinum complexes appear to be the leading alternatives to organotin catalysts. These have both advantages (no shrinkage, generally skin-safe) and disadvantages (higher cost, less easy to use, adverse effects from the presence of certain substances) compared to organotin catalysts. Nevertheless, platinum catalysts may be considered to be viable alternatives and consultation suggests that CES members are prepared to accept a regulatory decision to phase out the use of organotins in RTV-2 moulding compounds for the DIY market; and

- for RTV-2 dental silicone moulds, the position of the dental industry is that while titanium and platinum alternatives are available, the former would lead to increased curing times (i.e. increase treatment times for patients) and the latter would require changes in the practices of dentists/technicians and increased costs. On the other hand, CES suggests that alternatives to dibutyltin catalysts can be provided, however, it is not clear whether these unspecified alternatives are based on other metals of tin.

Overall, the introduction of alternatives appears to be easier in RTV-2 DIY silicone moulds than in the other two applications. In RTV-1 silicone sealants, the alternatives already appear to have a significant market share despite the catalyst manufacturers' claim of the criticality of this application. In RTV-2 dental moulds, alternatives exist but their use is accompanied with technical and cost issues and the dental industry appears to be more reluctant to replace the current DBT catalyst as compared to the main catalysts industry association.

5.6 Alternatives to Organotin-based Catalysts in Electrodeposition Coatings

As discussed in Section 2, this represents an industrial uses and suitable alternatives will not be considered in detail.

5.7 Alternatives to Organotin-based Catalysts in Polyurethane Manufacture

5.7.1 Use of Catalysts in Polyurethane Foam Manufacture

In polyurethane foam applications, amine catalysts, which provide a balance between gelling and blowing reactions are mainly used. Many typical metal catalysts are not as useful as they only promote gelling reactions (Kometani *et al*, 2001). Traditional catalysts used by polyurethane foam producers are amines such as bis-(dimethylaminoethyl) ether (BDMAEE) and triethylenediamine (TEDA) along with organometallic compounds such as potassium acetate and stannous octoate. Often combinations of several of the abovementioned catalysts are used in practice as each exhibit specific activities. For instance, amines will often preferentially catalyse the reaction of water with the isocyanate. However, amines are a major contributor to the volatile organic compounds (VOC) released from polyurethane foams. The VOC issue is of concern in the automotive industry where catalyst producers have developed low-emission types - so-called reactive amines - that contain an active hydrogen functional group integrated into their structures or "blocked" active hydrogen groups that are heat activated. This was achieved at the loss of reactivity and product quality especially in regards to hydrolytic stability such as humid ageing compression set (HACS) (Stengel, not dated-1).

The polyurethane industry continues to use conventional catalyst systems with stannous octoate and dibutyltin dilaurate (DBTDL) being the most commonly used. However, they are not without problems:

- reasons of hydrolytic stability requires them to be added as a third stream;
- in the case of stannous octoate, the 2-ethyl hexanoic acid released is a major contributor to the VOC released from a foam; and
- the presence of trialkyltin impurities such as tributyltin in DBTDL that are known to be toxic to both human health and the environment.

Some foam producers have converted entirely to tertiary amines such as TEDA, thereby further adding to the issues mentioned earlier. Recent developments in the field of polyurethane catalysis include catalysts based on organotitatanes (Stengel, not dated-1).

Organotitanate Alternatives

Traditionally, organometallic complexes were still not widely considered as viable alternatives to existing polyurethane catalyst systems such as tin, amines or mixture thereof. The main reason that organometallic complexes are not widely used is their poor hydrolytic stability and consequently short pot-life. This is especially true for polyurethane foam systems where often 0.5% by weight or greater of water is present. Little research and development has been carried out to date on organometallic compounds to address the problematic issues referred to above with regard to amines (Stengel, not dated-1).

Nevertheless, according to a manufacturer of titanate alternatives, titanium catalysts are water stable and suitable to be used as gel catalysts in any polyurethane foam production process. The areas of application where customers have found the greatest advantages over standard catalyst technologies include PIR foams, rigid foams, microcellular foams and flexible foams. These new catalysts allegedly result in better control over the foaming process and delivering a much smoother and more uniform surface. The most important achievements are the improved cell structure and the reduction in VOC release from the final product (Johnson Matthey, 2005).

For foam applications amine catalysts tend to be the main competitors to organotin catalysts rather than titanates; however, titanates do feature in this market, to a lesser extent. Titanates are reported as being less reactive than organotins for polyurethane applications and therefore, due to the need for higher addition levels, the use of titanium is more expensive than tin. Foam applications are generally volume applications and thus tend to source catalysts primarily on the basis of their cost. At the same time, it is suggested that a known EU-wide chain of home furniture and possibly a major European car manufacturer currently stipulate that their polyurethane products are completely free from all TBT and this affects the use of organotin catalysts in polyurethane foams (pers. comm.).

5.7.2 Use of Catalysts in Polyurethane Coatings, Adhesives, Sealants and Elastomers (CASE) Manufacture

In CASE applications, the gelling reaction plays an important role in determining the reaction profile and physical properties (Kometani *et al*, 2001). Contrary to foam applications, in CASE applications the formation of bubbles and foaming are highly undesirable as they would impart lower physical properties to the final polyurethane articles. In CASE applications, a long pot life is required with a sharp viscosity rise profile. In other words, after mixing all the ingredients, the system should maintain a low viscosity for a long time to allow good handling and processing or pouring before beginning to significantly cure. Pot lives vary from five minutes to more than one hour depending on the application (Kometani *et al*, 2001).

Heavy Metal Catalysts for Polyurethane CASE Applications

Heavy metals such as mercury, lead and tin are generally used as they exhibit high reactivity, high selectivity towards the reaction with active hydrogen containing compounds such as polyols, and in the case of mercury show a very distinct reaction profile (Stengel, not dated-2). Because of the low gelling catalytic activities of alkali metals, catalysts such as iron and aluminium are not used (Kometani *et al*, 2001). Table 5.16 gives examples of metal compounds that may in theory be used as catalysts.

Table 5.16: Example Metal Catalysts used in Polyurethane CASE Applications

Metal	**Example catalyst**
Mercury	Mercury neodecanoate
Lead	Lead octoate
Tin	Dibutyltindilaurate
Titanium	Titanium 2-ethylhexanoate
Zirconium	Zirconium naphthenate oxide

Source: Kometani et al, 2001

Heavy metal catalysts, especially mercury catalysts, typically provide a long pot life with a sharp viscosity rise profile and are widely used in CASE applications (Kometani *et al*, 2001). However, some of these heavy metal catalysts, such as mercury and lead, are associated with high toxicity issues. Tin catalysts are lower in toxicity, but may contain damaging endocrine disrupters such as tributyltin compound (Kometani *et al*, 2001). Because of these issues, CASE producers and suppliers are reducing the use of toxic substances and looking for alternatives. Over recent years, growing concern over the potential or in some cases proven toxicity of these catalysts has led to renewed interest in potential alternative metal catalysts. Already in some countries such as Japan, CASE producers will actively avoid the use of heavy metal catalysts. This is becoming a growing issue in Europe where mercury is banned from certain products used in the automotive industry under the End-of-Life Vehicles Directive (Stengel, not dated-2).

Currently, only mercury is able to deliver such a reaction profile however, other catalysts have recently been developed; this includes organotitanates (Stengel, not dated-2) and catalysts based on bismuth (for instance, bismuth neodecanoate which is claimed to be more selective than organotins), zinc (not a selective catalyst) and zirconium (with a claimed better selectivity than DBTDL which results in less gassing, fewer pinholes, longer pot life and higher gloss) have been developed (Shepherd, not dated).

Organotitanane and Zirconate Alternatives for Polyurethane CASE Applications

Regarding elastomer applications, the replacement of mercury is the main aim for titanium catalysts and not the replacement of tin. Titanium catalysts are primarily developed and marketed as replacements for mercury rather than tin (pers. comm.).

Polyurethane production involves complicated and competing chemical reactions. Due to this complexity, the catalyst used is integral to the formulation of a polyurethane system. Therefore, replacement of the catalyst would normally require the reformulation of the polyurethane concerned (pers. comm.).

The addition levels of tin and titanium catalysts are much lower than for silicone applications, for example, 0.01 % of formulation by weight[35]. The low addition levels make catalyst cost a relatively minor contributor to overall formulation costs. Titanium catalysts are more costly than organotin catalysts, however, the low catalyst loading results in a far smaller increase in the cost of the final polyurethane formulation; for example the increase can be less than 1% of the total formulation cost, a cost increase in the area of 0.67 Eurocents per kg of product (pers. comm).

On the other hand, it has been suggested that due to the higher cost of the titanates themselves, polyurethane producers tend to move from tin to titanium only when motivated to do so by other concerns, for example, by customer demands, voluntary or industry restrictions (pers. comm).

The difficulty with titanium catalysts as compared to organotin catalysts has always been that organotin catalysts are stable in water and titanium catalysts were not, as discussed under polyurethane foam applications. However, new water stable titanate catalysts have now been developed (pers. comm). The potential of organotitanates is confirmed in the paper by Kometani *et al* (2001). In their tests, the scientists showed that mercury catalysts exhibit 'long pot life with sharp viscosity rise'. Lead and stannous catalysts have high catalytic activity and exhibit a long pot life, however the viscosity rise becomes mild. Many metal catalysts like Cu, Ni, Co do not show a sharp viscosity rise profile, and only titanium catalysts exhibit sharp viscosity rise with long pot life. A manufacturer of such alternatives also argues that titanium and zirconium catalysts may also be used for elastomers where they can display the required characteristics (long pot life, with sharp viscosity rise profile towards the end of the reaction, followed by a 'fast' curing of the part) until recently only to be found in mercury catalysts (Johnson Matthey, 2005).

Titanium and zirconium catalysts can also allegedly be used in a variety of other polyurethane areas[36] such as catalysts in thermo polyurethane (TPU) products, binders, coatings and adhesives and benefiting from the reduced environmental impact of these catalysts (Johnson Matthey, 2005). New titanium and zirconium catalysts minimise the water-isocyanate reaction resulting in bubble free elastomers and are accompanied by improvements of up to 11% in tensile strength and up to 28% in abrasion resistance. They can also offer the benefit of faster hardness build up that may allow the user to demould earlier. Earlier demould times can result in significant savings by increasing product throughput and thereby reducing the unit cost of the elastomer (Johnson Matthey, 2007b).

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[35] Addition levels will vary depending on the formulation being used but as a guide a working range of between 0.01 – 0.5% w/w is suggested (Johnson Matthey, 2007b).

[36] Consultation with industry suggests that titanium catalysts have been recommended by a major producer of polyurethanes for flooring applications (pers. comm).

New Tertiary Amine Catalysts Polyurethane CASE Applications

Amines very often promote the foaming reaction (Stengel, not dated-2) and typically exhibit a short pot life and mild viscosity rise, therefore are seldom used in CASE applications (Kometani *et al*, 2001).

Scientific literature suggests that tertiary amines may also replace mercury catalysts in CASE polyurethane applications. Testing by Kometani *et al* (2001) showed that special acid blocked catalyst of diazabicycloundecene 50% in diethyleneglycol show a long pot life with a sharp viscosity rise profile. These catalysts are reportedly non-toxic and can be used as an alternative to mercury catalysts.

Note that the RAR concludes that polyurethane foams are unlikely to present a significant direct risk to consumers (conclusion ii).

6. POSSIBLE FURTHER RISK REDUCTION MEASURES

6.1 Rationale for Introduction of Further Risk Reduction Measures

Following from the analyses in the previous Sections, it is considered that further risk reduction measures are required on the basis of:

- the findings of the risk assessment (RPA, 2005) which show unacceptable risks to children exposed to organotins from fish/fishery products, indoor air/dust and PVC-printed T-shirts;

- the risk of individual members of the general population exceeding the TDI for organotins as a result of the cumulative exposure to organotins from a variety of consumer articles, products and pathways (where some of these contribute to organotin intake in the range 20% to 100% of the TDI); and

- the potential health (and environmental) hazards relating to the PBT, vPvB, CMR and endocrine disrupting properties of certain organotins. On the basis of these properties and under the REACH Regulation which came into force on 1 June 2007, these organotins may be subject to authorisation and included in Annex XIV of the Regulation - or alternatively, measures may be introduced under the restrictions procedure.

The Project Specifications (see Annex I) also state specifically that:

- as highlighted by SCHER, it is the total consumer exposure to organotins that should be used in the RAR, including all the identified pathways, such as those estimated to contribute <u>with less than 20% of the TDI</u>. Therefore, if the total exposure exceeds the TDI, there is a reason for concern and risk reduction measures should be considered, regardless if this exposure comes via one or a large number of pathways;

- for both health and environmental risks, risk estimates of the RPA report may not represent the worst case situations (actual risks may therefore be higher);

- for this study, an attempt should be made to focus on products that either lead to a relatively high level of possible exposure (as concluded in the RAR) or *that are relatively commonplace* so that an average consumer is likely to come into frequent contact; and

- appropriate restrictions on the marketing and use of a specific chemical may be proposed under Directive 76/769/EEC, if unacceptable risks from a chemical have been identified and if they cannot be adequately controlled by other measures.

The discussion in previous Sections indicates that in recent years, there has been a move away from the use of organotins in a number of applications due to regulatory, technical and socio-economic reasons. In considering the need for and impact of further risk reduction measures, it is important to make a distinction between those measures which control risks associated with existing/continuing uses of organotins and those associated with historical uses. This Section discusses the types of risk reduction measures which are available for achieving the objective of safeguarding consumer health by:

- reducing risks associated with the current uses in PVC and as catalysts (as set out in the Project Specifications); and
- ensuring that the risks associated with historical uses do not re-occur.

6.2 Identification of Possible Risk Reduction Measures

6.2.1 The Range of Possible Risk Reduction Measures

The types of risk reduction measures that could be applied to the use of organotins are outlined in the relevant TGD (EC, 1998). The measures relating to domestic and consumer uses are outlined in Table 6.1 below.

Table 6.1: Possible Risk Reduction Measures for Domestic and Consumer Use

- restrictions on the size of container;
- design of containers including non-spill or narrow-neck containers;
- limits on concentrations of components;
- product design changes, e.g. encapsulation;
- limits of the overall quantity available to each user;
- addition of an emetic, a stanching agent or a colorant;
- restrictions on use (i.e. Directive 76/769/EEC);
- classification and labelling;
- hazard warnings and/or use instructions on packaging;
- tactile danger warnings; and
- child resistant closures.

Source: EC, 1998

6.2.2 Initial Screening of Possible Risk Reduction Measures

The measures identified in Box 6.1 have been screened to eliminate from further consideration those that are not relevant to the risks from organotins. On this basis of the reasons provided in parenthesis below, the following measures have been eliminated:

- ***restrictions on the size of container*** (this measure is not relevant to the types of consumer products identified as giving rise to risks to consumers (e.g. T-shirts));

- ***design of containers including non-spill or narrow-neck containers*** (this measure is not relevant to the risks identified or types of consumer products being considered);

- ***product design changes, e.g. encapsulation*** (this measure is not considered relevant to the types of consumer products identified as giving rise to risks to consumers (e.g. PVC-printed T-shirts);

- ***limits on the overall quantity available to each user*** (this measure is not relevant to the substance, risks or consumer products of relevance, particularly where the quantity is linked to or determined by external factors such as performance);

- ***addition of an emetic, a stanching agent or a colorant*** (this measure is not relevant to the identified risks for the uses of concern);
- ***classification and labelling*** (proposing suitable classification and labelling is outside the remit of a RRS; furthermore, further action on the classification and labelling for DBT is expected in the 30th/31st ATP to Directive 67/548/EEC);
- ***hazard warnings and/or use instructions on packaging*** (this measure is not relevant to the types of consumer uses and the exposure routes of concern, e.g. those which may occur from wearing T-shirts);
- ***tactile danger warnings*** (this measure is not relevant to the consumer products being considered); and
- ***child resistant closures*** (this measure is not relevant to the risks or consumer products of relevance).

Therefore, only two potential measures are considered further. The first is placing *restrictions on the marketing and/or use of the substance* (under Directive 76/769/EEC). In theory, marketing and use restrictions could be applied to all or some of the uses of organotins, with various industry sectors required to either cease use by a specified deadline or to phase out use over a given period in time. Restrictions could also be designed so as to apply to only particular applications or processes; for instance, those applications that may have significant socio-economic importance and for which suitable alternatives are not currently available may either be exempted from any marketing and use restrictions or be granted a derogation which could be conditional (e.g. time-limited) or unconditional. Restrictions could also be worded so as to prevent the sale of finished products containing organotins in the EU (thus covering imported goods); however, to be effective, organotins would have to be identified and identifiable in all products and associated documentation (which is often not straightforward).

The second potential type of measure is *placing limits on concentrations of components*. For instance, for absorbent hygiene products (AHPs), there are concentration limits currently in place (albeit, voluntary) while for rigid films and sheets, a concentration limit may arise from the migration limits which have to be complied with under the food contact legislation (although these limits cannot, in practice, be transferred to non-food products). In the case of AHPs, the concentration limits reflect the fact that organotins are only present as an impurity at low levels (rather than the result of intentional use) while for rigid films, there are practical reasons for manufacturing all products on a particular site to the most stringent limit. However, in terms of extending these limits to other products and applications, it is not clear that placing concentration limits would be feasible in terms of the effect on the functionality or technical suitability of the actual end product(s) and in any case, such an approach does not adequately address concerns relating to the ‘group TDI’. It is, therefore, considered that this measure may, at best, have implications similar or equivalent to marketing and use restrictions (with associated derogations) and it is, therefore, not considered further in its own rights (but will be discussed, as relevant, under restrictions).

6.2.3 Possible Options for Risk Management

Following from the above, the main type of measure being examined at this time is the introduction at Community level of marketing and use restrictions under Council Directive 76/769/EEC. As discussed earlier, this option may take several forms; however, for the purposes of this study, the restrictions would cover (individually or collectively):

1. all uses of tri-substituted organotins, in particular TBT and TPT compounds, unless used in chemical synthesis;

2. use of dioctyltin (DOT) and dibutyltin (DBT) compounds as stabilisers in all consumer (PVC) products;

3. use of DOT and DBT compounds in plasticised PVC products; and

4. use of DOT and DBT compounds in specific consumer products, in particular: PVC T-shirts, PVC gloves, PVC sandals, female hygiene products, nappies, dental moulds and 2-part silicone moulds.

The rationale for selecting these restrictions is described briefly in Table 6.2 below. The measures are then described and assessed in further detail in the next Section.

