

RIVM - Dutch National Institute for Public Health and the Environment

Analysis of alternatives for a group of phthalates

Final Report



AMEC Environment & Infrastructure UK Limited

December 2013

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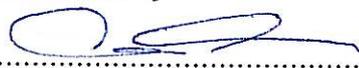
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1. Introduction

1.1 Purpose of this Report

The aim of this project is to provide a broad review of non (or low)-risk alternatives to a group of phthalates (those that are currently included in REACH Annex XIV or on the Candidate list) in various applications. In order to carry this out, a set of criteria are developed to identify and assess some of the most relevant applications, for which an analysis of alternatives is performed in terms of risks, technical and economic feasibility, suitability, availability and timing of substitution. The outputs of this analysis will be used as input to RIVM's considerations in the context of the RAC and SEAC opinion development on applications for authorisation for the phthalates.

1.2 Background

Four phthalates are currently included in Annex XIV of the REACH Regulation:

- Bis-2-ethylhexyl phthalate (DEHP);
- Benzyl butyl phthalate (BBP);
- Dibutyl phthalate (DBP); and
- Diisobutyl phthalate (DIBP).

In addition to this, four phthalates are currently on the Candidate List of Substances of Very High Concern for Authorisation:

- Dipentyl phthalate (DPP);
- N-pentyl-isopentylphthalate;
- Diisopentylphthalate (DIPP); and
- Bis(2-methoxyethyl) phthalate.

For the four phthalates included in Annex XIV, authorisation will be required in order for downstream users to continue to use them beyond the sunset date, which is 21 February 2015 for these substances. Companies wishing to do this had to apply for authorisation by 21 August 2013, 18 months before the sunset date.

Once the application is submitted, ECHA's Risk Assessment Committee (RAC) and Socio-Economic Assessment Committee (SEAC) consider the application and prepare draft opinions on it. During this process, a public consultation also takes place for interested parties to express their opinion. Once RAC and SEAC's draft opinions are set, the applicant has an opportunity to comment before the final opinions are adopted. These final opinions then feed into a Commission Decision, published in the Official Journal.

Whichever route to authorisation is taken (adequate control route or SEA route), it will be important to include all of the key elements, including information on substance uses, chemical safety assessment, analysis of alternatives and socio-economic analysis.

In this context, the overall aim of the study is to produce a detailed analysis of a selection of six alternatives to the phthalates in Annex XIV and on the Candidate List for six selected applications. The results of this study are provided in a way that will allow them to be readily used in reviewing applications for authorisation for the phthalates, with explicit consideration and analysis of risks, technical and economic feasibility, suitability, availability and timing of substitution, and existing R&D activities.

1.3 Approach

The invitation to tender (ITT) specifies the following tasks to be undertaken:

- Investigation of relevant applications for the phthalates: Preparation of a long list of alternatives, to include a variation of soft plastic applications (e.g. use in blood bags, electricity cables and inflatable items) and the use of phthalates as or in solvents;
- Selection of most relevant applications: Selection of the six most relevant applications from the long-list, based on selection criteria to be determined as part of the study. The selection criteria should include the extent to which industry assesses the use as crucial (i.e. with few technical and/or economic alternatives);
- Investigation of available alternatives: Investigation of alternatives per phthalate and per application, including non-phthalate substance alternatives, plastic material alternatives (including bio-based plastics), and non-plastic material alternatives;
- Selection of six of the most relevant alternatives: Selection six of the most relevant alternatives, based on criteria to be determined as part of the study. The six alternatives should together cover at least six of the selected uses; and
- Analysis of alternatives: Analysis of the selected alternatives in terms of risks, technical and economic feasibility, suitability, availability, timing of substitution and existing R&D activities. The ITT specifically highlights the evaluation of the technical feasibility of the alternatives as a particularly important aspect of the study.

In addition to this, the ITT highlights the importance of industry consultation in the assessment of alternatives.

On this basis, the key tasks that were proposed and agreed were:

- Task 1: kick-off meeting, to agree the overall scope of the study;
- Task 2: initial literature review, to produce long lists of applications (along with initial assessment for criticality) and then of alternatives for the selected applications;

- Task 3: selection of applications and alternatives, based on agreed criteria;
- Task 4: consultation, to further develop understanding relating to the applications and the selected alternatives, as well as address any identified information gaps if possible; and
- Task 5: analysis of alternatives and reporting.

Of these, it was agreed at project inception that the consultation (Task 4) would be particularly important in terms of gathering new information that might enable a critical analysis of the applications for Authorisation that would be received in due course. However, since the stated focus of the consultation was to gather additional information to that likely to be included in applications for Authorisation, it was also agreed that likely Authorisation applicants would *not* be contacted. Instead, the study team decided to focus consultation efforts on the following types of potential consultees:

- Downstream users for the selected applications;
- Upstream suppliers of alternative substances/products in those applications;
- Companies where substitution had already taken place.

More details concerning the approach to consultation for each selected application/alternative are given in the relevant application-specific sections below.

1.4 Report Structure

In line with the above, the report structure is as follows:

- Section 2 presents the information found on the phthalates and their applications based on an initial review;
- On this basis, Section 3 presents the application selection process;
- This is followed in Section 4 by an overview of the alternatives available in these applications, along with a presentation of the alternative selection process;
- Section 5-10 present the detailed analysis of alternatives for the six selected applications, specifically:
 - Section 5: Aero engine fan blades;
 - Section 6: Propellants;
 - Section 7: Indoor wires and cables;
 - Section 8: Maleic anhydride;
 - Section 9: Polypropylene catalysts; and

- Section 10: Ceramic sheets and printing pastes in the automotive industry.
- Section 11 presents the overall conclusions of the study, especially with regards to the overall Authorisation process and what lessons might be learned for stakeholders wishing to actively prepare for and participate in the public consultations for specific applications for Authorisation.

Note that the above applications were selected without detailed knowledge of what uses would be applied for in the authorisation applications, so the above list does not correlate directly with uses that have been applied for in 2013.

2. Phthalates and their Applications

2.1 Overview

The phthalates considered for the study are the four phthalates currently included in Annex XIV of the REACH Regulation (DEHP, BBP, DBP and DIBP), as well as the four phthalates currently on the Candidate List of Substances of Very High Concern for Authorisation (DPP, DIPP, N-pentyl-isopentylphthalate and Bis(2-methoxyethyl) phthalate).

The main use of these phthalate is as plasticisers, mainly in PVC. According to Denmark's Annex XV Restriction Dossier for the four Annex XIV phthalates [1], 94% of the four phthalates contained in articles is in PVC applications. Other general use categories include use as solvents; in insecticides; as antifoam agents; textile fibre lubricants; fragrance fixative; insect repellent, as well as in rubber cements [79]. For the purposes of this study, three main use categories are identified and used:

- Plasticiser uses, which may be further split into PVC plasticiser uses and non-PVC plasticiser uses (the distinction is made because PVC plasticiser uses are so much more common than non-PVC uses – as described above – and typically have greater levels of potential exposure associated with them – see below);
- Solvent uses; and
- Other uses.

In terms of potential exposure, for these use types, the following may be noted:

- Plasticiser PVC is the greatest use in terms of quantities, and hence in terms of number of people potentially exposed to the phthalates. There is potential for worker exposure during use of the phthalates and also for consumer exposure during e.g. use of articles;
- There are other uses where consumers might be exposed e.g. paints and varnishes;
- Many of the uses covered in this study are very 'niche' uses where the extent of use is small and so the number of people / extent of environmental releases is relatively small; and
- Some of the uses studied are purely industrial uses (e.g. in the manufacturing of maleic anhydride) and there probably exists much lower potential for exposure in such uses.

In order to identify the phthalate applications that might be the most critical (and hence likely to be applied for in authorisations), a literature review was carried out, and a phthalate-application 'mapping' produced. In this, every mention of a particular application for a given phthalate was noted in a single table, thus allowing for a visual representation of which are the applications that are cited the most often. This is presented in Table 2.1. Each reference is presented in square brackets, with the number referencing to the literature listed in Appendix A.

Table 2.1 Phthalate-application mapping carried out from literature review

	Annex XIV phthalates				Candidate list phthalates			
	DEHP	BBP	DBP	DIBP	DPP	N-pentyl-isopentylphthalate	DIPP	Bis(2-methoxyethyl) phthalate
Plasticiser uses								
Blood bags	Y [13] [15] [16]							
Packaging for medical material	[53]	[50] [51]	[52]					
Other soft plastic medical devices	Y [5] [9] [10] [11] [13] [14] [16] [18]		Y [16]					
Electricity cables	Y [5] [38]		Y [38]					
Inflatable items	Y [1]							
Interiors of cars, trains, ships, boats, aircrafts etc	Y [5] [11] [14] [15]	Y [15]						
Flooring and wall covering	Y [1] [3] [5] [9] [10] [11] [14] [15] [16] [18] [53]	Y [1] [3] [6] [15] [16] [50]	Y [1] [3] [7]	Y [1] [3]				
Insulation on wires used indoors	Y [1] [3] [38] [53]		P [1] [38]					
Insulation on cables used indoors in unsealed applications	Y [1] [5] [10] [18]							
Electric and electronic equipment	Y [1] [3] [5] [10] [14] [34] [38]	Y[34]	Y [1] [3][34] [38]	Y[34]				
Coated fabric and film/sheets used for furniture	Y [5] [11] [15] [53]		Y [15]					
Coated fabric and film/sheets used for bags and briefcases/suitcases and similar items	Y [1] [2] [3] [5] [9] [14] [18]	Y [1] [3] [6]	M [1] [3]	M [1] [3]				

	Annex XIV phthalates				Candidate list phthalates			
	DEHP	BBP	DBP	DIBP	DPP	N-pentyl-isopentylphthalate	DIPP	Bis(2-methoxyethyl) phthalate
Coated fabrics and film/sheets used for tablecloth, curtains, shower curtains and similar items	Y [1] [2] [3] [5] [14] [18]		M [1] [3]	M [1] [3]				
Carpet tiles/squares produced with foam as back cover	Y [14]							
Water mattresses and air mattresses	Y [1] [3] [5] [14]			Y [1] [3]				
Wallpaper/tapestry	Y [5] M [1] [3]		M [1] [3]	M [1] [3]				
Footwear	Y [1] [2] [3] [5] [9] [10] [11] [14] [15]	Y [6] M [1] [3]	Y [1] [2] [3]	Y [2]				
Textiles	Y [14] [15] [35] [36] [37] [53]	Y [6] [35] [37] [50]	Y [15] [35] [36] [37]					
Bathing equipment (swim jackets, wings, belts and pools - inflatable and others)	Y [1] [2] [3] [14]							
Erasers	Y [1] [2] [3]							
Balance balls for playing (not toys) and physical exercises	Y [1] [2] [3] [14]			Y [1] [2] [3]				
Sex toys	Y [1] [2] [5] [14]							
Garden hoses	Y [1] [5] [11] [14] [53]		Y [7]					
Insulation on wires and cables used outdoors	Y [5] [11] [18]							
Roofing material	Y [5] [11] [18] [53]							

	Annex XIV phthalates				Candidate list phthalates			
	DEHP	BBP	DBP	DIBP	DPP	N-pentyl-isopentylphthalate	DIPP	Bis(2-methoxyethyl) phthalate
Car undercoating	Y [5] [10] [11] [18]							
Food packaging	Y [10]		Y [15]	Y [17] (as for 2007)				
Plastic pipes	Y [11]							
Plasticiser in PVC or other uses (unspecified)					Y [27] (plasticiser in PVC)		Y [25] (plasticiser in various uses)	
Solvent uses								
General solvent use	Y [31]		Y [7] [65]					
Lacquers, paints and inks	Y [1] [3] [5] [10] [11] [14] [18] [53]	Y [6] [50] [51]	Y [7] [15]				Y [25]	
Adhesives & sealants	Y [5] [10] [11] [14] [31] [18] [53]	Y [6] [15] [50]	Y [7] [15]				Y [25]	
Immersion oil for microscopy		Y [39]						
Absorption oil in the manufacture of maleic anhydride (MAN)			Y [45] [46] [49] [58]					
Other uses								
Ceramic sheets and printing pastes for the automotive industry	[5] [10] [11] [14] [65]	[67]	[65] [66] [67]					
Propellants / explosives (ammunition)			Y [25] [52] [58] [65] [75] [78]		Y [27] (gunpowder)		Y [25]	
Catalyst in the production of polypropylene (PP)	[60]		[52] [58] [60] [59] [62]	[60]				

	Annex XIV phthalates				Candidate list phthalates			
	DEHP	BBP	DBP	DIBP	DPP	N-pentyl-isopentylphthalate	DIPP	Bis(2-methoxyethyl) phthalate
Analytical standard for test and measurement instruments	[53]		[52] [58]					
Reagent in the manufacture of medicinal products and active pharmaceutical substances	[53]		[52]					
Pressure transmitters for nuclear safety			[58]					

While the table above gives an overview of the identified phthalate applications, the sub-sections below relate the quantities of each phthalate that are known to be used in the major applications.

2.2 DEHP Major Application Quantities

The table below summarises the quantities of DEHP used in different end products based on data for 2007. Note that these data relate to a time prior to prioritisation of the substance for authorisation, meaning that recent shifts away from use of the substance are not taken into account.

Table 2.2 Estimated DEHP tonnage in end-products marketed in the EU based on EU manufacture, import, export data in 2007

End-product use area	Tonnage, t/y				% of total use
	EU Manufacture	Import	Export	End-product use	
Indoor uses:					
Flooring	33,000	2,000	4,800	30,200	10.6
Wall covering	11,000	700	1,600	10,100	3.5
Film/sheet and coated products made by calendaring	44,000	13,600	16,400	41,200	14.5

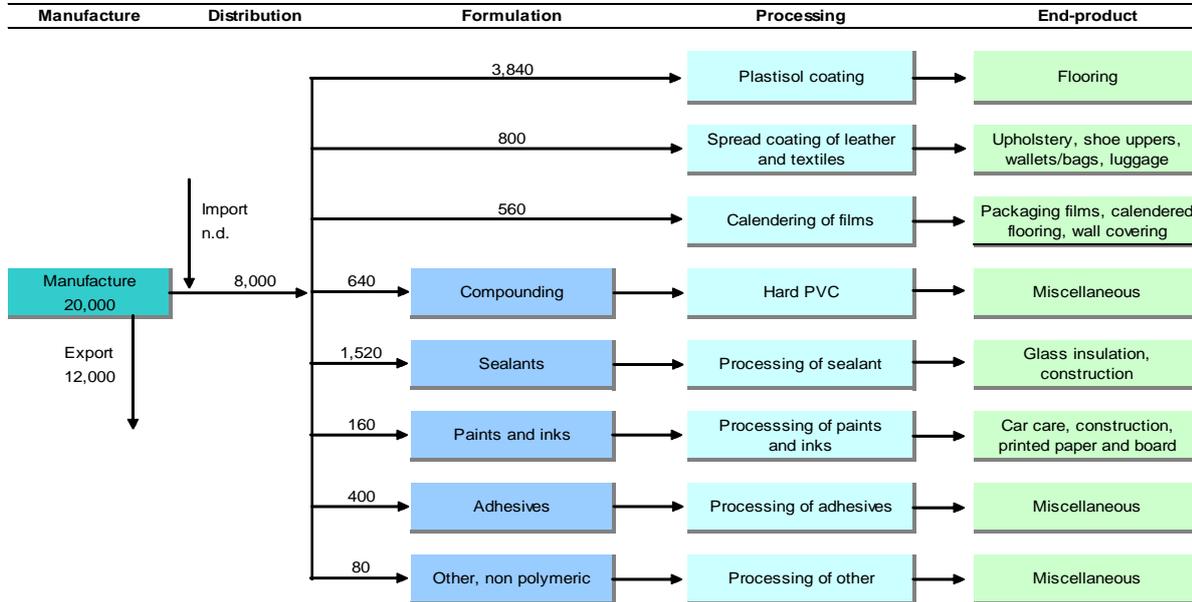
End-product use area	Tonnage, t/y				% of total use
	EU Manufacture	Import	Export	End-product use	
Wires and cables	52,000	6,200	5,600	52,600	18.5
Hoses and profiles	31,000	1,600	3,000	29,600	10.4
Coated fabric and other products from plastisol	31,000	2,200	1,400	31,800	11.2
Moulded products	3,000	2,700	700	5,000	1.8
Other polymer applications	12,300	10,900	3,100	20,100	7.1
Non polymer applications:					
Adhesives and sealant	4,000	n.d.	n.d.	4,000	1.4
Lacquers and paints	500	n.d.	n.d.	500	0.2
Printing ink	1,000	n.d.	n.d.	1,000	0.4
Other non-polymeric	20	n.d.	n.d.	20	0.0
Outdoor uses:					
Calendered roofing material	600	n.d.	n.d.	600	0.2
Coil coated roofing material	3,000	n.d.	n.d.	3,000	1.1
Wire and cables - air	2,400	n.d.	n.d.	2,400	0.8
Wire and cables - soil	9,700	n.d.	n.d.	9,700	3.4
Coated fabric	12,800	n.d.	n.d.	12,800	4.5
Car undercoating	4,000	n.d.	n.d.	4,000	1.4
Hoses and profiles	3,700	n.d.	n.d.	3,700	1.3
Shoe soles	19,400	n.d.	n.d.	19,400	6.8
Non polymer applications:					
Lacquers and paints	400	n.d.	n.d.	400	0.1
Adhesives and sealant	3,300	n.d.	n.d.	3,300	1.2
Total end-product use (round)	282,000	40,000	37,000	285,000	100

Source: (ECHA, ENTEC, 2009) [5]

2.3 BBP Major Application Quantities

The figure below presents the main application areas for BBP and the associated quantities, while the subsequent tables present the quantities used in each processing technique and the quantities present in different types of end product. These data refer to 2007, and thus to a time prior to prioritisation of the substance for authorisation, meaning that recent shifts away from use of the substance are not taken into account.

Figure 2.1 Overall flow of BBP through manufacturing processes. Tonnes BBP/year (2007). Figures are rounded and higher than actual figures



Source: ECHA, 2009 [6]

Table 2.3 BBP use for processing in 2007 and 2004

Process	Tonnage (t/y), 2007	% of total	Tonnage (t/y), 2004	Change 2004-2007
Formulation and processing (at same site):				
Plastisol coating for flooring	3,840	48	8,000	-52%
Coating of leather and textiles	800	10	1,800	-56%
Calendering of films	560	7	1,080	-48%
Processing from compound:				
Processing of hard PVC	640	8	1,080	-41%
Non-polymeric:				
Processing of sealants	1,520	19	6,000	-75%
Processing of coatings and inks	160	2	720	-78%
Processing of adhesives	400	5	360	11%
Processing of other non-polymeric	80	1	360	-78%
Total processing (rounded)	8,000	100	19,400	-59%

Source: ECHA, 2009 [6]

Table 2.4 Estimated BBP tonnage in end-products marketed in the EU based on EU manufacture, import, export data in 2007

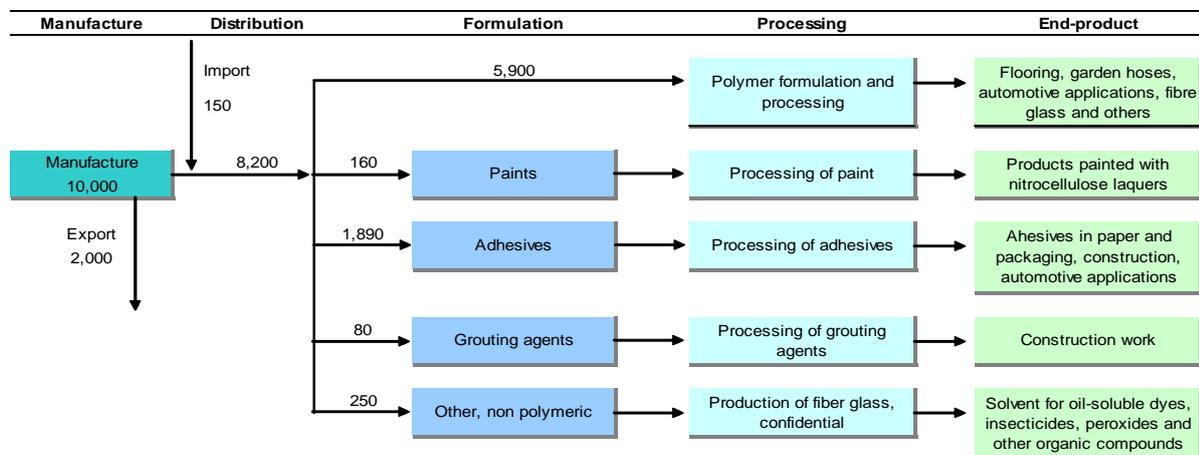
End-product use area	EU Manufacture	
	Tonnage, t/y	%
Flooring	4,290	54
Film	110	1
Coated fabric, upholstery, shoe uppers, luggage, etc.	800	10
Hard PVC	640	8
Non polymer applications:		
Sealant	1,520	19
Paints and ink	160	2
Adhesives	400	5
Other non-polymeric	80	1
Total end-product use (round)	8,000	100

Source: (ECHA, ENTEC, 2009) [5]

2.4 DBP Major Application Quantities

The figure below presents the main application areas for DBP and the associated quantities, while the subsequent tables present the quantities used in each processing technique and the quantities present in different types of end product. Note that these data relate to a time prior to prioritisation of the substance for authorisation, meaning that recent shifts away from use of the substance are not taken into account.

Figure 2.2 Overall flow of DBP through manufacturing processes. Tonnes BBP/year (2007). Figures are rounded and higher than actual figures.



Source: ECHA, 2009 [7]

Table 2.5 DBP use for processing in 2007 and 1998

Process	Tonnage (t/y), 2007	% of total	Tonnage (t/y), 1998	Change 1998-2007
Polymers formulation and processing	5,700	69	13,500	-58%
Formulation and processing of fiber glass	160	2	Not given	n/a
Non-polymeric, processing:				
Processing of paint	160	2	1,250	-87%
Processing of adhesives	1,900	23	2,500	-24%
Processing of grouting agents	80	1	200	-60%
Processing of other non-polymeric	250	3	550	-55%
Total processing (rounded)	8,300	100	18,000	-54%

Source: ECHA, 2009 [7]

Table 2.6 "Best estimated scenario" for DBP tonnage in end-products marketed in the EU27 based on EU manufacture data 2007

End-product use area	Tonnage, t/y		% of total use
	EU Manufacture	End-product use	
Polymers (incl. fiber glass), interior use	2,930	2,930	36
Polymers (incl. fiber glass), exterior use	2,930	2,930	36
Non polymer applications:			
Paint	160	160	2
Adhesives	1,900	1,900	23
Grouting agents	80	80	1
Other non-polymeric	250	250	3
Total end-product use (round)	8,250	8,250	100

Source: ECHA, 2009 [7]

2.5 DIBP Major Application Quantities

According to ECHA, the quantity of DIBP manufactured and/or used in the EU is in the range of 10,000 to 50,000 t/year. More specifically, the total figure is suggested to be 10,750t [1]. EU production and import used for production of articles is stated to be circa 13,000 tonnes [1]. These data refer to 2007, and thus to a time prior to prioritisation of the substance for authorisation, meaning that recent shifts away from use of the substance are not taken into account.

2.6 DPP Major Application Quantities

As of 2013, there has been no registration listed for DPP in ECHA's public dissemination database for information on registered substances. However, Poland's Annex XV dossier [27] relates the following:

- 102 companies had notified DPP on the C&L inventory database as at 18 February 2013;
- The European Chemicals Bureau (ECB) has listed DPP as a "low production volume chemical" (LPVC), with tonnage band 10-1000 t/year per producer or importer; and
- The SPIN database lists DPP use in 18 gunpowder preparations in Sweden from 2008-2011 (11 tonnes in 2008 and 2010, 15 tonnes in 2009 and 5 tonnes in 2011).

Poland's Annex XV dossier [27] further gives DPP's main use as being a plasticiser for PVC, with no further detail.

2.7 DIPP Major Application Quantities

DIPP has been registered in a total tonnage band of 10 – 100 tonnes per year as stated in the ECHA dissemination database. Based on the existing registration data there is no production of the substance in the EU in quantities > 1 tonne/year but the substance is imported into the EU (10-100 t/y) by 2 suppliers in Germany and another in "Europe" (no further detail provided). [25] There have been 3 notifications for the substance in the C&L inventory database, from 72 notifiers.

According to the Merck Index (2006, 2012), it is used as a plasticizer for nitrocellulose and resin lacquers; preventing foam in manufacture of glue; in rubber cements.

According to Austria's Annex XV dossier [25], the main uses are:

- Propellants / explosives in ammunition (military and civil), for which it is used to reduce the rate of burn. It is used in formulations containing 3-5% of phthalates (usually DBP, with DIPP being "not very common", although with an importance "expected to rise" as DBP becomes subject to authorisation); and
- Plasticisers for plastics (inc. PVC), adhesives, resin lacquers, glue, rubber cement.

DIPP does not feature on the SPIN database for use in Nordic countries.

2.8 N-pentyl-isopentylphthalate Major Application Quantities

No information was found on this substance:

- There are no identified REACH registrations;
- It does not feature in the SPIN database;
- No use data is included in the SVHC Annex XV dossier; and
- There are no notifications in the C&L inventory database.

2.9 Bis(2-methoxyethyl) phthalate Major Application Quantities

There have been 3 notifications for the substance in the C&L inventory database, from 289 notifiers.

Other than that, no information was found on this substance:

- There are no identified REACH registrations;
- It does not feature in the SPIN database; and
- No use data is included in the SVHC Annex XV dossier.

3. Application Selection

3.1 Selection Process and Criteria

3.1.1 Potential criteria for selection

In order to select six phthalate applications for further analysis, a number of possible criteria were taken into account, including:

- Indications in the literature / internet that use in a particular application is particularly problematic to replace / is crucial;
- Applications in which volumes of phthalates are high;
- Applications where there does not seem to be an existing significant trend away from the use;
- Applications in which potential exposure is high (e.g. as assessed in Annex XIV prioritisation documents prepared when substances were (or were not) selected for inclusion in Annex XIV);
- Applications expected (from the literature and expert judgement) to have high requirements in terms of technical specifications/parameters, thus making any material or process change more complex and costly;
- Applications likely to have strict approval processes for products (contractual, legal, etc.); and
- Data availability relating to phthalate use in the application, which might be applied either in a positive way (i.e. selecting applications for which data are available, potentially allowing for a greater degree of analytical depth) or in a negative way (i.e. selecting applications for which data are not available, with the hope that better data would be forthcoming through the consultation, thus helping to address identified gaps in the literature).

These criteria were not systematically applied to all the (hundreds of) applications identified, as the criteria are quite different in nature and purpose, comprising measures of potential exposure/risk, technical feasibility of substitution, economic and regulatory considerations and data availability. As such, a selection process based on direct comparison and ranking of all long-list applications based on all criteria (e.g. through use of an index) would lead to some useful aspects being overlooked in the aggregation process, as some criteria would necessarily have to be prioritised over others in order to produce a single ranking.

3.1.2 Criteria used

As an alternative to the approach described above, it was felt that a more useful approach would be to select the six applications for further analysis so as to provide an illustrative overview of the key issues pertaining to phthalate alternatives, particularly in the context of REACH authorisation. Specifically, the selection was based on achieving:

- coverage of the applications for which it was known that Authorisation would be sought;
- a range of different product types;
- a range of phthalates, including the candidate list ones (for which much less information is available);
- at least one application using large volumes of phthalates;
- at least one application linked to potentially high exposure levels (e.g. as assessed in Annex XIV prioritisation documents prepared when substances were (or were not) selected for inclusion in Annex XIV);
- at least one application with high technical specifications (from the literature and expert judgement);
- at least one use involving potential consumer exposure (i.e. with phthalates present in the finished article used by the general public); and
- at least one application from a purely industrial setting.

3.2 Selected Applications

On the basis of the phthalate-application mapping presented above and of further literature review, the above criteria were used to identify eleven applications that might be suitable for selection, which were presented to RIVM. These are presented in the table below, along with the reasoning behind their selection. Alongside these eleven applications, AMEC suggested six applications to RIVM to be taken forward for detailed analysis, with RIVM making the final choice.

