Annex XV dossier

PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CATEGORY 1A OR 1B CMR, PBT, vPvB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name(s):	**1,2-Benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich (DIHP)**
EC Number(s):	**276-158-1**
CAS Number(s):	**71888-89-6**

Submitted by:	European Chemical Agency on request of the European Commission
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- The substance is proposed to be identified as a substance meeting the criteria of Article 57 (c) of Regulation (EC) 1907/2006 (REACH) owing to its classification as toxic for reproduction 1B [1] which corresponds to classifications as toxic for reproduction category 2[2].

Summary of how the substance meets the CMR (1A or 1B) criteria

1,2-Benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich (DIHP) is covered by index number 607-483-00-2 of Regulation (EC) No 1272/2008 and classified in Annex VI, part 3, Table 3.1 (the list of harmonised classification and labelling of hazardous substances) as toxic for reproduction, Repr. 1B (H360D: “May damage the unborn child”). The corresponding classification in Annex VI, part 3, Table 3.2 (the list of harmonised and classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008 is toxic for reproduction, Repr. Cat. 2; R61 (“May cause harm to the unborn child”).
Therefore, this classification of the substance in Regulation (EC) No 1272/2008 shows that it meets the criteria for classification as toxic for reproduction in accordance with Article 57 (c) of REACH.

Registration dossiers submitted for the substance? No

[1] Classification in accordance with Regulation (EC) No 1272/2008 Annex VI, part 3, Table 3.1 List of harmonised classification and labelling of hazardous substances.

[2] Classification in accordance with Regulation (EC) No 1272/2008, Annex VI, part 3, Table 3.2 List of harmonised classification and labelling of hazardous substances (from Annex I to Council Directive 67/548/EEC).

PART I

JUSTIFICATION

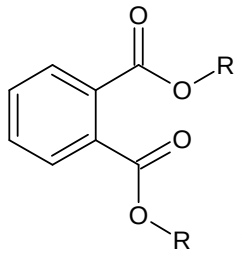
1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

1.1 Name and other identifiers of the substance

Table 1: Substance identity

EC number:	276-158-1
EC name:	1,2-Benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich
CAS number (in the EC inventory):	71888-89-6
CAS number:	71888-89-6
CAS name:	1,2-Benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich
IUPAC name:	$C_{6\text{-}8\text{-}(branched)}$-Alkyl benzene-1,2-dicarboxylate
Index number in Annex VI of the CLP Regulation	607-483-00-2
Molecular formula:	Unspecified
Molecular weight range:	Unspecified
Synonyms:	C6-8-(branched)-Alkyl phthalate Diisoheptyl phthalate DIHP

Structural formula:



R = C_6 – C_8 branched

1.2 Composition of the substance

Name: $C_{6\text{-}8\text{-}(branched)}$-Alkyl benzene-1,2-dicarboxylate

Description: ---

Degree of purity: 99 – 100 %

Table 2: Constituents

Constituents	Typical concentration	Concentration range	Remarks
$C_{6\text{-}8\text{-}(branched)}$-Alkyl benzene-1,2-dicarboxylate EC number: 276-158-1		99 – 100 %	

Table 3: Impurities

Impurities	Typical concentration	Concentration range	Remarks
No information available			

Table 4: Additives

Additives	Typical concentration	Concentration range	Remarks
No information available			

1.3 Physico-chemical properties

No information available

2 HARMONISED CLASSIFICATION AND LABELLING

1,2-Benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich (DIHP) is listed by index number 607-483-00-2 in Annex VI, part 3 of Regulation (EC) No 1272/2008 as follows:

Table 5: Classification according to part 3 of Annex VI, Table 3.1 (list of harmonised classification and labelling of hazardous substances) of Regulation (EC) No 1272/2008

International Chemical Identification	EC No	CAS No	Classification		Labelling			Spec. Conc. Limits, M-factors	Notes
			Hazard Class and Category Code(s)	Hazard state-ment code(s)	Pictogra m, Signal Word Code(s)	Hazard state-ment code(s)	Suppl. Hazard statement code(s)		
1,2-benzenedicarboxylic acid; di-C_{6-8}-branched alkylesters, C_7-rich	276-158-1	71888-89-6	Repr. 1B	H360D***	GHS08 Dgr	H360D***			

Table 6: Classification according to part 3 of Annex VI, Table 3.2 (list of harmonized classification and labelling of hazardous substances from Annex I of Council Directive 67/548/EEC) of Regulation (EC) No 1272/2008

INTERNATIONAL CHEMICAL IDENTIFICATION	EC NO	CAS NO	CLASSIFICATION	LABELLING	CONCENTRATION LIMITS	NOTES
1,2-benzenedicarboxylic acid; di-C_{6-8}-branched alkylesters, C_7-rich	276-158-1	71888-89-6	Repr. Cat. 2; R61	T R: 61 S: 53-45		

3 ENVIRONMENTAL FATE PROPERTIES

Not relevant.