Table 6.2: Rationale for Selecting Options for Restricting Organotins

Measure/Restrictions on:	Applications Affected	Rationale
1. All uses of tri-substituted organotins, in particular TBT and TPT compounds, unless used in chemical synthesis	• TBT-treated textiles imported into the EU • Other treated products imported into the EU containing tri-substituted organotins as biocides	Intended to address any concerns relating to borderline products (e.g. those relating to medicinal products) and the importation for sale in the EU of consumer articles treated outside of the EU with organotins (for biocidal purposes)
2. Use of DOT and DBT compounds as stabilisers in consumer (PVC) products, unless used in food products and food-related applications	• PVC (plasticised and unplasticised)	Use in PVC accounts for the majority of organotin use in the EU. A restriction on this major use could significantly reduce overall quantities available - potentially contributing to the TDI
3. Use of DOT and DBT compounds in plasticised PVC products	• Plasticised PVC • Catalyst applications	A number of the risk end-points in the RAR are associated with plasticised PVC products/applications. Restricting this use would, therefore, result in a reduction in risks and overall contribution to TDI
4. Use of DOT and DBT compounds in specific consumer products	• PVC T-shirts, gloves and sandals; • female hygiene products; • nappies; • dental moulds; and • 2-part silicone moulds	These products have been selected on the basis of the specific risks identified in the RAR

7. ASSESSMENT OF POSSIBLE RISK REDUCTION MEASURES

7.1 Introduction

7.1.1 The Assessment Criteria

The Technical Guidance Document (TGD) on Development of Risk Reduction Strategies (EC, 1998) specifies that possible further risk reduction measures should be examined against the following four decision criteria: effectiveness, practicality, monitorability and economic impact.

There are three sub-criteria against which the **effectiveness** of a risk reduction measure may be assessed:

- the *risk reduction capacity* of the measure: the most important characteristic of any risk reduction measure should be the ability of the measure to reduce the risk to acceptable levels. Generally, a measure that cannot ensure a sufficient level of risk reduction will either have to be complemented by another measure or will be eliminated from further consideration;

- the *timing* of implementation: the timing of implementation will be influenced by the scale of risk and the severity of its consequences. Generally, effective measures that lend themselves to quick implementation and enforcement will have a relative advantage over measures that require a longer timeframe to become effective; and

- the *proportionality* of the risk reduction measure: the proposed measure should be one that:
  - targets the identified risk;
  - corresponds in amount or degree to the impacts of the adverse effects suffered or the adverse effects that are being avoided taking into account the available scientific evidence;
  - requires that risk management action is taken by those responsible for the risks (and that these actors have the authority and information to act accordingly);
  - is consistent with other options taken forward in the past (but builds on past action and learns from past failures); and
  - ensures a good balance between costs and effectiveness.

  Issues of proportionality are relevant to the (potential) need for derogations and may also be addressed in an economic assessment of any proposed restriction.

There are three sub-criteria against which the **practicality** of a risk reduction measure may be assessed:

- *implementability*: a suitable measure should lend itself to practical implementation, i.e. the industry sectors affected should be capable of practically complying with the requirements. To achieve this, the necessary technology, techniques and alternatives (required by the selected risk reduction measure) should be available for adequate control of releases and exposure. As a general (non-binding) rule, measures that can be implemented within the existing infrastructure may be given priority;

- *enforceability*: a suitable measure is an enforceable option. An enforceable measure is one that introduces legally binding conditions on the way the substance is manufactured, marketed or used, the success of which is followed up by the responsible authorities and its compliance is ensured by monitoring, inspection and sanctions. Penalties imposed on offenders in the event of non-compliance may be an important deterrent. Monitoring mechanisms should either exist already (which would be the ideal scenario) or they should be able to be readily set up and operated; the most effective measure may have no effect if those supposed to comply with it fail to do so and the competent authorities in Member States are not able to oblige them to comply; and

- *manageability*: a suitable measure should be simple to manage (taking into account the characteristics of the sectors concerned, for instance, the number of SMEs) and understandable to affected parties; the means of its implementation should be clear to those involved and access to the relevant information should be easy. Enterprises, professionals and consumers are more likely to implement a measure if it is simple and does not require great levels of effort for compliance and monitoring of performance. It may also be helpful to a user of the substance if the measure results in a single straightforward binding requirement rather than a combination of regulatory measures that may or may not apply to him. The need for a non-excessive administrative burden is relevant to both industry and the authorities.

There are three sub-criteria against which the **monitorability** of a risk reduction measure may be assessed:

- *availability of appropriate indicators that could be used for the monitoring of the implementation of the option*: two types of indicators are needed:
    - those that allow monitoring of the presence of the chemical in the environment, biota and humans (for example, the concentration of the substance in specific environmental compartments or human tissue), and
    - those that allow monitoring of the manufacture, import and use of the substance across the Community (for example, import statistics from the Customs authorities in the Member States or the concentration of the substance in preparations placed on the market);

- *ease of monitoring*: the monitoring of a suitable measure should be easy to set up and administer and its cost and administrative burden should be proportional to the levels of use of the chemical and the number of actors involved; and

- *availability of monitoring mechanisms*: effective monitoring mechanisms should be in place to monitor both use and releases, and the implementation and success of the option. Monitoring should be capable of providing the necessary guarantees that industry is complying and that the measure is meeting its original objectives across the Community and within the required timeframe. Measures capable of utilising existing monitoring mechanisms may have a relative advantage over measures that require new ones.

Finally, the **economic impact** of the measure on producers, processors, users and other parties should also be estimated. In practice, such an assessment relies significantly on the quantity and quality of information provided by industry and stakeholders on the potential impacts, as well as wider information in the literature and from past experience.

Overall, very patchy and generic information on the potential cost implications from any restrictions has been received in the course of this study. For instance, while the manufacturers of organotins have provided an indication of the costs to them, very little information on the potential impacts on SMEs has been collected, despite requests for information addressed to both companies and industry associations. The discussion provided on the direct cost impacts of any restrictions (as well as on the wider effects, for instance, on trade, competition and employment, provided, where available and relevant) should, therefore, be viewed in the light of these limitations. Nevertheless, it is considered that the discussion presented herein describes the current uncertainties and generally provides an adequate basis for decision making.

7.1.2 Order of Assessment

Based on the described criteria, this Section provides an assessment of the potential risk reduction measures (identified in Section 6) for addressing the risks from certain organotins, where these include restrictions on:

- all uses of tri-substituted organotins, in particular TBT and TPT, unless used in chemical synthesis (Section 7.2);
- use of DOT and DBT as stabilisers in all consumer (PVC) products (Section 7.3);
- use of DOT and DBT as catalysts in the manufacture of esters used in plasticisers in consumer (PVC) products (Section 7.4); and
- use of DOT and DBT in specific consumer products, in particular: PVC T-shirts, PVC gloves, PVC sandals, female hygiene products, nappies, dental moulds and 2-part silicone moulds (Section 7.5).

In assessing these restrictions, it is important to bear in mind that the focus/aim of this RRS is to ensure that:

- the specific risks to consumers associated with specific products/applications as identified in the RAR are reduced to acceptable levels, particularly in PVC and catalyst applications;
- overall consumer exposure (calculated as TDI) to organotins is reduced to acceptable levels and any risks from historical or obscure (or unidentified) uses do not re-occur (potentially increasing the TDI);

- potential health hazards relating to the PBT, vPvB, CMR and endocrine disrupting properties of certain organotins are taken into account and are addressed; and
- where it is feasible and possible to substitute organotins with safer substances or processes (with minimal burden to industry and society), this is encouraged (as this will help in reducing the overall TDI).

7.2 Option 1: Restrictions on Uses of Tri-substituted Organotins (TBT and TPT)

7.2.1 Introduction

This measure will restrict all uses of tri-substituted organotins, in particular TBT and TPT. It is intended to address concerns relating to borderline products (e.g. those relating to biocidal and medicinal products) and the importation for sale in the EU of consumer articles treated outside of the EU with organotins (for biocidal purposes). The main applications affected would, therefore, be TBT-treated textiles imported into the EU and other treated products imported into the EU containing tri-substituted organotins as biocides. There would be derogations for use as an intermediate in chemical synthesis - as this is not identified as posing any risks in the RAR and an average consumer is unlikely to come into frequent contact with organotins via this route.

7.2.2 Effectiveness

In practice, this measure is unlikely to result in a significant overall reduction in risks or exposure to organotins as these are generally restricted or controlled at present; however, it would potentially have the effect of:

- strengthening or reinforcing existing controls which already restrict the use of organotins as a biocide (as it was not notified by any company under the Biocides Directive) and addressing any concerns relating to borderline products (e.g. those relating to medicinal products, e.g. foot sprays);
- addressing the importation for sale in the EU of consumer articles treated with biocidal organotins outside of the EU. For instance, it is understood that, under the Biocidal Products Directive, products (such as textiles) containing TBT can still be imported into the EU as long as they are not making biocidal claims. This measure would, therefore, have the effect of clarifying that TBT- and TPT-treated articles are not allowed in the EU[37];
- preventing a potential substitution of risks where companies move from known hazardous substances such as TBT to other tri-substituted organotins, whose risks are not be fully known at present; and

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[37] Note that the REACH Regulation also requires registration of substances in articles intended to be released (see Section 4.3.3).

- contributing to the achievement of the cessation of discharges, emissions and losses requirement for TBT which is a priority hazardous substance under the WFD.

7.2.3 Practicality

The procedure for restricting the marketing and use of substances at the EU level under Directive 76/769/EEC is well established, with various substances already subject to restrictions. Amendments to Directive 76/769/EEC have been introduced several times and in this respect, it is a simple measure to introduce and implement. Member States also have suitable procedures in place for implementing its requirements. Following from this, it is expected that EU competent authorities and industry should be capable of introducing and complying respectively with marketing and use restrictions on the use of TBT and TPT as the actual additional administrative burden are relatively minimal.

It is, however, likely to be the case that the major obligation for ensuring compliance (of imported articles) with this restriction would fall mainly on customs and border officers, rather than the main competent authorities in Member States, as the use of these organotins within the EU should have ceased and this measure is, therefore, mainly targeted at imports.

7.2.4 Monitorability

For monitoring purposes, any restrictions would have to be clearly worded so as to prevent the sale of articles and finished products containing tri-substituted organotins in the EU (thus covering imported goods) and to be effective, organotins would have to be identified and identifiable in all products and associated documentation (which is often not straightforward). It is, therefore, likely that this measure may be affected by the typical difficulties associated with monitoring and enforcing restrictions on substances in (imported) articles.

For instance, it has been suggested that any restrictions provide a derogation for the presence of these tri-substituted organotins as an impurity during the production of mono- and di-substituted organotins *at levels below the concentration limits given in Annex I to 67/548/EEC* (presumably to reflect the analytical difficulties). This does not, however, constitute an intentional use and the quantities of impurities are not indicated to be more than 0.5% w/w. It has also been indicated by an organotin manufacturer that impurity levels of tri-substituted organotins can be reduced by developing ‘high mono’ species or via post-treatment of selected products (using technologies such as solvent extraction). The company notes that industry is already developing these ‘high mono’ species for the methyl-, butyl- and octyl- compounds (albeit at higher costs to end products and applications) and, using post treatment, TBT impurities have been reduced to less than 500 ppm in DBTO for catalyst applications (at significant, but unspecified, cost).

Overall, monitoring the implementation of restrictions on the use of tri-substituted organotins should be relatively straightforward, given that suitable systems have been established through previous restrictions. Also, given that the restriction does not actually add a significant additional monitoring burden, but rather reinforces existing restrictions under other Directives, this measure should be straightforward. In terms of monitoring mechanisms and indicators, due to the use profile of tri-substituted organotins, the effects of this measure are more likely to be felt or measurable in the environmental compartment; the monitoring mechanisms which have been set up under the WFD may, therefore, be adopted (or adapted) for assessing compliance and progress made (especially for TBT).

7.2.5 Economic Impact

Overall, this measure is not expected to impact on EU industry. According to ETINSA, the production of TBT compounds for biocidal applications has strongly decreased and the sales in the EU have stopped (exports may still be on-going). The measure is, therefore, likely to affect non-EU companies exporting articles to the EU.

Some benefits may therefore be accrued by EU manufacturers, particularly from the creation of a more level playing field. Another benefit may relate to the potential for an increase in sales of alternatives (or their raw materials); however, the scale of this is unlikely to be significant (based on recent usage, production and marketing trends in the chemical sector).

7.2.6 Summary

In theory, this measure should address issues relating to the importation for sale in the EU of consumer articles treated with biocidal organotins outside of the EU, as well as, prevent a substitution of risks, where companies move from known hazardous substances such as TBT to other tri-substituted organotins, whose risks may not be fully known at present. However, the actual extent of the benefits is currently unclear; for instance, if there are no (longer) imports of articles containing tri-substituted organotins, then the restriction would simply serve to ensure that this use does not re-occur in future (which is also a desirable outcome). Overall, the effectiveness, practicality and economic impact of this measure appears to be satisfactory (relative to their objectives), although there may be some minor issues for further clarification at an implementation stage relating to monitorability (i.e. the identification of organotins in articles and imported finished products). No significant impacts are expected on EU trade, competitiveness and employment as a result of this measure.

Use of tri-substituted organotins in plant protection products will be outside the scope of the Limitations Directive. However, this should not constitute a problem as the approvals process under the plant protection products legislation also involves an assessment of the health and environmental impacts of ingredients vis-à-vis their benefits - and as such, is an equally suitable regulatory framework for determining the case for continued use (or non-use) of tri-substituted organotins. Under the REACH Regulation, active substances manufactured or imported for use in plant protection products and biocides and included in their respective legislation are to be regarded as being registered. This measure is, therefore, consistent with the spirit and text of the current EU regulatory framework for chemical risk management.

7.3 Option 2: Restrictions on Use of DOT and DBT as Stabilisers in Consumer (PVC) Products

7.3.1 Introduction

This measure will restrict the use of DOT and DBT in stabilisers used in all consumer (PVC) products (whether plasticised or unplasticised). As PVC stabilisers currently account for the largest use of DBT and DOT in the EU, a restriction on this major use could significantly reduce overall quantities available and potentially contributing to the TDI, hence, the reason for its consideration.

7.3.2 Effectiveness

Considering that the major commercial use of organotins is in PVC applications, a total ban on the use of DBT and DOT in PVC products is likely to result in significant reductions in the total concentration of these organotins in the environment and hence, human exposure. In this regard, this measure provides the best possible guarantee of reducing the overall emissions and/or exposure to these groups of organotins and thereon, their contribution to the TDI.

At present, it is expected that **DBT** will be included in the 30th/31st ATP of Directive 67/548/EEC as a reprotoxic category 2 substance and a number of companies have indicated that they are currently moving away (or planning to move away) from DBT (albeit, to other organotins, including DOT). In the event of restrictions on DBT, it is, therefore, considered to be the case that there are alternative compounds which can be used across the vast majority of (if not all) applications. Hence, placing restrictions on DBT would build on the requirements of the classification and labelling Directives (DSD/DPD) such that they apply to articles (rather than preparations only). A restriction on DBT would also reduce the amount of TBT which will be available in the environment as an impurity - and, therefore, help in achieving the targets of the Water Framework Directive.

For **DOT**, there are currently approvals for its use under the food contact legislation; it may, therefore, be argued that the specific migration limits (SMLs) provide a protective level for humans from direct exposure to DOT in food packaging. Industry have also indicated that where certain products at a given site have to comply with the SMLs set under the food contact legislation, all products manufactured at that site regardless of end-use tend to be produced to the same SMLs for production/process reasons (the extent to which this occurs (especially for SMEs) has not been confirmed).

The above argument does not, however, take into account the wide dispersive uses of DOT (e.g. construction products), the method of substance loss and subsequent human exposure (wear and tear as opposed to migration into foodstuff) and the long life-spans of these non-packaging related products (10 - 100 years). Taken together, these mean that emissions and exposure could be on-going for a considerable time and will still contribute to the total exposure of the individual, as noted by SCHER (2006).

It has also been highlighted that food and pharmaceutical packaging currently account for around 60% of all organotin use in unplasticised PVC (and have their own regulatory framework for approvals). Placing restrictions on the remaining 40% of uses (assuming none of these uses are derogated on technical grounds), therefore, runs the risk of being potentially disproportionate to the actual consumer exposure and/or the adverse effects that are being avoided (for instance, exposure via food versus exposure via construction products).

There are also known alternatives for use in food packaging and non-food contact applications. These are effectively the same for both categories of products and arguments relating to their suitability apply equally to both categories. If the need for risk management is considered to be the same regardless of application (where it is based on the substance itself), and alternatives are available and suitable, then it may be argued that a consistent approach to risk management be adopted across all uses of DOT (i.e. either restrictions (or limit values) should apply to both food and non-food applications).

However, where the aim of the restrictions is to reduce the risk of individual members of the population exceeding the TDI, restrictions on non-food packaging applications may be considered to be an appropriate and effective way of achieving this.

7.3.3 Practicality

The procedure for restricting the marketing and use of substances at the EU level under Directive 76/769/EEC is well established, with various substances already subject to restrictions and, as such, no critical problems are foreseen with the introduction or implementation of restrictions.

For **DBT**, a number of companies have indicated that they are moving away from DBT. It is, therefore, possible that by the time any restrictions are introduced, DBT may effectively have been removed from the majority of consumer (PVC) products. In such a situation, any restrictions would have a near neutral effect and would serve the purpose of preventing future use of DBT. In the event that some companies have not moved away from DBT, it is considered (based on the risks identified in Section 3 and the availability of alternatives in Section 5) that the health benefits of moving away from DBT outweigh the costs associated with the identified hazards/risks (whether as an individual substance or cumulative (or additive) with TPT, TBT and DOT).

Practically speaking, an immediate restriction on DBT should be straightforward to introduce and implement and Member States are considered to have suitable procedures in place for implementing its requirements. Moreover, no specific information has been received during consultation indicating that a restriction on DBT alone would impact on downstream users and/or on the quality of consumer products.

For **DOT**, the key issue relates to the discrepancies in the information received from various companies and the literature review relating to the technical suitability of alternatives (as set out in Section 5). In theory, industry should be capable of practically complying with an immediate restriction on DOT as the necessary technology, techniques and alternatives (required in the event of a restriction on DOT) are available. However, it appears to be the case that while most companies are aware of the need to act towards substituting organotins in plasticised applications ahead of any regulatory action, some companies have not anticipated the need to substitute in unplasticised applications. Some companies still believe, based on what appears to be past research and development, that the current alternatives are not suitable for achieving certain performance characteristics; however, information from other companies (and published literature or marketing material) have reached a different conclusion.