Table 3.1 Applications suggested for selection, reasoning, final selection

Application	Reasoning	Link to criteria	Selected by RIVM
Aero engine air blades *	The use mentioned in the first published authorisation application for DEHP and also expected to be a use for DBP), so clearly identified as a crucial use (at least until approvals for alternatives can be obtained).	<ul style="list-style-type: none"> • Application for Authorisation known to be sought (already published during application selection for this use) • Use type: solvent use • High technical specifications (aerospace) • Industrial setting 	Yes

Application	Reasoning	Link to criteria	Selected by RIVM
Blood bags and other medical devices *	<p>Articles expected to have a high degree of technical requirements specifying performance in use.</p> <p>Indicated in the literature as being a potentially critical application, (e.g. [13], [16]).</p> <p>Note: medical devices are subject to the following exemptions under REACH:</p> <p>Art 2.6(c) exempts medical devices which are invasive or used in direct physical contact with the human body from the provisions of Title IV, concerning information in the supply chain; and</p> <p>Art. 60.2 states that, when taking decisions on applications for authorisation, the Commission shall not consider the risks to human health arising from the use of a substance in a medical device regulated by Directive 90/385/EEC (active implantable medical devices), Directive 93/42/EEC (medical devices) or Directive 98/79/EC (in vitro diagnostic medical devices). To this end, it is likely that any applications for authorisation for phthalates in medical devices would be automatically granted.</p> <p>Art. 62(6) states that The application shall not include the risks to human health [but not environment] arising from the use of a substance in a medical device regulated by Directives 90/385/EEC, 93/42/EEC or 98/79/EC.</p>	<ul style="list-style-type: none"> • Large volume of phthalates (relative to industrial niche applications, if not other PVC uses) • Use type: plasticiser • Potentially high exposure levels • Potential consumer (patient) exposure • High technical specifications (medical) 	No
Explosives, ammunition, gunpowder *	<p>Indicated in the DPP and DIPP Annex XV SVHC dossiers [25, 27] as potentially critical uses.</p> <p>Little-studied use.</p> <p>One of the few uses that does not apply to DEHP, thus ensuring that project scope covers the phthalates as a group (a lot of phthalate literature focuses mainly/exclusively on DEHP)</p> <p>Use as a propellant expected to be one of the applied-for uses.</p>	<ul style="list-style-type: none"> • Application for Authorisation though to be sought (press) • Use type: other use • Potential consumer exposure • High technical specifications 	Yes
Erasers *	<p>Consumer article, so potentially high levels of public exposure, especially as they may be mouthed by children.</p> <p>Identified in Denmark's Annex XV proposal as responsible for "extensive exposure to humans" (p. 16).</p>	<ul style="list-style-type: none"> • Large volume of phthalates (relative to industrial niche applications, if not other PVC uses) • Use type: plasticiser • Potentially high exposure levels • Potential consumer (patient) exposure 	No
Electrical and electronic equipment	<p>Indicated in the Danish restriction proposal as being a potentially critical application, especially in non-polymer applications, for which "substitution may be particularly difficult", although little detail is provided.</p>	<ul style="list-style-type: none"> • Large volume of phthalates (relative to industrial niche applications, if not main PVC uses) • Use type: solvent/other • Potential consumer exposure 	No

Application	Reasoning	Link to criteria	Selected by RIVM
Insulation of wires/cables used indoors. *	<p>A high-volume use for some phthalates (>50,000 tpa for DEHP in 2007). Potentially safety concerns with use of alternatives and relevant fire safety requirements</p> <p>According to Denmark's Annex XV proposal, "there are no uses of indoor cable types for which DEHP cannot be substituted" (p. 40).</p> <p>DEHP authorisation application is expected for plasticiser use but extent of coverage is not known. This is the highest volume use so may well be covered (and hence could be broadly representative of other high-volume PVC plasticiser uses).</p>	<ul style="list-style-type: none"> • Large volume of phthalates • Use type: plasticiser • Potentially high exposure levels • Potential consumer (patient) exposure • High technical specifications (in some sub-uses) • Authorisation expected for some types of wires 	Yes
Artists' paints	<p>Artists' paints are exempt from the restrictions imposed on CMR substances in REACH Annex XVII (substances 28-30). On this basis, ECHA originally considered exempting them from Authorisation. However, this was not taken forward, following comment by the MSC. This is related in the Annex XIV prioritisation reports for DEHP, DBP and BBP.</p> <p>In this context, artists' paints may be likely to have authorisation applications.</p>	<ul style="list-style-type: none"> • Use type: solvent/other • Potentially high exposure levels • Potential consumer exposure 	No
Pressure transmitters in the nuclear industry	<p>Emerson Process Management – Rosemount Nuclear Instruments argued for an exemption from authorisation in their comment for ECHA's 2009 DBP prioritisation consultation, suggesting it is a critical use.</p> <p>Use description and criticality argument provided in comment.</p> <p>High technical specifications required, including to meet health and safety requirements as pressure transmitters play a "critical role" in nuclear safety.</p>	<ul style="list-style-type: none"> • Use type: other • High technical specifications (nuclear) • Industrial setting 	No
Absorption oil in the manufacture of maleic anhydride (MAN) *	<p>Huntsman (Europe) BVBA argued for an exemption from authorisation in their comment for ECHA's 2009 DBP prioritisation consultation, suggesting it is a critical use.</p> <p>The company further argues that there are no alternatives to DBP available in this use.</p> <p>Use description and criticality argument provided in comment.</p> <p>Authorisation application expected for this use.</p>	<ul style="list-style-type: none"> • Application for Authorisation though to be sought (press) • Use type: solvent • Industrial setting 	Yes
Catalyst in the production of polypropylene (PP)	<p>Belgium's "Company X" argued for an exemption from authorisation in their comment on ECHA's 2009 DBP prioritisation consultation, suggesting it is a critical use.</p> <p>Downstream uses of PP include food packaging, consumer products, medical applications, electrical/electronic devices, automotive, building and construction, pipes and textiles.</p> <p>The company argues that "attempts to substitute this phthalate by other chemicals have not been successful in the sense that the desired physico-chemical characteristics could not be preserved or that the manufacture of the polymer was not possible in the same industrial process conditions". Further details in the comment.</p>	<ul style="list-style-type: none"> • Use type: other • Potentially high technical specifications • Industrial setting 	Yes

Application	Reasoning	Link to criteria	Selected by RIVM
Ceramic sheets and printing pastes for the automotive industry	<p>Chemical Watch (30 August 2013) has related that Czech company Deza has submitted an authorisation application for DBP in this use. Few further details have been found on this application.</p> <p>The processes referred to are possibly those described in the patents available at http://ip.com/patfam/en/39265027 and http://www.google.co.uk/patents/US5897723.</p>	<ul style="list-style-type: none"> • Application for Authorisation though to be sought (press) • Use type: other • Potentially high technical specifications • Industrial setting 	Yes

Note: (*) indicates initial AMEC suggestion for selection

The selected applications for further analysis were agreed with RIVM as the following:

- Aero engine fan blades (potentially all phthalates, but DEHP in particular, with additional consideration of DBP), focusing particularly on the use in the manufacture of blades for aeroplanes, as described in the Rolls-Royce application for authorisation for DEHP;
- Propellant in explosives, ammunition and gunpowder (DBP and DIPP);
- Insulation of indoor wires and cables (primarily DEHP);
- Absorption oil in the manufacture of maleic anhydride (MAN) (DBP), as detailed by Huntsman in their comments provided to ECHA during the prioritisation of DBP for inclusion in Annex XIV;
- Catalyst in the production of polypropylene (PP) (DBP, DEHP, DIBP), as detailed by Belgium's 'Company X' in their comments provided to ECHA during the prioritisation of DBP for inclusion in Annex XIV and Borealis (the two may be the same company, as Borealis has production sites in Belgium). Note: Borealis argue that in this process the phthalates are (transported) isolated intermediates and therefore exempted from Authorisation under REACH. We have assumed that catalysts are not exempt from authorisation; and
- Ceramic sheets and printing pastes for the automotive industry (DBP), as detailed by Deza (ChemicalWatch, 2013).

4. Alternatives Selection

4.1 Types of Alternative

4.1.1 Substance alternatives

The most conceptually straightforward type of alternative is a substance alternative. In this case, a particular substance (e.g. a phthalate) is replaced with another substance or mixture of substances. While the use of an alternative substance may require some process changes or changes in operating conditions, it is generally expected that a substance alternative will be used in a very similar way to the substance it replaces.

In the case of the phthalates under consideration, the following distinctions can be made as pertaining to substance alternatives:

- The first is between phthalate substance alternatives (i.e. phthalates with lower risk profiles than those being substituted) and non-phthalate substance alternatives. Whilst in many cases the former are preferred in practice (e.g. see indoor wires section below), these were not a priority based on the study terms of reference, so are not given detailed consideration in the study;
- The second relates to the type of use in which the phthalate is used (i.e. plasticiser, solvent or other). This is an important distinction to make, as the main properties that are required from a substance alternative will clearly vary according to the type of use. Whilst non-phthalate substances may be suitable as alternative plasticisers, they may not also be suitable as alternative solvents, or vice-versa; and
- Third, in terms of plasticiser uses, a distinction is made between the use as a PVC plasticiser specifically, and in other plasticiser uses (which are categorised as 'other').

4.1.2 Material alternatives

In addition to substance alternatives, material alternative may also be considered. In this case, a material that contains phthalates or is dependent upon phthalates in its manufacture is replaced by a different material altogether. This particularly pertains to the use of phthalates as plasticisers, since the polymers produced might be replaced by other materials, which may be alternative plastics (i.e. non-PVC) or non-plastic materials (e.g. wood, cork or linoleum in flooring, or glass in medical devices).

Alternative materials may include bio-plastics. These are plastics or plastics additives that are derived from renewable biomass sources (e.g. vegetable oils) instead of non-renewable ones (such as petroleum). Bio-plastics are currently an active field of chemical research, which RIVM has a particular interest in. This was taken into account where possible in the analysis and selection of alternatives for more detailed analysis (see below).

4.1.3 Process alternatives

The third general type of alternative available is where a change of manufacturing (or other) process may be feasible. For instance, it may be possible to remove impurities from some products by burning them off rather than by using particular solvents. Similarly, the removal of impurities or pollutants using solvents (or other types of substances) may be precluded via the introduction of more controlled upstream processes that reduce the level of impurities/pollutant.

4.2 Specific Alternatives

In order to select six specific alternatives for further analysis for the selected applications, a literature review was carried out, and an application-alternative matrix drawn up. This is presented in Appendix B. Again, the cells are filled with literature references that mention use of the alternative in the application. This matrix is summarised in the table below for the selected applications.

It should be noted that this table represents the knowledge AMEC had at the time of alternative selection, and upon which the selection was based. However, following the selection and subsequent consultation and more detailed literature review, this understanding evolved. In particular, the ‘map’ of potential alternatives became more comprehensive and accurate, as knowledge of technical feasibility considerations and other potential alternatives was improved. Such evolution in understanding is presented in the relevant alternative-specific sections.

Table 4.1 Non-phthalate alternatives suggested for selection, reflecting understanding at the time of selection.

Alternative	Lit. Ref.	Type of alternative	Comment
Aero engine fan blades			
Glycerol	[31]	Substance alternative (solvent)	Only potential alternative identified for this specific application. More generally, [1] mentions its “high solvating properties” Glycerol can be made as a by-product of biodiesel production. It can be used to make PHA, a bio-plastic. Note: we are unlikely to gain more information than that contained in Rolls-Royce’s application for authorisation
Propellant			
Diphenyl urea derivatives (ethyl centralite)	[25] [44]	Substance alternative (other)	Only potential alternative identified for solid single base propellant modifiers in [44] Mentioned as example in [25] – no more information found
Camphor	[25]	Substance alternative (other)	Mentioned as example in [25] – no more information found
Diisooctylphthalate	[25]	Substance alternative (phthalate)	Mentioned as example in [25] Phthalate – not considered further

Alternative	Lit. Ref.	Type of alternative	Comment
Diocetylphthalate	[25]	Substance alternative (phthalate)	Mentioned as example in [25] Phthalate – not considered further
Alternative propellant types	[44]	Material alternative (other)	[44] relates that there are several types of propellant: solid single base, solid double base, solid triple base, solid composite and liquid. DBP is only specifically mentioned as being used for solid single base propellants. It is not clear whether other propellant types use DBP or not. There may therefore be scope for guns/ammunition to no longer use DBP by switching to another propellant type, although it is not clear on what basis the choice of propellant is made. (i.e. it is possible that some types of gun/ammunition can only use solid single base propellants).
Indoor wire/cable insulation			
DINCH / Hexamoll	[1]	Substance alternative (PVC plasticiser)	Proprietary chemical (BASF) Covers many other applications. A lot of information available
TOM / TOTM / TETM	[1] [5] [13] [15] [18]	Substance alternative (PVC plasticiser)	Covers many other applications. A lot of information available
DOTP/DEHT	[1]	Substance alternative (PVC plasticiser)	Covers many other applications. A lot of information available
COMGHA / Castor oil	[1]	Substance alternative (PVC plasticiser)	Covers many other applications. A lot of information available COMGHA is castor oil-based, and hence can be used in bio-plastics (see below)
Polyethylene	[14][16]	Material alternative (plastic)	One of the most-cited alternative plastics
Glycerol-based	No direct ref.	Substance alternative (PVC plasticiser)	Glycerol can be made as a by-product of biodiesel production. It can be used to make PHA, a (bio-) plasticiser for PVC. PHA can also be used for bio-plastics.
Castor-oil based bio-plastics	No direct ref.	Material alternative (bio-plastic)	Plastics (no direct link to selected applications identified) Most relevant use of COMGHA or castor oil derivatives is as a PVC plasticiser. However, it can also be used to manufacture bio-plastics, the potential relevance of which to the selected application may be investigated.
PHA	No direct ref.	Material alternative (bio-plastic)	Plastics (no direct link to selected applications identified) Most relevant use of PHA is as a PVC plasticiser. However, it can also be used to manufacture bio-plastics, the potential relevance of which to the selected application may be investigated.
Maleic anhydride			
Xylenes	[48]	Substance alternative (solvent) ⁽¹⁾	Xylenes mentioned as possible alternative in the Kirk-Othmer Encyclopedia of Chemical Technology [48], with no further detail given other than a reference to a non-public domain academic article: J. C. Burnett, R. A. Keppel, and W. D. Robinson, Catal. Today 1(5), 537 (1987).

Alternative	Lit. Ref.	Type of alternative	Comment
Alternative processes in patent history	[46]	Process alternatives	A number of different processes are described in the patent for a DBP-based process. Some also use DBP, others do not, and for some it is not clear as the summary only mentions use of an "organic solvent". The potentially non-DBP-based ones mentioned are: Alkenyl or alkyl substituted succinic anhydride as absorption liquid; "Liquid solvent comprising polymethyl-benzophenones" Dialkyl esters of hexahydrophthalic acid, tetrahydrophthalic acid, methyl tetrahydrophthalic acid, or methyl hexahydrophthalic acid [note: these may be phthalates] Dewaxed oil from refinery (as alternative to phthalic dioctyl ester) Tetrahydrothiophene 1,1-dioxide
PP catalyst			
Diethers	[61] [62]	Substance alternative (other)	Mentioned in the Kirk-Othmer Encyclopedia of Chemical Technology [61] and as constituent of the Basell Avant ZN product range
Ethyl benzoate	[61] [62]	Substance alternative (other)	Mentioned in the Kirk-Othmer Encyclopedia of Chemical Technology [61] and as constituent of the Basell Avant ZN product range
Succinates	[61] [62]	Substance alternative (other)	Mentioned in Kirk-Othmer Encyclopedia of Chemical Technology [61] and as constituent of the Basell Avant ZN product range
AVANT ZN	[61] [64]	Substance alternative (other)	Proprietary LyondellBasell product range, comprising four types of PP catalyst, with 3 out of 4 products phthalate-free
HYAMPP	[59] [63]	Substance alternative (other)	Proprietary Grace-Dow product, phthalate-free. Exact chemical composition could not be found, probably due to IP issues (see attachment).
Ceramic sheets			
Dibutyl sebacate	[67]	Substance alternative (other)	Only one reference to a non-phthalate alternative in this use found.

Note: (1) Xylenes were originally thought to be substance alternatives to DBP in the production of MAN, although it later became clear that they in fact represent a process change from solvent-based to water-based MAN recovery (see section below).

Based on this overview, potential alternatives were selected with the aim of:

- Covering all the selected applications (at least one alternative per application); and
- Including all the main alternative categories (alternative PVC plasticisers, alternative plastics, alternative non-plastic uses, alternative processes and bio-plastics).

Of these criteria, the most important one was the first, i.e. selecting alternatives so that all six applications would be covered. This greatly limited the choice of potential alternatives, as most of the selected applications are very 'niche', with little published information regarding both the processes themselves (i.e. role of phthalate in them) and potential alternatives. There was also relatively little overlap identified between the alternatives and

applications, although some alternatives did cover several applications, such as glycerol (which can be used in solvents for airblades, as an alternative PVC plasticiser and hence in wire insulation and can be used to manufacture bio-plastics).

Based on the selected applications and the initial proposal for alternatives, the primary alternatives identified for more detailed investigation was as follows:

- Glycerol use as alternative **solvent** in the manufacture of **aero engine fan blades**. Glycerol was primarily selected because it is the most suitable alternative for the solvent (airblades) application, with the Rolls-Royce application for Authorisation indicating that it is both technically and economically suitable, but still subject to various safety tests (detailed in the aero engine fan blade section below);
- COMGHA/castor oil: use as an alternative **PVC plasticiser in indoor wire/cable insulation**. This was selected due to its versatility/range of potential uses. Note: other PVC plasticisers could be studied instead, some of which are potentially more directly relevant to the application in question;
- Diphenyl urea derivatives (ethyl centralite): alternative for use (**other use type**) as **propellant**. This is selected because it is the only alternative propellant to have been mentioned in two sources, thus implying it may be more 'recognised' as an alternative in this use;
- Xylenes: alternative **solvent** (absorption oil) in the manufacture of maleic anhydride (**MAN**). Xylenes were selected because there appeared to be more information available than there is for the other possible alternatives. It later became clear that the use of xylene involves a significant **process change** and that other, more suitable potential alternative solvents might have been selected instead. These are presented in the maleic anhydride section below;
- An alternative catalyst (AVANT ZN) (**other use type**) in the manufacture of **PP**: Preliminary research indicates that possible alternative catalysts in the manufacture of PP include diethers, ethyl benzoate and succinates (from Kirk-Othmer Encyclopedia of Chemical Technology – entry on Ziegler-Natta catalysts), all of which are used in some of LyondellBasell's proprietary AVANT range of products. DOW also produces a non-phthalate PP catalyst called HYAMPP, the exact chemical composition of which could not be found. For this application, consideration was given to all of the above, with an eventual focus on diethers and succinates, as detailed in the section on PP catalysts below; and
- Dibutyl sebacate for the (non-PVC plasticiser, categorised as **other use type**) production of **ceramic sheets and printing pastes** for the automotive industry. This is the only non-phthalate alternative (non-PVC) plasticiser for ceramics found in the literature review at the time of selection.

Whilst these were the alternatives that were investigated in most detail for each application area, RIVM's aim was to get a good overview of the range of different alternatives that are available for each use. Therefore, in the following sections, details are provided on the range of different alternatives identified, as well as the more detailed consideration of the selected alternative for each of the six applications.

4.3 Review of Selection

It is important to note that the selection of alternatives was made on the basis of the information available at the time. Combined with the significant lack of knowledge on what would be in the authorisation applications (use

descriptions, which alternatives were being considered, what the arguments for authorisation would be), the selection of alternatives involved making decisions based on relatively little information. Many of the principal issues related to some alternatives only became clear relatively late on in the project. As more information became available, it became clear that in some cases more alternatives are in fact available than was evident at the time of selection, some of which may be more technically or economically suitable than the alternative that was originally selected.

Some of the main selection difficulties encountered at the time of selection can be summarised as:

- Too little information to base a fully informed decision on. This was the case, for instance, with propellants (for which only four potential alternatives were initially identified, of which two were other phthalates, and therefore excluded from scope), as well as with ceramic sheets and printing pastes (for which only one passing reference to a potential phthalate alternative was found);
- Too much information. In some cases (e.g. indoor wires and cables), there is a wealth of information available on different potential alternatives. The difficulty with this is that it is not possible to ensure that the best potential alternative is selected (in preference to all the other possibilities) without carrying out a significant amount of preliminary research into all of them. In the case of indoor wire and cables, castor oil was selected because of its bio-credentials (which we knew RIVM were interested in) rather than due to any specific technical or economic characteristics (these were investigated subsequently);
- Information provenance. In the case of aero-engine fan blades, only a single source of information was found, which was Rolls-Royce's application for authorisation, thus making independent assessment of the best alternative for detailed analysis impractical. As such, the alternative selection was based on Rolls Royce's own assessment of most promising alternative; and
- Information unclear or misunderstood during initial research stages. In at least one case (maleic anhydride), it only became clear late on how the alternative is used and the fact that the different substances involved relate to quite distinct production processes, when a substance alternative would likely be more (economically) feasible in practice, and hence a better candidate for detailed analysis.

Application and alternative-specific considerations are presented in more detail in the relevant application sections below.

5. Aero Engine Fan Blades

5.1 Phthalates in Aero Engine Fan Blades

According to Rolls-Royce's application for Authorisation for DEHP (Rolls-Royce, 2013a), the company manufactures the wide-chord fan blade (WCFB) for use in airplane engines using the compound *Stopyt-62A* as a bonding stop-off agent to prevent diffusion bonding in the printed areas of the blade. In general terms, this compound is used when three sheets of titanium are bonded to form the external and internal parts of fan blades. This agent ensures that only specific parts of the blades are bonded together to give the required strength and specifications. The active ingredient is Yttria (Yttrium(III) Oxide), whereas DEHP is added to the *Stopyt-62A* as a plasticiser to ensure a smooth and even coating of Yttria is printed onto the blade. Rolls-Royce has applied for an authorisation to continue using *Stopyt-62A* for the manufacture of aero engine fan blades (Rolls-Royce, 2013a), hence the selection of this application for the current study.

5.2 Overview of Alternatives for Phthalates in Aero Engine Fan Blades

Rolls-Royce has considered four alternatives for the *Stopyt-62A* mixture as a whole, as it is all the components that provide the desired properties to the bonding process and not necessarily DEHP alone. Along with the description of each of them, Rolls-Royce had to submit information about the health and environmental impacts, the technical and economic feasibility and justify whether research was continued or not and at which stage it is at the moment. This information is summarised in Table 5.1.

Table 5.1 Identified formulations that could be a substitute of *Stopyt-62A*

Substance	Manufacturer	Health and environmental implications	Technical feasibility	Economic feasibility	Stage of research
GG4400 B2	Acheson	Not available (No longer on the market)	The bond was of lower strength. All test blades failed earlier than the current ones.	Favourable analysis with modest costs.	No further analysis has been programmed due to technical unsuitability (Lower strength of bonds. Early failure of test blades)
Dag MS-401LR	Acheson	Risk phrase: 20/21, 52/53. Safety phrase: 23C, 36/37, 43E	Excessive drying time ⁽¹⁾ , need to change the process, probable pipe blockages, probable underperformance	Not conducted as it had already been discounted on grounds of technical feasibility	No further analysis has been programmed due to technical unsuitability (Excessive drying time, probable pipe blockages, and underperformance).

Substance	Manufacturer	Health and environmental implications	Technical feasibility	Economic feasibility	Stage of research
Stop-flo No2	Johnson Matthey	Not hazardous	Initial trials not yet done. Assumed to need design change as the composition and properties are completely different to Stopyt-62A.	In principle higher material costs. In total production, might be assumed as the quantity used is low. Trials will enlighten about the process parameters and other costs.	Selected for initial trials.
Stopyt-62G	Morgan Technical Ceramics – Wesgo Metals Division	Same implications as Stopyt-62A (related to isopropyl alcohol and MIBK) but it has glycerol instead of DEHP, which would decrease the hazardousness of the mixture (see section 5.3.2 below).	Successful tests (general use) conducted by the manufacturer. Initial tests successful at Rolls-Royce.	No capital or additional operational costs needed. Same manufacturer, which sells it at the same price.	Successful tests (general use) conducted by the manufacturer. Initial tests successful at Rolls-Royce. Further research in progress.

Source: Rolls-Royce (2013a)

Note: The assessments provided above are summaries of those provided in the Rolls-Royce application for Authorisation for DEHP and could not be independently verified as part of the study. (1) Excessive drying time is assessed in Rolls Royce's application for Authorisation as compromising technical feasibility because longer drying time or forced drying techniques would increase the likelihood of surface contamination and eventually affect product integrity. The eventual conclusion is that the alternative "did not allow for a repeatable high strength diffusion bond, leading to an unacceptable safety risk for aero-engine performance". This assessment could not be independently verified as part of the study.

Rolls-Royce has scheduled initial analysis for Stop-flo No2, while Stopyt-62G has passed initial tests. The latter seems to have similar properties to the current formulation and the manufacturing process does not seem to need major changes. Some small differences in the initial mixing time are expected to decrease as the mixing technique is developed and perfected (Rolls-Royce, 2013a).

In addition to these, two boron nitride-based products have been identified in the recent public consultation process on the Rolls-Royce authorisation application (Rolls-Royce, 2013a, Kooperationsstelle Hamburg IFE GmbH, 2013). According to this institution, these two products could be feasible alternatives that prevent diffusion bonding without the need for a plasticiser. One of them is in the form of an aerosol, which may lead to respiratory problems according to Kooperationsstelle Hamburg IFE. As reported in this submission of information, a compound based on boron nitride has already been successful in a company manufacturing similar products. It is worth noting that these alternatives were only identified relatively late in the current study, when the responses to the public consultation were made available.

As a result of the above, Stopyt-62G has been selected for further analysis due to the fact that Rolls-Royce has already identified it as a technically suitable alternative that would need minimal process/mixture modifications. The justification of an application for authorisation regards to the time that Rolls-Royce requires to implement this alternative. This is discussed below.

5.3 Detailed Investigation of Selected Alternative

5.3.1 Approach

The use of Stopyt-62G entails an alternative substance and not an alternative process for the substitution of Stopyt-62A for a phthalate-free substance as a bonding stop-off agent in the process of airplane fan blade manufacture. The substitution process for this alternative seems to have relatively low impacts on the manufacturing process, as the only difference is including glycerol instead of DEHP in its composition. Both formulations are provided by the same supplier.

Taking into account that Stop-flo No2 is still in the initial testing phase and that the company would incur higher material costs, the most likely alternative seems to be Stopyt-62G.

The information related to this use is limited, due to its small industrial niche. Little information is available relating to this use beyond that contained in the authorisation application submitted by Rolls-Royce (Rolls-Royce, 2013a), as well as some of the comments made on the application during the public consultation phase (ECHA, 2013). This literature therefore provides the starting point and main input for this analysis.

The information from literature was supplemented where possible with information from consultation. The companies approached as part of this were as follows:

- There are two major manufacturers of aero engine fan blades in the world. The other one (Boeing) manufactures in the USA, where REACH authorisation is not applicable. As Boeing manufactures its own aero engine fan blades, they were consulted to determine their research findings and corporate policy on phthalates. However, despite a phone call and several emails, this consultation was without success; and
- Morgan was successfully contacted, as the company supplying both the current and potential alternative mixture for the manufacture of aero engine fan blades in Europe.

Overall, it should be clear that very little independent information could be found to allow for a full and detailed analysis of potential alternatives (including the selected one: Stopyt 62G) to DEHP in this use. This is because the only information sources found were the Rolls-Royce application itself, which was further corroborated by Morgan, Rolls Royce's supplier of both Stopyt 62A and Stopyt 62G. While Boeing were also contacted to provide a potentially alternative view on the matter, this attempt to gather further information was not successful. Similarly, no other literature could be found specifically looking at phthalates and their alternatives in this use (until the comments on the public consultation were made public).

For these reasons, the study approach for this application/alternative is essentially a synthesis of the information contained in the Rolls-Royce application, supplemented with further information from consultation and literature where it was possible to do so.

5.3.2 Health and environmental impacts

DEHP is a male reproductive toxicant because of the specific testicular toxicity associated with exposure. The active metabolite responsible for the testicular toxicity of DEHP is the ester metabolite monoethylhexyl phthalate (MEHP). Dosing studies have shown that after oral exposure to DEHP, the only detectable metabolites found in the testis is MEHP and MEHP-derived compounds. The study further showed that only MEHP, and not DEHP, accumulates in the testes after oral administration.

Orally-administered DEHP is rapidly hydrolyzed to MEHP and 2-ethylhexanol (2-EH) in the digestive tract. This metabolism is facilitated by pancreatic hydrolases. Trace amounts or no intact DEHP have been found in the blood or liver tissues of rats or primates treated orally with DEHP at levels below 500 mg/kg. This supports the hypothesis that DEHP is poorly absorbed from the gastrointestinal tract and that it is MEHP that predominantly enters the circulation from ingested DEHP doses.

Dermal absorption involves the transfer of DEHP from the outer skin surface to the central circulation. It therefore bypasses the digestive tract. As a result, it represents a direct introduction of DEHP to the circulation akin to parenteral exposure in that it is DEHP and not MEHP that enters the bloodstream. Hence, the toxicity for dermal exposure is about 20-times lower than toxicity associated with ingestion.

Inhalation of DEHP is precluded by its low vapour pressure (0.13 Pa at 20 °C). This yields an equilibrium concentration of 0.98 ppm and a vaporization rate of practically zero. Therefore, inhalation is not a significant route of exposure.

This application is expected to result in occupational exposure only and be limited to those involved in manufacture. Once the Stopyt-62A cured, there would be no exposure to the product during maintenance operations due to spatial hindrance by the titanium laminates and extremely limited potential exposure after catastrophic failure since the DEHP would be bound in the matrix of the hardened Stopyt-62A.

Occupational exposure during manufacture would principally involve potential dermal exposure through skin contact and potential inadvertent ingestion through mouth contact with contaminated skin areas. This can be reasonably expected to be rendered insignificant with the use of minimal personal protections: gloves and coveralls and hand washing after use.

Glycerol is a simple polyol that is a by product of triglyceride metabolism and generally regarded as safe. The chemical is non-corrosive, non-sensitizing and possesses no apparent carcinogenic/mutagenic, reproductive or endocrine disrupting toxicity. While the no adverse effect dose for glycerol by ingestion is in excess of 10,000 mg/kg-day, long term inhalation exposure to mist by inhalation has been shown to impact respiratory volumes at concentrations in excess of 0.662 mg/m³. Environmentally, glycerol has a very low aquatic toxicity (> 10,000 mg/l in 48-hour fish mortality tests), low environmental persistence, and no potential to bioaccumulate in aquatic or terrestrial organisms.

Replacement of DEHP with glycerol would have a limited impact of the safety based on the very limited risk associated with the use of DEHP. That said, substitution of glycerol for DEHP would eliminate potential exposures

during manufacture. However, Rolls Royce has not evaluated the impacts of the exposure of Stopyt-62G during manufacture yet.