In order to address this potential imbalance, restrictions could be put in place with specific derogations granted to reflect the current state of substitution for specific applications. For instance, it has been suggested by ECVM (not dated) that the penetration of the newer forms of the calcium-organic stabilisers is almost complete in drinking water pipes, well advanced in cables but still limited in some pipes and profiles. Using this example, it would be relatively straightforward to place restrictions on the use of organotins in drinking water pipes (as this would constitute a mainly historical use) with conditional derogations of some sort placed on use in pipes and profiles.

The problem posed by such an approach is that it does not reflect the convoluted nature of PVC processes and products (i.e. the same product may be manufactured using different production processes/techniques and at the same time with other products which have different regulatory requirements). Other practical issues may arise from the fact that certain categories of products are often produced at the same factory and producers are keen on having one stabiliser suitable for them all (as is the case for credit cards, food packaging material and blister packaging). Also, for manufacturing and cost reasons, all the products manufactured under the rigid calendering process are made to comply with the limits set under the food contact legislation. If the use of organotins were restricted in one set of products while allowed in others, this may give rise to some difficulties in manufacturing processes or enforcement issues. In any case, industry has not provided the level of information required for such a product or application-specific analysis (leading to derogations) to be undertaken.

On this basis, it may be helpful to industry (as well as competent authorities) if any recommended measure results in a single straightforward binding requirement rather than a combination of regulatory measures that may or may not apply to a given user, as well as supports the need for a consistent approach to risk management to be adopted across all uses of DOT. Such a consistent approach would essentially mean that restrictions, if adopted, would have to be applied across all uses of DOT at the same time.

However, as it is possible that there may be genuine difficulties for some companies in finding the appropriate alternative for a given product or in retooling a plant or processing system, it is possible that these companies may have significant difficulties if restrictions were to be put in place immediately. As noted by ESPA (not dated), the complexity of processes, uses and applications of PVC means that the selection of the appropriate stabiliser system requires considerable knowledge and expertise of process equipment, polymer choice and final application - in addition to regulatory approval requirements and cost issues - and this is not straight-forward. These difficulties encountered by companies are likely to be more serious where a significant proportion of a given company's portfolio is based on DOT and DBT, as opposed to competitors who use calcium-organic stabilisers and/or methyltin stabilisers.

Based on the above, a simple time-limited derogation or phase-out period after which all applications should cease use of DOT is likely to be more practical than derogations based on critical applications (which in any case, industry has provided very little substantiated information on) or immediate restrictions. Such time-limited derogations would give industry time to react accordingly to any restrictions. Examples of the time-periods required for such substitution can been drawn from cadmium-based stabilisers (phased out in 2001) and lead-based stabilisers (which is to be phased out by 2015). In this regard, it is worth noting that lead-based stabilisers accounted for around 70% of the market and covered a wide range of complex uses at the time the phase-out was agreed. Organotin-based stabilisers currently account for around 8% and it is unlikely, based on the information in this Report, that a similar timescale would be required for a phase-out. Obviously, any time-limited derogation would not affect food and pharmaceutical applications which have their own approvals process (and which may require longer timeframes for phase-out).

Overall, while an immediate restriction on DBT may be considered practicable on the basis that industry appears to be moving away from these compounds, an immediate restriction on DOT may be considered less so (taking into account the differing positions on the state of substitution and the imminence (i.e. whether there are threats of serious or irreversible damage) and relatively lower hazard/risk profile (compared with TBT, TPT and DBT). A time-limited derogation or phase-out period may, however, be more appropriate, particularly as it allows for companies to develop a plan for substitution (as has been done for cadmium and lead stabilisers). It would also allow for the current limits in food contact to potentially be re-examined by DG SANCO in the light of more recent developments and the potential for a consistent set of measures to be applied across all uses of DOT.

7.3.4 Monitorability

In theory, monitoring the implementation of restrictions should be relatively straightforward, given that suitable systems have been established. Measures for ensuring that restrictions on uses of certain stabilisers are enforced are currently in place as part of the Vinly2010 initiative and these could possibly be extended (or serve as a 'template') for these restrictions relating to use of organotin stabilisers.

7.3.5 Economic Impact

Introduction

Information has been received from a number of companies on the potential impacts of restrictions on organotins (where the major use (>90%) is in PVC stabilisers, the target of this Option). In general, responses provided by companies indicated that broad restrictions on all organotins across all uses would be particularly damaging to the industry; it is, however, important to bear in mind that this Option is examining the impacts of restrictions on only DOT and DBT in consumer (PVC) products; food products and medical devices are outside the scope of the study and relevant legislation. The actual costs which would be incurred would, therefore, be a sub-set of those provided by respondents and presented below for completeness purposes. The companies which provided the information have also not been identified for business confidentiality reasons.

Overall Costs

A number of companies manufacturing organotins indicated that the impact of broad restrictions would be to significantly reduce turnover (up to half in one case) and result in calendering plants transferring their activities outside of Europe and then importing the finished goods into the EU. In the case of PVC film, it is suggested that the imported PVC film made with organotins would be much cheaper than film produced in the EU using higher cost and less efficient stabilisers and there would be no means of verifying the imported goods and their content of tin or other products[38]. It has also been suggested that since SMEs would not have the possibility to transfer their sites outside of Europe, they would have to close their production sites.

Two companies noted that a restriction on organotins would mean significant loss of business with the potential to decrease volumes down to levels where local European production would be unwarranted. One organotin manufacturer indicates costs of around €15 million (where this includes employee severance costs, plant decommissioning costs and loss of turnover and revenue) while a manufacturer of PVC products predicts potential loss of business of between 20,000 and 30,000 tonnes with a loss in revenue of as much as £20 million per annum.

According to ERPA, if they cannot replace DOT by another stabiliser system, they would have to shut down their calendering production plants (which cannot be used for other polymers) with the costs of this action estimated at between €3 billion and €4 billion[39]. If they can use an alternative stabiliser, they would have costs of reformulation of around €10,000 per company and €150 million for the EU PVC rigid films industry.

However, it is the case (as pointed out by some respondents) that there are a number of variables which could influence the scale of these costs. These include:

- **the extent of the restrictions (and associated derogations) put in place**: some companies indicated that if selected organotins are recognised as safe for rigid PVC and catalyst applications (or the study had focused only on the organotins and applications for which a conclusion (iii) or (ii)* had been reached in the RAR), then the impacts will be minor. Also, it has been indicated that the food and medical applications would be severely affected both on the basis of direct costs incurred but also the wider socio-economic costs.

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[38] This argument is interesting vis-à-vis substances in articles which are covered under REACH.

[39] Details of how these figures have been derived have not been provided.

Note that this Option is focusing on restrictions on only DOT and DBT (not methyltin compounds or mono-substituted organotins) in consumer (PVC) products. Food products and medical devices are also outside the scope of the study and relevant legislation. Therefore, the actual costs which would be incurred should, therefore, be significantly less than those indicated above; and

- **current manufacturing processes and potential volume losses**: it has been suggested that plants which are specifically designed to manufacture one substance (e.g. methyltin compounds) cannot be converted to other manufacturing uses, as these plants are very specific to the complex chemistry involved to make organotins. Other information received, however, suggests that some re-tooling of equipment will be sufficient, although this will be at some cost[40].

  It has been suggested that the restrictions could result in volume losses at production sites which would raise the cost of production of the remaining volumes of organotins produced at that location, potentially by as much as 15% at a given site. It has also been indicated that if substitution was required in rigid applications (like rigid film and profiles), the cost would be exorbitant from investments into new production equipment, substantial laboratory development, patent costs, etc. The global market is suggested to be extremely price sensitive, and such a cost impact could adversely affect a company's competitive position in other markets globally where there are no restrictions on organotins.

  In terms of the potential wider effects of restrictions on trade and competitiveness, the following will influence the costs to a given company:

  - **substance and product portfolios for individual companies**: if a company manufactured only DBT and DOT, the impacts of a restriction would be significantly higher than those for a company which manufactures mainly methyltins. Similarly, if a company has a portfolio which includes calcium-organic stabilisers, any losses from a restriction on organotins are likely to be compensated by an increase in sales of these alternatives (the market for which is growing quickly); and

  - **the level of preparedness of individual companies**: as indicated earlier, not all companies have anticipated the need to substitute organotins in unplasticised applications. One company has indicated that they have not developed any alternatives as they did not see any reason to, on the basis that no unacceptable risk conclusions ((iii) or (ii)*) were identified in the RAR for these applications. It is, therefore, considered that the costs which would be incurred by this company would relate to a potential loss of business from competitors who are better placed or prepared. Where changes to other technologies and products require substantial investment and there is insufficient time to react, the viability of manufacturing at certain sites may be lost.

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[40] It is known that industry has been able to switch from lead-based stabilisers to calcium-organic stabilisers.

Detailed information has not been obtained on employment effects, where these relate to restrictions on DBT and DOT only. However, one company notes that the impact of restrictions on organotins (where these account for between 10% and 20% of the company's sales value) would be a reduction in workforce of around 20 people (~15% of the work force) at a cost of around €750,000, in addition to the costs of moving the facility across continents of around €2 million.

Case Box 7.1 below presents the costs which have been provided by a company on the impact of restrictions on organotins for their operators; however, it should be borne in mind that the information provided reflects the company's own analysis of the market (and their research and development into alternatives). It is also not specifically indicated to be applicable for DOT and DBT and, even if it is, the costs do not reflect the implications of substitution using other organotins or calcium-organic stabilisers. It, however, highlights the fact that different companies have varying perceptions of the costs which may be incurred by them (relative to the uniqueness of their businesses) and the state of alternatives.

Case Study 7.1: Potential Impact on Single Company in the EU

Company A is one of the leading manufacturers across Europe of unplasticised PVC building products for roofline and rainwater applications. These products, used in domestic and commercial buildings, are versatile and are available in a range of colours and designs. Company A started researching into alternative stabilisers primarily as a result of a no lead policy, which it actively promoted. The main alternative researched was the calcium/zinc (calcium-organic) stabiliser system.

In general, Company A found that while these calcium-organic systems were suitable for white PVC products, they were unsuitable for coloured PVC products. They experienced significant discolouration of coloured PVC - resulting from the reaction between stearate (migrating through the plastic under certain environmental conditions) and silicone and other building materials (at the surface) to form a white colouration on the 'skin' (top surface). This does not occur with tin stabilised PVC where pigment fastness is the determinant of colour stability. It was also found that during the foam production process, the use of calcium-organic stabilisers caused plate-out, which resulted in shortened and inconsistent production runs (with a resultant impact on costs).

With regard to future trends in the use of calcium-organic stabilisers, Company A indicates that it is currently unclear whether the issues relating to heat stability will be resolved soon, although this is an area of a lot of on-going research work. It is also worth noting that there are no issues relating to the use of calcium-organic stabilisers in white PVC products (as any discolouration is not visible); the discolouration is only in coloured PVC products which are driven by customer demand (and account for around 30% of Company A's products). Also, discolouration depends on a number of environmental/weathering conditions, an example being proximity to the sea.

In terms of the costs of any potential restrictions on tin stabilisers, Company A indicates that the costs will result mainly from:

- the loss of their innovative and technical advantage in the market: Company A offers products which are unique (based on the colour variety) and guaranteed to customers for 20 years (which is not necessarily the norm for these types of products). A ban on tin stabilisers would imply that the efforts put into R&D will be lost as well as a share of the market; and

- customer dissatisfaction and replacement of discoloured products: Company A would have to replace sub-standard products for their customers (as a result of the above guarantee) at a multiple of the material cost.

The combined cost effect of these effects was estimated at €8million.

7.3.6 Summary

Considering that the major commercial use of organotins is in PVC applications, a total ban on the use of DBT and DOT in PVC products is likely to result in significant reductions in the total concentration of these organotins in the environment and hence, the exposure to humans. In this regard, this measure provides the best possible guarantee of reducing the overall exposure to these groups of organotins (and their contribution to the TDI).

However, considering that there may be genuine difficulties in finding the appropriate alternative for a given product or in retooling a plant or processing system, some companies may have significant difficulties if restrictions were to be put in place immediately. This also takes into account that some companies have not anticipated the need to substitute organotins in unplasticised applications. These problems are likely to be more serious where a significant proportion of a company's portfolio is based on DBT and DOT, as opposed to competitors who also manufacture/use calcium-organic stabilisers and/or methyltin stabilisers.

In order to address this potential imbalance, a time-limited derogation or phase-out period after which all applications should cease use of DOT is likely to be more practical than derogations based on critical applications (which in any case, industry has provided very little information on). Such a phase-out period would also give industry time to react accordingly to any restrictions while limiting the resulting economic impact on affected businesses.

7.4 Option 3: Restrictions on DOT and DBT in Plasticised PVC

7.4.1 Introduction

This measure will restrict the use of DOT and DBT in plasticised PVC.

In theory, organotins may be present in plasticised PVC from either the catalysts/plasticiser component or from the stabiliser component. While the discussion in Sections 2.4 and 5.3 has focused on the use in catalysts, this measure basically considers restricting the use in plasticised PVC as a more useful outcome of risk reduction, rather than a ban on use as an esterification catalyst alone. Evidently, there is some overlap between this Option and Option 2 (which restricts use of organotins in stabilisers) and Option 4. A number of the risk end-points in the RAR are associated with specific plasticised PVC products/applications (which are the subject of Option 4); restricting this use would, therefore, result in a reduction in risks and overall contribution to TDI.

7.4.2 Effectiveness

By placing restrictions on the use of DBT and DOT in plasticised PVC applications, a number of the specific products identified in the RAR as contributing to the TDI - as well as other plasticised PVC products that contain these organotins - would no longer be on the market; thereby, reducing consumer exposure to certain organotins and ensuring the protection of consumers. In terms of timing, this measure would also provide some benefits to industry as it will support on-going initiatives by industry to eliminate some of these uses, by providing a regulatory underpinning.

With regard to organotin being present from the catalyst/plasticiser component, Information received from the European Council for Plasticisers and Intermediates (ECPI) - representing European producers of the whole range of plasticisers (phthalates, adipates, trimellitates, polymeric plasticisers, etc. - indicates that organotins are not used as catalysts in the production of PVC plasticisers (ECPI, 2007a). Donnelly (2007) also notes that the use of organotins in the manufacture of plasticisers such as phthalates and adipates is unlikely for technical reasons, since there are far superior catalyst systems for these esters. The catalysts being used in practice, for esterification reactions, range from sulphuric acid to titanates and p-toluenesulphonic acid. Also, as noted earlier by one company, mono-alkyltin catalysts (which are not the subject of this Option) function in esterification reactions whereas di-alkyltin catalysts are better for trans-esterification reactions.

With regard to organotin being present from the stabiliser component, information from industry indicates that organotin stabilisers are rarely used in plasticised PVC, with the liquid mixed-metal systems being the favoured stabiliser type. Information has also been received from the European Resilient Flooring Manufacturers' Institute who have indicated that the few remaining users of these organotin stabilisers are not interested in defending organotin stabilisers since the phase-out process is nearly finished (ERFMI, 2007). Also, according to ESPA, the use of tin stabilisers in plastisol (suspension) PVC is highly unusual and these all use the liquid mixed-metal stabiliser systems (ESPA, 2007). Industry has, however, requested derogation for use of organotins in coil (or steel) coating - which strictly is not a consumer use. The RAR indicates that this use is unlikely to present a significant direct risk to consumers, suggesting a conclusion (ii).

Overall, the effectiveness of this measure would depend on the extent to which DBT and DOT are currently used in esters, as opposed to being a 'near' historical use - where the aim of the restriction would be to prevent a re-occurrence of use. Assuming that only mono-substituted organotins (and other alternative catalysts, such as titanates) are currently used in this application, the effect of this restriction could, therefore, be minimal (although the presence of TBT impurities in DBT products could mean that this measure may have indirect benefits in achieving the goals of the WFD with regard to TBT).

7.4.3 Practicality

The procedure for restricting the marketing and use of substances at the EU level under Directive 76/769/EEC is well established, with various substances already subject to restrictions. Amendments to Directive 76/769/EEC have been introduced several times and in this respect, it is a simple measure to introduce and implement. Member States also have suitable procedures in place or implementing its requirements.

Practically speaking, this Option should be straightforward to implement as the current use of organotin stabilisers in plasticised applications is indicated to be less than 5% of all PVC-related uses. A few companies have been keen to stress that while they have phased out organotin use in some plasticised PVC applications, this has come at some cost and impact on their business and customers. There is, therefore, the issue that companies who have already incurred costs in phasing out (and being proactive) would benefit from foreseeing the restrictions before they come into place. Overall, it has been indicated that for customers using organotins in plasticised PVC, there is the ability to change formulations but some companies may need some time to confirm that the new formulations are fully workable on their plant and do meet their customer's specifications (i.e. some R&D work may be required on a site-by-site basis).

This is why the organotin manufacturing industry has requested its customers to help them in this process. It is not yet clear how long would be required for the communication process to be complete; however, the general feeling is that the costs which are incurred from such a switch to alternatives are significant, but bearable. There has been no indication or suggestion of companies being put out of business as a result of switching to alternatives. Most companies indicated that they had explored alternatives to organotins in plasticised applications and the relevant industry associations have already been encouraging their members to find alternatives.

7.4.4 Monitorability

In theory, monitoring the implementation of restrictions should be relatively straightforward, given that suitable systems have been established through previous restrictions. Measures for ensuring that restriction on uses of organotins in plasticised PVC can be included as part of the Vinly2010 initiative and these could possibly be extended (or serve as a template).

7.4.5 Economic Impact

In general, the impacts of the measure should be limited in the sense that:

- plasticised PVC accounts for less than less than a third of the total PVC in the EU;
- organotins are rarely used in plasticised PVC applications (whether from the stabiliser or plasticiser components). Only small quantities (5 - 7% (see Table 2.8)) of tin stabilisers are used in plasticised PVC where the majority stabiliser systems used are the liquid mixed metal systems); and
- where used, organotins are currently being phased out in a number of remaining applications (apart from steel (or coil) coating, which is not a consumer use).

On the above basis, no significant adverse effects and/or disproportionate impacts have been indicated or are expected on the downstream markets or on the manufacturers of plasticisers. It is, however, possible that some companies would incur significant costs as a result of the measure; however, these may be considered 'delayed' costs since other companies have also changed their portfolios at their own cost to eliminate organotins in plasticised applications.