5.3.3 Technical feasibility

Morgan Advanced Materials reports that both formulations have the same properties. The main active ingredient remains the same and glycerol does not seem to change the properties of the stop-off agent. The process parameters remain the same, except that longer initial mixing is required, although this difference is expected to decrease as the mixing technique is perfected. The mixture has been assessed at Morgan's laboratories and has passed initial tests at Rolls-Royce.

It is of note that, in a different but similar use, one of Morgan's clients has already successfully replaced Stopyt-62A with Stopyt-62G (no further details provided, due to business confidentiality). This company was using the product for metal dyeing.

5.3.4 Economic feasibility

Rolls Royce states that capital and operational costs still have to be assessed, but the supplier has confirmed that the price of the new product would remain the same as that of Stopyt-62A. Indirect costs for R&D and suitability tests are expected to be high (Rolls-Royce, 2013a, interview with Stopyt-62A and Stopyt-62G manufacturer). This is based on Rolls Royce previous experience and the consultation with the manufacturer of the alternative and current used substance. The costs have been calculated and included in the confidential section of the application for authorisation.

Additionally, Boeing has reported that a fleet of aircraft operating in the EU contain phthalates in various parts and components. According to Boeing, a restriction could lead to difficulties in obtaining replacement parts (SEAC (ECHA), 2012; Rolls-Royce, 2013a).

5.3.5 Availability and timing

According to Rolls-Royce, the product is readily available and shall be as accessible as the current formula. However the necessary tests that the company has to conduct would delay its full-scale production 5-10 years beyond the sunset date of 21st February 2015 (Rolls-Royce, 2013a, 2013b).

This is not in line with the information included in the application for authorisation (Appendix A, Rolls-Royce 2013a). According to this, Stopyt-62G could be implemented in around 4 years from the initial laboratory assessment to the substitution planning and implementation. As the analysis of Stopyt-62G started in 2012, the whole process could potentially be finished in 2016. This is also concordant with an example of how Boeing selected the Trent 1000 engine to power their 787 Dreamliner model. This model achieved its airworthiness certificates in 3.5 years (Rolls-Royce, 2013a)

Due to the similarities of the two formulas, the period prior to the submission for approval is stated to be relatively small (around a year and a half from the start), although the design would have to comply with EASA requirements (as described in, for instance, EASA, 2007). Among them, the manufacturer has to submit an approved airworthiness limitations section of the instructions for continued airworthiness as defined by the applicable airworthiness code. According to EASA (2007), there will have to be enough evidence to confirm the safety standards stated in the application for validation of the design (bird impact resistance, rotor strength, over-temperature and others). Additionally, EASA may require witnessing some tests to ensure that the parameters stated in the application are correct. Notwithstanding this, Rolls-Royce does not envisage additional time for these approval procedures, so the stated total period of four years may be assumed.

On the other hand, Stop-flo No2 would involve a higher amount of tests (assessment of risk of performance, production scale testing, destructive testing) as the difference with the current products are significant. Therefore, the time required could double (according to Rolls Royce). After control and assessment of all the parameters that EASA requires (performance, resistance and environmental impacts), an application for approval is submitted to EASA. EASA specifications and requirements are very strict, which may delay the full scale production of these phthalate-free aero engine fan blades even more (Rolls-Royce, 2013a).

Provided that no unexpected failures/issues occur when conducting the final tests with Stopyt-62G (low cycle/high cycle fatigue bend testing, and non-destructive testing of blades and review of test data), there is no reason in principle for Rolls Royce to not have a technically feasible alternative ready for 2016.

5.3.6 Existing R&D activities

The second possible alternative of those initially considered by Rolls-Royce (Stop-flo No2) is undergoing initial tests. Existing R&D activities regarding Stopyt-62G include the fabrication of a testing WCFB for a Low Cycle Fatigue (LCF) testing. According to Morgan Advanced Materials, there are competitors producing similar compounds, but none with the same purity as theirs (Rolls-Royce, 2013a, interview with manufacturer of Stopyt-62A and Stopyt-62G).

5.3.7 Suitability

The current evidence suggests that glycerol is a suitable alternative for DEHP in the production of the stop-off agent with which Morgan Advanced Materials supplies Rolls-Royce. However, according to the authorisation application, the aeronautic industry requires years of additional tests and trials before the alternative is put in place for full-scale production and, therefore, no changes at short notice would be possible.

Rolls-Royce's application is submitted on the basis that adequate control can be demonstrated for the use of DEHP. If this is agreed, then the main issue is the length of the review period that should apply, taking into account the fact that an alternative has been identified which seems to be technically suitable. The R&D and other work to develop an alternative were estimated to take between 5-10 further years to complete, based on Rolls-Royce's recent experience of engine validation and flight test costs. This does not seem to be in line with the 'project plan for alternative analysis programme' in Annex A to the analysis of alternatives document, which seems

to suggest a period of around 4 years for alternative #4 (Stopyt-62G), which seems to be the most likely replacement (around 10 years seems to be indicated for alternative #3).

5.4 Overall Conclusions

Overall, it appears that Stopyt 62G is a suitable alternative to Stopyt 62A in this application.

The main potential point of contention regards the exact time required for Rolls-Royce to undergo all the safety testing and certification required in order to place WCFBs produced using Stopyt 62G on the market. According to Rolls Royce's assessment (2013a), it would appear that a substitution, testing and certification might be possible within a timeframe that would allow them to keep on producing WCFBs continuously without requiring Authorisation for DEHP to be granted. However, this would be contingent on all tests being successful first time round, and without any further needs being identified as a result of the tests. By applying for Authorisation for DEHP in this use, we assume that Rolls-Royce clearly wish to retain the *possibility* of using DEHP in case of any problems arising with the substitution process.

Whilst it has not been possible to independently verify the information provided in Rolls-Royce's application for Authorisation for DEHP, the overall conclusion is that the main information laid out and arguments presented seem reasonable, although the timescales indicated as being needed would merit further discussion.

5.5 References

EASA (2007) Certification Specifications for Engines CS-E, Amendment 1, 10 December 2007

ECHA (2013) Comments on public consultation 0001-01. Available from: <http://echa.europa.eu/addressing-chemicals-of-concern/authorisation/applications-for-authorisation/comments-public-consultation-0001-01>

Kooperationsstelle Hamburg IFE GmbH (2013) *Third party submission of information on alternatives for Applications for Authorisation. Comments on public consultation 0001-01* (in relation to Rolls-Royce application for authorisation under REACH). Available from: <http://echa.europa.eu/addressing-chemicals-of-concern/authorisation/applications-for-authorisation/comments-public-consultation-0001-01>

Rolls-Royce (2013a) *Analysis of alternatives for DEHP use. Non-confidential report*. Application for authorisation under REACH.

Rolls-Royce (2013b) *Non-confidential summary of the socioeconomic analysis for DEHP use*. Application for authorisation under REACH.

SEAC (ECHA) (2012) *Response to comments on the SEAC draft opinion on the Annex XV dossier proposing restrictions on four phthalates*. Committee for Socio-Economic Analysis, European Chemicals Agency.

6. Propellants

6.1 Phthalates in Ammunition

6.1.1 Phthalates used

Phthalates are used in the manufacture of propellants for ammunition, and have been for many decades, with initial research into their use carried out around the time of World War 2 (e.g. Phillips, 1942, Pring, 1948). According to consultation, the most common phthalate in ammunition is dibutyl phthalate (DBP), accounting for the vast majority of the phthalates used in the industry. Other phthalates such as diisopentyl phthalate (DIPP) were used in old formulations but are uncommon nowadays, according to personal communication with an industry expert. Dimethyl phthalate (DMP) and diethyl phthalate (DEP) have also been used in gun and rocket propellants according to Kirk Othmer (2000). In a list of 62 propellant formulations elaborated by a specialized website (Ammunitionpages.com, undated), the only listed phthalates were DBP and DEP, being present in 8 and 1 formulations respectively. No information was found regarding the tonnage of phthalates used in the manufacture of ammunition compared to the total use of these substances.

ECHA registration data confirm the use of DIPP in the manufacture of propellants and explosives. Propellants containing DIPP may be further used by producers of ammunition or used directly by the consumers to manually reload their cartridges (Austria 2013). The SPIN database, which collects records on use of chemicals in Scandinavian countries, indicates the use of DPP in Sweden as a component to gunpowder at 15, 11 and 5 tonnes in 2009, 2010 and 2011 respectively in 18 registered products used in explosives materials (SPIN Database).

6.1.2 Concentration

The content of phthalates in ammunition is variable. According to consultation with AFEMS (Association of European Manufacturers of Sporting Ammunition), phthalates represents around 2-5% by weight of the propellant charge. Literature offers similar figures: 2-5% (Austria 2013) and 3.5-7.5% of ball powder propellant (Kirk-Othmer 2000). The maximum concentration found in the literature has been 8% in ASN Solventless propellant (Ammunitionpages.com, undated).

6.1.3 Uses

DBP is used in propellants in two different ways: as a plasticiser and as a deterrent (Heramb and McCord 2002). Plasticisers are added to the mixture of the propellant in order to reduce the need for volatile solvents necessary to colloid nitrocellulose, soften the propellant, and reduce hygroscopicity. This improves processability and flexibility at low temperatures. Nitrated plasticisers can also increase the energy level of the propellant (Kirk-Othmer 2000).

Deterrents (or burning rate regulators) are applied to the exterior of the propellant grains, penetrating into the energetic substrate. This reduces the initial burning rate, flame temperature and ignitability, resulting in lower

barrel erosion. Deterrents also broaden the pressure peak and increase efficiency (Heramb and McCord, 2002). Basically, in the detonation of ball powder, combustion starts in the outside of the powder granules, which have a high surface area, releasing a high volume of gases. As the combustion moves to the core of the grain, surface area is reduced and combustion rate decreases. Deterrents are added to control the initial burning rate on the surface of the grains.

No information was found regarding the proportion of the ammunition or propellant market that uses phthalates relative. This information was sought both in literature and during consultation, but was not forthcoming.

6.1.4 Types of guns and ammunition

According to consultation, the use of deterrents in ammunition, and DBP in particular, is also related to the type of firearm. Three main types have been identified:

- **Shotgun ammunition:** Most ammunition in this category does not contain DBP. This is due to the relatively simple ballistics of shotguns, which does not require the addition of deterrents. They normally use single base propellant (see below) but double base propellants for shotguns can also be found in the market (Lovex, 2013);
- **Metallic ammunition (pistols, rifles, etc.):** most of these have deterrents (usually phthalates) due to their higher ballistic needs. They use single and double base propellants (Lovex, 2013); and
- **Large calibre artillery:** These all have deterrents (usually phthalates) in order to achieve the necessary mechanical performance. Double and triple base propellants are usually used in this type of guns, although single base ones are not uncommon.

The classification of propellants as single, double and triple base refers to the number of energetic compounds, which confer mechanical strength to the mixture during detonation (Kirk-Othmer 2000; Agrawal 2010).

- **Single-base propellants:** Derive energy primarily from nitrocellulose (NC). They are used in all kinds of guns from pistols to artillery weapons. This type of propellant is usually lower in energy (3100 – 3700 J/g) compared to the double or triple-base types;
- **Double-base propellants:** In addition to NC, these contain liquid energetic plasticizers (usually nitroglycerine (NG)). This type of propellant is used in pistols, mortars, rockets and missiles. The energy range of double-base propellants is between 3,300 and 5,200 J/g. As NG already has plasticising properties, the need for additional plasticisers is decreased. However, higher energy levels lead to increased barrel erosion as a result of higher flame temperatures. To prevent this, deterrents are usually needed and DBP may be present coating the granules of propellant; and
- **Triple-base propellants:** Crystalline additives (usually nitroguanidine) are added to the NC/NG mix in order to reduce flame temperature and muzzle flash. Triple-base propellants have energy values from 3,200 to 3,700 J/g and are normally used in tanks and large calibre guns. As with the previous case, DBP may be found as a deterrent, regulating the burning rate.

The classifications above are commonly used to identify different kinds of propellants and are related to the use of plasticisers and/or deterrents. However, there is no clear rule of thumb indicating in which circumstances phthalates

should be used and in which not. As a general indication, the table below summarises the main reasons behind the choice of one plasticiser and/or deterrent against other.

Table 6.1 Key considerations in the choice of plasticiser and/or deterrent

Factor	Plasticiser	Deterrent
Energy	The desired level of energy may direct the choice towards an energetic plasticiser or an inert one.	Higher energy propellants are more likely to require deterrents in order to regulate initial burning rate.
Chemical composition	The initial mechanical properties of the mixture, derived from its chemical composition, influence the choice of the plasticiser.	Some deterrents are required to diffuse into the granules while others are expected to be inert and coat them. This depends on the chemical composition of the propellant and the deterrent.
Manufacturing process	Different processing methods require different amounts and types of plasticisers: <ul style="list-style-type: none"> - Solventless extrusion: The lack of solvents requires higher amounts of plasticisers in order to achieve the desired mechanical properties. - Solvent-based extrusion: Less plasticiser is required. - Cast propellants: The interstices of the granules are filled with a fluid plasticizer that diffuses into the powder. 	The manufacturing process may limit the choice between water soluble/insoluble and solid/ liquid deterrents as well as the application method (dipping, spraying, etc.).
Migration/decomposition	Some plasticisers may migrate from the mixture over time degrading the performance of the ammunition round.	The life expectancy of some deterrents also varies and this can be affected by environmental conditions.

6.2 Overview of Alternatives for Propellants

As illustrated above, the factors affecting the choice of plasticisers and deterrents are various. Because of this, plasticisers and deterrents are chosen on a case by case basis during the development of the propellant. According to industry, this makes it impossible to find a single universal, drop-in alternative able to substitute phthalates in all the propellants.

Literature and consultation revealed the presence of several potential alternatives to DBP in propellants. These are detailed in the table below together with comments on their suitability to replace DBP.

Table 6.2 Overview of Alternatives for Propellants

Alternative	Comments
Plasticisers	
Inert plasticisers	Do not add explosive capacity to the mixture. Among them, the most common apart from phthalates seems to be triacetin (1,2,3-triacetoxypropane; CAS No. 102-76-1). Recent research (Osborn and Manning 2010) has explored other common inert plasticisers. More details can be found in section 6.3.6.

Alternative	Comments
Energetic plasticisers	Add explosive capacity to the mixture while gelling the NC. Nitroglycerine is the most common one and, together with NC, the core of double-base propellants. Examples of energetic plasticisers include tris(azido acetoxy methyl) propane (TAAMP) and bis(azido acetoxy) bis(azido methyl) propane (BABAMP). These are assessed as potential DBP replacements in triple base propellants by Gosh et al (2008).
Deterrent	
Diphenyl urea derivatives (centralites)	Ethyl centralite (N,N'-Diethyl-N,N'-diphenylurea; Centralite I; CAS No. 85-98-3): used frequently in gun propellants as a stabiliser and deterrent. It can also be used as a plasticiser in some specific occasions. Methyl centralite (N,N'-Dimethyl-N,N'-diphenylurea, Centralite II; CAS No. 611-92-7). Mostly used as a stabiliser in double-base and triple-base propellants. It has also been used as a deterrent in some compositions.
Dinitrotoluene	DNT (CAS No. 121-14-2) is widely used as a deterrent in several types of ammunition. Its concentration is usually around 10% but it can reach up to 23% in some propellants for artillery. Although this substance seems to perform well in a variety of ammunition types, it is classified as carcinogenic Category 1B under the CLP Regulation and is included in the Authorisation list. It is therefore unlikely to be suitable for substitution of phthalates.
Diphenylamine	DPA (CAS No. 122-39-4) is a very common stabiliser against exothermic nitrocellulose degradation reactions in many propellant formulations. It can also be used as a coating deterrent. It is usually found in concentrations between 0.4% and 1%, reaching 8% in some rocket propellants. However, DPA is a known toxin and contains a carcinogenic impurity (4-aminobiphenyl). This impurity can be absorbed into the body by inhalation of its aerosol, through the skin, and by ingestion (Manning et al. 2006). According to consultation, DPA has good chemical compatibility as a deterrent but also a short life, its deterring capacity being reduced over time and decreasing the shelf life of the final product. Stability over time is a critical problem, as large quantities of ammunition are purchased in bulk and usually stored for significant periods of time prior to use. It is essential that the ammunition remains usable and safe even after many months (or even years).
Citrates	Compounds based on calcium citrate and bismuth citrate have been used as deterrent agents in propellants (Song et al. 2010, Craig 1974). According to consultation, citrates may offer good potential as alternative deterrent. However, general knowledge on the industrial potential of these substances is limited and more research is needed.
Camphor	Obsolete in most of formulations but known to be still in use as a deterrent for some large calibre weapons (25mm)

Source: Kirk-Othmer 2001, Manning et al. 2006, Song et al. 2010, Craig 1974, AFEMS 2013, van Driel & de Klerk 2010, ECHA website.

6.3 Detailed Investigation of Selected Alternative

6.3.1 Approach

The approach was based on literature review combined with some key insights from a representative of the sporting ammunition industry and ammunition manufacturers. Data availability is good for general formulations. However, no details were found about recent developments in substitution efforts as the name of the selected substance alternatives was rarely disclosed. In addition, the fact that both DBP and many of the alternatives can have several different uses within the propellant (e.g. plasticiser, deterrent, stabiliser) adds more confusion and uncertainty as the specific uses of these substances in some of the literature sources are not specified.

In addition, the nature of the ammunition industry with dozens of calibres and ammunition types, results in hundreds of different formulations individually designed to meet the specific needs of particular types of weapons. This fact, together with the rapid development of the industry and the confidential classification of some documents, hindered efforts to obtain detailed information about substitution capacity of specific substances.

Based on information gathered during a preliminary literature review, diphenyl urea derivatives (centralites) were selected for detailed investigation, having a particular focus on ethyl centralite (Centralite I) as this substance is already widely used as a stabiliser and deterrent, but has also been listed as a propellant plasticiser (Heramb and McCord 2002).

It should be noted that the level to which ammunition is covered by REACH remains uncertain. Article 3(3) of the REACH legislation excludes the obligatory application of this regulation to military ammunition stating that “Member States may allow for exemptions from this Regulation in specific cases for certain substances, on their own, in a mixture or in an article, where necessary in the interests of defence”. On the other hand, civil ammunition (e.g. hunting and sport shooting) would not be excluded by this article.

6.3.2 Health and environmental impacts

DIPP, DBP, and DPP are on ECHA’s Candidate List of Substances of Very High Concern for Authorisation (published in accordance with Article 59(10) of the REACH Regulation). DIPP and DPP are both classified in Annex VI of Regulation (EC) No 1272/2008 (list of harmonised classification and labelling of hazardous substances) as toxic for reproduction, Repr. 1B (H360FD: “May damage fertility. May damage the unborn child.”). DIPP rat studies showed severe fetal effects¹ and slight maternal effects. (ECHA, 2012). Although there are no studies on fertility with DIPP available to date, a fertility reducing action is suspected because of its structural relationship to DPP and DBP and their respective fertility findings.

DPP demonstrates testicular atrophy and a fertility impairing effect in dose ranges of relevance for classification. (ECHA, 2013). The NOAEL of DPP for reproductive and maternal effects is 200 mg/kg/day based on significant changes in maternal body weight gain, number of live fetuses, total resorptions, and fetal mortality.

DBP is classified in Annex VI as toxic for reproduction, Repr. 1B (H360Df: “May damage the unborn child. Suspected of damaging fertility”). Based on the available developmental studies in mice, an oral NOAEL of 100 mg/kg bw was derived for teratogenicity, embryotoxicity, and maternal toxicity (ECHA, 2008). DBP is currently included in Annex XIV of REACH (the "Authorisation List").

Industrial sites exposure at the workplace may be possible during the production of propellants. Furthermore, manufacturers may also be exposed to phthalates in the production of ammunition and explosives containing propellants with DBP (during dismantling and disposal of ammunition). Powder for manual reloading of shotgun, rifle and pistol cartridges with a content of DBP between zero and 10% is currently being sold to the public in the EU (e.g. Winchester (2009) and Ramshot (2007) Smokeless Powders), posing a risk of exposure for consumers. However, once the propellant is encased during the manufacturing process, there is no assumed release during

¹ After oral administration of a mixture Di-n-pentylphthalate with di-iso-pentylphthalate to Wistar rats in the dose of 1,000 mg/kg from the 6th - 15th day of pregnancy, all fetuses were resorbed (100% post-implantation loss).

storage and handling. This raises an interesting question as to whether this is in accordance with the REACH provisions on supply of CMR substances in mixtures to the general public.

Professional users may be exposed to phthalates in the propellant powder during reloading of empty cartridges with the propellant and also to dust from unburned propellant residues. According to the literature, the combustion of propellant powders in general is not complete. There are several factors that affect the amount of unburned propellant residues that remain including the propellant, calibre of the projectile and the barrel length. In indoor shooting ranges, the unburned propellant residues may be deposited on the floor area in the first five to ten meters from the shooter in the firing direction. Studies have shown that the amount of propellant can range from 1 – 100 g per 1,000 shots. Also, in professional shooting operations, a daily amount of 0.5 kg of unburned residues may be assumed. Therefore, professionals during shooting activities and cleaning personnel of indoor shooting ranges may be exposed to DIPP from unburned propellant residues.

Although there is opportunity for inhalation exposure to unburned propellant dust at indoor shooting sites or to powder dust during manual reloading of cartridges, there is no information available on the extent of exposure, on particle size or the concentration of DIPP in the dust.

Alternatives to DIPP, DBP, and DPP used in propellants and ammunition include ethyl centralite and other diphenyl urea derivatives, such as methyl centralite. A hazard evaluation of ethyl centralite (CAS No. 85-98-3) was performed using rats, rabbits and guinea pigs (Weeks and McCreech, 1976). Data indicated little toxic hazard from accidental ingestion or acute vapour inhalation. Ethyl centralite has also been reported to be non-corrosive, non-sensitizing and possesses no endocrine-disrupting toxicity. There are no reports of reproductive toxicity associated with exposure to ethyl centralite. It has been suggested that gradual decomposition of ethyl and methyl centralite may form carcinogenic nitrosamines (Fryš et al. 2010). However, carcinogenicity and mutagenicity testing performed on these two chemicals have resulted in no detectable carcinogenicity or mutagenicity suggesting that this is not a biologically significant degradation pathway. The LD₅₀ for ethyl centralite is about 781 mg/kg (24 hrs) by ingestion and greater than 198 mg/l (4 hours) by inhalation. Environmentally, ethyl centralite has a moderate acute aquatic toxicity (16-20 mg/l in 48-hour fish mortality tests) but very high chronic fish toxicity (0.037 mg/l 14-day fish). Neither the methyl nor the ethyl derivatives bioaccumulate and neither has significant persistence in air or water. However, the ethyl centralite has been found to be moderately persistent in terrestrial soils.

It was recommended that personnel handling solid ethyl centralite wear approved eye and skin protective equipment. Similarly, methyl centralite (CAS No. 611-92-7) is moderately acutely toxic via oral routes and may cause respiratory irritation. It is not listed as a carcinogen and is not expected to bioaccumulate in aquatic organisms. It is also considered readily biodegradable.

6.3.3 Technical feasibility

As mentioned above, technical constraints in the replacement of phthalates as deterrents are variable and numerous. However, there are three key technical requirements that any deterrent must meet in each of the formulations:

- The alternative must not interact chemically with NC or NG (or any other energetic base used in the same ammunition);
- It should be stable over time: the thickness of the deterring layer must not alter over time; and
- It should have an adequate diffusion rate from the surface of the granules.

According to consultation, in general terms, centralites show adequate properties with regards to stability and diffusion rate, but have chemical compatibility problems. Centralites may not be always chemically compatible with NC/NG as they may react chemically with them and thus undermine the desired properties. It should be noted that centralites are also used as stabilizers (preservatives) and may have an influence on the chemistry of the gunpowder.

Information about what specific alternatives are suitable for each use could not be provided by consultees or literature. This is due to the high number of factors that condition the need and suitability of the deterrent. In any case, it seems that the replacement of DBP in all cases with a single substance is not possible. Ammunition manufacturers declared that centralite may work for some of their products, but not to totally replace phthalates. The technical feasibility to replace phthalates must be addressed on a case by case basis, selecting the most appropriate substitute for each use.

6.3.4 Economic feasibility

DBP is widely manufactured on a global scale, being used in many other fields. This ensures affordability and supply, especially considering that propellants are likely to represent a small proportion of the overall use of DBP.

According to consultation, ethyl centralite is two to three times more expensive than DBP. However, they are used in a similar concentration to DBP (2-5%) so the impact on the final price is limited compared to the overall propellant cost. The main economic impact is expected to be on R&D and, particularly, in testing and certification.

Testing and certification pose a particular burden for the military industry. Military ammunition has to withstand harsher environmental conditions than civil ammunition (humidity, extreme temperatures, etc.). In addition, NATO and national regulations impose strict standards (e.g. STANAG 4496 on fragment impact test, STANAG 4241 on bullet impact test, STANAG 4382 slow cook-off test, etc). Therefore, testing and certification can be very costly and, in some cases, logistically complicated (e.g. testing rounds of tank ammunition). No specific cost scales for testing and certification could be provided by the consultees.

6.3.5 Availability and timing

Time is a significant constraint in the ammunition industry. As mentioned above, testing and certification in the ammunition industry is an important burden. As there are more than 100 calibres and several types of ammunition for each calibre, the time taken to replace any one substance is likely to be significant as each of these types must be individually tested and certified. This makes the testing of a whole product portfolio a long and expensive procedure. In addition, this industry is heavily regulated, which forces producers to undertake many certifications, such as the NATO STANAG tests mentioned above. However, market development of a tested and certified

product seems to be much faster. In the civil ammunition industry an implementation time of 6 months (from lab to production) is expected for each ammunition type. No time scales were provided for the military industry.

Available stock may be affected by the sunset date of the authorisation process. As pointed out by the Finnish Defence Forces (RCOM 2009), considerable amounts of military propellants are currently stored as they are a key element of military preparation. In the same way, reserves of DBP as one of the raw materials for these propellants are stored in significant quantities. Such propellants are kept in store for considerable lengths of time, often for decades. This can pose a burden in the development of alternatives as a significant proportion of the stock would need to be replaced, with its associated cost. In the same way, if the legislative timeframe is too short, armies may be forced to replace a large part of their stored DBP by alternative substances. However, as noted above, military applications may be exempt from the authorisation requirement.

6.3.6 Existing R&D activities

During recent years, there has been increasing research undertaken by private business and public research centres in the development of safer and more environmentally friendly propellants. According to consultation, many propellant manufacturers are involved in R&D activities in this sense.

The German based company Rheinmetall Defence conducted a research for the development of a “green” propellant for large calibre ammunition (76mm) (Wiehahn, 2012). Their objective was the reduction or elimination of solvents in the manufacturing process and the replacement of some toxic components including DBP, DNT and DPA. After conducting several tests, they developed three potentially suitable formulations, two of them based on the addition of “inert plasticisers”. A final selection and further tests are expected to occur but no specific timescale was detailed. Details of the specific substances included were not provided and it is not possible to determine the extent to which they have replaced DBP.

Another significant initiative has been running for more than seven years in the USA. Coordinated by the US Army Picatinny Arsenal in collaboration with other organisations and private companies, in 2006 the team developed a propellant that eliminated DBP, DNT and DPA among other substances for medium calibre ammunition (25 mm) (Manning et al. 2006). This double-base propellant, denominated PAP-8386, involved the use of NG as a plasticiser in a solventless process. Coating deterrents were added but no details about the specific substance were made public.

Further phases of the project explored the use of this propellant in larger calibres (120 mm) (Manning et al, 2007). For this purpose, changes in the formulation of PAP-8386 were investigated, including the addition of inert plasticisers. The plasticisers studied were:

- Castor oil;
- Diethylene glycol (DEG);
- Di n-propyl adipate (DnPA);
- Dioctyl sebacate (DOS);

- Glycerol;
- Glycerol carbonate; and
- Trioctyl trimellitate (TOTM).

Only one of these (not disclosed) is reported to have provided good technical results (Osborn & Manning, 2010). Although PAP-8386 is already DBP-free, the selected plasticiser may offer potential as a replacement of DBP in other types of propellants.

Recently, researchers at Picattiny Arsenal have also been investigating the use of inert coatings as an alternative to classic deterrents like DBP or ethyl centralite (which diffuse into the energetic substrate rather than simply coating). Three inert coatings have reportedly been selected for further study (without specific details) (Park, 2012).

6.3.7 Suitability

Considering all the factors affecting the choice of plasticisers and burning regulators, no single alternative to DBP can be identified as a universal replacement. However, there are a series of factors that affect present and potential alternatives:

- Technically, the main requirements for a suitable deterrent are
 - No chemical interaction with the energetic substrate (other than deterrent properties);
 - Stability over time; and
 - Adequate diffusion rate.
- Economically, the price differential of alternatives is likely to be surpassed by R&D, testing and certification costs. This is expected to occur for any alternative, as any change in formulation can have a significant impact on the properties and safety of the ammunition.
- Health and environment: The alternative should be safer than DBP and unlikely to be restricted in the future.

In the specific case of centralites, it seems that these can be a good substitute for some particular formulations but it cannot cover the whole range of propellants. This is true not only for centralite, but possibly for any other alternative to DBP, based on the consultation undertaken for the current study.

6.4 Overall Conclusions

Overall, there are a range of different substances that are currently used as plasticisers or deterrents in propellants for ammunition. Phthalates, particularly DBP, are some of the most popular and have been used for decades in the manufacture of ammunition. The alternatives selected for detailed analysis were diphenyl urea derivatives (centralites), having a particular focus on ethyl centralite (Centralite I). Ethyl centralite has been used for many years in propellants and is already one of the most popular alternatives to DBP in ammunition. However, this

substance is not always compatible with the chemical composition of the propellant or may not offer the necessary technical requirements for all ammunition types. Regarding health concerns, ethyl centralite seems to be non-mutagenic, non-bioaccumulative and have low toxicity. However, it has been suggested that daughter substances from its gradual decomposition may be carcinogenic. This substance is also substantially more expensive than DBP, although the effect on the price of the final product is expected to be limited.

The main conclusion of this section is that, while ethyl centralite can successfully replace DBP in some formulations, none of the available deterrents can be considered as a universal drop-in substitute in propellants. This is due to the myriad of formulations, uses, environmental conditions and calibres with varying ballistic requirements. In addition, the stringent tests and reliability requirements that regulate the ammunition industry allow for a very limited degree of flexibility in the composition and performance of propellants.

Other substances that may replace DBP in some formulations are citrates (as a deterrent) and several inert and energetic plasticisers. Alternatives need to be investigated on a case by case basis, but given the regulations of the ammunition industry, changes are expected to occur slowly. Research in this field seems to be active, with some positive results and further developments are expected to take place.

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7. Insulation of Indoor Wires and Cables

7.1 Phthalates in Insulation of Indoor Wires and Cables

Use of the Authorisation and Candidate List phthalates in wire and cable insulation was selected as an application for detailed investigation, on the basis that it is probably the largest use of the phthalates in a commodity, general purpose PVC product². It is expected that there may have been authorisation applications for general PVC plasticiser uses (as well as some of the more specialised uses considered elsewhere), and this application is therefore taken to be representative of some of the issues that may arise in considering alternatives for those uses³.

PVC is used in cable insulation because it provides both inherent flame retardancy and resistance to oils, chemicals, ozone and sunlight. As PVC is inherently rigid and stiff, plasticisers are required to impart flexibility. It is used as jacketing for a wide variety of cables, including power cables, and is also used as insulation in wires such as those used in audio transmission, low voltage cables in buildings and portable applications (applications where its level of dielectric power loss is deemed acceptable (Kirk Othmer, 2000)). There are various performance test criteria developed specifically for PVC compounds used in wires and cables, set out in relevant fire safety standards⁴.

PVC was reported in 2006 to be the world's leading electrical material, with over 250,000 tonnes used each year for wire and cable insulation and sheathing, electrical conduit, boxes, and components (Kirk Othmer 2006).

An estimated 0.5 million tonnes of cables are imported into the EU each year, with production around 2.9 million tonnes. PVC content is reported to range from 30% (single solid copper conductor wire used for 230-400V installations), to 65-70% for 2-3 conductors flexible connecting cords used in the home or office or and 3-5 conductors construction cables (230-400V) (Denmark, 2011).

Of the phthalates on the Candidate and Authorisation Lists, it is understood that the primary (or even only) one used is DEHP, which was used in the EU in quantities of 52,600 tonnes in 2007 (Denmark, 2011). However, the primary plasticiser used in cables is understood to be di-isodecyl phthalate (DIDP), at around 80% of the market and there is understood to be a trend away from use of DEHP, due to regulatory pressures, including the classification as a CMR and inclusion on the REACH authorisation and candidate lists (highlighted in consultation for the current study).

Indoor wire and cable often undergoes heating (typically up to 60°C) and can be in near-constant use (e.g. with refrigerators), which makes some of the other lower molecular weight phthalates (such as DBP and BBP) unsuitable, due to the greater potential for volatilisation.

Exxon (2011) indicate that the key processing and end use requirements for wire and cable include dry blending time, extrusion rate, ageing performance, heat resistance, abrasion resistance and retained properties over time.

² For instance, as reported for DEHP in Denmark (2011).

³ For example, similar issues in substitution are likely to arise with other plasticiser uses, such as flooring, film/sheet and hoses/profiles, some of the other historical major uses of DEHP and other phthalates.

⁴ For example, EN 60332 on tests on electric and optical fibre cables under fire conditions.

Plasticisers used in PVC are indicated to require low volatility and viscosity, extraction resistance and good processability amongst others.

7.2 Overview of Alternatives for Indoor Wires and Cables

7.2.1 High-level listing of potential alternatives

One key finding from the research undertaken for the current study is that other phthalates are likely to be the main substances used as replacements for those on the candidate and authorisation lists. In particular, some of the higher molecular weight phthalates, particularly di-isonyl phthalate (DINP) and DIDP, are reportedly usable in many of the applications in which DEHP has historically been used. Since these substances do not have harmonised classification under the CLP Regulation, it seems that many companies would tend to use these substances as alternatives, not just for indoor wire and cable, but also for many other commodity, general purpose applications.

There is a wide range of **alternative PVC plasticisers** (non-phthalates), with those identified in the current study including:

- (2-ethylhexyl) adipate (DEHA) (CAS No. 103-23-1) (ECHA, 2009; SCENIHR, 2008; Lowell Center, 2011);
- Acetyl tributyl citrate (ATBC) (CAS No. 77-90-7) (ECHA, 2009);
- Alkylsulphonic phenylester (ASE) (CAS No. 91082-17-6 (Denmark, 2011; SOCOPSE, 2009);
- Castor oil derivatives (COMGHA) (CAS No. 736150-63-3) (Denmark, 2011);
- Di(2-ethylhexyl) phosphate (CAS No. 298-07-7) (Lowell Center, 2011);
- Di-(isononyl)-cyclohexan-1,2-dicarboxylate (DINCH) (CAS No. 166412-78-8 or 431-890-2) (Denmark, 2011);
- Diethylene glycol dibenzoate (DEGD) (CAS No. 120-55-8) (Denmark, 2011);
- Dioctyl terephthalate (DOTP/DEHT, Eastman 168) (CAS No. 6422-86-2) (Denmark, 2011);
- Dipropylene glycol (CAS No. 27138-31-4) (Denmark, 2011);
- O-toluene (CAS No. 88-19-7) (Lowell Center, 2011);
- Tri(2-ethylhexyl) phosphate (TEHPA) (CAS No. 78-42-2) (SOCOPSE, 2009); and
- Trioctyl trimellitate (TOM/TOTM, TETM) (CAS No. 3319-31-1) (Denmark, 2011; ECHA, 2009; SCENIHR, 2008; Lowell Center, 2011; SOCOPSE, 2009).

Finally, there are a number of potential **alternative materials** that are used in wire and cable applications, including, for example, polyethylene and silicone rubber. The main non-PVC building wires for 110-220V use

include polyethylene. For data cables and appliances, flame retardancy is critical and alternatives to PVC include fluorinated ethylene-propylene polymers (such as PTFE or FEP), with polyethylene being more suitable in outdoor applications where it is more cost-effective and does not always require the same flame retardant properties (Kirk-Othmer, 2006).

Other materials identified in the literature have been tested as potential alternatives to phthalates in power cords, including: styrene-ethylene, butylene-styrene (sebs) polymer (CAS No. 66070-58-4), polyphenylene ether (ppe) (CAS No. 25134-01-4), high impact polystyrene (HIPS) (CAS No. 9003-55-8), polystyrene (CAS No. 9003-53-6) and thermoplastic co-polyester; polymer with 1,4-butanediol and .alpha.-hydro-.omega.-hydroxypoly(oxy-1,4-butanediyl) (CAS No. 9078-71-1) (SUBSPORT, 2012).

The above is by no means an exhaustive list, but serves to illustrate the range of different alternatives that are potentially available for use in this application. Each has advantages and drawbacks, and the uptake of each in the event of non-authorisation is difficult to predict.

The following section is intended to provide a good picture of the range of some of these potential alternatives for this application, to the extent that useful information has been identified regarding their potential suitability for indoor wire applications.

The final section in this part of the report provides a more detailed review of the merits of one specific alternative (COMGHA), which was selected for further investigation not because it is the most likely used alternative for this application, but because it includes some useful considerations in relation to alternatives that can be produced from substances of biological origin (castor oil).

7.2.2 Alternative plasticisers

Higher molecular weight phthalates (e.g. DINP, DIDP)

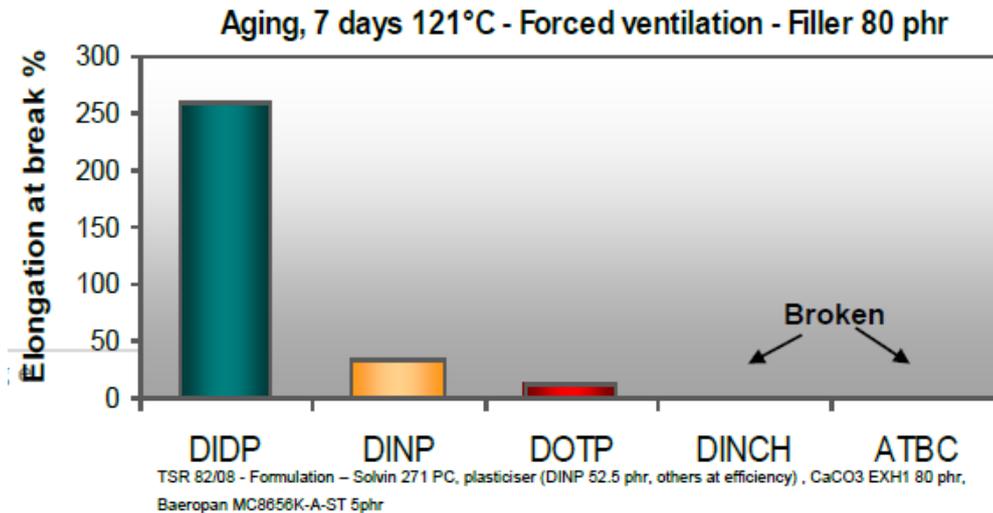
The primary focus area of the current study is to consider non-phthalate alternatives to the substances on the authorisation and candidate lists. However, it is vital to be aware that, in many cases, it is expected that the alternatives that would be used for wire and cable applications will be other, higher molecular weight, phthalates, such as DINP and DIDP.

Neither DINP nor DIDP are classified under the CLP Regulation. Therefore, it is likely that many companies currently using lower molecular weight phthalates such as DEHP would use DINP or DIDP in wire and cable applications. Indeed such a move towards these substances is already evident within the EU, having taken place over recent years in response to regulatory pressures on DEHP (Exxon, 2012).

DINP has around half the volatility of DEHP and DIDP around one third that of DEHP (Exxon, 2011). These are important factors in the context of plasticiser loss from articles during their service life. Clearly for indoor wire applications, it is important that the wire remain plasticised over its lifetime, in order to ensure adequate performance in use. Similarly, the rate of diffusion of DIDP in PVC is around four times slower than that of DEHP.

Exxon (2011) compared the ageing of PVC with reference to high-temperature-rating cables (in terms of loss of elongation at break), highlighting the poorer performance of some alternatives compared to DIDP in particular. Whilst the same high-temperature performance is not necessarily required for indoor wire and cable applications, there are clearly some such applications where temperature can affect the flexibility of the polymer.

Figure 7.1 Elongation at break for PVC plasticised with different phthalates after ageing



Source: Exxon (2012)

Denmark (2011) suggest that the price of DINP is around 11% higher than that of DEHP, comprising a 4% increase in price per unit weight, and a substitution factor of 1.06. Consultation for the current study confirms that the price differential is around 10%, though this may be partially offset by more effective formulations due to the lower density of the higher-MW phthalates.

Consultation with industry⁵ (as well as ECPI's (2013a) statement regarding the use of phthalate esters plasticisers in cables) suggests that the majority of EU PVC converters (10s of thousands) have moved away from the use of DEHP over the last 10 years, primarily to higher-MW phthalates. Available information suggests that the technical performance of these plasticisers is comparable or better to that of DEHP and that substitution can typically take place fairly rapidly (e.g. within several months to one year for wire and cable applications).

DINP and DIDP are reportedly widely available on the market and it is assumed that there would be no particular issue with availability. As reported by Denmark (2011), the share of the plasticisers market for DINP/DIDP went from 35% to 67% between 1999 and 2008, while the share for DEHP went from 42% to 18%. More recent data suggests that the share of the market for the higher phthalates (DINP, DIDP and DPHP) is over 75%, with lower phthalates (DEHP, DBP, DIBP, BBP) representing less than 10% (ECPI, 2013a).

⁵ Personal communication with plasticiser producer

It is also indicated that other high molecular weight phthalates (e.g. tri-isodecyl phthalates, linear undecyl phthalates), as well as trimellitates (see below) have become the first choice for high-temperature resistant cables (ECPI, 2013a).

Trioctyl trimellitate

TOTM does not have harmonised classification under the CLP Regulation, and the majority of notifiers have indicated that the substance is not classified. However, it is of note that several companies notified classification as a category 2 reproductive toxin, and there are various other notified classifications listed on the CLP Inventory Database.

Trimellitates (such as TOTM) can be used in wire and cable coatings. They are reported to have good technical performance and are well suited to high temperature (e.g. automotive) applications. Their molecular weight reportedly makes them harder to process due to their higher viscosity and lower solvation power for PVC. They are also reported to have poorer cold-temperature performance than phthalates⁶.

Whilst TOTM is widely used in some applications, a primary barrier to their more widespread uptake in applications such as indoor wire and cable is their higher price, which is estimated at around three times that of DEHP and DINP⁷.

Overall, it seems that their use is more likely to be limited to high temperature applications, such as automotive, rather than the indoor wire and cable applications that are the focus of this section of the report.

Diocetyl terephthalate

Terephthalates, such as dioctyl terephthalate (DOTP), are structurally very similar to the ortho-phthalates. The key differentiation in technology relates to the parent alcohol, which is the same in DOTP as it is in DOP, and the only difference is the production from terephthalic acid compared to phthalic anhydride.

DOTP is structurally analogous to DOP. This substance is not classified under the CLP Regulation, and it is likely that some companies would choose to use this substance as a replacement for phthalates such as DEHP. However, consultation for the current study highlights the fact that this substance has been far less extensively studied than the phthalates.

DOTP reportedly has lower resistance to high temperature compared to other phthalates used in wire and cables, and is reported to be less compatible with PVC than ortho-phthalates⁸. It is expected that this substance is more likely to be used in less demanding wire and cable applications, which may include some commercial and domestic indoor applications.

The price of DOTP is understood to be similar to that of DEHP, as the production process is similar, though the esterification process takes more time.

⁶ Personal communication with plasticiser producer

⁷ Personal communication with plasticiser producer

⁸ Personal communication with plasticiser producer

Production is understood to take place in the EU (1-2 producers), USA, Turkey and China (several producers in the latter), though the overall consumption and market capacity for this substance are unknown.

Phosphate esters

Phosphate ester plasticisers are reportedly commonly used in wire and cable when additional flame-retardant and smoke-suppressant properties are important (ECPI, 2013a).

An example is tris (2-ethylhexyl) phosphate, which is reportedly compatible with PVC and provides flame retardancy and good low temperature performance, as well as 2-ethylhexyl diphenyl phosphate (ECPI, 2013).

Relatively little information has been identified on this substance. It has no harmonised classification under the CLP Regulation but several notifiers indicated self-classification as category 2 for skin and/or eye irritation.

Di-(isononyl)-cyclohexan-1,2-dicarboxylate (DINCH)

DINCH is worthy of mention due to the substantial increase in production capacity in the EU in recent years⁹, and its likely adoption in a number of other commodity PVC applications. It is reportedly more widely used in products such as toys, childcare articles, hoses, sealants and cap closures, crown corks, artificial wine corks, gaskets and gloves (Denmark, 2011).

The substance is structurally similar to DINP, but based on a cyclohexane, rather than a benzene ring structure. It does not appear to be classified under the CLP Regulation.

Investigation for the current study indicates that the substance is unlikely to be suitable for wire and cable applications, primarily due to its higher volatility and lower compatibility with PVC, resulting in poorer ageing performance (which is not such an issue for products such as toys)¹⁰.

Alternative plastics

The main alternative plastic materials for this use are understood to include polyethylene and fluorinated ethylene-propylene polymers (such as PTFE or FEP). These materials have not been investigated in any detail at the current time, but it is hoped that additional information may be forthcoming following two interviews planned for early November 2013.

⁹ For example, BASF raised its capacity from 25kt to 100kt in 2007 (Denmark, 2011).

¹⁰ Personal communication with plasticiser producer

7.3 Detailed Investigation of Selected Alternative

7.3.1 Approach

The alternative selected for more detailed investigation for this application is acetylated monoglyceride derived from hydrogenated castor oil (COMGHA), which is marketed as an alternative for DEHP, DBP and BBP (Denmark, 2011).

This application was selected for more detailed investigation not because it is the most likely used alternative (that would be DINP and DIDP), but because it raises issues of interest to RIVM being produced from a supposedly more 'sustainable' source (the terms of reference for the project incorporated the desire to investigate bio-based plastic products).

The main information sources used in this analysis are a review of relevant literature, supplemented with consultation with suppliers of relevant plasticisers (specifically a supplier of the substance itself, as well as a supplier of high molecular weight phthalates).

The key gap in the information collected for this application as a whole is relevant input from representatives of the users of the phthalates in wire and cable applications. Following several attempts to contact relevant organisations, it was not possible to interview representatives of the main trade body contacted (Europacable). However, it is expected that an interview with them, along with a company that has replaced phthalates in its cables, will take place in early November 2013.

7.3.2 Health and environmental impacts

DEHP is a male reproductive toxicant because of the specific testicular toxicity associated with exposure. (NIOSH 1990, USFDA 2001). The active metabolite responsible for the testicular toxicity of DEHP is the ester metabolite monoethylhexyl phthalate (MEHP) (Astill, 1989). MEHP forms predominantly in the digestive tract as the result of the action of protease enzymes produced in the pancreas. With the exception of a small amount of activity in the liver, there is very little potential for DEHP introduced to the blood through inhalation or dermal absorption through the skin. (Ono et al, 2004).

Studies on animals indicate an age specific sensitivity of immature males to both testicular toxicity and endocrine impacts from DEHP exposure. This is particularly true for neonates potentially exposed within 1-2 years post partum (human equivalent).

Orally-administered DEHP is rapidly hydrolyzed to MEHP and 2-ethylhexanol (2-EH) in the digestive tract. This metabolism is facilitated by pancreatic hydrolases. Trace amounts or no intact DEHP have been found in the blood or liver tissues of rats or primates treated orally with DEHP at levels below 500 mg/kg. (Kessler et al, 2004). This supports the hypothesis that DEHP is poorly absorbed from the gastrointestinal tract and that it is MEHP that predominantly enters the circulation from ingested DEHP doses (Astill, 1989).

Dermal absorption involves the transfer of DEHP from the outer skin surface to the central circulation. It therefore bypasses the digestive tract. As a result, it represents a direct introduction of DEHP to the circulation akin to parenteral exposure in that it is DEHP and not MEHP that enters the bloodstream. Hence, the toxicity for dermal exposure is significantly lower than toxicity associated with ingestion.

Inhalation of DEHP is precluded by its low vapour pressure (0.13 Pa at 20 °C). This yields an equilibrium concentration of 0.98 ppm and a vaporization rate of practically zero. Therefore, inhalation is not a significant route of exposure.

Although transfer rates tend to be slow between PVC cable and insulation, it is expected to result in consumer exposure through both dermal absorption as well as incidental ingestion. Dermal uptake is expected to have a maximum rate of 0.24 $\mu\text{g}/\text{cm}^2\text{-hr}$ of contact. This would be expected for most applications of DEHP as a plasticiser since flux across the epidermis is the rate-limiting step in most absorbance situations. Incidental oral contact will vary by circumstance, but would be expected to be on the order of 1-3 $\mu\text{g}/\text{hr}$ for an adult male. Hence, it is unlikely that any situation short of extraordinary contact (i.e. chewing, ingesting plastic, etc.) would exposure be expected to rise to the DNEL of 34 $\mu\text{g}/\text{kg}\text{-day}$ oral or 672 $\mu\text{g}/\text{kg}\text{-day}$ dermal.

Substitution for DEHP will have minimal impact on consumer risk for this application. This is because the risk of adverse effect from interacting with DEHP-containing cables is minimal with only cases outside the expectation of average use representing an issue. That said, even this minimal risk will be alleviated with the substitution of a non-reprotoxic plasticiser.

Since the DEHP is added early in the manufacture of the PVC, occupational exposure during processing would be expected to be widespread and occur along the majority manufacturing chain. Exposure rates can be significantly impacted by temperature not so much through inhalation, but through reduced phthalate and plastic viscosity thereby increasing the rate at which it may leaches out of plastic. Activities at greatest risk include thermal moulders and finishers. Personal protection such as gloves and coveralls as well as mandatory post work washing will significantly limit potential exposure.

Substitution of a safer alternative for DEHP will likely have the greatest impact in the occupational setting since this is the situation of highest and most widespread potential exposure.

The primary reason for considering COMGHA is its potentially lower environmental impact, as it can be based on biologically-generated substances. It is derived from castor oil, which is a plant-based fatty acid triglyceride composed primarily of C₁₈ ricinoleic acid. Castor oil is generally regarded as safe and is used as a direct food additive as well as a stimulant laxative. Castor oil does not contain ricin that is found in the native castor bean, therefore post-extraction, castor oil has no sensitizing or irritant properties. Furthermore, it is not carcinogenic/mutagenic and is not a reproductive toxicant or an endocrine disruptor. Environmental impacts are extremely mild with the exception of potential eutrophication if released in high volumes.

While the product is safe as the oil extract, extreme care must be taken in its production. Along with the presence of ricin, the castor bean contains a number of seed coat proteins that are known human sensitizer proteins (both respiratory and skin). Exposure to the raw extraction mashes must be limited with isolation through engineered controls and/or personal protection.

It is also of note that growing castor oil for production of phthalates could, like biofuels, lead to displacement of land from food production or other land applications.

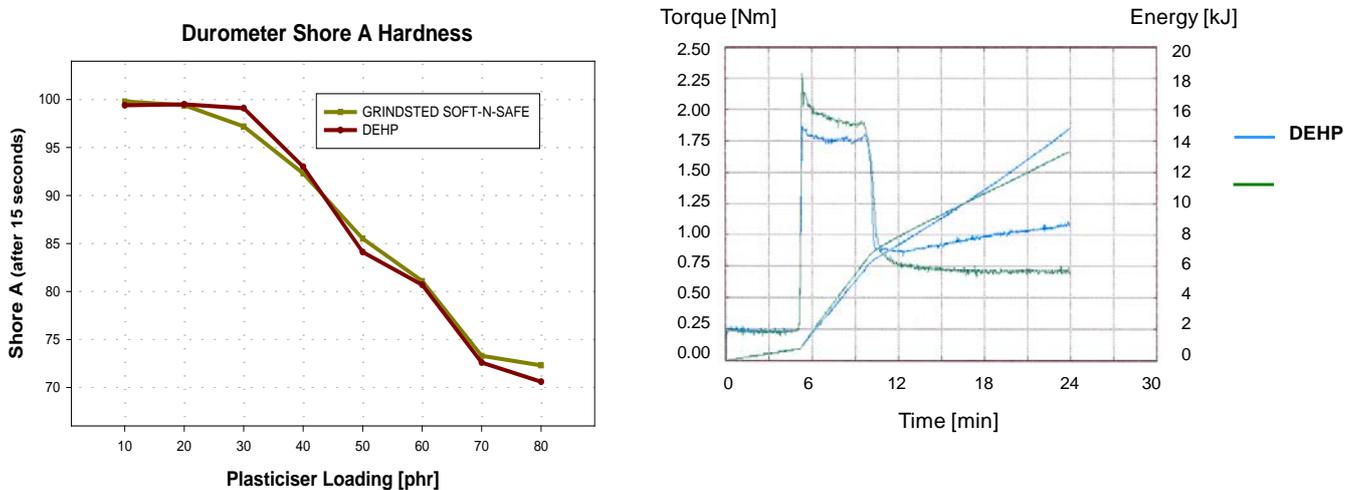
7.3.3 Technical feasibility

A supplier of the substance indicates that COMGHA does not require significant changes in PVC formulations or investments in new equipment. It has reportedly been shown to perform well in domestic and household cables and wires up to 60°C. However, its performance in high tension or automobiles is reportedly poorer due to the higher temperatures involved¹¹. It is more widely reported to be used in toys, food contact and other applications¹².

The supplier of the substance has indicated that customers in the automotive industry have indicated that the substance allows fogging tests for wires in the automotive industry to be met (Danisco, 2013). However, they have confirmed the view of the suppliers of high-molecular-weight phthalates that cable manufacturers are more likely to move to higher molecular weight phthalates than to COMGHA.

The figures below illustrate that the substance is comparable to DEHP in terms of gelation/efficiency and in terms of fusion time.

Figure 7.2 Shore A hardness variation with plasticiser loading / fusion time for COMGHA vs DEHP



Source: Danisco (2013)

¹¹ Personal communication with plasticiser producer

¹² In terms of the temperature requirement for indoor wire and cables, it is understood that many indoor applications will not need to have a temperature rating above 60°C. However, there are some wire and cable applications which have higher temperature ratings (see e.g. UL 2012), meaning that COMGHA may not be a technically suitable alternative if only the 60°C standard can be met.

Overall, while the substance appears to be suitable for at least some types of PVC wire and cable, this does not appear to be an application in which it is expected to be particularly widely used and there is at least anecdotal information which suggests that it is not suitable for use in applications subject to higher temperatures.

7.3.4 Economic feasibility

A supplier of the substance suggested that the purchase price of the substance is around 50% more than that of DEHP, with a price differential expected to remain regardless of any increase in production¹³. Suppliers of other substances have suggested the price could be substantially higher (5-6 times that of DEHP) (ECPI 2013, and personal communication with plasticiser producer).

The substance supplier suggested that, in cable applications, the implications for the overall price is relatively small (in the order of 3-4%) due to the significant impact on price of the copper in PVC wire and cables. Consumers may therefore be more able to bear an increase in price compared to other applications in which the plasticised PVC is the primary product (such as cling film for food).

7.3.5 Availability and timing

The substance is registered under REACH at 1,000 to 10,000 tonnes but the current and projected future production capacity are unknown.

The EU plasticisers trade association highlights the fact that harvesting time and seasonality of the raw materials limits the production capacity of these substances (ECPI, 2013). Similarly, the supplier of the substance contacted for this study indicates that, although availability is adequate at present, total substitution of phthalates would not be realistic due to production capacity constraints¹⁴.

For use in large quantities, availability will be affected by land requirements for growth of the castor beans which are used to produce COMGHA. Likewise, use of agricultural land for this purpose could have unintended consequences in terms of e.g. land availability for food crops. By way of example, it is estimated that 10m²a (square metre years) are required to produce 1kg of COMGHA (Danisco, 2011). If a 1:1 replacement ratio for DEHP use in wire and cable were assumed, and taking historical DEHP use for wire and cable in the EU of 52,600 tonnes in 2007 (see above), the amount of land required to grow the castor beans for this use would be around 530 million m², or over 1% of the total surface area of the Netherlands¹⁵.

The supplier of the substance indicates that, as a drop-in substitute, replacement can be done in a very short time (e.g. laboratory phase to production in 6 months), which is comparable to that for higher phthalates. However, as highlighted by a supplier of the higher phthalates (Exxon, 2013), the time taken for reformulation of wire and cable products may be longer, due to the additional testing requirements on product performance.

¹³ Personal communication with plasticiser producer

¹⁴ Personal communication with plasticiser producer

¹⁵ Assumed 41,530 km² total surface area.

7.3.6 Existing R&D activities

The extent to which the EU wire and cable industry is actively pursuing this substance type as an alternative to phthalates in PVC wire and cable is unknown.

7.3.7 Suitability

Overall, it appears that COMGHA is suitable for some, lower temperature, wire and cable applications, but the suitability in higher temperature applications appears to be questionable. The available information does not suggest a worse health/environmental profile than phthalates such as DEHP, although it is likely that the substance has not been studied to the same extent. The price of the alternative is considerably higher than that of the phthalates, which is expected to limit its use in some applications, though this may be less of an issue for PVC cable, due to the relatively small share of the overall cost accounted for by the PVC plasticiser. It appears that availability of the substance is likely to be an issue if considering more widespread replacement of general commodity phthalates.

7.4 Overall Conclusions

PVC wire and cable represents one of the largest historical uses of phthalates that are on Annex XIV, particularly DEHP. The analysis above reveals some findings with this application that are likely to be applicable to other historical uses of DEHP. Of particular note is the significant move away from use of DEHP to higher molecular weight phthalates such as DINP and DIDP. This is a trend that has occurred across numerous PVC applications over recent years due to the various regulatory pressures on DEHP. DINP and DIDP are likely to be the most-used alternatives for many other PVC applications, as well as for wire and cable.

The alternative substance that underwent more detailed examination was the castor-oil-based COMGHA, selected on the basis that it can be produced from biologically-generated substances (of particular interest to RIVM for the current study). Whilst COMGHA may not have been studied to the same extent as e.g. DEHP, the substance does not seem to be classified under the CLP Regulation. It is reportedly technically feasible to implement with minimal process changes for various applications, with good technical performance in certain applications (e.g. food contact materials and toys) specifically mentioned. It is reportedly suitable in PVC wire and cable with a temperature rating up to 60°C, which will encompass many indoor wire and cable applications, but not all, as some appliances have a requirement for a higher temperature rating. The availability of the substance as a replacement for high-volume uses of phthalates is reportedly limited by the seasonality of supply due to the growing season for castor oil. The substance is more expensive than DEHP and also more expensive than the higher molecular weight phthalates that are more widely used as alternatives in wire and cable. As a result of the above, COMGHA does not seem to be widely used in PVC wire and cable as an alternative to DEHP.