7.4.6 Summary

Overall, this measure would serve to prevent re-occurrence of past uses and restrictions on DBT would also reduce the amount of TBT which is available as an impurity - and, therefore, help in achieving the targets of the WFD. Also, because industry has found alternatives to organotins in most plasticised applications, any restriction on the use of organotins can, therefore, be implemented quickly, with the exception of a few cases (coil or steel coating). The overall effectiveness of this measure (as a stand-alone) in reducing the contribution to the overall TDI may, however, be limited, seeing that it only deals with 5 - 7% of the total source of organotin in PVC.

7.5 Option 4: Restrictions on Specific Consumer Products Containing Organotins

7.5.1 Introduction

This measure will restrict the use of di-substituted organotins in specific consumer articles, in particular: PVC T-shirts, PVC gloves, PVC sandals, female hygiene products, nappies, dental moulds and 2-part silicone moulds. These products have been selected on the basis of the conclusions of the RAR and their contribution to the TDI.

7.5.2 Effectiveness

By targeting the specific products assessed in the RAR, this measure is likely to be effective in reducing consumer exposure associated with the conclusions (iii) and (ii)* - which are most likely to result in exceedance of the TDI (whether individually or collectively) and would mean that the major contributor(s) to human exposure to these organotins are reduced to acceptable levels.

However, this Option does not take into account the SCHER opinion, that it is the total consumer exposure to organotins that should be used in the RAR, including all the identified pathways, such as those estimated to *contribute with less than 20% of the TDI*. Therefore, if the total exposure exceeds the TDI, there is a reason for concern and risk reduction measures should be considered, regardless if this exposure comes via one or a large number of pathways.

It is also important to bear in mind that the RAR did not attempt to assess every single consumer product that contains organotins, and as such, a non-risk characterisation does not automatically mean that there is an acceptable risk associated with a given product. In this case, even if it is accepted that the products which have been assessed in the RAR reflect those of concern based on type and/or frequency of exposure and availability of monitoring data, these products can only be considered as providing solely an indication of the kind of exposure which may be obtained using similar products.

Another key issue with restricting the use of organotins in specific products is the uncertainty which is associated with the particular source of organotins in some of these products. This poses a problem for the phrasing of restrictions, for instance, where:

- the same product (e.g. carpet) can be manufactured using polyurethane, polyvinyl chloride or polyolefins (which could all be sources of organotins); or
- the same product can be manufactured using any combination of polyurethane, polyvinyl chloride or polyolefins in different parts of the same product (e.g. where the lining, backing and top of carpets have different materials).

Overall, while this measure has its merits, in effectiveness terms, it is not considered to be sufficiently robust for effectively reducing consumer exposure or addressing the risk of exceeding the TDI.

7.5.3 Practicality

In practical terms, the impact of restrictions on the use of organotins in:

- *female hygiene products and nappies* (and AHPs in general) should be minimal as organotins are not intentionally used in these products and occur only as impurities. There is currently a voluntary agreement by EDANA to ensure that raw materials that come into contact with the user contain less than 2 ppb of TBT, <10 ppb for each species of organotins individually. These limits refer to the organotin concentration in the raw materials used and not to the final consumer products (AHPs) and the 2 ppb is indicated to be below the current detection limit. On this note, marketing and use restrictions on the use of organotins in AHPs are likely to be neutral, both in terms of their practicality as well as reducing exposure to the selected organotins.

  However, it is the case that the exact source of organotin impurities in AHPs is currently unclear (where such sources could include the polythene bags to carry samples for analysis, PVC flooring and machine cables on production sites, etc.). Hence, while marketing and use restrictions would have little effect in reducing or eliminating impurities, there is the risk that an outright restriction could result in industry stopping current testing and monitoring currently being undertaken under the terms of the existing VA.

  This brings to the fore a key point for this RRS which is that the recommended risk management measure(s) must not result in a reduction in the levels of consumer protection (or actions in that respect) compared with the status quo. On this note, it should be borne in mind that the current limits of 2 ppb and <10 ppb are far below the typical threshold of 0.1% usually employed in marketing and use restrictions. In other words, a restriction on the use of organotins in *concentrations equal to or greater than 0.1 % by weight* for this sector or application would effectively amount to relaxing the limits in the voluntary agreement.

  If, as indicated by EDANA, the use of organotins in the production of silicone coated release sheets and in polyurethane foam in nappy waist bands has since been phased out, a more reasonable risk reduction measure would appear to be a monitoring of progress made as a result of these actions, as well as those resulting from the recommendations from this study, to identify any impacts on the levels found in these products. This measure is justified on the basis that there is currently no evidence that the current voluntary agreement is not adequately controlling the concerns or risks. If after monitoring over time, the levels or organotins are found to decrease significantly or remain insignificant, the effects may be comparable to a restriction; however, where the levels are found to be significant, further measures may then be introduced on the basis of the better information available.

In order to achieve this goal, the industry needs to take steps towards formalising the voluntary agreement and ensuring the agreement of the test protocols currently being used (with the appropriate authorities). They also need to ensure that the terms of the voluntary agreement apply across the whole of their industry sector;

- *PVC T-shirts* should be minimal as these T-shirts are generally not produced in the EU, but imported from outside the EU. ESPA companies are also looking to ensure that such use ceases in the EU. For *PVC gloves and sandals*, the impact should also be minimal as industry is currently moving towards alternatives. With regard to *wall coverings and flooring*, ESPA companies are currently working with their customers to change to alternative stabiliser systems with the aim of phasing out this use by the end of 2007; and

- *RTV silicone applications* is unclear. As discussed in Section 5, it appears to be the case that the introduction of alternatives is easier in RTV-2 DIY silicone moulds compared with RTV-1 silicone sealants. In RTV-1 silicone sealants, the alternatives already appear to have a significant market share despite the catalyst manufacturers' claim of the criticality of this application. There appear to be commercially available alternatives such as titanates and zirconates although organotins are the established catalysts of choice. Issues have been raised with regard to the increased costs of alternatives, the colour of the produced sealant and the expected shelf-life of alternatives, however these technical issues may be overcome as more research is put into the development of these alternatives. As noted further above, titanium catalysts are competitive products in this market with a significant market share. On the other hand, CES has argued in favour of the criticality of construction applications of organotin catalysts in this area; however, with the exception of the increased cost, the case for the criticality of these applications has not been adequately made. It is also important to note that not all construction applications are consumer applications, however, RTV-1 silicone sealants may generally be available in DIY stores to both consumers and professional users alike.

In summary, restrictions on specific products will provide a useful option for addressing the risks associated with conclusions (iii) and (ii)* in the RAR; however, it may be necessary to consider some derogations for uses for which suitable alternatives have not been identified. It should also be borne in mind that Option 3 effectively restricts the use of organotins in PVC T-shirts, PVC gloves and sandals.

7.5.4 Monitorability

In theory, monitoring the implementation of restrictions should be relatively straightforward, given that suitable systems have been established through previous restrictions. However, issues of imported good may still need consideration by the relevant authorities in Member States.

7.5.5 Economic Impact

Very limited information has been provided on the scale of the costs from replacing organotins in the selected applications. It is, however, the case that any costs incurred from restrictions on these uses are likely to be incurred or passed on to the consumer. It is, however, considered that the health benefits of moving away from DBT outweigh the costs associated with the identified hazards/risks (whether as an individual substance or cumulative with other groups of substances). For DOT, a three-year phase-out period is recommended to allow for companies to review their product portfolios and identify suitable alternatives for them and their customers.

7.5.6 Summary

Overall, while this measure has its merits and provides a useful option for addressing the risks from individual applications, in effectiveness terms, it is not considered to be sufficiently robust for effectively reducing consumer exposure or addressing the risk of exceeding the TDI. It may also be necessary to consider some derogations for uses for which suitable alternatives have not been identified.

Very limited information has been provided on the scale of the costs from substitution. It is, however, the case that any costs incurred from restrictions on these uses are likely to be passed on to the consumer.

It is also considered that the health benefits of moving away from DBT outweigh (the costs associated with) the identified hazards/risks (whether on its own or cumulatively with other groups of substances). For DOT, a three-year phase-out period is considered to be suitable to allow for companies to review their product portfolios and identify suitable alternatives for them and their customers.

8. RECOMMENDED RISK REDUCTION STRATEGY

8.1 Recommended Risk Reduction Measure

Based on the analysis presented in the previous sections and the information made available by industry for this RRS, the following risk reduction measure is recommended:

Recommendation

To consider at Community level, marketing and use restrictions under Council Directive 76/769/EEC (marketing and Use Directive) on all uses of:

- tri-substituted organotins, in particular tributyltin (TBT) and triphenyltin (TPT) compounds (Option 1);
- dibutyltin (DBT) compounds as stabilisers in all consumer (PVC) products (Option 2);
- dioctyltin (DOT) compounds as stabilisers in all consumer (PVC) products with a three-year phase-out period (Option 2);
- dibutyltin (DBT) and dioctyltin (DOT) compounds in plasticised PVC, unless used in steel (or coil) coating (Option 3); and
- dibutyltin (DBT) and dioctyltin (DOT) compounds as silicone catalysts for RTV-2 DIY moulds, baking trays and baking paper coatings and in RTV-1 sealants, with a three-year phase-out period for use of dioctyltin (DOT) compounds in RTV-1 sealants (Option 4).

Uses of organotins in plant protection products, food and food contact materials, biocides, medical devices and applications, and as intermediates in chemical synthesis, are not covered by these recommendations as these uses (apart from intermediates) fall under specific regulatory frameworks (or legislation) which are more appropriate for addressing the identified risks.

8.2 Summary Justification for Recommended Risk Reduction Measure

The above recommendation is based on the following key considerations (amongst others detailed in the Report):

- **contribution to the TDI**: the SCHER opinion that it is the total consumer exposure to organotins from all identified pathways which should form the basis of the risk assessment, where this includes all the identified pathways, such as those estimated to contribute less than 20% of the TDI. Any risk reduction strategy should, therefore, aim to ensure that the risk of individual members of the general population exceeding the TDI for organotins as a result of the cumulative exposure to organotins from a variety of consumer articles, products and pathways is reduced (regardless if this exposure comes via one or a large number of pathways); and

- **additive effects of the organotins**: the SCHER view that the four groups of organotins (DBT, TBT, DOT and TPT) represent the organotin compounds of most concern and their effects should be viewed as additive both for the target organs (thymus) and for the modes of action (immunotoxicity);

- **hazardous properties of individual organotins**: the potential health (and environmental) hazards relating to the PBT, vPvB, CMR and endocrine disrupting properties of certain organotins have to be taken into account. As noted earlier, in relation to the marine environment, TBT and TPT are likely to be classified as both PBT and vPvB substances, as well as being endocrine disruptors, while DBT is to be classified as a Category 2 reproductive toxin;

- **for tri-substituted organotins, in particular TBT and TPT (Option 1)**: these substances are rarely used without a detailed 'approvals' process (such as under the plant protection products legislation) or for chemical synthesis; however, there may still be importation for sale in the EU of consumer articles treated with biocidal organotins outside of the EU. The restriction is intended to address this issue and also prevent a substitution of risks, where companies move from known hazardous substances such as TBT to other tri-substituted organotins, whose risks may not be fully known at present;

- **for DBT compounds**: these are likely to be included in the 30th/31st ATP of Directive 67/548/EEC as reprotoxic category 2 and a number of companies have indicated that they are currently moving away (or planning to) from this substance (albeit, to other organotins, including DOT). Placing restrictions on DBT would therefore build on the DPD/DSD requirements such that they apply to articles, rather than preparations only. A restriction on DBT would also reduce the amount of TBT which will be available as an impurity - and, therefore, help in achieving the targets of the Water Framework Directive (where it is a priority hazardous substance for which a cessation of emissions, losses and discharges to the aquatic environment is required). In the event of an immediate restriction on DBT, it is considered to be the case that there are alternative compounds which can be used across the vast majority of (if not all) applications. Overall, it is considered that the benefits of moving away from DBT outweigh the costs associated with the identified hazards/risks (whether from DBT compounds themselves or in addition to those from TPT, TBT and DOT);

- **for DOT compounds**: there are current regulatory approvals for use in food packaging (within specific migration limits) and pharmaceutical packaging. Since food and pharmaceutical packaging currently account for around 60% of all organotin use in unplasticised PVC (and have their own regulatory framework for approval), placing restrictions on the remaining 40% of uses (assuming no further derogations on technical grounds are granted) runs the risk of being potentially disproportionate to the actual consumer exposure or the adverse effects that are potentially being avoided (for instance, exposure via food versus exposure via construction products).

There are known alternatives for use in food packaging and non-food contact applications. These are effectively the same for both categories of products and arguments relating to their suitability apply equally to both categories. If the need for risk management is considered to be the same regardless of application (where it is based on the substance itself), and alternatives are available and suitable, then it may be argued that a consistent approach to risk management should be adopted across all uses of DOT (i.e. either restrictions [or limit values] should apply equally to food and non-food applications).

However, the aim is to reduce the risk of individual members of the population exceeding the TDI, therefore, restrictions on non-food packaging applications may be considered to be an appropriate way of achieving this.

Furthermore, the relative safety of using SMLs in food contact materials cannot be directly transposed to other non-food articles, as it does not take into account the wide dispersive uses of DOT (e.g. in construction products), the method of substance loss and subsequent human exposure (wear and tear as opposed to migration into foodstuff) and the long life-spans of these products (10 - 100 years). Taken together, these mean that emissions and exposure could be on-going for a considerable time and will still contribute to the total exposure of the individual, as noted by SCHER.

In this regard, it appears to be the case that while most companies are aware of the need to act towards substituting organotins in plasticised applications ahead of any regulatory action, some companies have not anticipated the need to substitute in unplasticised applications. As it is possible that there may be genuine difficulties in finding the appropriate alternative for a given product or in retooling a plant or processing system[41], some companies may have significant difficulties if restrictions were to be put in place immediately. These problems are likely to be more serious where a significant proportion of a company's portfolio is based on DOT and DBT, as opposed to competitors who may also have or use calcium-organic stabilisers and methyltin stabilisers. For these reasons, a three-year phase-out period is considered to be suitable to allow for companies to review their product portfolios and identify suitable alternatives for them and their customers; and

- **for use of organotins in silicones**: uses in baking trays and baking papers represent historical uses and, as such, restrictions are intended (amongst other things) to prevent a re-occurrence of use. For RTV-2 moulding compounds, there are suitable alternatives to organotins and CES members are prepared to accept a regulatory decision to phase out this use of organotins. The three-year phase-out period applies

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[41] As noted by ESPA (not dated), the complexity of processes, uses and applications of PVC means that the selection of the appropriate stabiliser system requires considerable knowledge and expertise of process equipment, polymer choice and final application - in addition to regulatory approval requirements and cost issues - and this is not straight-forward.

in RTV-1 sealants to allow industry sufficient time to identify suitable alternatives to move to.

Overall, it is considered that restriction on three of the four groups of organotins (whose effects should be viewed as additive, according to SCHER) are sufficient as a short-term measure (i.e. for the three years) for protecting the health of consumers and the environment.

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ANNEX I

PROJECT SPECIFICATIONS

Terms of Reference for a socio-economic impact assessment concerning:

Potential restrictions on the marketing and use of certain organotin compounds as catalysts or PVC stabilisers

1. GENERAL INFORMATION AND OBJECTIVES

It falls within the responsibility of the Chemicals Unit of DG Enterprise and Industry to manage the risks from chemicals and to propose the appropriate restrictions on the marketing and use of a specific chemical in the framework of Directive 76/769/EEC, if unacceptable risks from this chemical have been identified and if they cannot be adequately controlled by other measures. A framework contract concerning socio-economic evaluation arising from proposals for risk reduction measures related to specific chemical substances was signed 04 July 2006 and will be used for this study.

The objective of the present study is to collect the information necessary for assessing the potential impacts of a restriction on the marketing and use of certain organotin compounds used as PVC stabilisers or catalysts in the production of consumer articles.

2. SUBJECT OF THE SERVICE REQUEST

Organostannic or Organotin compounds (OTs) are substances composed of tin directly bound to a number of organic groups, which find widespread use in industrial applications. Di-substituted OTs (such as Di-Octyl Tin compounds - DOT, Di-Butyl-Tin compounds - DBT) usually in combination with mono-substituted OTs are used as stabilizers in PVC and as catalysts in the production of various products. Tri-substituted OTs (such as Tri-Butyl-Tin compounds - TBT, Tri-Phenyl-Tin compounds - TPT) have been used historically as biocides.

Restrictions have already been imposed at EU level on certain antifouling applications of organotins by means of amendments to Directive 76/769/EEC concerning restrictions on the marketing and use of certain dangerous substances and preparations, by Directives: 89/677/EEC, 1999/51/EC and 2002/62/EC. Moreover, Regulation (EC) No (782/2003) of the European Parliament and the Council prohibited the use, as from 1 July 2003, of organotin compounds as biocides in anti-fouling systems on EU ships and, as from 1 January 2008, on any ship entering the EU waters.

Organotin compounds are not included in the list of priority substances in the framework of the existing substances regulation (793/93). *However, prolonged exposure to certain tin-organic compounds has been scientifically proven to disrupt the endocrine system and cause harm to human health and the environment.* Organotin compounds in their various forms are used in a large number of different applications, including many consumer products. Therefore, consumers within the EU are exposed to a range of different products containing OT compounds.

The Commission (DG Enterprise and Industry) awarded a contract to Risk & Policy Analysts Ltd (RPA) to examine possible risks from the applications of organotin compounds in areas outside their use as biocide in antifouling systems. The final report (published in September 2005): (i) focused on the presence and effects of four specific groups of OTs: dibutyltin (DBT), tributyltin (TBT), dioctyltin (DOT) and triphenyltin (TPT); (ii) adopted a group TDI (tolerable daily intake) for the effects on human health of the four listed organotins in combination.

The RA report provides an overview of various consumer products, in which these organotin compounds have been detected and reported. According to the results, unacceptable risks were concluded: (a) for children's exposure to fish/fishery products, indoor-air/dust and T-shirts, (b) for any consumer due to the presence of organotins as catalysts in silicon-coated baking paper for cookies, (c) for people living near industries that produce or using OTs where there is a high exposure via the local environment.

In addition, as risks to consumers may arise from a wide range of products containing OTs, the report also identified OT uses that contributed to exposure in the range of 20<%TDI<100. Such a cumulative risk was observed for the following consumer applications:

(1) For adults, via: Fish and fishery products, PVC gloves and sandals, T-shirts, female hygiene products, foot spray, dental moulding, 2-part silicon moulds and PVC food packaging.

(2) For children, via: PVC sandals, nappies, and PVC food packaging.