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8. Maleic Anhydride

8.1 Phthalates in the Manufacture of Maleic Anhydride

8.1.1 Process overview

Maleic anhydride (MAN) is usually produced via the reaction of either benzene or *n*-butane with oxygen, although it can also be produced as a by-product of phthalic anhydride. Of these, using *n*-butane as feedstock is by far the most common process. This is due to the high cost and risk profile of benzene on the one hand, and the low MAN yields when produced as a by-product of phthalic anhydride on the other (5-6% of MAN relative to phthalic anhydride (Brandstaedter, 2007)).

Using either benzene or *n*-butane as feedstock, the main process steps in the production of MAN are (ChemSystems, 2009):

- Feed preparation: the feedstock (hydrocarbon) is mixed with compressed air and delivery to the reactor;
- Oxidation reaction: the reaction takes place in the presence of catalysts in one of three types of reactor:
 - Fixed-bed reactors: the feed gas is passed over fixed beds of catalyst pellets in multiple tubes. As the reaction is highly exothermic, the tubes are cooled by molten salt and hydrocarbon concentration is limited to prevent explosion (1-2.5% for *n*-butane) (Brandstaedter, 2007);
 - Fluid-bed reactors: catalyst powder is kept in suspension by the gas flow, at velocities high enough for fluidisation. Heat is removed by steam coils within the reactors (Brandstaedter, 2007); and
 - Transport-bed reactors: the feedstock only contains *n*-butane, with the oxygen provided by the catalyst in a transport bed reactor. The reduced catalyst is then re-oxidised in a regenerator reactor, before being fed back into the transport bed reactor Luciani (2009).
- Crude MAN recovery: The reaction produces MAN, water and carbon oxides. There are two main processes for MAN recovery from the reactor off-gas (Brandstaedter, 2007), Luciani, 2009):
 - Aqueous recovery: the off-gas from the reactor is cooled, with some MAN liquid droplets condensing out and recovered. The rest of the gas is fed into a water scrubber, in which the MAN is washed out as maleic acid. MAN is then recovered from the maleic acid by thermal dehydration, or azeotropic distillation, usually using a xylene as the azeotropic agent; and
 - Solvent recovery: the cooled off-gas is passed through an organic solvent stream (which may be DBP). This absorbs the MAN, which is then recovered using vacuum-stripping or fractional distillation.
- Purification: in both cases (aqueous and solvent recovery), the MAN is finally purified using batch or continuous distillation.

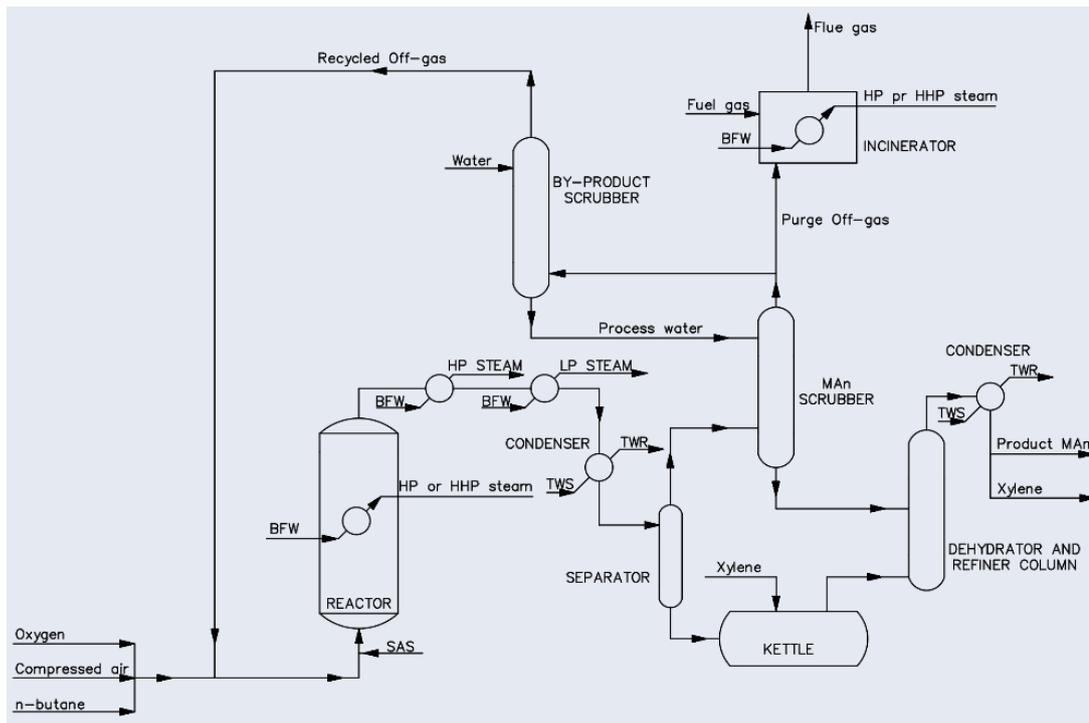
There are therefore three main process options for MAN manufacturers:

- Feedstock: either benzene or *n*-butane;
- Reactor type: fixed-bed, fluid-bed or transport-bed; and
- MAN recovery: aqueous or solvent.

In addition, there are other possible process differences that are less relevant to this study (e.g. energy integration options, feed recycle or one through).

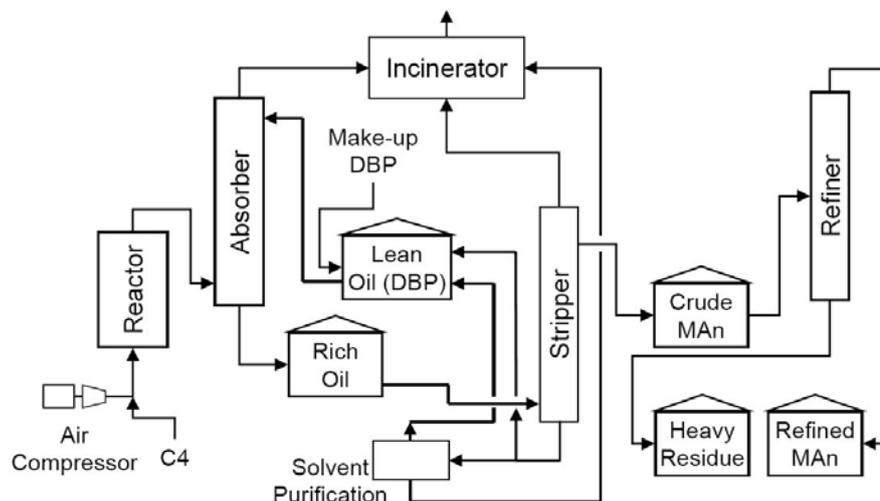
Examples of common process flows (both using *n*-butane as feedstock) are presented in Figure 8.1 and Figure 8.2. The first represents a fixed-bed process with aqueous recovery using xylene (as licensed by Technobell), and the other represents a fixed-bed process with solvent (DBP) recovery (as licensed and used by Huntsman).

Figure 8.1 Fixed-bed with aqueous recovery maleic anhydride process flow (Technobell)



Source: Technobell (undated)

Figure 8.2 Fixed-bed with solvent recovery maleic anhydride process flow (Huntsman)



Source: Hunstman attachment in ECHA (2009)

Regarding feedstock, it has already been noted that benzene is essentially no longer used due to price and safety concerns. It is reported as no longer used at all in the US (ChemSystems, 2009), and that there are only two benzene-based plants remaining in the EU¹⁶. An overview of the main processes used in practice (for *n*-butane plants only) is presented below.

Table 8.1 Principal industrial technologies for MAN production from n-butane(1)

Process ⁽¹⁾	Type of reactor	Recovery	Dehydration / solvent used	EU manufacturers known to use
ALMA (by Lummus-Polynt)	Fluid-bed	Anhydrous	ALMA, proprietary solvent (composition not in public domain)	Polynt (IT) ⁽²⁾
Mitsubishi / BOC gases	Fluid-bed	Aqueous	Uncertain	Pilot plant reported in Japan. ⁽³⁾ No known EU manufacturers
INEOS (originally Sohio-UCB and then BP Chemicals)	Fluid-bed	Aqueous	Thermal dehydration ⁽⁴⁾	Compania Espanola de Petroleos SA (CEPSA) (ES) ⁽⁵⁾
Huntsman (originally Monsanto)	Fixed-bed	Anhydrous	Solvent can be DBP (as for Sasol-Huntsman plant) ⁽⁶⁾	Sasol-Huntsman (DE)

¹⁶ Personal communication with a European MAN manufacturer

Process ⁽¹⁾	Type of reactor	Recovery	Dehydration / solvent used	EU manufacturers known to use
Scientific Design	Fixed-bed	Aqueous	Azeotropic distillation using xylene	Technology licensed and sold by Technobell Ltd (UK) ⁽⁷⁾ Hungarian Oil and Gas (MOL) ⁽⁸⁾
DuPont	Transport-bed	Aqueous	n/a (maleic acid is converted directly to tetrahydrofuran (THF) ⁽⁹⁾)	No known EU manufacturers. Only one known plant worldwide (in US), which was shut in 2005. ⁽¹⁰⁾

Source: First three columns based on Luciani (2009); source of supplementary information indicated in the notes

Notes: (1) This list of processes is not exhaustive, as there are some existing plants for which the process is not identified (see below) and Brandstaedter (2007) states that there are nine known different industrial processes for the manufacture of maleic anhydride, without describing them all in detail. (2) Polynt have two MAN plants, one of which is benzene-based fixed bed (recovery system not known), and the other *n*-butane-based fluid-bed ALMA. Benzene source: ICIS (2010a). ALMA source: Polynt (undated) (3) Source: IHS (2003). (4) Source: Felthouse (2001) (5) Source: PR Newswire (1991) (6) Source: Huntsman attachment in ECHA (2009) (7) The exact nature of the relationship between Technobell and Scientific Design has not been ascertained, but the processes are the same and the Technobell website lists Scientific Design as a key business partner. (8) It is not confirmed that MOL uses the Scientific Design process, but clear business links can be ascertained between MOL and Technobell, as the Technobell website lists MOL as a reference for their chemical process technologies. (9) Source: Felthouse (2001) (10) Source: Luciani (2009).

A company wishing to produce maleic anhydride may devise their own system, or they may purchase a licence from an existing manufacturer or licence holder. The EU manufacturers for which a specific process licence could be identified or inferred are presented in the table above. In addition to these, there are some manufacturers for which it was not clear whether a specific process licence was acquired. It should be noted that Brandstaedter (2007) relates that there are nine known different industrial processes for the manufacture of maleic anhydride, without describing them all in detail. It is therefore possible/likely that some of these EU manufacturers use a process not given in the table above. The EU producers of maleic anhydride are presented in Table 8.2.

Table 8.2 EU maleic anhydride producers and capacity (2011)

Company	Location	Capacity (1,000 tonnes)
Sasol-Huntsman	Moers, Germany	105
Polynt	Bergamo, Italy	36
	Ravenna, Italy	65
DSM Fine Chemicals	Linz, Austria	36
Hungarian Oil and Gas (MOL)	Szazhalom-Batta, Hungary	16
Compania Espanola de Petroleos SA (CEPSA)	Algeciras, Spain	12
Zaklady Azotowe Kedzierzyn (ZAK)	Zedzierzyn-Kozle, Poland	8

Company	Location	Capacity (1,000 tonnes)
BASF	Ludwigshafen, Germany	3
Kemiplas	Koper, Slovenia	2

Source: ICIS (2010b)

Concerning the technologies employed by the EU producers not featured in Table 5.1:

- DSM has two MAN production plants in Austria (Umweltbundesamt, 2001), both of which use *n*-butane:
 - One is a fixed-bed reactor with aqueous recovery using xylene, making it akin to the Scientific Design process; and
 - One is a fluid-bed reactor with aqueous recovery using xylene; making it potentially akin to the Mitsubishi/BOC gases process (although the plant has been operating since 1993 and Mitsubishi/BOC gases process started being licensed in 1999).
- BASF produces MAN at its Ludwigshafen (DE) site; its Felui (BE) plant was closed in 2009. The production process BASF uses at Ludwigshafen is not publicly available, but it may be as a by-product of phthalic anhydride production with aqueous recovery (Weissermel & Arpe, 2008, p. 366);
- Kemiplas (SI) may produce MAN as a by-product of phthalic anhydride, as the two are produced jointly at the same plant (ICIS, 2005), but this has not been specifically confirmed. It is not clear which MAN recovery method is used; and
- Zakłady Azotowe Kędzlerzyn (ZAK) (PO) produces MAN from benzene. It is not clear which MAN recovery method is used.

8.1.2 Use of phthalates in manufacturing process

As described above, there are several established processes for the production of maleic anhydride. Of these, the only one which definitely uses phthalates is the Huntsman process, and the only EU producer that definitely uses this process is the Sasol-Huntsman plant in Moers, Germany. It is also possible that other producers may use it. Specifically, it is not clear exactly what recovery process is used by BASF (likely to be aqueous with xylene – see above), Kemiplas or ZAK. Also, while it is known that Polynt uses the ALMA process in one of its plants, it is not known whether this does or does not involve phthalates as the process is proprietary with very few details in the public domain. However, it is worth noting that the Mediobanca Securities (2007) analysis of Polynt does not include any phthalates in its description of inputs into Polynt’s MAN business model, but does include ortoxylylene.

This might imply an aqueous recovery process, in opposition to the categorisation in Luciani (2009) which was the basis for Table 5.1 above¹⁷.

Broadly, it is estimated that around 60% of plants use aqueous recovery (i.e. without phthalates) and 40% anhydrous recovery¹⁸ (with high likelihood of phthalate use - mainly DBP, but also DEP).

An overview of the Huntsman process flow is provided above (Figure 8.2). From this, it can be seen that in this process DBP is added to reactor gases in the absorber before being stripped of MAN, purified and recycled, with some parts also incinerated.

It is already known that Huntsman intends to apply for DBP Authorisation in this use, arguing that “Adequate Control is robustly demonstrated” (Huntsman, 2013), since DBP is used in a closed system, under strictly controlled conditions, with only trace amounts remaining in the final product (MAN), and with all DBP waste streams incinerated on site ECHA (2009).

8.2 Overview of Alternatives to Phthalates in the Production of Maleic Anhydride

Most of the literature on maleic anhydride production tends to focus on the type of reactor bed used, occasionally considering the choice of benzene or *n*-butane as feedstock or the choice of specific reactor catalyst in more detail. In these analyses, the choice of MAN recovery process tends to be limited to a brief presentation of aqueous vs. anhydrous-based recovery processes in general. Examples of papers in which this is the case include Ruitenbeek (1999), Felthouse et al (2001), Brandstaedter (2007), Chandru & Anujar (2008), Luciani (2009) and ChemWeekly (2010).

No study has been found specifically focusing on the use of phthalates in the production of maleic anhydride, or the possibility of substitution of phthalates with other organic solvents. However, it should be clear from the above that a phthalate-using producer of maleic anhydride would almost necessarily use an anhydrous MAN recovery process and would have one of two choices to remove phthalates from their process:

- Retaining anhydrous MAN recovery, but using an alternative (non-phthalate) organic solvent; or
- Switching to an aqueous MAN recovery process, which would be likely to involve either thermal dehydration or azeotropic distillation of the maleic acid produced in the post-reactor scrubber.

In terms of the former, some information is available from the patent literature, with the most comprehensive list of possible organic solvents in an anhydrous recovery system provided by Tuck et al (1997). The main examples it mentions that are related in other literature (such as Duda et al, 2005, or Brandstaedter, 2007) are DBP, tricresyl phosphate and dibutyl maleate. A full list of the organic solvents mentioned is presented below, alongside the patent reference given.

¹⁷ A possible conclusion is that Polynt uses an aqueous recovery process with orthoxylene in its benzene plant in Bergamo (IT), and a proprietary solvent (which may or may not contain phthalates) in its *n*-butane ALMA plant in Ravenna (IT).

¹⁸ Personal communication with MAN process licence holder

Table 8.3 Organic solvents used in anhydrous recovery of maleic anhydride

Solvent	Patent reference
DBP	GB-A-727828 GB-A-763339 GB-A-768551 US-A-4118403
Carboxylic acid anhydride (such as C ₁₂₋₁₅ -alkenyl substituted succinic anhydride)	US-A-3818680
Tricresyl phosphate	FR-A-1125014
Dimethyl teraphthalate	JP-A-32-8408
Dibutyl maleate	JP-A-35-7460
High molecular weight wax	US-A-3040059
Diphenyl pentachloride	US-A-2893924
Dibenzylbenzene (or other aromatic hydrocarbon solvent with molecular weight between 150 and 400 and a boiling point above 140° C)	FR-A-2285386
Dimethylbenzophenone	US-A-3850758
Polymethylbenzophenones	US-A-4071540
Dialkyl phthalate esters	US-A-3891680
Ester of cycloaliphatic acid (e.g. dibutyl hexahydrophthalate)	ZA-A-80/1247

Source: Tuck et al (1997) – Patent WO 97/43242

Also, it might be noted that there are some instances (Felthouse, 2001, p.9, Luciani, 2009, p.12) in which xylenes are mentioned (or implied as) as a possible type of organic solvent for use in an anhydrous recovery system. These provided the starting point of this analysis, as described in Section 4.2 on the selection of alternatives. However, further research indicated that the use of xylenes in a MAN recovery process is indicative of azeotropic distillation as part of aqueous recovery, rather than the use of an alternative solvent in anhydrous recovery. Later on in both these studies (Felthouse, 2001, p. 21, Luciani, 2009, p. 12), xylene is mentioned as an azeotropic agent in aqueous recovery, with no more mention of it being a potentially suitable solvent in an anhydrous recovery system.

8.3 Detailed Investigation of Selected Alternative

8.3.1 Approach

Xylene was originally selected as the alternative to DBP in this application because of the reference in Felthouse (2001, p. 9) implying that it may be used in the same way. Upon further investigation, it became clear that this reference to xylene was in fact a reference to an altogether different process for MAN recovery.

In practice, the likely favoured approach to substitution would be to seek an alternative solvent and thus retain an anhydrous recovery system. However, the selected alternative for detailed analysis in this use remained the switch from an anhydrous recovery process (using DBP) to an aqueous recovery process, using xylene as azeotropic agent. This was for several reasons:

- As described above, most of the literature comparing manufacturing processes for MAN focuses on the difference between aqueous and anhydrous recovery processes (when the recovery process is considered at all);
- Very little literature was found considering the relative merits of different solvents in anhydrous recovery. The references found, as presented above, were mainly in the patent literature;
- For the consultation, no producer other than Huntsman is known to use a combination of fixed-bed reactor with anhydrous MAN recovery (there is therefore limited opportunity to identify other companies with experience of the issues associated with substituting phthalates in this application). Of the European producers for whom specific technology could be identified, only Polynt use anhydrous recovery, although they do this as part of a fluid-bed ALMA process, the details of which are secret and therefore not applicable to Huntsman; and
- For these reasons, as well as the relatively advanced stage of study at the time it became clear that the use of xylene in fact represents a process change rather than a straight substance substitution, this was retained as the selected alternative for detailed analysis in this use.

While it is unlikely that a phthalate-using MAN producer would choose a process change to aqueous recovery with xylene to eliminate the use of phthalates (they would probably look for a different solvent), it is nonetheless a useful process to study in detail:

- It is a well-established process, which is currently competitively used in the EU and worldwide (it is estimated that around 60% of plants use aqueous recovery)¹⁹;
- The use of azeotropic distillation in aqueous recovery is retained (as opposed to thermal dehydration), as it is much more energy-efficient (hence its relative popularity), and reduces the formation of fumaric acid (see economic feasibility below) in the process. It is therefore deemed more likely to be a workable alternative in practice; and
- The use of xylene as azeotropic agent is retained as it is clearly the most commonly used azeotropic agent in this type of process (no references to other azeotropic agents have been found).

For analytical simplicity, it is assumed that there is no other change to the process, i.e. any company implementing the process change would seek to keep the same feedstock and type of reactor. In practice, as there is only one EU MAN producer known to use DBP, this means a switch from an *n*-butane fixed-bed reactor with anhydrous recovery using DBP (as the Sasol-Huntsman plant uses) to an *n*-butane fixed-bed reactor with aqueous recovery

¹⁹ Personal communication with MAN process licence holder

using xylene (akin to the Scientific Design and/or Technobell process). Both of these processes have been presented above in Figure 9.1 and Figure 8.2.

The detailed analysis of such a switch has been assessed primarily based on literature, combined with some key insights from consultation with a MAN process (aqueous recovery) licence holder.

8.3.2 Health and environmental impacts

DBP is a reproductive toxicant because of the specific testicular and prenatal developmental toxicity associated with exposure. (NIOSH, 1990, USFDA, 2001). The active metabolite of DBP is its corresponding monobutyl phthalate (MBP) (Astill, 1989).

Orally-administered, DBP is rapidly hydrolyzed to MBP in the digestive tract. This metabolism is facilitated by pancreatic hydrolases. Dermal absorption bypasses the digestive tract. Bypassing most of the hydrolases and thereby reducing exposure to the toxic metabolite.

Inhalation of DBP is precluded by its low vapour pressure (0.1 Pa at 20 °C). This yields an equilibrium concentration of 0.98 ppm and a vaporization rate of practically zero. Therefore, inhalation is not a significant route of exposure.

Because the DBP is used in a closed system with no significant residues in the resulting products, occupational exposure during manufacture would principally involve potential dermal exposure through skin contact and potential inadvertent ingestion through mouth contact with contaminated skin areas. This can be reasonably expected to be rendered insignificant with the use of minimal personal protections: gloves and coveralls and hand washing after use.

The alternative selected for detailed analysis in this use is a change of process to aqueous MAN recovery, using xylene as azeotropic agent. Xylene possesses a much higher vapour pressure than DBP meaning that exposure through inhalation must be considered along with dermal and oral exposure. While moderately toxic through ingestion, the xylenes have low toxicity by inhalation and dermal absorption. The chemical is not a sensitizer, but has been found to be irritating in high volume skin contacts. This is most likely the result of the chemical's dewaxing properties that can cause skin drying through skin oil removal. Carcinogenicity of this chemical is still under debate. While chemically similar chemicals have been shown to be carcinogenic and/or reproductive toxicants, all tests specific to isomers of xylene have been negative. This may be the result of its rapid metabolism and excretion *in vivo*. Xylene is metabolized in the liver by oxidation and conjugation with glycine to yield methyl hippuric acid, which is excreted in the urine. Environmentally, xylene has a moderate acute (47-150 mg/l fish, 0.6-14 mg/l invertebrate) and high chronic toxicity to fish (0.056 mg/l) and invertebrates (150 mg/l). While possessing a relatively long half-life in air, xylenes are readily biodegradable in both water and terrestrial soils.

Personal protection would likely not vary between the phthalates and the alternatives except for the additional consideration of vapour control and isolation. Therefore, such a process change would have a limited impact of the safety based on the very limited potential exposure and current risk associated with the use the phthalates in the manufacture of MAN.

In addition to this, a switch from a DBP-based anhydrous recovery system to a xylene-based aqueous recovery system would entail significant increases in both energy and water usage, and would therefore lead to wider environmental impacts that should be considered. The main wider environmental impacts to be expected would be:

- Greenhouse gas (GHG) emissions. In terms of energy input differentials, it is estimated that anhydrous recovery systems consume about one third that of aqueous recovery ones (Shelley et al, 1993). Therefore, the switch from the former to the latter would roughly triple energy usage and hence GHG emissions (assuming no change in power supply source). The exact energy input or GHG emissions for either process have not been found, so cannot be further quantified. However, it is clear that the differential involved is significant;
- Water usage: aqueous recovery systems clearly use much more water than anhydrous ones, although the exact quantity could not be ascertained from publicly available sources. According to the European Environment Agency (EEA, 2005), Moers (location of the Sasol-Huntsman plant) was in a region of medium water stress in 2000 (water exploitation index of 20-40%), which is expected to be low water stress (water exploitation index of 0-20%) by 2030; and
- Water pollution: the switch to an aqueous recovery system may lead to increases in water pollution, depending on the efficiency and effectiveness of the waste water treatment that is applied. No information has been found on specific water pollution arising from aqueous MAN recovery processes or on associated treatment efficiencies, so this aspect is not considered further, although it is worth noting as a potential impact.

8.3.3 Technical feasibility

For new plants, there should be no issues concerning the technical feasibility of building either an anhydrous (DBP-based) recovery process or an aqueous (with xylene) one. Both processes are well established in industry, with aqueous recovery actually more common. The *n*-butane water-based system has been used for 40 years while the phthalate-based one is more recent (~15 years).

However, this may not be the case for exiting plants, as a DBP-using company would have their plant specifically configured to use their process, as is the case with the Sasol-Huntsman plant described in Figure 8.2 above.

According to a MAN process licence holder consulted, the main changes required in order to convert an existing anhydrous MAN recovery process in this way would be (c.f. Figure 9.1 and Figure 8.2 above):

- adding a separator, to separate out the MAN liquid droplets condensing out as the gas is cooled after exiting the reactor from the rest of the gas;
- adding a kettle, where the xylene is added to the condensed MAN droplets from the separator;
- converting the stripper (where the gas is washed in solvent) into a scrubber (in which the remaining post-separator gas is washed with water); and
- converting the refiner into a dehydrator.

Overall, while there would clearly be costs associated with such a conversion, there are no technical reasons why any plant could not do this (according to a MAN process licence holder consulted).

In terms of eventual quality and supply chain impacts, these are also expected to be minimal. According to a water-based process licensee (personal communication), using aqueous recovery (with xylene) offers a higher quality final product, but at higher operational cost (see economic suitability below). If this is correct (this assessment could not be independently verified), the technical impacts on the supply chain would be for downstream users to have to accept a higher quality product than is actually required. This would therefore be more of an economic issue than a technical one.

The same source also mentioned that DBP may damage some process catalysts to some extent, reducing performance and shortening the catalyst life. Again, if this is the case, the switch in process would be technically beneficial.

8.3.4 Economic feasibility

The economic feasibility of switching from one process to another would primarily depend on the scale of initial capital costs, as well as any subsequent changes in operational costs and the ability of companies to pass these costs onto consumers through increased prices.

Capital costs

The exact capital costs involved in such a process conversion could not be established. However, according to a water-based process licensee (personal communication), the main changes required in practice would be the addition of a separator and a kettle. Changes in the scrubber and dehydrator may also be required. The costs involved would be variable and would depend on the size of the installation and the existing equipment. This consultee thought that for a relatively modern plant, this would not be “prohibitive”. The same consultee assessed that for older plants, costs may be much higher and, in some cases, unachievable. This latter statement should be treated with caution as older plants are likely to have lower residual value of capital, which should make such conversions more economically achievable.

It should be noted that the only EU plant known to use DBP is the Sasol-Huntsman one. A scale of investment costs for the plant can be gauged by considering the recent expansion in capacity at the plant. This occurred between 2009 and 2011 and expanded capacity from 60,000 to 105,000 tonnes per year by adding a new reactor and purification section (Sasol, 2008). This expansion required an investment of €2 million (ICIS, 2009).

An indication of the order of magnitude of the costs involved in converting a MAN plant from one process to another can be obtained by assuming that half of this cost covered the new reactor, and half the new purification section, meaning that a new large purification section requires about €40 million investment. This is itself a high end estimate, as the technical requirements for the reactor may be supposed to be more exacting than those of a purification section, due to the highly exothermic nature of the reaction requiring it to take place in multi-tubular beds with complex molten salt cooling systems to be put in place.

According to a water-based process licensee (personal communication), water-based systems cost about 20% less than solvent-based ones. Based on the above estimate for a solvent based system, this indicates that a new water-based system might cost in the region of €30 million.

For the Sasol-Huntsman plant, this would need to be carried out for both the old and the new purification systems, so a rough estimate would be in the region of €60 million. While these figures are necessarily somewhat speculative, they nonetheless provide an indication of potential scale of required investment.

In the context of authorisation, the ability to afford the costs (as set out in ECHA, 2012) will be assessed at the level of the specific product line or supply chain. In this case, it might be assumed that the plant operates near capacity and thus produces about 100,000t per year (see above). Further assuming a sales price of roughly €1,000/t (ICIS, 2011), this implies revenues in the order of €100 million per year.

As a comparison, Cefic estimate the Gross Operating Surplus²⁰ (GOS) for the chemicals sector as 12.8% (Cefic, 2011), meaning around €13 million GOS per year would relate to MAN in the plant under consideration. This implies that the potential costs could be equivalent to GOS for several years if they are of the order of magnitude derived above.

Operational costs

The main difference in operational costs between the two systems would relate to energy consumption, which is much higher in an aqueous recovery system, as the dehydration process requires high energy inputs. According to ChemSystems (2005), energy considerations are the key component in the production costs of MAN, with fixed costs forming “only a modest proportion of production cash costs in the 18-25% range”. In terms of energy input differentials, it is estimated that anhydrous recovery systems consume about one third that of aqueous recovery ones (Shelley et al, 1993).

Another key factor is the production of fumaric acid as a by-product. This occurs in aqueous recovery systems due to the higher temperatures involved and reduces MAN yields (Brandstaedter 2007, Tuck et al, 1997). Together, the higher energy input requirements and reduced MAN yields are the key reasons underlying the development of anhydrous recovery processes.

Overall, the switch from one process to the other would therefore be expected to result in an increase in operational costs, although this has not been quantified due to lack of sufficient data to do so.

It is worth noting that this increase might be offset by longer catalyst lifespan in an aqueous recovery system. It is noted in the literature that catalyst bodies need to be replaced about every five years in fixed-bed systems, which requires the reactor to cease operations while it is partially disassembled, with the spent catalyst removed and replenished (Brandstaedter, 2007). According to a water-based process licensee (personal communication), DBP

²⁰ Gross operating surplus (GOS) is the excess amount of money generated by incorporated enterprises' operating activities after paying labour input costs. In other words, it is the capital available to financial and non-financial corporations which allows them to repay their creditors, to pay taxes and eventually to finance all or part of their investment.

may damage the catalyst to some extent, reducing performance and shortening the catalyst life, thus requiring more frequent replenishment.

Supply chain impacts

According to a water-based process licensee (personal communication), using aqueous recovery (with xylene) offers a higher quality final product, but at higher operational cost. The supply chain impacts therefore depend on the relative value that downstream users place on price vs. quality.

In general, it may be assumed that the downstream users requiring aqueously-recovered MAN (independently of their reasons for requiring this) are already using producers using this process. Therefore, the downstream users most likely to be affected would be those for which price is the most critical aspect. According to a water-based process licensee (personal communication), companies using solvent-recovered MAN include those that use MAN for the synthesis of butanediol through the Davy process; in this case the quality of MAN as an input material is not a key factor.

Overall, the supply chain impacts would be primarily determined by the market structure for MAN, which is relatively competitive, with a number of different producers using different production processes. While there have been a few supply bottlenecks recently (see below), suppliers have been able to increase production capacity in response to these. Nonetheless, it should be noted that since the Sasol-Huntsman MAN plant is now the largest in Europe (since the extension in 2011), even a temporary closure might lead to significant supply disruptions and consequent price rises for the duration of the closure. This was the case during a temporary closure of the plant extension in 2011 (due to technical problems linked to the new extension), which was credited as being responsible for record MAN spot prices in the weeks immediately following it (MRC, 2011). Similarly, it is worth noting the general context of tight MAN supply in the European market following the closure of BASF's Feluy plant in 2009 (MRC, 2011), although this was attenuated by the opening of Sasol-Huntsman's extension, as well as a number of other plants.

Regulatory aspects

From a legal point of view, the new process could presumably not be too similar to the existing Scientific Design (and/or Technobell) one without potentially violating patent law. This would imply either reaching an agreement with Scientific Design and/or Technobell (or possibly another technology supplier) or developing a new alternative process based on the same (or similar) principles. Both of these options would entail additional costs, which are not quantified here.

Overall assessment

Overall, it is likely that a process switch from DBP-based anhydrous recovery to aqueous recovery would impose significant capital costs on the affected operators, and would also stand to increase their operational costs (especially energy). As such it is likely that this may not be the preferred method of meeting any regulatory requirement to eliminate DBP. Instead, it is likely that companies would seek an alternative solvent to use, although more research would be required to assess exactly which one(s) would be the most suitable.

8.3.5 Availability and timing

Both technologies are well developed and readily available. The basic raw materials are the same in both cases (oxygen and *n*-butane with reaction catalysts) and they are available in large quantities. Therefore, no issue of material availability was identified.

Nonetheless, it is clear that reconfiguring the production process would take some time. Based on the time that was required for Sasol-Huntsman to build the extension described above (2 years), this might be estimated at about 2 years.

Acquiring rights to the process technology might also require some time. Broadly, it is expected that one of two approaches might be taken:

- purchasing process rights from an existing supplier, which would be unlikely to require significant time in itself; or
- developing a new proprietary process based on similar principles, which would take longer.

In both of the above cases, it is unlikely that this additional time would significantly alter the overall time requirement of commissioning, designing and implementing the change of process.

8.3.6 Existing R&D activities

It has not been ascertained as part of this study whether current users of phthalate-based recovery processes are currently undertaking R&D activities to replace the substance, as this should be clear from the applications for authorisation once they are made public.

However, given the wide prevalence of existing alternative processes, it is thought unlikely that significant R&D effort would be required for phthalate-using MAN producers to switch to an alternative production process.

8.3.7 Suitability

The suitability of process change to aqueous MAN recovery (with xylene as azeotropic agent) as an alternative to phthalate use in MAN production is not clear cut:

- Technically, the change should be feasible, unless if the plant in question is space-constrained and thus unable to add the necessary separator and kettle for that reason;
- Environmentally, the overall impacts would be likely to be negative, with few risk/health benefits being combined with substantial increases in energy consumption (and hence GHG emissions) and water usage. There would also be the possibility of an increase in water pollution, although this could not be exactly ascertained; and
- Economically, while a process change might be feasible, there would likely be potentially substantial capital costs involved, as well as non-trivial increases in operational costs, which could affect business viability based on the illustrative cost estimates above.

Overall, while the alternative is possibly feasible in practice, it is likely that operators would prefer to find an alternative solvent to use, as this would clearly entail lower costs. More research would be required to assess exactly which one(s) would be the most suitable.

8.4 Overall Conclusion

As discussed above, the overall suitability of switching from anhydrous DBP-based MAN recovery to aqueous recovery using xylene is not clear-cut. While the switch is almost certainly technically feasible, there would be clear costs entailed (both capital and operational), which might compromise the economic feasibility of the alternative. In addition to this, there would likely be negative wider environmental impacts centred on increases in GHG emissions and water usage, and possibly water pollution.

Because of these clear drawbacks, it is likely that DBP-using MAN producers would likely prefer to find a direct substance alternative that would have similar properties to DBP and could be used as a solvent in an anhydrous recovery process. Ideally, such a substance would be able to act as a direct drop-in replacement, thus offering the regulatory and risk benefits of substitution away from DBP, but while minimising the costs of substitution and the wider potential environmental impacts. It is not clear exactly what substances might be suitable in this respect, but, based on the information presented in Table 8.3, they might include carboxylic acid anhydride, tricesyl phosphate, dibutyl maleate or diphenyl pentachloride.

8.5 References

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9. Polypropylene Catalysts

9.1 Phthalates as Polypropylene Catalysts

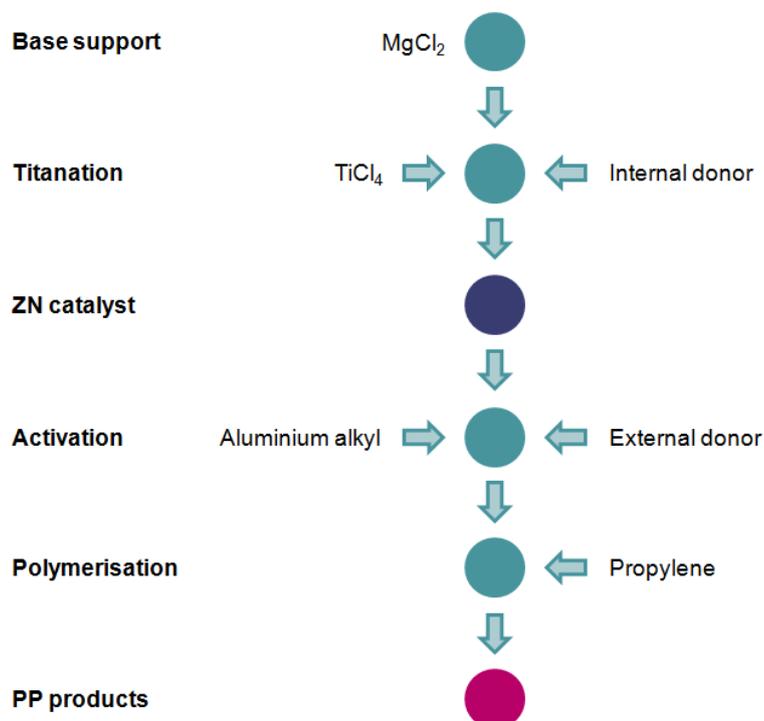
9.1.1 Process overview

The polymerisation of ethylene using catalysts was discovered in 1953 by Ziegler. The following year, Natta discovered that a similar process could be applied to propylene to form polypropylene (PP). Catalysts used in these processes are now known as Ziegler-Natta (ZN) catalysts, and the scientists were awarded the 1963 Nobel Prize for their discovery.

The production of polypropylene has several steps. Summarising those presented in Cecchin et al (2003) and Lieberman et al (2006):

- The catalyst is prepared from a pre-catalyst mixture. This is composed of:
 - The active part of the catalyst, which is a transition metal salt, usually TiCl_4 ;
 - A base support, usually MgCl_2 . This not only provides a physical support for the catalyst complex, but its particle shapes and sizes can also influence catalyst productivity (i.e. amount of polymer produced per unit catalyst), as well as eventual polymer properties. This is because the shape and size of the support (and hence catalyst) alters the number and location of active centres where polymerisation takes place so that, eventually, “the polymer flake size and shape is a large copy of the size and shape of the catalyst particle” (Lieberman et al, 2006); and
 - An internal electron donor, which may be a phthalate. This plays an essential role in controlling the stereoregularity of the polymer (see Box 1 below), as well as other polymer properties, such as the polymer molecular weight (MW) and molecular weight distribution (MWD). The role of the internal donor is explained in more detail below.
- Prior to polymerisation, the catalyst is activated using a cocatalyst, typically an aluminium alkyl, such as diethyl aluminium chloride (DEAC) or triethyl aluminium (TEAL). This turns the potential active sites into actual active centres through the formation of a Ti-C bond. This is carried out immediately prior to polymerisation, as the unactivated catalyst is more stable than the activated one, and hence more durable and safer to handle (personal communication with ZN catalyst producer);
- An external electron donor (typically a silane) may also be used, depending on the type of internal donor, and on the desired polymer properties. This has a similar function to the internal donor, with the internal-external donor combination being the key characterising feature of the different types (generations) of ZN catalyst and polymerisation process; and
- The polymerisation of propylene occurs when the activated ZN catalyst and external donor are fed into either a gas or liquid stream of propylene. Ethylene may also be added to produce copolymers.

Figure 9.1 Key steps in the polypropylene production process



Source: Based on Merz (2002)

Since the discovery of polypropylene in 1954, there have been five widely recognised generations of ZN catalyst in use. In addition to this, two relatively new compositions have been labelled “6th generation”, although this term is not widely used in the literature. The composition of the main ZN catalyst generations is presented in Table 9.1.

Table 9.1 Generations of Ziegler-Natta Catalysts

Generation	Base	Internal donor	Activating agent	External donor
1 st	$TiCl_3$ and $AlCl_3$	None	DEAC	None
2 nd	$TiCl_3$ and $AlCl_3$	None	DEAC	None
3 rd	$TiCl_4$ and $MgCl_2$	Benzoate	TEAL	Benzoate
4 th	$TiCl_4$ and $MgCl_2$	Phthalate	TEAL	Silane
5 th	$TiCl_4$ and $MgCl_2$	Diether	TEAL	Silane (although not always necessary)
	$TiCl_4$ and $MgCl_2$	Succinate	TEAL	Silane

Generation	Base	Internal donor	Activating agent	External donor
6 th	Zirconocene	Uncertain	MAO	Uncertain
	Consista/HYAMPP: Chemistry a trade secret			

Notes: DEAC = diethyl aluminium chloride, TEAL = triethyl aluminium, MAO = methylaluminoxane

Source: based on Cecchin et al (2003), Lieberman et al (2006), Suba et al (2007) and SpecialChem (2012).

The uses of TiCl_4 as active ingredient, MgCl_2 as base support, , an aluminium alkyl as activation agent and a silane as external donor have all been well established since the 1970s and feature in both 4th and 5th generation ZN catalysts, with the main differences between the ZN catalyst generations since then being the internal-external donor combination.

In addition to this, Dow and Grace have recently started marketing a “6th generation” ZN catalyst (Grace, 2012) under the name Consista (Dow) and HYAMPP (Grace, under licence from Dow). The exact composition on these catalysts is not publicly available, but company representatives (personal communication) have confirmed that the internal donor is not a diether, succinate or phthalate. It is possible that the chemistry of Consista/HYAMPP may be based on zirconocene-MAO, as there are some reports in the academic literature of these making effective ZN catalysts (for instance Dam & Gianni (1992) or Hagihara et al, 2008). However, no reports have been found of the industrial use of zirconocene-MAO catalysts in PP production.

The exact market share of the different generations of catalyst is not in the public domain. However, consultation with a PP catalyst producer indicates that the vast majority are 4th generation catalyst (i.e. phthalate-based). More detail is provided in the confidential Appendices.

9.1.2 Use of phthalates in process

As described above, phthalates are used as internal donors in 4th generation ZN catalysts. Phthalates known to be used in this application include DEHP (Borealis, 2013), DBP (Cecchin et al (2003), Refinery Operations (2012), Borealis (2013)) and DIBP (Ma et al (2004), Makwana et al (2009), Borealis (2013)), as well as DEP and DNOP (Ma et al (2004), Makwana et al (2009)).

The main role the phthalate plays is that of ZN catalyst donors in general, specifically (Cecchin et al, 2003):

- To achieve high levels of polymer stereoregularity (see Box 1 below) in combination with high productivity (1st and 2nd generation ZN catalysts, without donors, could only achieve high stereoregularity at the expense of productivity, as a high proportion of atactic PP had to be washed out in order to achieve requisite isotacticity - see Box 1 below for definitions); and
- To control key polymer parameters, such as molecular weight (MW) and molecular weight distribution (MWD), as well as comonomer incorporation, when required, e.g. with ethylene.

Beyond these general aims of donors, phthalates are particularly prized because they produce mid-MWD polymers, which are the types most commonly sought by PP producers and downstream users²¹. For this reason, “phthalate-based catalysts can be regarded as a family of general-purpose systems with which it is possible to cover the majority of product properties and application” (Cecchin et al, 2003).

It should be noted that ZN catalyst producers consider phthalates in this use to be transported isolated intermediates (components in a catalyst mixture), and therefore not subject to Authorisation under REACH. This position has been published by Borealis [60] and confirmed by all the ZN catalyst producers consulted as part of this study. A representative of a PP producing company consulted expressed the belief that some catalyst suppliers are seeking authorisation for phthalates in PP catalyst use, which would run contrary to the positions stated above, although it should be noted that the company in question produces a range of products and the individual consulted was not a ZN catalyst specialist.

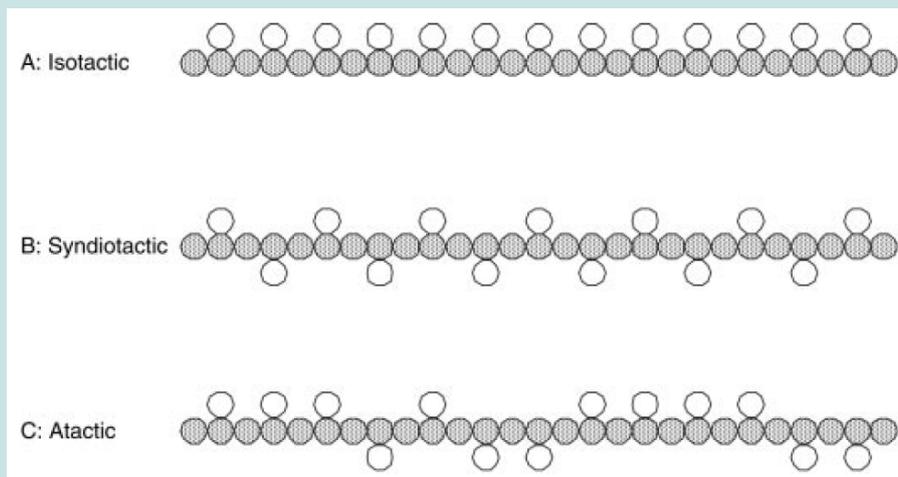
It might also be noted that the ECHA (2010) guidance on intermediates specifies that “a substance used as catalyst in the manufacturing of another substance on its own cannot be regarded as an intermediate under REACH because the catalyst is not used to be itself converted into the manufactured substance”. Similarly, the Cefic (2012) REACH Authorisation guidance for downstream users recommends that, since any “rejection of the intermediate status would automatically imply a need for a granted authorisation”, it follows that “an authorisation strategy relying on exemption is at risk of failure”.

²¹ Personal communication with ZN catalyst producer.

Box 1 Polypropylene stereoregularity and the isotactic index
Stereoregularity

During the polymerisation process, three types of PP may be produced, depending on the position of the methyl groups in the polymer chain. In each case, the methyl groups are attached to every other carbon atom in the polymer chain:

- Isotactic PP: all the methyl groups are on the same side of the carbon chain.
- Syndiotactic PP: the methyl groups alternate sides of the carbon chain; and
- Atactic PP: the methyl groups are randomly dispersed along the carbon chain.



Of these, atactic PP is the least useful, as it is “soft and sticky and of little value as a material” (Lieberman et al, 2006). Syndiotactic PP has a few niche uses (estimated at 1% of PP use – personal communication with ZN catalyst producer), but requires the use of specialized catalyst and donor systems. Isotactic PP is by far the most industrially useful and is the main PP component in about 99% of PP that is produced.

The Isotactic Index

PP stereoregularity/isospecificity (i.e. configurational regularity) is one of the most important technical features of PP, and has an important impact on PP properties and its usability. It is measured by the isotactic index, which is a measure of the proportion of PP by weight that is isotactic. In practice, it is a measure of the proportion of PP that is insoluble in xylene, as atactic PP dissolves in xylene but isotactic PP does not.

Source: Lieberman et al (2006)

9.1.3 Contextual comment

It is worth noting that PP is often mentioned as a possible (and actual) material alternative to PVC in many applications. For instance HCWH (2006) presents PP products as alternatives to PVC product for some medical devices and Vycon (undated) present PP as a PVC alternative in plastic folders and boxes.

In this context, the use of phthalates in the production of PP might be viewed as making it less suitable as a PVC material alternative. However, this should be tempered by the fact that while the use of PVC may lead to consumer products with potentially significant phthalate content being placed on the market, the phthalates used in PP production are not present in any significant quantity in the final PP product. As such, PP products would be expected to have significantly lower exposure potential for the phthalates, compared to phthalate-containing PVC.

9.2 Overview of Alternatives to Phthalates in the Production of Polypropylene

9.2.1 Substance alternatives

Phthalates are by definition only used in 4th generation ZN catalyst. The alternatives to phthalates in this use therefore require the use of a different generation of ZN catalyst, as presented in Table 9.1 above.

The starting point of the study was the analysis in Cecchin et al (2003), which identifies diethers and succinates as possible drop-in replacement for phthalates in ZN catalysts (in that 5th generation catalysts share all catalyst components with 4th generation ones apart from the internal donor). In addition to this, it was clear that LyondellBasell market 3rd to 5th generation ZN catalyst as part of their AVANT ZN product range [61], i.e. using benzoates, diethers and succinates as well as phthalates in their product range. For this reason, the AVANT ZN product range as a whole formed the starting point for our selection of alternative for detailed analysis, with particular consideration given to benzoates, diethers and succinates.

Dow-Grace's Consista-HYAMPP is also interesting, in that it is marketed as 6th generation and therefore different from all preceding types of ZN catalyst. However, a detailed analysis is precluded by the fact that all its chemistry is secret and there is therefore no data to cross-check the producer's assertions against.

The zirconocene-MAO ZN catalyst may also be a very promising alternative, in that it is relatively new and that some information is available in academic journals. Unfortunately, the information currently available to the study team is insufficient for it to be subject to detailed analysis. It may nonetheless provide a useful starting point for future studies.

9.2.2 Material alternatives

In addition to the substance alternatives (other PP catalyst internal donors), material alternative may also be available, i.e. end products might be produced using polymers other than PP. Potential alternative materials for many PP uses might include polyethylene (PE), polypropylene carbonate (PPC), or some bio-plastics, such as polyhydroxyalkanoates (PHA) or corn-based polylactic acid (PLA). However, due to the wide variety of PP uses, it is unlikely that a single polymer would be able to act as a material substitute in all cases. To determine the potential viability of other (bio-)polymers as PP material alternatives, the specific properties required in the specific end-product would have to be carefully considered.

9.3 Detailed Investigation of Selected Alternative

9.3.1 Approach

The approach was based on literature review and consultation with several ZN catalyst producers. Data availability is good for all ZN catalyst generations up to the 5th generation, since they are all established technologies. As such, there is good data availability on catalysts using benzoates and diethers.

There is slightly less data available for succinates, as the technology is more recent. For instance, Cechin et al (2003) and point out that succinates are “a very new family of donors, whose mechanism of action is still under investigation”. Since then, more information has become available and they are now well established as internal donors in 5th generation ZN catalysts, as is the case in Lieberman et al (2006), Suba et al (2007) and by LyondellBasell (undated). Despite this increase in interest over the last 10 years, there is nonetheless less information available for succinates than for diethers in this use.

Little information is available on Consista/HYAMPP, other than that provided by the companies themselves in, for instance, press releases (e.g. Grace, 2012). Also, since the catalyst composition and chemistry is a trade secret, a detailed analysis is not possible. Nonetheless, useful insights have been gathered from consultation with the companies, which is related where relevant.

Little information is publicly available regarding zirconocene-MAO catalysts. In the general ZN catalyst literature reviewed, only a single mention is made in Lieberman et al (2006), with no further detail provided. Most of the other information found on this technology is in academic journals, with only the abstract publicly available (e.g. Cam & Gianni 2003, Hagihara et al 2008) although the University of Southern Mississippi does host an educational website explaining the zirconocene polymerisation mechanism in detail (PSLC, 2005).

9.3.2 Health and environmental impacts

DEHP is a male reproductive toxicant because of the specific testicular toxicity associated with exposure. (NIOSH 1990, USFDA, 2001). DBP has also been found to be a male reproductive toxicant as well as a developmental toxicant. As with DEHP where the ester metabolite monoethylhexyl phthalate (MEHP) is the active metabolite, the active metabolite of DBP is its corresponding monobutyl phthalate (MBP) (Astill, 1989) and that for DIBP is mono-iso-butyl phthalate (MIBP) (ECHA, 2009).

Orally-administered, the phthalates are rapidly hydrolyzed to MEHP, MBP or MIBP respectively in the digestive tract. This metabolism is facilitated by pancreatic hydrolases. Dermal absorption bypasses the digestive tract, thus bypassing most of the hydrolases and thereby reducing exposure to the toxic metabolite.

This application is expected to result in occupational exposure only and be limited to those involved in the immediate process of preparing and maintaining the polymerization reactors. The phthalates' instability during polymerization results in virtually no detectable residues in the resulting polymer. For instance, Borealis (2013) relate that “the potential residual traces of phthalates in polypropylenes are decades below the limits defined by REACH (0,1 wt%)”. As such, there is virtually no potential risk to downstream users. Occupational exposure

during manufacture would principally involve potential dermal exposure through skin contact and potential inadvertent ingestion through mouth contact with contaminated skin areas. This can be reasonably expected to be rendered insignificant with the use of minimal personal protections: gloves and coveralls and hand washing after use.

Because of the proprietary nature of these new phthalate free ZN catalysts, it is hard to be precise as to the full toxicological and environmental impacts associated with these alternatives. Generally, succinate and benzoate are regarded as safe and are used as food additives and preservatives. Diethers are common industrial solvents. Most members of these chemical families possess low acute and chronic toxicities, no potential for sensitization, and no evidence or consideration for carcinogenicity or reproductive toxicity especially when compared to other constituents typically used in a ZN catalyst. However the benzoates and succinates are strong organic acids with relatively high vapour pressures and may represent an inhalation hazard at high concentrations. Diethers may also represent potential skin irritation as the result of their dewaxing properties. Environmentally, the benzoates and succinates represent a moderate toxicity risk to fish and invertebrates. The diethers tend not to be a significant issue because of their high vapour pressure and low water solubility. All of these classes tend to be readily biodegradable in water and soil and have no potential for bioaccumulation.

Based on the alternatives' inhalation and dermal irritation hazards, the personal protection required would likely not vary from that required for the phthalates-based ZN catalysis except for the additional consideration of vapour control. Therefore, replacement of DEHP or DBP with these chemicals would have a limited impact on worker safety, based on the very limited potential exposure and current risk associated with the use the phthalates in polypropylene manufacture.

9.3.3 Technical feasibility

The technical feasibility of the alternatives depends on properties such as the catalyst productivity (amount of polymer produced per unit catalyst), the Isotactic Index (see Box 1 above) and the molecular weight distribution (MWD) of the polymer that is produced. These are presented for the different ZN catalyst generations in Table 9.2.

Table 9.2 Technical characteristics of the generations of Ziegler-Natta Catalysts

Generation	Internal donor	Productivity (kgPP/g _{cat})	Isotactic Index (%)	MWD (M_w/M_n)
1 st	None	1 - 4	90 – 94	Not given
2 nd	None	4 - 15	94 – 97	Not given
3 rd	Benzoate	15 - 30	90 – 97	8 - 10
4 th	Phthalate	30 - 70	95 – 99	6.5 - 8
5 th	Diether	70 - 130	95 – 99	4.5 - 5.5
	Succinate	40 - 70	90 – 99	10 - 15

Generation	Internal donor	Productivity (kg _{PP} /g _{cat})	Isotactic Index (%)	MWD (M_w/M_n)
6 th (zirconocene / MAO)	Uncertain	Not found	90 – 99	Not found
6 th (Consista / HYAMPP)	Uncertain (trade secret)	Not found	Not found	Broader but higher than 4 th generation

Source: based on Cecchin et al (2003), Lieberman et al (2006), Suba et al (2007), personal communication with Dow representative

From the above, the following broad comparison can be made regarding the technical characteristics of the alternatives relative to the phthalates:

- The advent of 4th generation ZN catalysts (i.e. phthalate-based) represented a significant improvement in terms of catalyst productivity. Since then, 5th generation ZN catalysts have managed to maintain or improve on this (in the case of diethers). Dow claim Consista/HYAMPP also represent productivity gains relative to 4th generation catalysts (personal communication), although this could not be independently verified;
- The relatively low productivity of 1st-3rd generation catalysts is due to the high atactic content of the PP produced. This necessitates its removal (by washing) in order to achieve the required isotacticity, thus lowering overall yield;
- It might also be noted that the shift from 3rd to 4th generation catalysts was also associated with better taste and odour²², which is important in some applications, such as food packaging;
- Diethers perform well on isotacticity and very well on productivity, but are limited to narrow MWDs;
- Succinates also perform well on isotacticity and on productivity, but are limited to high MWDs;
- Phthalates cover the critical mid-range MWD; and
- According to Dow (personal communication), the MWD of Consista/HYAMPP is broader but higher than for 4th generation catalysts, i.e. it performs as well or better when mid-high MWD is required, but less well when mid-low MWD is required.

Overall, the main conclusion is the main technical difference between the alternatives considered and phthalates relates to MWD, with diethers and succinates performing well at the low and high end MWDs respectively, but less so in the mid-range. As such, diethers and succinates are viewed as more “specialised”, with phthalates being more “general purpose” (Cecchin et al, 2003).

PP MWD can affect some important PP properties, such as stiffness, stickiness and rubber content. Specifically, Lieberman et al (2006) relate that narrow MWD is beneficial for non-woven fibre applications (such as technical filters, ropes, furniture fabric, medical fabric) (Raghavendra et al, 2004), while broad MWD is suited to oriented films (used when moisture resistance, high tensile strength and optical clarity are required, e.g. for packaging for

²² Personal communication with ZN catalyst producer.

some food and personal care products, medical packaging, and tamper evident films) (Dunmore, 2013). For most PP applications, though, phthalate-based catalysts remain the “benchmark” against which others are assessed, particularly for films and sheets and cast film (personal communication with ZN catalyst producer).

Overall, the technical feasibility of substitution depends mainly on the specific portfolio of the individual PP producer, as they are likely to require a single catalyst that can cover their entire product range (i.e. PP for different end uses), according to personal communication with ZN catalyst producer. As this is more of an economic than a technical consideration, it is further detailed in operational costs below.

Because of these general purpose qualities, phthalates remain the internal donor of choice in PP production and it is estimated that the vast majority of ZN catalysis in PP production remains phthalate-based (personal communication with ZN catalyst producer – specific figure in confidential annex).

9.3.4 Economic feasibility

Capital costs

According to all the ZN catalyst producers consulted, changing catalyst should not require any direct capital investment, as the same production lines could be used, even though the process conditions would need some adjustment and testing to replicate the same PP properties.

Operational costs

Changing catalyst would require some process conditions changes (e.g. pressure, temperature). While this might impact on operational costs (e.g. energy costs), these differences might be increases or decreases depending on the specific PP polymer being produced (and specific catalyst used). Over a whole product portfolio, the overall effect might therefore be expected to be neutral.

As mentioned under Technical Feasibility, the main disadvantage of switching to alternative catalysts is that they are unlikely to cover the whole product range of a PP producer, as both diethers and succinates perform best at very narrow or very broad MWDs. Phthalates produce mid-range MWD PP polymers (and copolymers) and are thus more versatile, allowing for greater portfolio diversity from a single production line.

Technically, it would be possible for PP producers to use several catalysts, and change them according to the exact polymer being produced at any one time. However, this would be likely to have several consequences with cost impacts:

- More frequent and complex changeovers (machines would need to be stopped, cleaned and reconfigured each time a new catalyst was used to make a different type of PP), leading to lost productivity during downtime;
- Potential problems of compatibility with external donors. A change in internal donor might require a change in external donor to maintain the same final properties; and

- According to a ZN catalyst producer (personal communication), this would make operations much more complex and costly.

The above would clearly depend on the exact product range of the producer. For some, substitution would be simpler than for others.

According to a ZN catalyst producer (personal communication), these increased operational costs might affect plant viability in some cases (small producers in competitive markets). This assertion is difficult to verify, as it would critically depend on several highly company/plant-specific variables (company size, product range, exact product type, proportion of products that could be produced using a single catalyst type, exact costs associated with changeovers, competitiveness of market, etc.).

Testing requirements

Another important issue is the testing requirements necessary throughout the supply chain prior to, during and following a change of catalyst. Changing catalyst alters the PP properties and hence its functionality for downstream products. For a product to maintain functionality, a range of tests is therefore required throughout the supply chain. This is especially problematic when the final product must itself meet specific quality requirements and undergo a range of testing, e.g. automotive or medical uses.

For a PP producer, each product line will need to be tested. This may be required several times, if the product is used in a range of downstream applications with different requirements. This is one of the reasons why a single catalyst for all product lines is preferred (and explains the current popularity of 4th generation ZN catalysts – see above).