The Scientific Committee on Health and Environmental Risks (SCHER) was invited by DG Enterprise and Industry to assess the overall scientific quality of the report and comment on specific questions concerning the validity of the risk assessment conclusions. Following five meetings of the OT Working Group, which carefully reviewed the RPA report, the SCHER issued a draft opinion in October 2006 entitled: "Revised assessment of the risks to health and the environment associated with the use of the four organostannic compounds TBT, DBT, DOT and TPT".

The SCHER is of the opinion that it is the total consumer exposure to OTs that should be used in the risk assessment, including all the identified pathways, such as those estimated to contribute with less than 20% of the TDI. Therefore, if the total exposure exceeds the TDI there is a reason for concern and risk reduction measures should be considered, regardless if this exposure comes via one or a large number of pathways.

Moreover, the SCHER underlines that:

(a) the most important exposure pathways are food, indoor air, household dust and via dermal contact with different polymer materials;

(b) the risk for an individual of the general population to exceed the TDI for OTs is high and some people maybe exposed to much higher doses (considering that at least 70% of the children and 25% of the adults are exposed to more than the TDI according to the RA results).

(c) for both health and environmental risks, risk estimates of the RPA report may not represent the worst case situations.

The main objective of the proposed study is to complement the already available information regarding the current uses of organotins as PVC stabilisers or catalysts in the production of various articles, which are used by relevant industry or eventually by the consumers for do-it-yourself activities.

Among specific targets would be:

- to identify potential alternatives to OTs and their risks and benefits,
- to check the existing national restrictions for certain uses of organotins,
- to propose possible options for the management of identified risks at Community level.

For each of these options the potential health, environmental, and economic impacts should be described.

3. DESCRIPTION OF THE TASKS TO BE PERFORMED

The aim of the study is to collect the necessary information in order to assess the impact of potential restrictions on the marketing and use of certain organotin compounds in various consumer applications. Recent developments in methodologies for impact assessments shall be taken into account. These are available at:
http://europa.eu.int/comm/enterprise/regulation/better_regulation/impact_assessment/docs/sec_2005_791_guidelines_annexes.pdf

The study is to focus, starting on the basis of the already existing information, on certain consumer uses of organotins. In particular, the following areas should be covered:

- The study should prioritise, using the available production and marketing data, those OT-consumer applications which have the greatest overall risks and size in the market (tonnes of use), including:
    i. PVC stabilisers, which constitutes the single largest use of these substances, primarily for rigid and also for flexible PVC applications.
    ii. Catalysts in the production of various consumer articles.

  In agreement with the Commission services, the study should examine the possibility of OT replacement in a range of selected consumer uses and assess currently available alternative substances, providing with sufficient information regarding their volume, availability, price, suitability and their efficiency. Moreover, the study should specify any uses for which there are no suitable alternatives available and if possible provide estimation by when alternatives could be developed.

- The study should identify the health and environmental risks and incidents already observed in the Member States. Though it is obviously not feasible to conduct an assessment for all potential routes of consumer exposure, an attempt should be made to focus on products that either lead to a relatively high level of possible exposure, as concluded in the risk assessment, or that are relatively commonplace so that an average consumer is likely to come into frequent contact.

- The study should provide an overview about the national situations of the EU Member States. More specifically, it should identify the respective scopes of any national measures, if any exist further to the restrictions imposed by the previous amendments of the Limitation Directive 76/769.

- Starting from existing measures in the Member States and the measures proposed in the latest RPA report, the study should identify all other possible options for risk management with different stringency levels. All the information and views expressed by different stakeholders (latest scientific opinions of SCHER and EFSA, recent remarks of ETINSA etc.) should be considered in this process.

- For each of the potential risk reduction measures, the study should describe the expected positive and negative impacts on the protection of human health and the environment and particularly also the economic, commercial, employment and social consequences, including investment one-off costs, operating costs that the measures would entail. It should also investigate the wider implications on trade, competition etc. In this context, as certain restriction of organotins would certainly lead to an increase of the volumes of alternative substances on the market and in use, it will be especially relevant to consider also the health and environmental impacts and the performance of alternative substances.

- The study should provide clear conclusions and recommendations with regard to the risk reduction measures considered most appropriate.

4. ESTIMATED EXPERTISE REQUIREMENT

Risk management, impact assessment and legal expertise from EU Member States are required.
Estimated expertise requirements are:

- Experts on risk management and impact assessment,
- Experts for National analyses,
- 90 w.d. in total including management.

w.d. = 1 working day for 1 expert (remuneration shall be payable to the Contractor only in respect of services actually rendered).

5. ESTIMATED PRICE

The total estimated budget (including travel costs) should not exceed 60.000 Euro
Travels should include 2 meetings of one day in Brussels for 2 persons.

6. ESTIMATED TIME TABLE

It is mandatory to complete the study within the time period of 10 months.
The contractor will provide a work programme including a detailed time scale.

7. REPORTS AND DOCUMENTS

For the purpose of this specific study the following reports will be required:

Interim report(s) are due after	4 months
The draft final report is due after	8 months

The contractor is asked to submit all required reports in English and electronically to Mr. Sotirios Kiokias (sotirios.kiokias@ec.europa.eu)

After the final report has been accepted by the Commission, the Contractor must send 4 copies (three bound and one unbound) and one electronic version on CD-ROM to the Commission addressed to Sotirios Kiokias. The report on CD-ROM should preferably be delivered as a single document in PdF Format (Acrobat TM). The software to be used for all reports should be compatible with the Commission's operating system (at present Windows XP).

The **interim report** will indicate the progress to date with sufficient information to permit reorientation if appropriate and required and will contain at least the following information:

- All information with regard to the existence of possible alternatives used in the higher prioritised (as previously explained for either PVC stabilisers or catalysts) consumer applications, as well as the structure of the relevant industry.
- Complete collection of adopted measures of MS concerning any consumer application of OTs.
- Table of different risk management options.
- Indications for positive and negative impacts of possible restrictions on the marketing and use of these specific OTs uses in consumer products.
- Comparison between results obtained and the overall objectives of the study.
- Information on the remaining work to be carried out.
- Any particular problems encountered that would have a notable effect on the tasks to be carried out.
- Clear indications and detailed planning of the work to be carried out during the rest of the period for the completion of the tasks.

The Commission shall have 30 days to approve or reject the interim report and the Contractor shall have 30 days to submit new documents.
The interim report will be deemed to have been accepted by the Commission if it does not expressly inform the contractor in writing of any comments within 30 days of its receipt.

The contractor shall deliver a **final report** containing at a minimum:

- An executive summary setting out the conclusions of the report;
- Analysis and conclusions per MS concerning the impact of a restriction on the marketing and use of certain OTs as catalysts or PVC stabilisers;
- A comparison between results and objectives set out in the proposal; description of problems encountered and steps taken to overcome these; consequences of these problems on the results; impact on the validity and completeness of the conclusion.
- Information and clear references on sources of information used and the value of their methodologies as appropriate.
- A summary of the resources spent on the specific contract, including details of travel expenses.

The Commission shall have 30 days to approve or reject the final report and the Contractor shall have 30 days to submit new documents.

The final report will be deemed to have been accepted by the Commission if it does not expressly inform the contractor in writing of any comments within 30 days of its receipt.

8. REQUIRED MEETINGS

Attendance at 2 meetings: Kick-off meeting and Presentation of final report in Brussels.

ANNEX II

LIST OF CONSULTEES

ANNEX II: LIST OF CONSULTEES

An asterisk indicates an organisation that has responded, either by providing information or completing an RPA Questionnaire.

Note that some trade associations (without an asterisk) circulated the questionnaire to their members to complete on individual basis (as requested by RPA), without sending a consolidated association response.

Trade Associations

Alliance of Independent Retailers Limited
Association of European Adhesives and Sealants Manufacturers (FEICA)
Association of the Suppliers of the Garment Industry (ASSOCONFEZIONE)
Camera di Commercio Belgo-Italiana
Centre Europeen des Silicones (CES)*
European Apparel and Textile Organisation (EURATEX)
Europoean Association of Automotive Suppliers (CLEPA)
European Association of Chemical Distributors (FECC)
European Association for Textile Polyolefins (EATP)
European Automobile Manufacturers' Association (ACEA)
European Catalyst Manufacturers Association (ECMA)
European Chemical Industry Council(CEFIC)*
European Catalyst Manufacturers Association (ECMA)
European Confederation of the Footwear Industry (CEC)*
European Council of Paint, Printing Inks and Artists' Colours Industry (CEPE)
European Council for Plasticisers and Intermediates (ECPI)*
European Council of Vinyl Manufacturers (ECVM)
European Disposables and Nonwovens Association (EDANA)*
European Light Stabilisers and Antioxidants Association (ELiSANA)*
European Lubricants Working Group
European Plastics Converters (EuPC)*
European PVC Floors Manufacturers (EPFLOOR)
European Resilient Flooring Manufacturers' Institute (ERFMI)*
European Rigid PVC Film Association (ERPA)*
European Rubber Chemicals Association (ERCA)
European Stabiliser Producers' Association (ESPA)*
European Synthetic Rubber Association (ESRA)
European Textile Services Association (ETSA)
Eurpean Thermoplastic Independent Compounders (ETHIC)
European Tin Catalysts Association (ETICA)*

Trade Associations

European Tin Stabilisers Association (ETINSA)*
European Tyre and Rubber Manufacturers' Association (ETRMA)
European Union of Skilled Craft and Small and Medium-sized Enterprises (UEAPME)
Federation of the European Dental Industry (FIDE)*
Federation of the European Play Industry (FEPI)
Federation of European Screen Printers Associations (FESPA)
Federation of the European Sporting Goods retail associations
Fédération des Industries Chimiques de Belgique (FEDICHEM)
Federation of Sports and Play Associations
Independent Footwear Retailers Association (IFRA)
Institute of Materials, Minerals and Mining (Plastics and Rubber Division) (IMMM)
International Council of Chemical Associations (ICCA)
International Council for Toy Industries (ITCM)
Joint Committee of the Textile Finishing Industry in the EU (CRIET)
Kemianteollisuus ry (Chemical Industry Federation of Finland) (KT RY)
Organotin Environmental Programme (Association) (ORTEP(A))
Plastics Europe (Association of Plastics Manufacturers)
Polyester Powder Resin Manufacturers (PPRM)
Scottish Plastics And Rubber Association (SPRA)
Society of Motor Manufacturers and Traders Limited (SMMT)
Sport Manufacturers and Retailers Trade Association (SMART)
Sports Traders Alliance Group Ltd (STAG)
Standing Committee of the European Glass Industries (CPIV)*
Toys Industry of Europe (TIE)*

Companies

Abiel SA
Accantia Health & Beauty
ac-Folien Gmbh
Advansa
Aiscondel*
Altro
Ambrogio Pagani S.p.A.*
Amtico
Albermerle
Akcros*
Arkema*
Arbora & Ausonia

Companies

Armstrong DLW AG
Arquest
Artsana
Asahi Glass
ASUA*
Axens
Baerlocher*
BASF
Basell Polyolefins
BAYER Material Science
Betten Stumpf
Bluestar Silicones
BNT
Bonar Floors
Borchers
Borealis
Browning Enterprises
Chemopetrol
Chemson Polymer Additive AG*
Chemtura Corporation (formerly Crompton & Gt. Lakes)*
CIBA
CIFRA
CIRES SA
Cri/Criterion
Degussa*
D. Jacobson & Son
Dr Foot
Dr Scholl
Dow Corning Europe*
Dunlopillo
Dyeon
Eastman Chemical
Elana*
Elastogram
Eurocat
Exxon Mobil Chemicals
Fater
Fatra Napajedla
Ferro*

Companies

Floridienne Chimie
Fogarty Filled Products Ltd.
The Forbo Group
Ford
Freefoam Plastics Ltd.*
Georgia-Pacific
Gerflor
Goldschmidt TIB
Grace GmbH & Co. KG*
Guardian Europe*
Haldor Topsoe A/S*
Heraeus*
Hexion Speciality Chemicals
H.M.T. Design Aps
HMV Group
Huntsman Polyurethanes
Hydro Polymers*
Hyga
Hygiene Oederan
Ineos - Polyolefins
Ineos Vinyls
Invista Resins and Fibers GmbH & Co. KG*
Jade B.V.
Jaguar/Rover Cars*
Johnson & Johnson*
Johnson Matthey*
Kimberly-Clark*
KMZ Chemicals
Laboratorios Indas
Lonza*
Lubrizol*
LVM
M & G Polymers*
Momentive Performance Materials
Mycota
Ontex
OXEA Group
OXENO Olefinchemie (subsiduary of Degussa)*
Northern Feather Ltd.

Companies

PaperPak
Paul Hartmann
Pilkington Flat Glass*
Polimeri Europa*
Polyflor Ltd
PolyOne
Premier Automotive Group
Procter & Gamble
Reagens S.pA.*
Renault
Riolon
Resilia (Arkema)*
Rohm & Haas*
Sabic Europe
Sapsa Bedding srl
SCA Hygiene Products
Selenis -Indústria de Polímeros, S.A.
Shell Chemicals Europe*
Shepherd Chemical Company*
Shin Etsu PVC*
Shin Etsu Silicones
SILIS S A
S.I.L.C.
SIR Industriale
Solvay - Solvin
Solvay - Caprolactones
Somnis
Spolana*
Stanley Smith Ltd.
Süd-Chemie
Tarkett Floors*
Tessenderlo Chemie (Sotraseperef)*
Tyco Healthcare
UOP
Upofloor Oy
Vulcaflex S. P. A.
Wacker-Chemie

Competent Authorities

Country	*Department/Agency*
AT	Federal Ministry of Agriculture, Forestry, Environment and Water Management
AT	Federal Ministry for Economic and Labour
AT	Federal Ministry of Social Security, Generations and Consumer Protection
AT	Ministry of the Environment
BE	Federale Overhidssdienst Voksgezondheid, Veiligheid van de Voedselketen en Leef milieu Directoraat-generaal: Leefmilieu
BE	Federal Ministry of the Environment
BE	DG5 : Environnement - Service Maîtrise des Risques
BG	National Centre of Public Health Protection
BG	Ministry of Health
BG	Ministry for Environment and Water
CY	Department of Agriculture, Ministry of Agriculture, Ministry of Agricultre Natural Resources and Environment
CZ	Ministry of Health of the Czech Republic: Chemical Substances Register
CZ	Ministry of Environment, Department of Environmental Risks
CZ	Ministry of Industry and Trade - Department of Manufacturing Industry and Construction
DE	Federal Institute for Occupational Safety and Health, Division for Chemicals and Biocides Regulation
DE	Federal Institute for Occupational Safety and Health (BAuA)*
DE	Federal Ministery for the Environment, Nature Conservation and Nuclear Safety (Bundesministerium fur Umwelt, Naturschutz and Reakorsicherheit)*
DE	Federal Environment Agency (Umweltbundesamt)*
DK	Danish Environmental Protection Agency (Miljostyrelsen) (EPA)*
DK	Danish Ecological Council
DK	Danish Working Environment Authority
EE	Chemicals Notification Centre
EE	Ministry of Social Affairs, Public Health Department
ES	Ministerio de Sanidad y Consumo.Dirección, General de Salud Pública, Subdirección General de Sanidad Ambiental y Salud Laboral
ES	Ministry of Environment
FI	Finnish Environment Institute
FI	National Product Control Agency for Welfare and Health
FI	STTV-National Product Control Agency
FI	Ministry of Social Affairs and Health
FR	Ministere de l'Ecologie et du developpement durable DPPR/SDPD/ Bureau des Substances et Preparations Chemiques
FR	Agence Fracaise de Securite Sanitaire de l'Environment et du Travail (AFSSET)

Competent Authorities

Country	*Department/Agency*
GR	Hellenic Republic Ministry of Economy and Finance Directorate General, General Chemical State Laboratory, Division of Environment (GXK)
HU	Ministry of Environment
HU	Ministry of Health*
IE	Health and Safety Authority*
IT	Ministry of Environment
IT	Environmental Protection Agency
LV	Environment, Geology and Meteorology Agency
LV	Ministry of Environment Projection and Regional Development
LV	Ministry of Health / Department of Public Health, Environmental Division
LT	State Environmental Health Centre
LU	Ministere de la Sante
LU	Inspection du travail et des mines
MT	Malta Standards Authority
NL	National Institute for Public Health and the Environment (RIVM)*
NL	Ministry of Housing, Spatial Planning and the Environment, Directorate-General for Environmental Protection, Dir. for Chemicals, Waste, Radiation Protection / IPC 645 (VROM)*
PL	Ministry of Environment
PL	Bureau for Chemical Substances and Preparations
PT	Ministry of Economy (Ministério da Economia e Inovação - Direcção Geral da Empresa)
RO	Ministry of Environment and Water Management, General Directorate for Waste Management and Dangerous Substances
SE	Swedish Chemicals Inspectorate (KemI)*
SE	Ministry of the Environment
SE	Ministry of Sustainable Development
SI	Ministry of Health, National Chemicals Bureau
SI	Ministry of Labour, Family and Social Affairs
SI	Ministry of Health, National Chemicals Bureau
SK	Centre for Chemical Substances and Preparations
SK	Ministry of the Environment of the Slovak Republic
UK	Department for Environment, Food and Rural Affairs (Defra)
UK	Department for Trade and Industry (DTI)
UK	Health and Safety Executive (HSE)

Chambers of Commerce

Country	*Organisation*
EU	Association of European Chambers of Commerce and Industry (Eurochambres)
EU	Network of Insular Chambers of Commerce and Industry of the EU (INSULEUR)
AT	Eurochambres - Austria
BE	Fédération des Chambres de Commerce et d'Industrie de Belgique (CCI)
BG	Bulgarian Chamber of Commerce and Industry (BCCI)
CY	Cyprus Chamber of Commerce and Industry (CCCI)
CZ	Economic Chamber of the Czech Republic
DK	The Danish Chamber of Commerce
EE	Estonian Chamber of Commerce and Industry
FI	The Central Chamber of Commerce of Finland
FR	Assemblée des Chambres Françaises de Commerce et d'Industrie (ACFCI)
DE	Deutscher Industrie- und Handelskammerstag (DIHK)
GR	Union of Hellenic Chambers of Commerce
GR	The Athens Chamber of Commerce and Industry
HU	Hungarian Chamber of Commerce
EI	Chambers Ireland
IT	Association of Italian Chambers of Commerce (Unioncamere - Union Italiana delle Camere di Commercio Industria Artigianato e Agricoltura) (UNIONCAMERE)
LV	The Latvian Chamber of Commerce and Industry
LT	Association of Lithuanian Chambers of Commerce, Industry and Crafts
LU	Chambre de Commerce du Grand-Duché de Luxembourg
MT	The Malta Chamber of Commerce
NL	Vereniging van Kamers van Koophandel en Fabrieken in Nederland
NL	Netherlands Chamber of Commerce (kamer van koophandel en Fabrieken voor Amsterdam-Harlem)
PL	Polish Chamber of Commerce
PO	Associacao Comercial de Lisboa, Camara de Comercio e Industria Portuguesa
RO	Chamber of Commerce and Industry of Romania
SK	Slovak Chamber of Commerce and Industry
SI	Chamber of Commerce and Industry of Slovenia
ES	Consejo Superior de Camaras Oficiales de Comercio, Industria y Navegación de España
SE	Svenska Handelskammarförbundet
SE	Oslo Chamber of Commerce (Oslo Handelskammer)
UK	British Chamber of Commerce

Consumer Protection Organisations

Country	*Organisation*
EU	European Consumers Organisation
CH	Bureau Federal de la Consommation
DE	Bundesministerium für Verbraucherschutz, Ernährung und Landwirtschaft
EL	Directorate of Technical Inspection and Consumer Protection
EL	Ministry of Development, General Secretariat of Consumer Protection
FR	Civil Sous-Directeur de la sous-direction C Protection des consommateurs (DGCCRF)
IE	Office of the Director of Consumer Affairs
IE	Consumer Association of Ireland
IT	IMQ Legal Department
HU	Fogyasztóvédelmi Főfelügyelőség
LU	Ministere de l'Economie
LV	Consumer Rights Protection Centre
MT	Ministry for Economic Services
NL	General Inspectorate for Health Protection and Veterinary Public Health
NL	Food and Consumer Product Safety Authority (VWA)*
NO	Direktoratet for samfunnssikkerhet og beredskap
SI	Market Inspectorate of Republic of Slovenia
ES	Instituto Nacional de Consumo (M° Sanidad y Consumo)
SE	Konsumentverket (Swedish Consumer Agency)
UK	Consumer Safety and Strategy - Department of Trade and Industry
UK	WHICH

Other Consultees

European Trade Union Technical Bureau for Health and Safety (ETUC)
Friends of the Earth (FoE)
World Wildlife Fund for Nature, European Policy Office (WWF)
Greenpeace European Unit

ANNEX III

SCHER OPINION AND RPA'S COMMENTS/RESPONSES

ANNEX III: SCHER OPINION AND RPA'S COMMENTS/RESPONSES

SCHER Opinion, Comments and Responses to Questions	Further RPA Comments/Responses
OPINION	
The SCHER, supported by external experts including representatives from EFSA Scientific Panels has reviewed the new RPA report (September 2005) on organotin compounds (OTs). First the comments on the report and, to some extent, the OTs in general will be presented, and then the specific questions forwarded to the committee will be addressed.	
The assessment of environmental and human health risks caused by the OTs is difficult. The large number of compounds with very different properties in the group makes it difficult to make general conclusions. An unknown fraction of the added substances are also changed to new compounds in some of their functions (e.g. as stabilisers) and in the environment. There are not measured data available for the physical and chemical properties for all these substances. Properties like water solubility, dissociation and octanol-water distribution are also dependent on a number of conditions like temperature, pH and salinity (Laughlin et al, 1986b; Inaba et al, 1995; Arnold et al, 1997), which makes it difficult to estimate these properties. The picture is further complicated by the wide use of the OTs for very different purposes, including applications in consumer products, and the assessment has to be based on a number of assumptions.	Agreed.
Environment	
Environmental exposure The environmental exposures have been estimated using the procedures described in the TGD and complemented with measured data where such were available. The uncertainties in the assessment are large due to the limited amount of data available for the OTs, and that their physical and chemical properties make the well established model calculations less useful (e.g. logKow for dioctyltin ethylhexylmercaptoacetate (DOT- EHMA) is calculated to more than 15 by the KOWWIN program). The authors also point at the uncertainties at several places in the report.	Agreed.
One of the EHMA ligands in OTs added to PVC is partly exchanged with a chloride ligand during the processing of the material, and the remaining EHMA ligands are immediately exchanged with other groups (mainly chloride) after emission to water or soil. The environmental assessment should therefore be focussed on the formed substances, but it has to be kept in mind that it is mainly the EHMA derivatives that are emitted.	Agreed.

SCHER Opinion, Comments and Responses to Questions	Further RPA Comments/Responses
The OTs usage data are converted to corresponding alkyltin chlorides volumes (RPA Report, Annex 3). For the PVC stabilisers it is then assumed that "there is a 50:50 split between mono- and di-substitutes", and as the mono-substituted compounds do not contribute to the critical effect this will reduce the critical emissions. All of the stabilisers are also given as EHMA compounds, which further reduces the exposure to tin. The SCHER would have preferred to see some arguments for these assumptions. The 50:50 split mentioned above is also used for the plant losses (RPA Report, Annex 4). In the case of air emissions this would not be applicable as the vapour pressure of the mono-alkyl compounds is much lower than that of the poly-alkylated, and thus the correction factor of 0.6 is doubtful. In this Annex also air emission factors are calculated, and the result is that DOT has two times higher factor than DBT, which in turn has a 3 times higher factor than TBT. If the compounds produced are EHMA esters the reversed order would have been expected.	The assumed 50:50 split was based on industry advice dating back to 2002 (and hence used in the 2002 and 2003 Reports as well as the 2005 RAR). Air emissions will depend not only on vapour pressure (one uncertainty) but also on the conditions of release (another uncertainty). It is accepted that Annex 4 represents 'estimates' of plant emissions.
The amount of remaining OTs catalysts in polyurethane (PU) varies between 0.01% and 0.2% (RPA Report, Table 2.12) and the total production of PU is claimed to be 3352 kt/y (Table 2.13). The total volume of OTs in PU is estimated to be 400 t/y (Table 2.14) and this corresponds to an average concentration of 0.012%, which seems to be a best rather than worst case estimate. The emission factor for DOTC is claimed to be almost 5 times that of TBTC (RPA Report, Table 3.4). This is not in line with the vapour pressures given, where the value for TBTC (1 Pa, Table 3.26) is more than 1000 times higher than that of DOTC (2.6E-04 Pa, Table 3.27). The emissions from extrusion and calendering of PVC stabilised with OTs has been estimated using an ESD from OECD. That document identifies two groups of additives with different vapour pressure, and the DOT-EHMA and degradation products all belong to the group with high volatility. The predicted emission is reduced by 80% with a reference to "some limited monitoring data". More recent analyses of grass samples taken around a large PVC calendering plant (processing nearly 100,000 ton PVC annually) shows concentrations of up to 5 µg DOTC / kg ww 300 m from the emission (de Wolf, 2006). This is considerably lower than the 422 µg DOTC / kg ww predicted by EUSES and support a reduced estimate.	Incorrect. Table 2.13 (of the RAR) refers to total PU markets by sector (i.e. with and without OTs). Table 2.14 uses the data to generate market values for PUs with OTs. Overall, Table 2.14 says 400t of OTs used in 425kt PU - hence, overall concentration is about 0.1%. As above (but one). As discussed in Section 3.3.1 (of the RAR), the emission factors are derived from measurements (albeit limited). The issue of grass measurements is quite different. The RAR suggested that consideration should be given to the presence of DOT-EHMA, DOT-Cl-EHMA and DOTC (Sections 3.6.4 and 5.2.1 refer). To be informed that measurements indicate 5 µg DOTC/kg ww provides no evidence as to whether the associated concentrations of DOT-EHMA and DOT-Cl-EHMA are greater or lesser than those of DOTC. As such, there is no basis on which to 'support a reduced estimate'.

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Some OTs have been used as plant protection products, in particular as acaricides and fungicides. These include azocyclotin, cyhexatin and fenbutatin oxide used as acaricides on fruit and vegetables plus fentin acetate and fentin hydroxide used as fungicides on potato, sugar beet and beans. Now their use is strongly reduced, and the use of fentin and cyhexatin is not authorised since 2002.	Azocyclotin, cyhexatin and fenbutatin oxide are all discussed in the RAR (Section 2.4.3 refers) using the synonyms TCTT, TCTH and TNTO respectively. As noted, fentin (TPT) (but not cyhexatin) pesticides have been banned since 2002.
Environmental fate OTs are mainly used as stabilisers in PVC and as has been mentioned above in this function they will partly be transformed to new substances during use and after release. The EUSES2 modelling described in the report is done for the dialkyltindichlorides and dialkyltinoxides. Several constants for distribution between media have been calculated with equations developed for non-dissociated compounds, but the OTs are partly dissociated. There is a special section (Appendix XI, Part II) in the TGD describing this problem. This may explain some of the questionable data obtained, e.g. for DOT-EHMA the solubility in water is given as 8.5 mg/L (Table 3.31) and the log Kow as 15.3, two values that seem to be incompatible. The leaf – air distribution has a significant influence on the predicted value for the indirect human exposure. As the calculation of this parameter involves several factors that are connected to a high uncertainty the outcome will be highly uncertain as well. The water solubility demonstrates the difficulties as that of DOT-EHMA is given to be more than six orders of magnitude larger than that of DOT-Cl-EHMA (Table 3.31). The chlorine ligand in the latter will probably make that compound more soluble than the first.	It is accepted that figures relating to organotin properties must be treated with caution and this is highlighted in the RAR (Section 3.6 refers).
From the registration dossiers for TPTH and fentin acetate several data are available like the sorption constants to organic matter and the degradation rates in soil. For TPTH also information on the photo-degradation is available. The mean half life of TPTH in soil is about 26 days (n=4), whilst the photo-degradation half life has been determined to be about 14 days in natural sunlight. The sorption constant to organic carbon are established around 2200 dm^3/kg (median of 3 values) for TPTH. (RIVM, 1992 and RIVM, 1993)	Noted.
Environmental effects PNECs for the freshwater environment are derived from a large database on several organisms not including molluscs and have been calculated from long term toxicity data on *Daphnia magna* that is mentioned as the most sensitive freshwater organism, and a PNEC of 6 ng Sn/L has been calculated for TBT. The SCHER is of the opinion that the proposed value cannot be assumed enough protective for the aquatic environment without taking into account data on freshwater molluscs. Imposex was observed in freshwater gastropods at a concentration of TBT of about 40 ng/L as Sn (Schulte-Oelmann et al, 1995). Taking into account that this value is not a NOEC but a LOEC, a PNEC should be below 4 ng Sn/L, lower than those calculated for *Daphnia.* A careful search of the recent literature is needed to assess if additional data on freshwater molluscs are available. As suggested in the literature, a PNEC for the marine environment of 0.1 ng/L for TBT seems the most suitable (not explicitly proposed by the report). For other OTs no PNECs are proposed, except an indicative value (“perhaps” 10 ng/L) for DBT.	The referenced study used concentrations of 50 and 200 ng/L (TBT as Sn). Clear evidence of imposex was found at the higher concentration. Although degrees of imposex were detected at 50 ng/L, it is important to stress that similar evidence was also detected in the control group (due to ‘natural imposex’). As such, the observed effects at 50 ng/L cannot be associated with TBT.

SCHER Opinion, Comments and Responses to Questions	Further RPA Comments/Responses
Classification Classification of TBT and TPT as PBT and vPvB is appropriate. For DBT, the classification of T must definitely be applied (NOEC *Daphnia* = 4.1 µg/L, T threshold < 10 µg/L) instead of indicated a "probable" (Table 4.3 in the RPA report). A careful BCF assessment for DBT is needed for the classification of B. The same is needed for DOT.	The PBT criteria were developed for the marine environment and, as such, the P, B and T values should be based on values for the marine environment.
Justifications must be provided for the inconsistencies between observed and EUSES predicted BCF values. Many papers found in the literature, not mentioned in the RPA report, indicate high bioaccumulation and bio-magnification potential for OTs (see for example Iwata et al., 1995; Kannan et al., 1997, 1998; Tanabe et al., 1998; Hu et al., 2006). Laughlin et al. (1986b) found BCF values in marine animals for TBT higher than those predictable from Kow. The authors hypothesize a conjugation mechanism to biological molecules, increasing the simple process of partition on lipids. A more careful literature search on bio-accumulation and bio-magnification processes is needed.	Noted.
Risk characterisation The comments given above regarding both hazard and exposure assessments also have implications on the risk assessment. As most of the comments indicate an underestimate of at least the exposure, the conclusion must be that the risk estimates may not represent realistic worst case situations.	Based on the views presented above, the 'case' is not considered to have been made.
Human health	
Human exposure via food Several food items contain organotin compounds, especially those from the aquatic environment due to the use of such compounds as antifouling agents on boat hulls. In a recent opinion from EFSA (2004) the possible risks connected to consumption of food containing these substances have been assessed. The EFSA Panel on Contaminants in the Food Chain focused on TBT, DBT and TPT, primarily found in fish and fishery products. Based on SCOOP data (SCOOP, 2003) the panel estimated the median intake in Norway to 0.007 µg Sn/kg bw/day and the corresponding value based on mean data was 0.033. High consumers were exposed to 0.0 15 (median) and 0.070 (mean) µg Sn/kg bw/day.	EFSA/SCOOP data are reported in Table 5.3 of the RAR.
Children are generally, because of their lower body weight, considered as a group at risk for food chemicals when the dietary exposure is compared with a tolerable daily intake expressed in µg/kg bw. Based on this fact, a factor 3 is commonly used to estimate children dietary exposure when only data on adult consumption are available, i.e. the daily exposure for adults is multiplied by a factor 3. On the other hand children are expected to eat less in absolute value than adults in particular certain food categories like fish. In a recent study (Verger, 2006) focusing on the long term frequency of fish consumption on a population of consumers of fish located on the western coast of France, it was observed that the frequency of fish consumption is similar for adults, children between 6 and 15 years old and children below 6 years old with respectively 2.9 ± 1.4, 2.1 ± 1.1 and 2.1 ± 1.2 servings per week. On a quantitative point of view, based on the French national food consumption survey (Volatier, 2000), the average fish consumption (consumers only) for adults is 249 grams per week when the average consumption for children below 15 years old is 185 grams per week. Consequently for the current opinion, the SCHER can assume on a long term basis that the consumption of fish by children corresponds at least to 75% of the consumption of adults. In other EU Member States this percentage can even be higher. Considering both the difference in body weight and food consumption, a factor 3 can be used to estimate the exposure of children from the one of adults.	The factor of 4 used in the RAR is the same factor as that used in the 2003 Report which was adopted following CSTEE comments on the 2002 Report. It is accepted that it errs on the side of caution.
Several investigations of organotin compounds in food have been reported since the EFSA opinion. A recent study (CALIPSO, 2006) analysed the contamination by OTC of fish on the French market. It consists in sampling the fish and seafood mainly consumed by the population studied, taking into account the form of purchase	Noted.

SCHER Opinion, Comments and Responses to Questions	Further RPA Comments/Responses
(fresh, frozen, canned, etc.) and provisioning (bought or self-procured). The list of sampled food is based on an analysis of the individual dietary consumptions of the respondents. The final list included 138 products from which 95 fish and 43 molluscs and crustaceans. The sum of DBT, TBT, DOT and TPT was about 0.004 µg/g fresh weight for fish and sea food. For a hypothetical portion of 100 g/day, the total dietary exposure from fish would be 0.4 µg OTC.	
In another study (Rantakokko et al, 2006) the average intake of organotin compounds from foodstuffs was estimated in a Finnish market basket. The study was conducted by collecting 13 market baskets from supermarkets and market places in the city of Kuopio, eastern Finland. Altogether 115 different food items were bought. In each basket, foodstuffs were mixed in proportion to their consumption and analysed for seven organic tin compounds (mono-, di-, and tributyltin, mono-, di-, and triphenyltin, and dioctyltin). Organotin compounds were detected in only four baskets, with the fish basket containing the largest number of different organotin compounds. OTs were not detected in cereals, peas and nuts, milk and milk products, fats and oils, sugar, juices and soft drinks. On the contrary OTs were quantified in fish and sea foods, potatoes, vegetables and fruits. In potatoes, vegetables and fruits, the predominant compound was MBT at a concentration up to 0.57 ng/g fresh weight. In fish and sea foods, the predominant compounds were TBT, MBT, TPT, DBT and DPT measured at levels up to respectively 2.53, 1.52, 1.11, 0.25 and 0.14 ng/g fresh weight. Overall results of this study are reinsuring and show dietary exposure corresponding to a limited fraction of the Tolerable Daily Intake established by EFSA. However, it should be mentioned that the methodology used in the Finnish study combines average contamination levels with average food consumption and for consumers eating fish from contaminated areas the intake may be much higher. Moreover the exposure assessment is based on an average fish consumption of 39.5 grams per day representing 1.8 % of the total food consumption. High consumers of fish can also be highly exposed to OTs even considering an average level of contamination.	Noted.
A monitoring project (Sternbeck et al, 2006) that analysed fish samples from Swedish waters found higher concentrations than those reported from Finland. The values for fish were nd – 2.8 (DBT), nd – 7.8 (TBT) and 2.2 – 12 (TPT) ng/g fresh weight for background areas. Fish from Stockholm had even higher concentrations and values up to 14 (DBT), 71 (TBT) and 171 (TPT) ng/g fresh weight were measured.	Noted.
Human exposure via the local environment The RPA report identifies high intake of TBT (mainly from wood preservation) and DOT (mainly from PVC processing) via the local environment (Tables 5.1, 5.2 and 5.4). For DOT, however, the picture is complicated by the fact that it may be mainly DOT-EHMA that is emitted and then converted to the chloride in the environment. The daily intake was therefore also predicted for the compounds containing one or two EHMA ligands. DOT-EHMA and DOTC gave a similar result, but the DOT-Cl-EHMA gave three orders of magnitude lower intake. It is then assumed that 80% of the emission is in the form of DOT-Cl-EHMA and 10% each of the other two compounds and the predicted intake is reduced dramatically. This is not in line with the information from industry that approximately 10 to 15% of the DOT-EHMA is reacted in the PVC during processing. It is also mentioned at several places in the report that DOT-Cl-EHMA is effectively degraded to DOTC in the environment, and if that is the case the exposure via the local environment would have been 0.61 µg Sn/kg bw/day.	As acknowledged in the RAR, analysis of DOT emissions from PVC processing is complex. As such, the associated calculations are uncertain and this uncertainty has not been reduced by the 'grass study' (as mentioned above).