An added problem is that some key changes in properties might not be revealed during quality control. This is because catalyst performance might not be exactly the same in laboratory tests as it is in industrial conditions (Merz and Mulrooney, 2002). As such, PP property differences might only be picked up by downstream customers, as they perform their own, different tests on their own products (personal communication with ZN catalyst producer, with no specific example related).

To summarise, testing will be required throughout the whole supply chain, from catalyst producer to end product producer (via polymer producers).

According to a ZN catalyst producer (personal communication), the following timescales may apply:

- Catalyst testing: Consists of initial tests by the catalyst producer (a few months), with the new catalyst then passed downstream to the PP producer, who tests it again in their own production processes. Then there is a feedback loop between catalysts producer and PP producer. This is done for each PP line at a time, with the process for the whole portfolio of PP lines being proportional to the number of products (potential number discussed below). This is estimated at 3-5 years overall by the consultee;
- PP testing, happens in parallel to the catalyst testing above, with feedback. This was estimated to take 18-24 months to industrial trial; and

- Downstream users then need to carry out their own tests, which varies considerably according to the product. For some uses (automotive, medical), this may be significant (e.g. 3-4 years for medical).

The main problem facing PP producers would relate to testing all the product lines in parallel across the supply chain. Realistically, any given company would only be able to do a few lines at a time, with the exact number depending on company size, portfolio size and diversity, market size, client location, etc.

According to a ZN catalyst producer (personal communication), the scale of this can be estimated by considering that a small PP producer might have 1 or 2 product lines (polymers), and a large one about 10. Each of these then has several downstream users. In total, an average PP producer might have about 100-120 specific products. Since polymers tend to consist of a range of different polyenes, there is an added compounding effect. Including the compounding effect, a producer might have about 900 different unique (co)polymers, of which 80% might need thorough testing due to high technical specifications. These estimates could not be independently verified. Similarly, no specific number was found for the number of PP producers in Europe, although it is known that PlasticsEurope has a membership of 53 polymer producers (PlasticsEurope, undated). However, it should be clear that not all polymer producers that are members of PlasticsEurope will necessarily produce PP, and not all PP producers are members of PlasticsEurope.

Input costs and price impact

According to Lieberman et al (2006), a typical input price for catalyst and process stabilisation chemicals was in the range \$22-25 per tonne of PP (no date given, so 2006 assumed). Adjusting for inflation and converting currency, this was equivalent to €22-24 in 2012. In comparison, the price of polypropylene (as given by the Platts Global Polypropylene Price Index (Platts, 2013)) was in the range \$1,200-1,700 in 2012, or €30-1,320. This leads to the estimate that the input costs of catalysts and other chemicals is about 2% of the value of the PP produced. As it is not known what proportion of this is catalyst and what is other chemicals, it may be assumed (to test the range of potential costs) that the catalyst proportion is between 10% and 90%. Applying this assumed range results in an estimated cost of catalyst of between 0.2% and 1.8% of the value of PP produced.

According to consultation with a ZN catalyst producer, the key points regarding the price of alternatives are:

- Diether and succinate catalysts: 50-60 times more expensive than phthalate catalysts. This ratio could not be fully independently verified. However, there are clear indications that diethers and succinates are relatively expensive:
 - Dong (2000) refers to a diether as “expensive”, although not in the context of PP production;
 - Merz and Mulrooney (2002) imply that 5th generation catalysts are more expensive, but still only represent a “very small cost” in the overall cost of production and might be offset by the “opportunity to realize value by upgrading product capability”;
 - Potera (2005) relates that in 2001, the average price of succinates was about \$2 per pound, which, converting to euros and adjusting for inflation, is about €7,000/t in 2012. For comparison, an internet search (Alibaba.com, 2013) for DPB result in quotes in the range \$1,000-2,000/t, or about €700-1,400/t. These figures are all subject to high uncertainty (the former for being old, and the

latter due to the reliability of the internet source), but nevertheless suggest that while succinates are likely to be significantly more expensive than phthalates, this is unlikely to be 50-60 times the case; and

- Hepburn (2011) includes a discussion on issues relating to the high expense of succinates, without mentioning a specific price;

Overall, while the price ratio given in consultation seems very high, it is nonetheless likely that diethers and succinates are more expensive than phthalates. If the quoted ratio is correct, this would imply that the catalyst cost as proportion of PP production value would go from 0.2%-1.8% to 10%-108%. These figures are clearly highly uncertain for a number of reasons (data sources, assumptions, not taking account of productivity differences between catalysts), but they nonetheless indicate that input cost factors may represent significant barriers to substitution. Even if production volumes increase (leading to economies of scale), consultees expect that these substances will never be price competitive with phthalate-based catalysts.

- Ethyl benzoate is, relatively speaking, more affordable (about 6 times more expensive than phthalates), but technical problems preclude its widespread use as an alternative. These technical problems were not fully explained during consultation, but are likely to be linked to the relatively high proportion of atactic polymer produced when using benzoate internal donors (see above). This both reduces overall productivity, but also requires additional processes to remove the atactic PP fraction, thus making the polymerisation process much more complex (Cecchin et al (2003), Lieberman et al (2006)); and
- Consista/HYAMPP is reported to be more expensive than phthalate-based catalyst, but with increased productivity, so that the overall cost per unit PP produced remains equivalent.

Overall, it seems likely that non-phthalate catalysts are more expensive than phthalate-based ones. However, the full input cost implications (which remain uncertain, given that there is very little publicly data on costs and prices of the different catalyst systems and their input) would also need to be compared against potential productivity gains achieved by alternative catalysts. These productivity gains are reported as being more important than the differences in input costs in several sources, including by Dow (personal communication) and by Merz and Mulrooney (2002).

Competitiveness

According to consultation with a ZN catalyst producer, the main issue is testing the new catalyst (and PP line) across the whole supply chain. If this is too complicated (e.g. due to large portfolio size), it may be simpler to relocate production outside the EU, or change supplier (in the case of downstream PP users) (PP polymer and related products from outside the EU would not be subject to the authorisation requirement).

The industry contacts suggest that this is especially relevant under the current economic conditions. Many companies do not have significant capital to invest in R&D, testing etc. As such, relocation (of production or supply) is comparatively more attractive than it would otherwise be. This is especially the case given that

authorisation is only granted for a limited period of time (ECHA have indicated typically 7 years, with a shorter review period being 4 years and a longer period being 12 years or more.). The option of relocation is more open to larger companies that may already have access to adequate non-EU production facilities.

9.3.5 Availability and timing

All potential alternatives are currently available and on the market. According to consultation with catalyst producers, there are no supply constraints for any of the alternatives, or capacity issues, as the tonnage of catalyst required is low relative to the overall market for all the internal donors under consideration (both phthalates and alternatives).

In terms of timing of substitution, ZN catalyst producers estimate that it may take up to five years for a typical PP producer to undergo the necessary testing across all products lines (in conjunction with upstream and downstream testing), as has been described above. The timescales quoted have not been independently verified, as they are likely to be highly company and portfolio-specific.

9.3.6 Existing R&D activities

All ZN catalyst producers consulted have carried out significant R&D efforts to move away from phthalates (for both technical and regulatory reasons – see below), as evidenced by the development and availability of 5th and 6th generation ZN catalysts. This research is ongoing, with some company-specific details provided in the confidential annexes.

The main drivers for substitution, other than regulatory context, are:

- Technical features: some 5th and 6th generation catalysts perform better than phthalates for some applications. For instance, diethers and Consista/HYAMPP have higher productivity; diethers perform better in the production of narrow MWD polymers; and succinates perform better in the production of wide MWD polymers; and
- Consumer pressure and brand image: large producers of consumer goods tend to be very sensitive to their image/brand/consumer pressure. For instance, several large companies are reported by consultees to put significant pressure on their suppliers to reduce / stop use of SVHCs, as well as other substances that may damage their brand (independently of actual risk).

9.3.7 Suitability

Overall, the suitability of the potential alternative to phthalates in the catalysis of PP polymerisation depends critically on a number of factors, both technical and economic:

- Technically, the suitability depends on the specific type of PP being produced by individual companies, especially the MWD required;
- Economically, the suitability also depends on a number of company-specific factors including:

- Size and range of portfolio, and proportion that is potentially covered by any given type of catalyst;
- Size of company, and ability to invest in the necessary tests across the product range (though this would not necessarily affect the determination of economic feasibility);
- Technical specificity of the company's product(s), which influences the level of testing and quality control required across the supply chain; and
- Input prices of catalyst, especially relative to eventual product price.

9.4 Overall Conclusion

Overall, it is clear that alternatives are available to phthalates in PP catalysts in some cases, although not necessarily in all of them. This is because the catalyst composition has an impact on the eventual PP properties (such as isotacticity and MWD), and therefore needs to be considered separately for each end-use application.

The alternative selected for detailed analysis was LyondellBasell's AVANT ZN product range, which includes third generation (benzoate-based) catalysts and two fifth generation ones (diether- and succinate-based). Taken together, these alternatives show good potential to replace fourth generation (phthalate-based) catalyst in many cases, although possibly not in all cases (see above). It is likely that companies substituting away from fourth generation catalyst would require the use of *several* catalyst types (e.g. diethers and succinate-based ones) in order to cover their entire product range. Whilst this might be technically feasible, there would be some costs associated with this, principally linked to cleaning and reconfiguring production lines as different catalysts were used for different end products. Even then, it is possible that some specific products might lose key functionality in the process (e.g. those requiring mid-range MWD).

Another promising alternative that might have been selected is Dow-Grace's HYAMPP, which, due to the MWD range of the PP it catalyses, may in fact be more technically suitable than the diethers and succinates that formed the main focus of this analysis.

Also, other 6th generation ZN catalysts (e.g. zirconocene-MAO ones) could also prove to be promising, although little information is currently publicly available on them.

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10. Ceramic Sheets and Printing Pastes for the Automotive Industry

10.1 Phthalates in Ceramic for the Automotive Industry

Ceramics are used in the automotive industry as a substitute for metal, due to their physical, thermal and electrical properties. Ceramics are reported to perform better than metals for several uses (ceramic rotors, comfort systems, sensors), to be more resistant to wear, temperature and corrosion; and to provide an improved accuracy to sensors due to the dimensional changes that ceramics with piezoelectric properties have when an electric field is applied (Morgan Technical Ceramics, n.d.; CeramTec, n.d.; Okada, 2009). Examples of uses include but may not be limited to fuel level sensors, transducers, piezoceramics in comfort systems of car seats, tyre pressure monitoring systems, seals, bearings, valves, accelerometers or electronic subassemblies (Morgan Technical Ceramics, n.d.; 2010), sensors for detecting oxygen in the exhaust (Roseman and Buchanan, 2002) and possibly spark-/glow-plugs²³ (NGK Spark Plug, 2007, 2013).

It is not clear from the literature in which specific automotive ceramic applications phthalates are used. Phthalates are used in ceramic sheets as plasticisers to improve their processability. BBP, DBP and DEHP are known to be used in the production of ceramic sheets (Yasuda *et al.*, 2008). The preferred phthalates are usually DBP and DEHP due to their low vapour pressures, low volatilities and high boiling points (ECHA, 2009a; Yasuda *et al.*, 2008). Other industrial processes for forming ceramic sheets (but not necessarily for the automotive industry) include tape casting; which consists of casting slurry (ceramic powder in a solvent, with addition of plasticisers, dispersants, and binders) onto a stationary or moving surface, in order to manufacture ceramic components and multilayered structures (Hotza and Greil, 1995). This manufacturing process is used to produce exhaust gas sensors, where phthalates are used as plasticisers (adding flexibility and plasticity to the sheet to improve its manageability prior to the firing process) (Symons *et al.*, 2003; Solutia, 2013). Along with plasticisers, an organic binder is normally added. Both reduce the size and frequency of flaws after the sheet is fired and add flexibility and elasticity to the mixture before it is finally fired (Gallimore *et al.*, 2003; Solutia, 2013). A plasticiser that dissolves efficiently in the binder (or in the same solvent in which the binder is dissolved) is normally sought. Examples of organic binders include isoparaffin, polyvinyl butyral resins, polyvinyl formol, or polymethyl metacrylate (Huber *et al.*, 1997; Symons *et al.*, 2003; Solutia, 2013). These are typically used in combination in order to produce odourless and higher quality colour pastes for decoration of glass, porcelain or ceramics as well as thin ceramic sheets, (for undefined use) exhaust gas sensors or multilayer structures. Phthalates are also included in ceramic coatings (Khadilkar *et al.*, 2009). After the ceramic sheets are fired, the residues of binders, plasticisers or dispersants are negligible in the final product as they are burned off in the firing process (Symons *et al.*, 2003; interview with academic expert in the ceramic processing industry).

²³ DBP and DEHP were reportedly used in some NGK Japanese factories in 2006, for the manufacture of ceramic products. 2013 catalogues include ceramic spark- and glow-plugs. Their composition is not stated, but in view of the aforementioned information, the term possibly has been used.

The volume used in this application is low, as the total use of phthalates for the production of ceramics in the EU was estimated to be 20 tonnes per year in 2007 (ECHA, 2009a).

10.2 Overview of Alternatives for Ceramics in the Automotive Industry

The use of phthalates in ceramic sheets and printing pastes in the automotive industry was selected as a critical application due to the application for authorisation that Deza is reported to have submitted on the use of DEHP and DBP for this application (Chemical Watch, 2013).

The use of plasticisers in the ceramic processing industry (of any kind) is quite extended/common (interview with academic expert in the ceramic processing industry). After a literature review, several alternatives to the aforementioned phthalates (adipates, sebacates, tricresyl phosphate²⁴) were found for their application in ceramics in general (e.g. ceramic colour paste, slender or thin ceramic green body, multilayered structures), but not specifically for the automotive industry (Khadilkar *et al.*, 2009; Huber *et al.*, 1997; Chida *et al.*, 1991). Within the specific use in the automotive industry, dibutyl sebacate (DBS) was the only specific alternative mentioned in the literature, due to the similar properties that this substance shares with DEHP and DBP (see technical feasibility) (Yasuda *et al.*, 2008). This single specific reference led to the selection of DBS for more detailed analysis.

Overall this seems to be a relatively niche use, with little information readily available on the specificities of use in the automotive industry, or on alternatives for this use.

10.3 Detailed Investigation of Selected Alternative

10.3.1 Approach

As the use of phthalates in the production of ceramic sheets was selected as a critical application and taking into account that DBS was the only alternative identified in this specific application, the literature review focused on assessing the availability and feasibility of this substance as an alternative to DEHP and DBP for this industry. The review included ECHA documents on the use of DEHP and some of its alternatives (including DBS) in several applications (including the production of ceramics but not specifically of ceramics in the automotive industry); patents documentation and specifications; automotive component suppliers' public information and technical brochures; the Kirk-Othmer Encyclopaedia of Chemical Technology; and several scientific articles on the evolution of ceramics in the automotive industry. As a result of the narrow industrial niche of this application, the findings have been more related to specifications on why and how plasticisers are used in the production of fine ceramic sheets in general rather than to an assessment of which plasticiser has comparably the best performance amongst potential alternatives and how feasible would it be to replace DEHP or DBP with DBS in this specific application.

²⁴ It might be noted that tricresyl phosphate has been potentially linked to aerotoxic syndrome, possibly linking oil/hydraulic fluid smoke/fumes contamination of air cabin pressurised air with neurological effects on aircrew. See, for instance, Bagshaw (2008).

Several stakeholders were identified for consultation in order to obtain specific information and the industry's view of the possibilities of DBS as a possible substitute for DEHP and DBP in ceramic sheets. Several DBS users, a manufacturer, two automotive ceramic components' manufacturers, the European Association of Automotive Suppliers (CLEPA) and the European Automobile Manufacturers' Association (ACEA) were contacted for consultation, but only the latter agreed on a consultation. In addition a large automobile manufacturer that was known by the study team to be particularly active regarding the health and safety aspects of supply chain management was also contacted, but without success. Whereas some stakeholders were not available for consultation at this stage of the project and were not aware of the potential of DBS as alternative to phthalates (manufacturer), others refused to collaborate according to their policy (alternative users). CLEPA agreed to inform its members about the project in case they were interested in participating. None of them has agreed to collaborate as yet. Additionally, an academic expert/researcher in the advanced structural ceramics field was contacted, so that general information on the use of ceramics in the automotive industry could be collected, but not specifically about phthalates.

The European Automobile Manufacturers' Association (ACEA) was consulted in order to establish whether DBS was already used in the European automotive industry (especially in ceramic sheets) and the proportion at which it might have replaced DEHP in this application. ACEA could confirm the use of both substances in ceramic applications for the automotive industry as plasticisers among other uses but not the proportions of each of them in the European industry. Similarly, ACEA were unable to confirm or clarify whether DBS is used: a) as a DEHP substitute specifically; b) alongside DEHP in some applications; or c) completely independently of DEHP in automotive ceramic and printing paste applications. Without further details on this question, it is not possible to undertake more detailed analysis.

According to them, the main driver for a possible replacement of phthalates with DBS in this industry is the REACH legislation.

10.3.2 Health and environmental impacts

Bis(2-ethylhexyl) phthalate (DEHP) is a commonly used plasticiser found in a variety of consumer products. However, data shows sufficient evidence in animals of DEHP-induced toxicity to the liver, kidney, testes, uterus, ovary, fetus and thyroid. (USPCSR, 2010). According to Annex I to Directive 67/548/EEC, DEHP is classified as a substance toxic to reproduction, Repr. 1B (H360FD: "May damage fertility. May damage the unborn child"). DEHP is considered a male reproductive toxicant because of the specific testicular toxicity associated with exposure. (NIOSH 1990, USFDA 2001).

Benzyl butyl phthalate (BBP) was identified as a Substance of Very High Concern pursuant to Article 57(c) as it is classified as Toxic to Reproduction, Category 2 and was therefore included in the candidate list for authorisation. At present, BBP is banned in all toys and childcare articles (European Directive 2005/84/EC) and in cosmetics, including nail polish as it is considered to be carcinogenic, mutagenic or toxic to reproduction (CMR-substance; European Cosmetics Directive).

Dibutyl phthalate (DBP) is classified in Annex VI as toxic for reproduction, Repr. 1B (H360Df: “May damage the unborn child. Suspected of damaging fertility”). Based on the available developmental studies in mice, an oral NOAEL of 100 mg/kg bw was derived for teratogenicity, embryotoxicity, and maternal toxicity. (ECHA, 2008).

A ceramic sheet patent states that the adhesion sheet of a ceramic composite body may have five parts of plasticiser for every 100 parts by weight of powder (e.g., zirconia, alumina, etc.), while green ceramic sheets may have 8.2 parts of plasticiser for every 100 parts by weight of powder. (Patent 5897723).

Dibutyl sebacate (DBS) is a dibutyl ester of C₁₀ sebacic acid. It is generally regarded as safe and is used as both a flavouring agent in foods as well as a lubricating agent in personal care products. It has a low vapour pressure. Therefore, exposure would be almost exclusively by incidental ingestion. It possesses very low acute and chronic toxicity and is not sensitizing or irritating in rat and rabbit studies, respectively (REACH registration information for DBS)²⁵. There is no indication of either carcinogenicity or reproductive toxicity. It is metabolized very quickly in the liver yielding non-toxic nutrient metabolites that can be used directly in energy metabolism. Environmentally, dibutyl sebacate has a low acute aquatic toxicity, but may potentially be a significant fish toxicant under chronic exposure conditions. It is readily biodegradable and does not bioaccumulate.

10.3.3 Technical feasibility

DBS has been identified as a possible alternative to DEHP and DBP in the production of printing inks, paints, lacquers and moulding agents (ECHA, 2009a, 2009b). Also (Yasuda *et al.*, 2008) mentions DBS as one of the plasticiser options for the production of ceramic sheets along with DBP and DEHP. Dibutyl sebacate (DBS) is a dibutyl ester of sebacic acid. Its boiling point is 344.5 °C, which is similar to that of DEHP (385 °C) and DBP (340°C). The high boiling points of these plasticisers are one of the reasons why they are preferred (Yasuda *et al.*, 2008). Another property shared by these three compounds is low volatility.

As confirmed by ACEA (European Automobile Manufacturers' Association), the automotive industry is very strict regarding the technical specifications of the ceramic products purchased from suppliers. As a result, the ACEA representative consulted assumes that if there has been a replacement of phthalates with DBS, the technical performance should be the same. However, this could not be confirmed with reference to any actual data or expert technical input, as the automobile manufacturers' suppliers could not be consulted.

10.3.4 Economic feasibility

As confirmed by ACEA, normal practices of the automotive industry include a price-neutral strategy when suppliers offer an alternative article. This is reflective of the significant buyer power Original Equipment Manufacturers (OEMs) have in the automotive supply chain. It has not been possible to establish a comparison between the prices of DEHP and DBS for this particular application. As for DEHP and DBS used in laboratory equipment (Sigma Aldrich, 2013), DBS seems to have relatively higher prices (€101 to €155 per litre) than DEHP (€10-€65 per litre) or DBP (€15-€33 per litre). When querying an online global trade service (Alibaba.com), DBS

²⁵ REACH Registration information is available at <http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances>

seems relatively more expensive (commonly €900-€300) per metric tonne in the query conducted) than DEHP (€1200-€1815 per metric tonne) or DBP (€725-€1340 per metric tonne)²⁶. If OEMs have to face differences of this proportion in the price of these plasticisers, the margins would be significantly decreased, which could lead to a significant reduction of the substitution viability of DBS. No conclusive statement on this point can be made in this study, taking into account the lack of available information on the current/prospective prices that automotive industry pays for these products as a proportion of overall costs.

10.3.5 Availability and timing

DBS is readily available and might have partially replaced DEHP and/or DBP in ceramics for the automotive industry, although the proportion of DEHP and DBS in this market is unknown. However, taking account the tight requirements of the certification process in the automotive industry and that all the vehicle components are certified at the same time; any time scale for the substitution of phthalates may need several years (Interview with a wire coating manufacturer).

10.3.6 Existing R&D activities

No evidence was found of any specific R&D activity for the substitution of DEHP or DBP in this application.

It is worth noting that a supplier of DBS that was approached for this study was unwilling to be interviewed because they were not aware of any potential use of DBS as a phthalate alternative. As such, they felt that they would not have any useful input to provide.

10.3.7 Suitability

Taking into account the information gathered, DBS seems to be already in use as one of the options when applying a plasticiser in ceramics for the automotive industry, although it could not be confirmed that the substance is used in comparable applications. No evidence has been found to confirm whether DBS would be a suitable alternative to DEHP or DBP in this application, though they have similar properties.

Despite an extensive review of literature and contact with key industry organisations (automotive manufacturers, suppliers to the automotive industry and suppliers of the only identified alternative), it has not been possible to draw conclusions on the suitability of DBS as an alternative to phthalates in this application. The fact that this seems to be a fairly small/niche use may partially explain the lack of available information/knowledge on the potential to substitute phthalates in this application.

²⁶ Prices available in US Dollars (USD, \$). Prices in Euros (EUR, €) calculated with the exchange rate on 25th October 2013 (€0.72/\$1)

10.4 Overall Conclusion

Overall, it is not possible to draw clear conclusions relating to the use of phthalates or their potential alternatives in this application, due to the paucity of publicly available information on the matter.

The study team's initial assessment that DBS may be a suitable alternative remains potentially valid in that it can be ascertained that both phthalates and DBS are used in this application, and may be used for the same (or similar) plasticising purposes. Other possible substance alternatives that have been identified include adipates and tricresyl phosphate, although insufficient information has been found to determine whether any of them may be more or less suitable than DBS, whether technically or economically.

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11. Conclusion

11.1 Context and Timelines

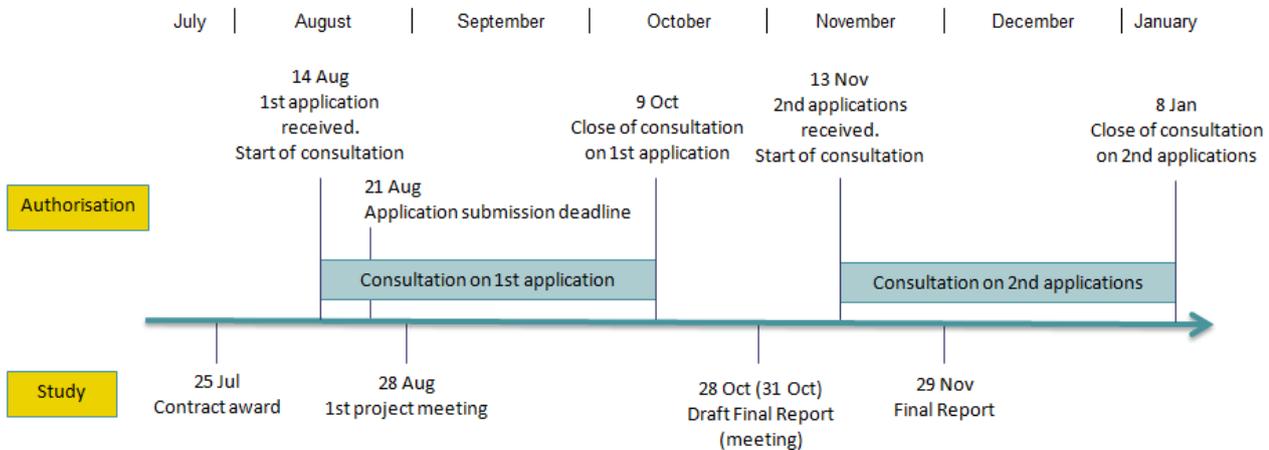
The present study was mainly intended to help the Dutch authorities (RIVM) prepare for discussions in ECHA's Risk Assessment Committee (RAC), Socio-Economic Assessment Committee (SEAC) and Member State Committee (MSC) on the authorisation applications received for the four Annex XIV phthalates. An objective of the Netherlands is to focus on the substitution principle behind REACH authorisation (i.e. stimulate substitution, especially where there are more significant health and environmental risks). For the phthalates in question, it was considered important to have knowledge in advance of discussions on authorisation applications so that RIVM might comment effectively on the applications for authorisation (and on prioritisation for Annex XIV for those that are currently on the candidate list).

The wider context is the RIVM work within Europe and globally on discussions on the principles and practice of chemical substitution more generally (e.g. Stockholm Convention and OECD discussions), especially as relating to sustainable chemical alternatives. Nevertheless, the focus of this project was primarily on the REACH context.

As the applications for Authorisation for the Annex XIV phthalates are the first to be received, processed and consulted upon, a number of lessons can be learnt relating to the Authorisation process as a whole, the role of the analysis of alternatives and public consultation within it, and how authorities might best prepare for it.

In order to derive such conclusions from the overall study, its timeline needs to be considered alongside that of the Authorisation process. Specifically, the timing of the official receipt and publication of the applications for Authorisation is especially relevant, as they define the moments when the exact nature and content of the applications become publicly known. For context, these timelines (i.e. for the public consultations relating to the applications for Authorisation for the Annex XIV phthalates and for the study) are presented below.

Figure 11.1 Timelines for the public consultations on Authorisation applications and for the study (2013-2014)



As can be seen above, the present study started around the time when the first application had been received (Rolls-Royce application for DEHP in aero engine fan blades) and the bulk of the work then took place over a two-month period, between the 1st project meeting on 28 August and the submission of the Draft Final Report on 28 October.

At the start of the study, no official information was available to determine exactly what the subsequent applications might be, what application routes would be taken (i.e. adequate control or socio-economic route – the former was expected to be more likely as the DNEL had already been set), what their key application arguments would be, or what alternatives would be considered. As such, the expected application uses (other than Rolls-Royce's) were deduced from media reports and other sources, such as comments on the Danish phthalates restriction proposal (e.g. on critical uses). This clearly had implications for the level of knowledge on the uses to be applied for, alternatives likely to be considered and the arguments that would be used for authorisation. This uncertainty remained until the closing stages of the study, with the actual applications for Authorisation made public on 13 November, about two weeks after submission of the Draft Final Report. (Note that the technical contents of the report have not been modified to take into account the actual contents of the authorisation applications received.)

In this context, the rest of this section considers what the main lessons learnt have been, focusing first on the positive outcomes from the project, then the challenges encountered, and finally considering potential options for similar work in the future.

11.2 Positive Outcomes from the Project

The positive outcomes from the project can be summarised as follows:

- In the light of the applications for Authorisation published on 13 November, it is clear that overall the study successfully identified the uses that Authorisation would be applied for. Of the six uses selected, five have had applications for Authorisation submitted. For the sixth (PP catalysts), the study identified that applications may not be received due to the industry considering phthalates to be

isolated intermediates in this use (although anecdotal information obtained during the study suggested that some applications might have been considered/prepared, but not ultimately submitted);

- For the use of phthalates in PP catalysts, while no applications for Authorisation have been submitted, it might be noted that the industry assertion that phthalates are isolated intermediates in this application is not certain to be accepted by the authorities. If it is not, the relevant chapter in the study should provide useful background information for authorities and other stakeholders;
- Within a two month period we were able to investigate and describe the context involved in substituting phthalates in several different uses, including some niche applications for which relatively little public information already exists (e.g. MAN, PP catalysts, propellants). We were also able to provide some information that could allow read-across to similar uses of the phthalates (e.g. from wire and cable);
- Overall, this provided good knowledge of what alternatives might be considered (or should be considered) in the eventual applications;
- The project acted as an awareness-raising process for companies involved in the supply and use of alternatives, increasing the flow of information through the public consultation process (both through our report and also by increasing the chances of companies providing inputs during the public consultation);
- Some consultees were very willing to discuss the issues involved in substitution. The focus of the consultation was on suppliers of alternatives and users of the substance (as they would be best placed to know if the alternatives will be suitable). This is useful compared to many other studies (e.g. of restriction proposals) where the focus of consultation is often mainly on the impacts for companies involved in supply and use of the substance potentially subject to restriction/authorisation, with less attention given to the supply chains of the alternatives;
- The timing of the project meant that RIVM will be well prepared for the start of the public consultation; and
- The project provides a good indication of the types and level of detail of information that can be gathered within the timescales (2 months) and resources available for the project (although the project team actually used over 70 man-days, compared to the c. 60 man-days estimated at the start of the project). As it was necessary to select applications and alternatives for analysis within these resources, it is likely that an equivalent amount of time would generate more detailed analysis of alternatives if the work were started in parallel to the public consultation (i.e. following the publication of the applications for Authorisation).

11.3 Challenges with the Project

The main challenges encountered during the project were:

- A main challenge was the significant lack of knowledge throughout the project on what would be in the authorisation applications (use descriptions, which alternatives were being considered, what the arguments for authorisation would be);

- As a result, the project involved quite a lot of guesswork, it is likely that there are some cases (uses/alternatives) where the study focused on the wrong issues²⁷. For instance, in the case of MAN production, it only became clear late on how the selected alternative is used and the fact that the different substances involved relate to quite distinct production processes. In this case, a focus on alternative solvents might have been more appropriate. The project was probably therefore less efficient than it would have been had the application details been known during the course of the work;
- There were quite a few consultees who were either unwilling to provide inputs to the study, or were unable to get their members (for trade associations) to be sufficiently interested in providing inputs;
- The study team did not seek the applicants' perspective (deliberately), because it was decided to focus the available resources on suppliers and (potential) users of alternatives. This was because it was deemed that there would be limited value in contacting the authorisation applicants at this stage in the authorisation process;
- Even after detailed investigation, there is relatively little information on the alternatives for some of the uses (most notably for ceramics and printing pastes in the automotive industry). In some respects, this is probably because the uses chosen were mainly those that were identified as 'critical' due to the probable lack of available alternatives;
- In terms of the application selection process, some applications/uses considered provide less valuable information than others. For example, the value added from considering the Rolls-Royce use applied for is more limited, though this is probably a facet of the argument they used for authorisation (i.e. that suitable alternatives are available, but time is required for aviation safety tests). Had Rolls-Royce's application suggested that alternatives are not suitable, the study team could have done more investigation to corroborate or refute the information in the application; and
- Overall, while the study provides useful context and knowledge of what alternatives might be considered (or should be considered) in the eventual applications, it is unclear at the time of writing exactly how useful this information will be in terms of allowing for critical analysis of the applications for Authorisation.

11.4 Options for Similar Work in the Future

Study aims

Overall, the main value of the study as it was performed is likely to be able to give RIVM (and potentially other interested parties) a better understanding of the context (technical and economic) within which the applications for Authorisation are submitted. At the time of writing, it remains unclear how useful the study will prove to be in terms of critically assessing the actual applications.

When considering options for future work, it is important to consider what the key objectives of such a study would be. These are essentially twofold:

²⁷ Due to the timing of publication of the bulk of applications for Authorisation, these have not been reviewed in detail to precisely assess the extent to which this may be the case.

- Assisting Member State authorities (and/or other interested stakeholders) in critically assessing the applications for Authorisation, especially relating to the analysis of alternatives. For this, the following is noted:
 - The main information requirements to assess the availability of alternatives and their technical and economic feasibility would relate to i) detailed understanding of how and why the substance is used, so that alternative can then be compared in terms of technical feasibility; ii) clear mapping of as many potential alternatives as possible, so as to assess whether applications for Authorisation have ‘missed’ any; iii) understanding of the relevant technical characteristics of the alternatives to assess their applicability in the use, which will depend on the exact use; iv) understanding of the practical/technical changes (e.g. process changes or new machinery) that would be required for substitution by individual companies; and v) key economic considerations, such as alternative price, capital and operational cost differentials linked with substitution;
 - This information is likely to be mainly gathered from initial literature review, and then supplemented with consultation. Given the likely timescales of the study (< 6 months), it is unlikely (although not impossible) that a study team would be able to uncover completely new information that had escaped the attention of the applicants for Authorisation, especially given the context that some applicants are reported to have spent in the region of €0.5-1 million (or more) on their applications. As such, the information gathered is highly likely to remain much more general in nature than that required to fully assess the detail contained in the applications for authorisation. However, the key issues relating to the uses and alternatives may be identified, as well as potential approaches to address them. If the analysis contained in the applications differs substantially from this, then this may be queried in the public consultation. Likewise, this type of literature review and consultation could be valuable where there are markets where some companies that have moved away from use of a substance and others that have not;
 - It is also worth noting that an independent assessment of the key issues relating to the use and potential alternatives may be valuable for RAC and SEAC members, as they are generally not process and material experts, but do require such an understanding to assess the technical and economic feasibility of the alternatives;
 - Overall, a study such as this may hope to identify and critically analyse some of the issues and data sources relevant to applicants’ analyses of alternatives (and hence allow for effective scrutiny and challenge where appropriate), but there will inevitably be cases where unforeseen issues are raised by applicants (e.g. points specific to their process/circumstances), meaning that a study such as this could never hope to identify and address all of the key parts of applicants’ cases for authorisation.
- Stimulating third parties to engage in the public consultation, for instance, by making the aware that is it happening and that they might have useful contributions to make.

Selection process

The main challenge when attempting to produce an analysis of alternatives that might be used to critically assess applications for Authorisation under REACH related to the timescale of their publication and public consultation. In this case, the work took place before publication of the applications for Authorisation. The focus of the study therefore first involved selecting uses that were deemed likely to have applications for Authorisation submitted, and then selecting likely potential alternatives to phthalates in these uses. Both of these selection processes involved elaborating criteria for selection. However, due to the number of potential uses and alternatives, in both cases it was

deemed that systematically applying all the criteria to all the uses and alternatives would probably not be a best use of the study team's time, as this would have eaten into the time available for actual analysis of alternatives. As such, a more pragmatic approach was taken, in which the applications and alternatives were selected so that they would cover a range of different types of use overall. Relatively little-studied uses were generally preferred so as to maximise the likelihood of the study providing 'new' information.

Under the circumstances (i.e. lack of definite information regarding the applications for Authorisation), this approach was successful overall, as the uses and alternatives selected match well with those eventually applied for (the applications were only made public after the draft final report for the present study). However, a study taking place with more knowledge as to the nature and content of the applications for Authorisation would clearly be more efficient, as there would be no need for a prior time-consuming selection process, which may or may not be successful in identifying critical uses and best alternatives.

In essence, such a study can either be performed before the publication, in which case it will necessarily involve some guesswork to address the significant uncertainty as to the nature and content of the actual applications (thus leading to the possibility of the 'wrong' uses or alternatives being selected); or it can be performed following publication, in which case time availability might be an issue (the public consultation lasts 60 days following the publication).

In order to meet the identified study aim while getting around the selection problem, two possible approaches are considered.

Approach 1: starting when applications are published

A shorter-term analysis might be launched as soon as the content of the authorisation applications is available, to focus on the real issues (alternatives, authorisation arguments). Such an analysis would be performed in parallel with the public consultation. However, this is high-risk given the short timescales of the public consultation process (in terms of mobilising the study team), and there will undoubtedly be challenges in getting useful information from people within the timescales involved. (Although it should be noted that two months is the timescales over which most of the work for this study took place.) Also, such an approach would be less likely to stimulate third parties to respond to the public consultation process, as it would necessarily give parties less time to formulate their responses within the public consultation window.

Approach 2: two-phase study

Another option might be to have two phases to the work. The first phase would take place before the publication of the applications for Authorisation and could involve early literature review and making initial contacts with the likely key consultees so that they are ready and available to provide information once the content of the applications is known. A potential deliverable for this phase might be an Interim Report assessing use criticality, a preliminary identification of potential alternatives and a list of potential parties to contact in a project consultation. It would not include detailed analysis of technical feasibility/suitability, economic feasibility or health/environmental impacts. This first phase would likely require a similar selection process to that undertaken for this study (assuming that, like the phthalates, the substances considered have many different uses). However,

with the detailed analysis pushed back to the second phase, there would be more scope for a more systematic elaboration and application of selection criteria. As was presented in the application selection and alternative selection sections, selection criteria/approaches might include:

- For application selection:
 - Indications in the literature / internet that use in a particular application is particularly problematic to replace / is crucial;
 - Applications in which volumes of phthalates are high;
 - Applications where there does not seem to be an existing significant trend away from the use;
 - Applications in which potential exposure is high (e.g. as assessed in Annex XIV prioritisation documents prepared when substances were (or were not) selected for inclusion in Annex XIV);
 - Applications expected (from the literature and expert judgement) to have high requirements in terms of technical specifications/parameters, thus making any material or process change more complex and costly;
 - Applications likely to have strict approval processes for products (contractual, legal, etc.); and
 - Data availability relating to phthalate use in the application, which might be applied either in a positive way (i.e. selecting applications for which data are available, potentially allowing for a greater degree of analytical depth) or in a negative way (i.e. selecting applications for which data are not available, with the hope that better data would be forthcoming through the consultation, thus helping to address identified gaps in the literature).
- For alternatives selection:
 - Indication in the literature of technical feasibility;
 - Indication in the literature of the alternative being subject to R&D in the use;
 - Systematic identification of substance and material alternatives, along with preliminary rating of potential feasibility;
 - Systematic preliminary appraisal of the potential applicability of a range of bio-products; and
 - Cross-alternative checking (i.e. preliminary appraisal of whether an alternative identified in one use might be applicable to another and why or why not).

The second phase could then start as soon the applications are published and could provide a critical review of the applications within, for example, six weeks.

This two-phase approach would also have good potential to be used as a basis for raising awareness of opportunities to input to the public consultation process, especially where the level of awareness is initially low.

Overall, these possible approaches might have led to more accurate and relevant conclusions than was possible within the present study. It might also involve a more efficient use of resources.

Finally, another option to increase the effectiveness of public consultation on authorisation applications could be prior publication of some information on uses to be applied for (and potentially other information, such as whether the application is under the adequate control or socio-economic route, what the key arguments are in the application, or what alternatives are included in the analysis of alternatives) in advance of the start of the public consultation. However, it is not known whether this would be a feasible option.

Appendix A

Literature reviewed for Sections 2-4

Ref	Author	Year	Title
1	Denmark	2011	Annex XV Restriction Report for DEHP, BBP, DBP and DIBP
2	RAC & SEAC (ECHA)	2012	Opinion on an Annex XV dossier proposing restrictions on four phthalates (final)
3	RAC & SEAC (ECHA)	2012	Final background document to the Opinion on the Annex XV dossier proposing restrictions on four phthalates
4	SEAC (ECHA)	2012	Response to comments on the SEAC draft opinion on the Annex XV dossier proposing restrictions on four phthalates
5	ECHA/ENTEC	2009	DATA ON MANUFACTURE, IMPORT, EXPORT, USES AND RELEASES OF BIS(2-ETHYLHEXYL)PHTHALATE (DEHP) AS WELL AS INFORMATION ON POTENTIAL ALTERNATIVES TO ITS USE (non-conf)
6	ECHA/ENTEC	2009	DATA ON MANUFACTURE, IMPORT, EXPORT, USES AND RELEASES OF BENZYL BUTYL PHTHALATE (BBP) AS WELL AS INFORMATION ON POTENTIAL ALTERNATIVES TO ITS USE
7	ECHA/ENTEC	2009	DATA ON MANUFACTURE, IMPORT, EXPORT, USES AND RELEASES OF DIBUTYL PHTHALATE (DBP) AS WELL AS INFORMATION ON POTENTIAL ALTERNATIVES TO ITS USE
8	RPA	2000	The Availability of Substitutes for Soft PVC Containing Phthalates in Certain Toys and Childcare Articles. Final report
9	TURI	2005	DEHP alternatives identification
10	TURI	2006	Five Chemicals Alternatives Assessment Study
11	ENTEC	2008	Water Framework Directive Supporting Plan - DEHP
12	Hansen	2008	New Developments in PVC. Draft layout
13	SCENIHR	2008	OPINION ON THE SAFETY OF MEDICAL DEVICES CONTAINING DEHP PLASTICIZED PVC OR OTHER PLASTICIZERS ON NEONATES AND OTHER GROUPS POSSIBLY AT RISK
14	Environment Agency/ENTEC	2011	Abatement cost curves for chemicals of concern
15	The Lowell Center for Sustainable Production	2011	Technical briefing Phthalates and Their Alternatives: Health and Environmental Concerns
16	Deutsche UBA	2007	PHTHALATES – USEFUL PLASTICISERS WITH UNDESIREED PROPERTIES
17	BfR	2007	Minutes of the meeting of the working group “Paper and board”
18	SOCOPSE	2009	An inventory and assessment of options for reducing emissions: DEHP.
19	Denmark	2012	Import of goods containing phthalates
20	ECHA	2008	MEMBER STATE COMMITTEE SUPPORT DOCUMENT FOR IDENTIFICATION OF Benzyl butyl phthalate (BBP) AS A SUBSTANCE OF VERY HIGH CONCERN

Ref	Author	Year	Title
21	ECHA	2008	MEMBER STATE COMMITTEE SUPPORT DOCUMENT FOR IDENTIFICATION OF DIBUTYL PHTHALATE (DBP) AS A SUBSTANCE OF VERY HIGH CONCERN
22	ECHA	2008	MEMBER STATE COMMITTEE SUPPORT DOCUMENT FOR IDENTIFICATION OF BIS(2-ETHYLHEXYL)PHTHALATE (DEHP) AS A SUBSTANCE OF VERY HIGH CONCERN BECAUSE OF ITS CMR PROPERTIES
23	ECHA	2009	MEMBER STATE COMMITTEE SUPPORT DOCUMENT FOR IDENTIFICATION OF DIISOBUTYL PHTHALATE AS A SUBSTANCE OF VERY HIGH CONCERN
24	ECHA	2011	SUPPORT DOCUMENT FOR IDENTIFICATION OF DIISOPENTYLPHTHALATE (DIPP) AS A SUBSTANCE OF VERY HIGH CONCERN BECAUSE OF ITS CMR PROPERTIES
25	Austria	2013	Annex XV Dossier: PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CMR CAT 1A OR 1B, PBT, vPvB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN - Diisopentylphthalate (DIPP)
26	ECHA	2011	SUPPORT DOCUMENT FOR IDENTIFICATION OF BIS(2-METHOXYETHYL)PHTHALATE) AS A SUBSTANCE OF VERY HIGH CONCERN BECAUSE OF ITS CMR PROPERTIES
27	Poland	2013	Annex XV Dossier: PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CMR CAT 1A OR 1B, PBT, vPvB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN - dipentyl phthalate (DPP)
28	ECHA	2013	RESPONSES TO COMMENTS ON AN ANNEX XV DOSSIER FOR IDENTIFICATION OF A SUBSTANCE AS SVHC AND RESPONSES TO THESE COMMENTS - dipentyl phthalate (DPP)
29	ECHA	2013	SUPPORT DOCUMENT FOR IDENTIFICATION OF DIPENTYL PHTHALATE (DPP) AS A SUBSTANCE OF VERY HIGH CONCERN BECAUSE OF ITS CMR PROPERTIES
30	ECHA	2011	SUPPORT DOCUMENT FOR IDENTIFICATION OF N-PENTYL-ISOPENTYL PHTHALATE AS A SUBSTANCE OF VERY HIGH CONCERN BECAUSE OF ITS CMR PROPERTIES
31	Rolls-Royce	2013	Application for authorisation under REACH - DEHP. Several documents, including: * Analysis of alternatives [31a] * Exposure assessment [31b] * Socio-economic analysis [31c]
32	OFSF (Swiss Federal Office of Public Health)	2012	Phthalate Factsheet (Fiche d'information : les phtalates)
33	SUBSPORT	various	Subsport database of substitution case studies, including many on phthalates. Warrant further research/inspection. (see [28] above for e.g.s) http://www.subsport.eu/case-stories
34	BASF	2011	Non-Phthalate Plasticizers for PVC: Hexamoll® DINCH®
35	INDITEX	2013	Substitution of phthalates in textile print applications (case study, no doc, web only: http://www.subsport.eu/case-stories/377-en?lang=)
36	G-Star	2013	An alternative to PVC and phthalates in high density plastisol prints. (case study, no doc, web only: http://www.subsport.eu/case-stories/371-en?lang=)
37	M&S	2013	Substitution of phthalates from childrenswear prints. (case study, no doc, web only: http://www.subsport.eu/case-stories/373-en?lang=)
38	HP	2012	Polyvinyl chloride (PVC) Power Cord Alternatives. (case study, no doc, web only: http://www.subsport.eu/case-stories/114-en?lang=)

Ref	Author	Year	Title
39	Uppsala county council	2012	Substitution of immersion oil containing dibutyl phthalate and chlorinated paraffin with an oil containing benzyl benzoate. (case study, no doc, web only: http://www.subsport.eu/case-stories/108-en?lang=)
40	DELL	2012	Proactively eliminating the phthalates DEHP, BBP, DBP and DIBP from electronic products (case study, no doc, web only: http://www.subsport.eu/case-stories/304-en?lang=)
41	SEMCO	2012	List of available safer products for use in the healthcare sector http://www.subsport.eu/wp-content/uploads/2012/10/substlista_EN_120921.pdf
42	Bio-Pol blog	2011	A biobased plasticizer for PVC from castor oil - http://biopol.free.fr/index.php/new-biobased-plasticizer-for-pvc-from-castor-oil/
43	Smock	2013	Bioplastic PHA puts new muscle in flexible PVC compounds - http://www.plasticstoday.com/articles/bioplastic-pha-puts-new-muscle-flexible-pvc-compounds061201301
44	UK Dept. Of the Environment	1995	Chemical works - explosives, propellants and pyrotechnics manufacturing works
45	Huntsman	2013	How Industry Can Cooperate in Making an Application for Authorisation
46	WIPO (World Intellectual Property Organisation)	2012	AN IMPROVED PROCESS FOR RECOVERY OF MALEIC ANHYDRIDE BY USING ORGANIC SOLVENT
47	Danisco	nd	GRINDSTED® SOFT-N-SAFE The safe and sustainable plasticiser for PVC
48	Versar & SRC	2010	Review of exposure and toxicity for phthalate substitutes
49	Felthouse et al	2001	MALEIC ANHYDRIDE, MALEIC ACID, AND FUMARIC ACID - entry in Kirk-Othmer Encyclopedia of Chemical Technology.
50	ECHA	2009	Background document for benzyl butyl phthalate (BBP) Document developed in the context of ECHA's first Recommendation for the inclusion of substances in Annex XIV
51	ECHA	2009	"RESPONSES TO COMMENTS" DOCUMENT FOR BENZYL BUTYL PHTHALATE (BBP) (EC NUMBER: 201-622-7)
52	ECHA	2009	Background document for dibutyl phthalate (DBP) Document developed in the context of ECHA's first Recommendation for the inclusion of substances in Annex XIV
53	ECHA	2009	Background document for bis(2-ethylhexyl) phthalate (DEHP) Document developed in the context of ECHA's first Recommendation for the inclusion of substances in Annex XIV
54	ECHA	2009	RESPONSES TO COMMENTS" DOCUMENT FOR BIS(2-ETHYLHEXYL)PHTHALATE (DEHP)
55	ECHA	2010	Background document for Diisobutyl phthalate (DIBP)
56	Germany	2010	PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS SVHC(CMR)
57	ECHA	2010	RESPONSES TO COMMENTS DOCUMENT (RCOM) FOR DIISOBUTYL PHTHALATE
58	ECHA	2009	RESPONSES TO COMMENTS" DOCUMENT FOR DIBUTYL PHTHALATE (DBP)
59	Refinery operations	2012	New Polypropylene Technology Employs Non-Phthalate Donor Based Catalyst
60	Borealis	2013	Polypropylene products BOREALIS' POSITION ON PHTHALATES IN PP CATALYSTS

Ref	Author	Year	Title
61	Basell	undated	Avant ZN Ziegler-Natta catalyst introduction
62	Cecchin et al (Kirk-Othmer encyclopedia)	2003	Ziegler-Natta Catalysts
63	SpecialChem	2012	Grace & Dow Collaborate to Develop Catalysts for PP Production to be Sold Under HYAMPP™ Brand
64	SpecialChem	2012	LyondellBasell Launches 5th Generation of Non-phthalate Catalysts for PP Production
65	Chemical Watch	2013	Phthalates authorisation application window closes
66	Tatumoto et al	1999	US patent: Method for fabricating a ceramic composite body having at least one hollow portion therein
67	Yasuda et al	2008	US patent: Method of manufacturing ceramic sheet and method of manufacturing gas sensing element
68	web ICIS	2013	Maleic Anhydride (MA) Production and Manufacturing Process
69	Nicholson	2009	Commercial PHA Production
70	Mutlu and Meier	2010	Castor oil as a renewable resource for the chemical industry (Abstract)
71	Ferro	2013	Ferro announces new investment in dibenzoate manufacturing capacity
72	Kawata	nd	Bioplastic PHA Production using Biodiesel Waste Glycerol by Newly Isolated Halomonas sp. KM-1 Strain
73	BASF	2007	General information on DINCH
74	Gravel and McBride	2010	Dibenzoate Plasticizers Offer a Safer, Viable Solution to Phthalates
75	Croft	2008	The analysis of unfired propellant particles (MSc Thesis)
76	RIVM	2009	Risk assessment non-phthalate plasticizers in toys
77	NVWA	2011	Plasticizers in toys (in Dutch) - Weekmakers in speelgoed
78	Heramb	2002	The Manufacture of Smokeless Powders and their Forensic Analysis: A Brief Review
79	O'Neil et al	2006	The Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals (14th Edition - Version 14.9)

Note 1: It states it may not be useful for some of the uses in which contact with lipids is important.

Note 2: COMGHA, DEGD & DGD used in wires and cables only at full-scale examples.

Note 3: Stated as cables and wires for toys.

Note 4: Possible alternatives with less health effects but still more research needed. Cannot be promoted for all uses.

Note 5: Only listed as TPU.

Note 6: Analysis on toy ball use but it is argued that it can be extrapolated to other uses like medical devices.

Note 7: COMGHA can also be used to make bioplastic, depending on the other ingredients involved.

Note 8: Castor oil may include COMGHA for bioplastics but also for other non-bio materials.

Note 9: Taken from a health risks analysis of BBP alternatives for medical devices.

Note 10: Risk info in [48].

Note 11: It refers to power cords.

Note 12: Mentioned but not detailed. Requires confirmation through consultation.

Note 13: High solvating properties.

Note 14: DEHPA use in these applications could be harmful.

Note 15: Refers to cables outdoor.

Note 16: Breathing ventilators.

Note 17: Urine drip collectors .

Note 18: Urine collection bags.

Note 19: "Blood bags for longterm storage/freezing of erthrocytes in glycerol at -80 °C."

Note 20: Some tubes

Note 21: Not stated, but glycerol can be used to make PHA.

Note 22: EKG electrodes, hospital blankets

Note 23: Concerns on tin residues.

Note 24: Dioctyl terephthalate (DOTP): Despite its name it is considered an "phthalate-free" substance.

Note 25: Polyurethane resins: based on aliphatic polyester (neutral and anionic) polyurethanes and non-TDI or MDI based polyether and polyester aromatic polyurethanes

Note 26: Appliances cases.

Note 27: PHA can be made from glycerol, which can be a bi-product of biodiesel production.

Note 28: It refers to castor oil.

Note 29: Medical devices: The literature generally refers to medical devices other than blood bags. For blood bags specifically, see [10], [13], [41] (DEHA, BTHC, TOTM, polyolefins, glass but it can break so not suitable for that reason).

Note 30: [46] mention a number of processes in the manufacture of MAN, some of which appear not to involve DBP

Note 31: Triacetin can be used both as a plasticizer and as a solvent. In gunpowder it is used as a plasticizer for non-plastic use.

Appendix B

Mapping of alternatives for selected applications

Alternative	CAS No.	Aero engine fan blades	Propellants	Insulation of wires/cables used indoors.	Maleic anhydride (MAN)	PP catalyst	Ceramics
Di-(isononyl)-cyclohexan-1,2-dicarboxylate (DINCH, Hexamol)	166412-78-8	-	-	[1, p199] Note 3	-	-	-
Triooctyl trimellitate (TOM/TOTM, TETM)	3319-31-1	-	-	[1, p. 40]; [5, p. 48] [13, p. 89] [15, p. 9], [18, p. 21]	-	-	-
Dioctyl terephthalate (DOTP/DEHT, Eastman 168) (Note 24)	6422-86-2	-	-	[1, p. 187]	-	-	-
Acetyl tributyl citrate (ATBC)	77-90-7	-	-	[5, p. 48]	-	-	-
n-Butyryl-tri-n-hexyl citrate (BTHC)	82469-79-2	-	-	-	-	-	-
(2-ethylhexyl) adipate (DEHA)	103-23-1	-	-	[5, p. 48], [13, p. 78], [15, p. 10]	-	-	-
Diisononyl adipate (DINA)	33703-08-1	-	-	-	-	-	-
Alkylsulphonic phenylester (ASE)	91082-17-6	-	-	[1, p. 148], [18, p. 21]	-	-	-
Diethylene glycol dibenzoate (DEGD)	120-55-8	-	-	[1, p. 173] Note 2	-	-	-
Dipropylene glycol dibenzoate (DGD)	27138-31-4	[1, p. 181] Note 13	-	[1, p. 180] Note 2	-	-	-
Di (2-Ethylhexyl) Sebacate (DEHS, DOS)	122-62-3	-	-	-	-	-	-

Alternative	CAS No.	Aero engine fan blades	Propellants	Insulation of wires/cables used indoors.	Maleic anhydride (MAN)	PP catalyst	Ceramics
Di(2-ethylhexyl) phosphate (DEHPA)	298-07-7	-	-	[15, p. 11, note 14], [18, p. 21]	-	-	-
Tri(2-ethylhexyl) phosphate (TEHPA)	78-42-2	-	-	[18, p. 21]	-	-	-
O-toluene sulfonamide (OTSA)	88-19-7	-	-	(15, p. 11]	-	-	-
2,2,4-trimethyl 1,3-pentanediol diisobutyrate (TXIB)	6846-50-0	-	-	-	-	-	-
COMGHA (Note 7)	736150-63-3	-	-	[1, p166] Note 2	-	-	-
Polyurethane resin (Note 25)	-	-	-	-	-	-	-
Acrylic resins	-	-	-	-	-	-	-
Silicon prints: Dimethyl siloxane, hydrogen terminated	70900-21-9	-	-	-	-	-	-
Silicon prints: Dimethyl methylhydrogen siloxane	68037-59-2	-	-	-	-	-	-
Styrene-ethylene, butylene-styrene (sebs) polymer	66070-58-4	-	-	[38] Note 11	-	-	-
Polyphenylene ether (ppe)	25134-01-4	-	-	[38] Note 11	-	-	-
Polystyrene	9003-53-6	-	-	[38] Note 11	-	-	-
Thermoplastic co-polyester; polymer with 1,4-butanediol and .alpha.-hydro-.omega.-hydroxypoly(oxy-1,4-butanediyl)	9078-71-1	-	-	[38] Note 11	-	-	-

Alternative	CAS No.	Aero engine fan blades	Propellants	Insulation of wires/cables used indoors.	Maleic anhydride (MAN)	PP catalyst	Ceramics
Thermoplastic polyurethane (TPU) with 1-4 butadiol, HDMI and PTMEG	-	-	-	-	-	-	-
High impact polystyrene (hips)	9003-55-8	-	-	[38] Note 11	-	-	-
Polyethylene	9002-88-4	-	-	[1, p. 40] 16, p. 13, note 15]	-	-	-
Meliflex	-	-	-	-	-	-	-
Polyurethane	9009-54-5	-	-	-	-	-	-
Ethylene vinyl-acetate copolymer EVA	24937-78-8	-	-	[16, p. 13, note 15]	-	-	-
Silicone	-	-	-	-	-	-	-
Polypropylene	9003-07-0	-	-	-	-	-	-
Polyolefin based elastomer (?)	-	-	-	-	-	-	-
Chloroprene rubber (Neoprene)	-	-	-	-	-	-	-
Kraton (SEBS)	-	-	-	-	-	-	-
Acrylonitrile butadiene styrene (ABS)	9003-56-9	-	-	-	-	-	-
Polyester	-	-	-	-	-	-	-
Kapton-Teflon material	-	-	-	-	-	-	-
Benzyl benzoate	120-51-4	-	-	-	-	-	-
Glass	-	-	-	-	-	-	-
Glycerol (bio??? - can be bi-product of biodiesel production)	56-81-5	[31, p. 15, 25]	-	-	-	-	-
Nonwoven fabric	-	-	-	-	-	-	-

Alternative	CAS No.	Aero engine fan blades	Propellants	Insulation of wires/cables used indoors.	Maleic anhydride (MAN)	PP catalyst	Ceramics
Diphenyl urea derivatives (ethyl centralite)	-	-	[25] [44] [78]	-	-	-	-
Camphor	-	-	[25]	-	-	-	-
Xylenes	-	-	-	-	[49]	-	-
Diethers	-	-	-	-	-	[61] [62]	-
Ethyl benzoate	-	-	-	-	-	[61] [62]	-
Succinates	-	-	-	-	-	[61] [62]	-
Avant ZN	-	-	-	-	-	[61] [64]	-
HYAMPP	-	-	-	-	-	[59] [63]	-
dibutyl sebacate (DBS)	-	-	-	-	-	-	[67]
Glycerol triacetate (aka triacetin)	102-76-1	-	[75] Note 31	-	-	-	-
Alternative processes	-	-	-	-	[46] Note 30	-	-