SCHER Opinion, Comments and Responses to Questions	Further RPA Comments/Responses
Individual consumers can be exposed to OTC via local environment including crops, vegetables, meat and milk. Such an exposure can occur in the case of food produced at home or of local purchases in rural areas. The French National Institute of Statistics (Bertrand, 1991) described the home production of food as the major component of local consumption and estimated its importance as a function of various food groups and for various populations of consumers. For farmers the consumption of home produced food represents on the average 25 % of the total food consumption (ranging from 0.2 % for bread to 89 % for rabbits) when for non-farmers it represents 9.5 % (0.2 to 66 %) and 4.6 % (0.1 to 36 %) of the total consumption respectively for consumers living or not in a rural area. For the current opinion, considering the worst case assumptions made on the food contamination, assuming the regular consumption of food produced locally to 20 % of the total food consumption seems reasonable.	The assessment presented in the RAR follows the TGD. As such, exposure via the 'local' environment is based on 100% consumption of local produce which is the 'worst case' but is also precautionary. Some PVC processing plants are in rural areas and, without supporting data, there is limited justification for not adopting this precautionary approach.
Consumer exposure assessment PVC is probably one of the most common materials in consumer goods and we are exposed to the additives used in this material via a number of pathways. Some of them have been assessed by RPA and some worst case exposures were calculated. The assessors have made some wide ranging assumptions in this work, but as our knowledge is so limited in this field that is probably the only way to do it.	Agreed and it is worth noting that PVC is the third commonest plastic (after polyethylene and propylene).
The intake via PVC food packaging has been estimated based on a study by Piringer et al. (2005), in which the values for aqueous food simulants in the primary table (µg/dm^2) disappears and are reported as non detects in the following table (µg/kg food) and furthermore the wrong factor seem to have been used for the remaining values. The values used by RPA were for fatty food and those seem to be right (104 and 417% of the TDI for adults and children, respectively, in Table 5.35 in the report). RPA also used a report from CSL (2005) for a refined assessment, which is based on the results of the Piringer (2005) study. Fortunately the original (µg/dm^2) were used, but there are also data on a Simulant A that the SCHER is not able to locate in the original study and one result from Simulant D is tabled as a Simulant B result.	Raw migration data (µg/dm^2) from Fabes (2005) was recalculated using slightly different molecular weight (hence slight differences between the RAR and Fabes)
The RPA report claims that the level of OTs in indoor air is below the detection limit (but there is no reference to either a report or even a value for the limit of detection). Air levels are therefore estimated with loss factors and reduced by a factor of 100 under the assumption that 1% is going to air and 99% to water based on migration measured to air and water, respectively (Piringer et al., 2000). If there is no water present evaporation is the only possible emission pathway, and if the data for emission to air is used, the investigated material would give an adult exposure of about 0.1 µg/kg bw, day of each of DBT and TBT. The ventilation rate used in the example was 0.5 exchanges/h, which probably is too high in many regions. Furthermore, the results presented by Piringer et al. (2000) indicate that it is not the diffusion of the organotin compounds within the PVC matrix that determines the emission rate, but rather the removal from the surface. This is well demonstrated by the relative concentrations of MBT, DBT, TBT and TeBT in the octane, water and air extracts from the same PVC matrix. Thus the calculations of loss factors based on diffusion rates can be questioned. A recent paper (Xu and Little, 2006) also shows that the emissions of semi volatile compounds from polymeric materials are subject to "external" control, e.g. partitioning into the gas phase and the convective mass transfer coefficient.	In fairness, Section 5.2.4 of the RAR states: *There are no data on measured levels of organotins in indoor air (in other words, there are no available direct measurements of organotins in indoor air as the very low concentrations are below the limits of detection).* The 1% factor allows for losses due to abrasion to be in solid form (so air-water partitioning is not relevant). There is no evidence to suggest that the TBT intake due to inhalation alone will be around the TDI (i.e. 0.1 µg/kg bw/day).
The exposure to DBT from the domestic use of silicone moulds is calculated to be close to the TDI, but it is assumed that the catalyst is pure dibutyltin laurate. As the melting point of that compound is over 200^{0}C this is probably used in a solution, and may thus give a lower exposure than that calculated in the report. Another type of silicone moulds could, however, be of interest from the human exposure point of view. This is the moulds used to bake cookies, where the high oven temperature will favour emission both to the cold cookies and the kitchen air. This may thus be a more serious source than the baking papers now being phased out.	Disagree as: 1) DBTL can be bought at 95% concentration in liquid form; and 2) silicone 'bakeware' uses platinum catalysts

SCHER Opinion, Comments and Responses to Questions	Further RPA Comments/Responses
It is surprising that the assessor did not look at the use of OTs in medical devices. There is a debate on the exposure to DEHP from PVC materials, but if OTs are used as stabilisers the emission of those may also constitute a risk. OTs may also be used as catalysts in the production of silicones for medical devices. A couple of breast implants can probably contain a kg of silicone, and if that contains 0.1% OTs it would correspond to 1 gram. An emission factor as low as 0.000007 would thus give a 70 kg person the TDI. Silicones are also used in many other medical devices, such as tubes and bags, and a further look into this should have been done.	There is no evidence to suggest that OTs would be used as catalysts for the low molecular weight polydimethyl siloxanes (PDMSs) used in breast implants or indeed in other medical devices.
The SCHER would also have liked to see some information on the possible levels of catalysts remaining in esters used as plasticizers, e.g. DEHP. That volume may add to the exposures now calculated from the volume used as stabilisers in PVC. Also other esters used for e.g. food packaging may be important exposure pathways for the consumers and should have been included in the assessment.	Noted.
The exposure to DBT and TBT from non-allergenic pillows also has an inhalation component in addition to the dermal route assessed in the report. If the sleeping person is inhaling 10 m3 saturated with TBTC (Vp=1Pa @ 25 C) that would be 100 mL of pure TBTC gas, which is more than 1 g and corresponding to more than 10,000,000% of the TDI. If only 1% of the inhaled air comes from the pillow and it is only saturated to 1% the inhaled dose would still correspond to 1000% of the TDI. This is an application where further studies of the exposure are needed.	Whilst there may be some inhalation, the figures presented are spurious (not least because a pillow contains less than 1g of TBT).
The SCHER recommends that measurements of OTs are included in some future biomonitoring programs in order to get better information on the total body burden of the OTs.	Noted.
Effect assessment The RPA report follows the CSTEE recommendation to use a group TDI for the four OTs based upon the immunotoxicity and assuming that the effect of the compounds are additive. A similar approach has been taken by the EFSA opinion on organotin compounds in foodstuff (EFSA, 2004). The group TDI, corresponding to 0.1 µg Sn/kg bw/day, is assuming the same molecular mechanism of the four compounds and the same potency (per µg Sn), but the mechanism of these compounds has not been investigated in a systematic way. The new RPA report does not give any further information on human health effects of OTs compared to the earlier versions of this report. The SCHER has therefore done a review of the present knowledge to see if there is reason to change the earlier adopted TDI. *[there follows two pages concerning inhalation studies, dermal exposure studies, oral exposure studies, mechanism of immunotoxicity, genotoxicity and reprotoxicity which have not been reproduced here]* These findings have three implications for the risk assessment of OTs. First, they confirm the validity of the currently used TDI value, because they were observed at dose-levels similar with (or even slightly lower than) those causing immunotoxicity after chronic administration, the most sensitive set of endpoints that form the basis of current organotin risk assessment. Therefore, there is no need to adjust the current TDI value. Second, they indicate that in addition to immunotoxicity, also a previously uncharacterized type of toxic effect is possible after exposure to low doses of organotin compounds. Third, they provide scientific justification for the future use of endpoint specific relative potency factors for different organotin compounds.	The RAR followed the Specification (Section 6.1 refers) which dictated use of the group TDI.

SCHER Opinion, Comments and Responses to Questions	Further RPA Comments/Responses
Risk characterisation The comments given above, especially on the exposure assessment also have implications on the risk characterisation. As most of the comments indicate an underestimate of the exposure, the conclusion must be that the risk estimates may not represent realistic worst case situations.	As for comments on exposure assessment above.
3.1 Question 1 **The Scientific Committee on Health and Environmental Risks (SCHER) is invited to comment on whether the recommendations made by the SCTEE in its former opinion on the same topic dated 28 May 2004 have adequately been taken into consideration by RPA.**	
Response to question 1 In the present RPA report on organotin compounds the reaction on the comments from CSTEE on the former report is described in an annex. Generally the comments have been accepted and the present document has been improved compared to the previous version. There are, however, a few points where RPA and the Scientific Committee still disagree.	Agreed.
Freshwater toxicity In the report the availability of data on freshwater molluscs is not mentioned. This information is essential in this case as the freshwater species are also sensitive. It was already observed in the previous CSTEE Opinion that imposex was observed in freshwater gastropods a 125 ng/L of TBT (corresponding to about 40 ng/L as Sn). This figure (not a NOEC but a LOEC) is a little bit lower than those on *Daphnia magna.* On this point, the new report does not give satisfying answers to the criticisms of the previous CSTEE Opinion. Moreover, it is the opinion of the SCHER that recent literature has not been adequately taken into account.	Disagree - see comments above *(Environmental effects)*.
Human exposure As described in the review above the SCHER does not support the reduction of emissions of OTs to indoor air from PVC. The use of the air concentrations measured by Piringer et al. (2000) indicates that the inhaled amounts are much higher than the “worst case” described in the report.	Disagree - see comments above *(Consumer exposure assessment - 3rd para)*
3.2 Question 2 **SCHER is requested to assess whether the 2005 revision of the RPA report has adequately addressed the risks posed by the four organotin compounds TBT, DBT, DOT and TPT, both for human health and the environment. Content from the previous RPA reports carried out from 2002 and 2003 as well as the opinion of the relevant EFSA panels on additives, flavourings and materials in contact with food (AFC) and on contaminants in the food chain (CONTAM) should also be taken into account.**	
Response to question 2 The assessments of several exposure pathways, important for both environmental and human health, have been found to have shortcomings. In most cases it is possible that the estimated exposure does not represent a worst case as it is stated in the report. There are also several additional pathways (such as via moulds for baking, medical devices, via esters (used as e.g. plasticizers) produced with OT catalysts and inhalation of OTs from non-allergenic pillows) that should have seen assessed. SCHER also have comments on some environmental effects that need to be reviewed. The conclusion must be that the risk may be even larger than that described in the RPA report	Disagree - as evidence has not been provided to substantiate these claims.

SCHER Opinion, Comments and Responses to Questions	**Further RPA Comments/Responses**
3.3 Question 3 **SCHER is requested to assess the overall scientific quality of the 2005 revision of the RPA report. SCHER is specifically requested to comment on the methodology and the assumptions used (e.g. exposure and emissions calculations) and on the conclusions given in the report.**	
Response to question 3 The assessment in the RPA report is based on the methodology described in the TGD and is the recommended for risk assessment of chemicals in the EU. A central role is therefore the prediction of both exposure and no-effect concentrations, which is based on properties for the investigated substances. If data for those properties are missing, which is the case for many OTs, there are also ways to estimate several of those. Some of the values for properties essential for exposure assessment, mainly delivered by industry, seem unreliable and thus the assessment will have a high uncertainty. In absence of data the assessor has to make assumptions to be able to do the risk assessment. Some of the disputable assumptions made in the present report have been highlighted in the review above. Examples are ➢ The assumption of the relative amounts of different OTs being produced and emitted; ➢ 80% of the OT emission from manufacturing of PVC products is assumed to be in the form of DOT-Cl-EHMA; ➢ The emission from PVC is assumed to be 1% to air and 99% to water. The basis for the assumptions made to estimate the exposure of the typical consumer (section 6.4 in the RPA report).	All risk assessments are uncertain and involve a degree of judgement. Where assumptions have been made, explanations have been provided in the RAR (as well as in the earlier 2002 and 2003 Reports).
3.4 Question 4 **The SCHER is requested to comment and give an opinion on the health risks to consumers that result from exposure to organotin compounds from the various non-food consumer product sources of exposure, or from environmental sources as reported in the studies (tables 3 and 4 of the executive summary, and on each specific exposure scenario of the 2005 RPA report).**	
Response to question 4 The SCHER supports the group TDI for DBT, TBT, DOT and TPT corresponding to 0.1 µg Sn/kg bw/day. The health risk is therefore determined by the total exposure to substances containing any of these four groups.	No further response.
The exposure is very complex due to the many applications of the OTs, and the wide use of the materials containing them. There are several possible pathways other than those described in the RPA report, e.g. via medical devices and products containing esters produced with organotin catalysts.	Although complex, major pathways have been identified.
In Tables 3 and 4 all results except those for dietary intake are related to point estimates of the exposure. Many of those are based on assumptions and are trying to describe worst case exposures. As have been discussed above some of these assumptions may be questioned and make the estimated exposure considerably lower than real worst cases. Indoor air is an example of an important exposure pathway for the OTs that is underestimated in the RPA report.	Although there are uncertainties, disagree that indoor air has been substantially underestimated.
The Tables 3 and 4 don't give a correct description of the risks connected to the OTs. Many individuals are exposed via several of the pathways described in the Tables and those have to be combined to get the total exposure. This will be addressed further under question 5.	This issue is clearly addressed in the accompanying text (Executive Summary, RAR).

SCHER Opinion, Comments and Responses to Questions	Further RPA Comments/Responses
Some of the sources are classified as "Eliminated", but it has to be remembered that products already in use may be there for a considerable time and will still contribute to the total exposure of the individual. Sources like old wood treatment plants is also known to act as important sources long after the use of a chemical is ceased.	Agreed.
There may also be a couple of pathways that need be added to the list. The exposure from OTs in both silicones (e.g. in medical devices and cookie moulds) and esters (e.g. used as plasticizers) need to be further assessed, as well as the possible inhalation exposure from non-allergenic pillows.	As previous comments.
3.5 Question 5 **In collaboration with the EFSA panels and taking into account the exposures of humans to organotin materials from foods, food contact materials, and non-foods as presented in the RPA reports and EFSA panel opinions, the SCHER is requested to assess and quantify (if possible) the total integrated (food and non-food) risks of humans from organotin compounds. SCHER is in particular requested:** **5A - to comment, on whether conclusion (ii*) risk sources should be considered separately (on an exposure by exposure case basis) to estimate the real level of risk to adults and children, or whether conclusion (ii*) risks sources should be considered collectively, taking into consideration the fact that TBT, DBT, DOT and TPT shall be viewed as additive both for the target organs and for the mode of actions.**	
Response to question 5A The SCHER is of the opinion that it is the total exposure that should be used in the risk assessment. That includes all identified pathways also those estimated to contribute with less than 20% of the TDI. The consumer risks estimated in section 6.2 for the different exposure pathways are regarded as worst cases and the probability that one person experiences worst case situations via all pathways on a long term basis is very small (see further under 5B)	Agreed
5B - If the answer to 5A is that risk (ii*) sources should be considered collectively: SCHER is requested to comment on whether it is realistic to conclude that the risks for 25% of adults and 70% of children are likely to exceed 100% group TDI taking into consideration that it is likely that a consumer will be exposed to more than one exposure route i.e. that a consumer may be exposed to several conclusion (ii*) risks sources.	
Response to question 5B It is obvious that consumers are exposed to OTs via more than one pathway. The use of probabilistic methods would be a way to estimate the overall risk, but to do that a lot of information on use pattern and concentration distributions would be needed. This information is only available for the dietary intakes, and not easy to obtain for the other pathways. The RPA assessor therefore assumed, without presenting the motivations in the report, intake distributions by setting the ratio between median and high. It is also unclear how the fact that only a rather limited part of the population is exposed to the local environmental levels has been dealt with. In the RPA report the description of the whole process would need to be more detailed. SCHER believes that the most important exposure pathways are food, indoor air, household dust and via dermal contact with different polymer materials. A large fraction of the population is exposed via several of the following pathways: ➢ EFSA (2004) assessed the OTs in food and concluded that fish and seafood give about 7% of the TDI based on median concentrations and about 33% based on the mean concentrations. For high consumers the corresponding fractions were 15 and 70%, respectively. The EFSA opinion does not say anything about children, but as they consume more per kg bw (a factor of four is used in the RPA report, a factor of three suggested in this opinion) it can be assumed that	Clearly, evaluating OT exposures across all pathways across the EU is complex. The purpose of analysis presented in Section 6.4 was to illustrate that by using various simplifying assumptions, it is possible to generate meaningful probabilistic estimates of the overall exposure. Such estimates rely, in turn, on identifying exposure pathways and associated (ranges of) exposures. As illustrated in the SCHER response, there are uncertainties associated with some of the identified ranges of exposure. However, it is

SCHER Opinion, Comments and Responses to Questions	Further RPA Comments/Responses
some children's dietary intake exceeds the TDI. ➢ The indoor air levels were in the RPA report calculated for a room with both floor and walls covered with PVC, but the ventilation rate was rather high, and it may therefore be regarded as a realistic worst case. It was also assumed that the persons stayed 24h/d in the room; 12h/d may make it even more realistic. The 99% reduction of the OT emission is not appropriate and the air concentrations may thus be up to 100 times higher. That would give exposure to 600% of the TDI for an adult and 1500% for a child, and there is an obvious need for further measurements. ➢ The RPA estimate of the exposure to OTs via dust is based on a 200 mg/d intake and on maximum reported concentrations. Dust intake data in the literature span over a wide range, and 200 mg seems reasonable for children, while it is probably lower for adults. The use of maximum concentrations is justified by the fact that several samples were pooled. A reasonable conclusion would be that adults are exposed to less than 10% of the ADI via dust, while children may be in the region of 100%. The uncertainty of this estimate is high due to both the limited information on dust intakes and the bioavailability of the OTs. ➢ The dermal exposure pathways (T-shirts, gloves, sandals, hygiene products etc.) have to be assessed based on default values for the uptake fractions. Values between 10 and 100% are normally used and the 10% chosen by RPA can be supported by the SCHER. The different pathways contribute, according to the RPA report, each with up to 62% for adults and 189% of the TDI for children. In the SCHER review of the RPA report above a number of further possibly very important OTs exposure pathways have been identified. Massive doses of OTs may be obtained from medical devices of PVC and silicones, as well as inhalation of the vapours from anti-allergenic pillows. SCHER concludes that the probability for an individual of the general population, especially a child, to exceed the TDI for OTs is high, and that some people may be exposed to doses much higher than the TDI. People living in regions where industries are producing or using OTs may also get an extra high exposure via locally produced food. The highest value in the RPA report is describing the situation around a timber treatment plant. Assuming this will be decreased in the future the major source would be the processing of stabilised PVC. As there is no support for the assumption that 80% of that emission is as DOT-Cl-EHMA, a worst case has to be calculated as if the total emission is DOT-EHMA. This corresponds to 0.73 µg Sn/kg bw/day from locally produced food. An assumption that only 20% of the food is locally produced will reduce this to 0.15 µg Sn/kg bw/day which is 150% of the TDI for an adult. In view of the physico-chemical characteristics of the organotin compounds the model EUSES2 is not fully applicable as the log Kow is outside the valid range. In addition EUSES2 is not able to handle ionisable substances correctly. Therefore the results calculated with EUSES2 should be interpreted with great care. The recent measurements (de Wolf, 2006) also indicate that the intake via locally produced food may be overestimated.	important to note that where SCHER considers that some exposure pathways have been neglected (medical devices, etc), no supporting evidence has been put provided. However, even allowing for such uncertainties, there appears to be a consensus that OT exposures will exceed the TDI for significant numbers of adults and children in the EU.
5C - SCHER is requested to comment whether it is realistic to conclude that, even if a consumer is exposed to several conclusion (ii) risks sources (< 20% TDI), the corresponding risks from these conclusion (ii) sources combined would be below 100 % TDI (for a group TDI both for adult and children), and therefore lead to a negligible risk.	
Response to question 5C If the total exposure exceeds the TDI there is reason for concern regardless of whether this exposure comes via one or a large number of pathways. The uncertainty of the exposure assessment will be larger if many pathways are involved, but as the amount of data available for the assessment of exposure to OTs is very limited it is very difficult also to estimate the uncertainty in those exposure predictions	No further response.

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3.6 Question 6 **In preparing this integrated assessment, the SCHER is requested to comment as to whether the total ban of organotin compounds in anti-fouling paint (2003), and the ban of the presence of these compounds in EU waters by 2008 will, by itself, reduce the risks (from a conclusion (iii) to (ii)) associated with the consumption of fish/seafood contaminated with the organotin compounds under consideration within a reasonably short period? Should other organotin compounds be taken into consideration when considering the possible establishment of a maximum threshold limit concentration in fish?**	
Response to question 6 The major source of OTs in the marine environment is antifouling paints. Additionally these substances may be used as antifouling agents is the application in cooling-water pipes for electric power plants or industries (UNEP, 1989). This use is not taken into account in the RPA report and is not included in Regulation EC 782/2003, but seems to be regulated by Directive 2002/62/EC, even if this Directive is not very explicit to this specific use. Moreover, this use will in the future be regulated by the biocides directive 98/8/EC once it fully enters into effect. Finally, for this kind of use, treatment with chlorine is usually preferred. Thus emissions due to cleaning of cooling-water pipes do not seem to be of high concern.	The RAR acknowledges that TBT (in particular) has been used in cooling water pipes (Section 2.4.3 refers).
At present no recent data are available to assess the effects of the total ban of organotin compounds in anti-fouling paint. A French survey, performed in 1999 along the coasts of Corsica, demonstrates concentrations of high concern for TBT and DBT, not only in harbours and marinas, but also in two Natural Reserves (Michel et al., 2001). The authors underline that, although past measures were effective in reducing organotin concentrations, they were not sufficient for a complete solution of the problem. More recent data for the same sites are not available. A survey on shellfish in 2004 along the coasts of England (Vazquez, 2005) indicates a large variability of total concentrations of OTs in molluscs. Maximum concentrations may indicate a potential risk for high consumers, but as no data are reported for the past it is not possible to evaluate the temporal trend. A Swedish study (Tesfalidet, 2004) reports data on water, sediments and biota from selected sampling sites at the Swedish west coast. Water samples were collected in 2001-02 (before the total ban) and in some cases a comparison with data from 1987 is possible, indicating a concentration decrease of more than two orders of magnitude. The use of TBT on boats shorter than 25 m was banned in Sweden 1989. On the other hand, a recent monitoring project found high concentrations of TBT in fish from Stockholm area and even higher (around 0.1 µg/g ww) of TPT (Sternbeck, 2006). In a recent OSPAR document (OSPAR, 2005a) the results of some studies performed in Denmark, Norway and UK are reported. The studies measured the content of TBT and the occurrence of sexual disorder (imposex/intersex) in different mollusc species. In all studies a large spatial variability was recorded, with levels of concern, mainly in the proximity of harbours. The UK study covers all national shoreline during a period from early 1990s up to 2003. In spite of the extension of the survey, the results cannot be used to assess a temporal trend, since different areas were sampled in different years. The Norwegian study is less extensive but more systematic, covering 9 stations from 1997 to 2003, but does not show a statistically significant trend. In the Danish study a statistically significant decrease from 1998 to 2003 was observed in a few sampling stations (3 of 25). All studies were performed before the total TBT ban. Experimental evidence seems to indicate that control measures before the total ban have been effective in reducing OTs concentrations in the marine environment, at least in some European coastal areas, but situations of concern were still present before 2003. The few data available need to be confirmed with more information. As a consequence of the total ban in 2003, emissions have not been immediately reduced. Emissions from ships painted before the ban will continue for some time.	Whilst it is accepted that comprehensive temporal/spatial datasets for individual OTs do not exist, the commentary provided by SCHER supports the general arguments presented in the RAR for butylins (Section 3.7.3 refers) and phenyltins (Section 3.7.4 refers) that measured levels are declining.

SCHER Opinion, Comments and Responses to Questions	Further RPA Comments/Responses
Daily OTs emissions from painted ships are initially in the order of some µg/cm^2. A large ship (hull area 6900 m2) would then release around 2-300 g TBT per day, but the leaching rate is rapidly decreasing with time (UNEP, 1989; EC, 1998). Most OTs are accumulated in sediments. The degradation rate and pathways in sediments is still controversial. Values used in the RPA report (that need to be supported by more information) indicate half-lives in the range 120-150 days for DBT, TBT, DOT and TPT. From a rough calculation, it derives that reduction will be of about one order of magnitude in a couple of years. This should indicate that, if emissions will be reduced and stopped in a relatively short time, sediment cleaning will occur in a few years. Michel and Averty (1999) hypothesize that in oligotrophic sediments of open coastal areas, the half-lives may be substantially higher, so the cleaning time for indirectly polluted sites could be longer. This process will be improved and accelerated by the cleaning of harbour sediments. Most OTs have bio-concentration and bio-magnification potential. Nevertheless, if exposure stops, complete clearance will take place in a reasonably short time (Laughlin et al., 1986a). More experimental evidence is however needed to quantify the length of the period and to better describe differences in clearance patterns in harbours and in open coasts. The SCHER therefore fully support the need for regular monitoring performed according with suitable protocols. The guidelines proposed by OSPAR (OSPAR, 2005b) are perfectly adequate to this goal. The data on toxicity of other organotin compounds is relatively sparse and described in the answer to Question 8.	
3.7 Question 7 **SCHER is requested to comment on whether risk conclusion (iii) predicted for child consumers due to organotin-based fish products intake > 100 % TDI is reliable, both at local, regional and continental levels.**	
Response to question 7 The SCHER is not aware of any facts that reduce the estimated dietary intake of OTs for children. Possible reasons for lower exposure could include that children eat other fish species or less shellfish than adults, but it has not been possible to find data to support that this is the case. The opinions from EFSA have triggered further studies in member states and more information on dietary intake of OTs can be expected in the near future. The SCHER also again underlines the importance to assess the total exposure to describe the risk connected to OTs, and taking that into account the number of children at risk may be considerably higher.	No further response.
3.8 Question 8 **SCHER is requested to comment on whether significant additional risk may be posed to consumers and environment by the additional exposure to organotin compounds such as MBTO, DBTO, etc in addition to the targeted group TBT, DBT, DOT and TPT.**	
Response to question 8 The data on the toxicity of mono- and dibutyltin oxide are limited and only few studies addressing the toxicity of these compounds have been located. Unfortunately, none of these studies investigates endpoints related to the major health effects of tributyl tins (immunotoxicity) in detail. However, since alkyl tin oxides are rapidly transformed to the respective alkyltin chlorides in the human stomach, data on the different alkyltin species may be used for an assessment. Monobutyltin has limited application and the toxicology data are scarce, indicating low toxicity, and an oral LD50 in rats of 2140 mg/kg bw has been reported (HSDB, 2006). In a comparative toxicity study in rats using TBTC, DBTC, and MBTC no effect on body weight and relative organ weights of thymus, spleen, liver	The human health effects have been previously examined in some detail - see 2002 Report and subsequent 2003 CSTEE Opinion. SCHER comments appear to confirm that the focus should remain firmly on TBT, DBT, DOT and

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and adrenals were noted when a single oral dose of 180 mg/kg bw was applied, while toxic effects, notably thymus atrophy, was seen from 10 mg TBTC and 5 mg DBTC onwards (Snoeij 1987). Therefore the contribution of MBT which occurs mainly as a metabolite of TBT and DBT is considered of no importance when the group TDI is considered. MOT stabilisers are normally used as a mixture with DOT. This mixture causes thymus atrophy but further research has pointed out that this was exclusively due to DOT. For DOT a group TDI of 0.6 µg Sn/kg bw was established, for MOT 20 µg Sn/kg BW (SCF, 1999). Target organ for MOT is the kidney, and the effect appears at much higher doses. Dibutyltin oxide caused reproductive toxicity (craniofacial and musculoskeletal abnormalities) when given in a single dose of approx. 20 mg/kg bw on day 8 of pregnancy. Moreover, other studies have also shown embryo-toxicity of dibutyltins in dose ranges > 10 mg/kg bw/day when administered during pregnancy. There also seems to be a 90-day oral study with a NOAEL of 2 mg/kg (no further information on effects). In vitro, dialkyltins have been shown to be as or even more potent regarding induction of cell death as compared to trialkyltins. Regarding the mode of action for toxicity responsible for cell death and ensuing toxicities (specific interactions of organotin compounds with sulhydryl containing proteins of the plasma membrane and the cytoskeleton), dialkyltins also have a high affinity binding site at the plasma membrane of cells. A high reactivity of DBTO with SH-containing proteins is also supported by chemistry of this compound. Dialkyltin oxide is present as an oligomer and retains a high reactivity with SH-groups. Based on these considerations, DBTO may have a similar potency as compared to tributyltins in vivo and the SCHER therefore recommends including dibutyltin oxide in the risk assessment approach and the group TDI. Regarding MBTO, results from a 90-day oral study suggest that this compound has a lower potential for toxicity with a NOAEL of 96 mg/kg bw/day based on effects on the liver (immunotoxicity unknown). MBTC also seems to have a lower potential for reproductive toxicity since administration of up to 685 mg/kg bw of that compound during pregnancy and up to post natal day 4 did not cause effects. As a general observation, monoalkyl tins have a lower potential for toxicity as compared to di- and trialkyltins. For example, MBTO, in a developmental neurotoxicity study using maternal doses of up to 25, respectively 94 mg/kg bw per day (with drinking water) during gestation and lactation did not induce developmental neurotoxicity. However, monomethyltin oxide caused a low incidence of specific brain lesions in the high dose off-spring, but the available data are too limited to make a conclusion regarding inclusion into the group TDI. Neurotoxicity is an endpoint of toxicological relevance for OTs. The best-known organotin compounds with neurotoxic potential are trimethyltin and triethyltin, but also TBT and TPT have been shown to be neurotoxic. Recent studies have identified DBT as a relatively potent developmental neurotoxicant in rats (Jenkins et al., 2004). In addition, monomethyltin was shown to induce vacuolization in cerebral cortex of rats (Moser et al., 2006). Due to lack of systematic *in vivo* data the significance of neurotoxicity for organotin risk assessment remains uncertain, but based on available data neurotoxicity is not likely to be the critical endpoint for setting organotin TDI, because neurotoxic effects are observed at higher dose levels than immunotoxicity. Due to differences in the mechanisms of neurotoxicity among different organotin compounds there seem to be no scientific basis for using a group TDI for this endpoint.	TPT.

SCHER Opinion, Comments and Responses to Questions	**Further RPA Comments/Responses**
3.9 Question 9 **SCHER is requested to give its opinion on whether emission of the targeted group TBT, DBT, DOT from plant processing and recycling PVC (flexible and rigid) or at landfill pose a significant risk for adults or children via environment, at local, regional or continental levels.**	
Response to question 9 The outcome of the RPA assessment indicates that the local environment around industries producing and using OTs is exposed to levels that make human intake exceeds the TDI. This result is also produced under an assumption that 50% of the produced/used OTs are mono-alkylated which is not proven, and the actual exposure could be even higher. However, the uncertainties in the exposure assessment are considerable, mainly due to uncertainties in the data for the properties of the compounds. The regional and continental levels of these substances are mainly influenced by more diffuse sources.	The 50:50 split between mono- and di-substituted tins is not an assumption but is based on advice from industry dating back to 2002. Obviously, this factor has been a central feature of the analyses presented in the 2002 and 2003 Reports as well as in the RAR.
Regarding recycling of PVC the information available to the SCHER is limited, but it is assumed that the processing of the recycled material is similar to that of new PVC. If that is the case the similar human exposure can be expected from both types of industries, and it is also expected that some industries are using both new and recycled PVC. Most landfills in Europe receive a mixture of solid waste of different origin. Common are the deposit of household waste, commercial waste, construction and demolition waste and in the 70-ties and 80-ties of the last century sometimes sewage sludge and hazardous wastes. Some PVC products contain organotin compounds as stabilizers. In particular mono– and dioctyltin compounds can be assumed to originate from PVC products (Mersiowsky et al. 1999). Methyl– and butyltin compounds may also emanate from a number of other sources put onto the landfill. An X-ray survey of waste material show that PVC articles contained tin and/or lead and tin levels up to 0.68 % were found (Bilitewski, personal communication). TBT is used as a biocide in water based vanishes (amount unknown) and heavy textiles like tents and lorries (only until 1999 in Germany), disinfectants, wood fungicides (only until 1990 in Germany) and other preservations like silicon for the sanitary area (until 1999 in Germany) and roof linings (until 1994 in Germany).	No further response

<table>
<tr><th>SCHER Opinion, Comments and Responses to Questions</th><th>Further RPA Comments/Responses</th></tr>
<tr><td>Another relevant source of OT compounds is sewage sludge and Table 1 gives some examples of data levels found in Germany. Kuballa et al. (1998) indicated 100 mg/kg dw to be a conservative estimate of the contents of organotin compounds.
<table>
<tr><th>Organotin</th><th>No. of samples</th><th>Minimum</th><th>Average</th><th>Median</th><th>90percentile</th><th>Maximum</th></tr>
<tr><td>Dibutyltin</td><td>156</td><td>0.008</td><td>0.22</td><td>0.13</td><td>0.35</td><td>4.8</td></tr>
<tr><td>Dioctyltin</td><td>156</td><td>0.0025</td><td>0.056</td><td>0.021</td><td>0.05</td><td>3.0</td></tr>
<tr><td>Monobutyltin</td><td>156</td><td>0.009</td><td>0.17</td><td>0.12</td><td>0.32</td><td>2.7</td></tr>
<tr><td>Monooctyltin</td><td>156</td><td>0.0025</td><td>0.031</td><td>0.019</td><td>0.043</td><td>1.3</td></tr>
<tr><td>Tetrabutyltin</td><td>156</td><td>0.0025</td><td>0.0067</td><td>0.0025</td><td>0.0025</td><td>0.4</td></tr>
<tr><td>Tributyltin</td><td>156</td><td>0.0025</td><td>0.033</td><td>0.027</td><td>0.065</td><td>0.3</td></tr>
</table>
Table 1: Concentration (mg/kg dw) of OTs in sewage sludge from North Rhein-Westfalia in Germany (MUNLV 2005).</td><td>The same German data were also presented in the RAR (Table 3.48 refers).</td></tr>
<tr><td>The possible fate of organotin compounds in landfills has been summarized by Mersiowsky et al. (2001). The OTs may be retained in the solid waste matrix, either being included in e.g. rigid PVC products or being adsorbed on organic matrix surfaces. Parts of the substances are transported in the leachate, either as solute or adsorbed to colloids or suspended solids. The relative relevance of the latter route seems to be comparatively low. A third possibility is that the compounds may be volatilized into the landfill gas. A screening investigation of the occurrence of OTs in leachate samples of landfills from Sweden, Germany and Italy indicate that monobutyltin is the most widely detectable species. Findings of all target compounds (MMT, DMT, MBT, DBT, TBT, MOT and DOT) range between not detectable (< 0.1 mg/L) and maximum levels of 1 mg/L (2-4 mg/L in the case of MBT and MOT) (Mersiowsky et al. 2001). The high levels of monobutyl– and monooctyltin were found in a German landfill with fresh not older than 2 years material. Landfills undergo a pH value drop in the first 1 to 2 years, so this might be a possible explanation of the high values. The highest value of TBT (0.9 µg/L) was found in a sample in Germany of an old already closed landfill (Mersiowsky et al. 2001).</td><td>The work of Mersiowsky et al was reported not only in the RAR but also in the 2002 and 2003 Reports.</td></tr>
</table>

<table>
<tr><th>SCHER Opinion, Comments and Responses to Questions</th><th>Further RPA Comments/Responses</th></tr>
<tr><td>
<p>Sanjay et al. (2005) reported about the identification and quantification of alkylated tin compounds in landfill gas from three landfills in Germany and one in Scotland.</p>
<table>
<tr><th>Landfill</th><th>A</th><th>B</th><th>C</th><th>D</th></tr>
<tr><td></td><td colspan="4">μg Sn/m^3</td></tr>
<tr><td>Me_4Sn</td><td>1050</td><td>12.6</td><td>14.8</td><td>14-17</td></tr>
<tr><td>$BuSnH_3$</td><td>0.06</td><td>0.06</td><td>N.d.</td><td>N.d.</td></tr>
<tr><td>$EtSnMe_3$</td><td>55</td><td>1.1</td><td>1.2</td><td>0.89</td></tr>
<tr><td>Et_2Me_2Sn</td><td>13</td><td>0.45</td><td>0.50</td><td>0.20</td></tr>
<tr><td>n-$PrSnMe_3$</td><td>117</td><td>2.8</td><td>1.1</td><td>0.21</td></tr>
</table>
<p>Table 2: Concentrations (μg Sn/m^3) of selected OTs in landfill gas (Sanjay et al. 2005)</p>
<p>The concentrations of the different tin species were two orders of magnitude higher in one landfill than in the other three studied sites. The relative species distribution is however site independent indicating that this formation is a general process (Sanjay 2005). So far sources of airborne organotin compounds have not been established, but Feldmann (2003) also reported that landfill gas contains volatile tin compounds in concentrations up to 100 μg Sn/m^3. A cubic meter of waste gives about 240 m3 gas emissions, containing some 10 to 100 mg of volatile OTs. The fate and effect of these substances are not known to the SCHER.</p>
</td><td>Noted but published after submission of the draft RAR.</td></tr>
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