4 HUMAN HEALTH HAZARD ASSESSMENT

Not relevant.

5 ENVIRONMENTAL HAZARD ASSESSMENT

Not relevant.

6 CONCLUSIONS ON THE SVHC PROPERTIES

6.1 PBT, vPvB assessment

Not relevant.

6.2 CMR assessment

1,2-Benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich (DIHP) is covered by index number 607-483-00-2 of Regulation (EC) No 1272/2008 in Annex VI, part 3, Table 3.1 (the list of harmonised classification and labelling of hazardous substances) as toxic for reproduction category 1B (H360d: “May damage the unborn child”). The corresponding classification in Annex VI, part 3, Table 3.2 (the list of harmonised and classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008 is toxic for reproduction category 2 (R61: “May cause harm to the unborn child”).

Therefore, this classification of the substance in Regulation (EC) No 1272/2008 shows that it meets the criteria for classification as toxic for reproduction in accordance with Article 57 (c) of REACH.

6.3 Substances of equivalent level of concern assessment.

Not relevant.

PART II

The underlying work for development of Part II of this Annex XV report was carried out under contract ECHA/2010/175 SR28 by COWI A/S[3], IOM Consulting Ltd[4], BRE[5] and Entec UK Ltd[6].

INFORMATION ON USE, EXPOSURE, ALTERNATIVES AND RISKS

1 INFORMATION ON MANUFACTURE, IMPORT/EXPORT AND USES

1.1 Manufacture, import and export

1.1.1 Manufacturing

DIHP has previously been manufactured by at least one company in the EU. However, it is understood that manufacture has ceased within the last two years (as of the end of 2010).

According to the European Council for Plasticisers and Intermediates (ECPI), none of the Council's member companies currently produce DIHP. Questionnaires to collect data on uses, releases and alternatives have also been sent to all companies that have been identified as manufacturers of phthalates in the EU but which are not members of ECPI (in total seven manufacturers). Six of the seven manufacturers have answered that they do not manufacture or import the substance, whilst one manufacturer in Eastern Europe has not provided any response. ECHA has not received a registration dossier from industry for the substance, indicating that it is not manufactured or imported into the EU as a substance on its own.

Therefore, the number of manufacturing sites in the EU is considered to be zero on the basis of the available information.

The general trend observed in recent years is that the manufacturing of DIHP in the EU has ceased. According to a former manufacturer in the EU, the main reason is that DIHP has been classified as toxic to reproduction by amendment to the CLP Regulation in 2009. Based on discussion with industry it is understood that, due to the classification of DIHP and the availability of suitable alternatives, it is unlikely that DIHP will be reintroduced.

[3] Parallelvej 2, 2800 Kongens Lyngby, Denmark

[4] Riccarton, Edinburgh, EH14 4AP, United Kingdom

[5] Bucknalls Lane, Garston, Watford, WD25 9XX, United Kingdom

[6] 17 Angel Gate, City Road, London, EC1V 2SH, United Kingdom

The worldwide DIHP production volume in around 2005 was reported to be in the range of 20,000 to 200,000 tonnes per annum, with production sites in both Europe and in the USA (OECD, 2005). No historical data on the manufacturing in the EU have been available.

According to information from the sole manufacturer in the USA in 2010, their manufacturing of the substance had also stopped by the end of 2010 and stocks were due to be consumed within a three month period.

The other potential market that has been considered is in Asia. However, to the knowledge of the former manufacturer of DIHP, the substance is not manufactured in Asia. Some chemicals websites (e.g. www.chemicalbook.com and www.chemicalregister.com) list some manufacturers of DIHP in China. It has not been possible to obtain any confirmation that the companies actually manufacture the substance by searching the websites of the companies (in English and Chinese).

1.1.2 Import of the substance on its own

As mentioned above, it is understood from industry that DIHP is not imported into the EU by manufacturers of phthalates. The substance was pre-registered by more than 100 companies and questionnaires have been sent to the 12 companies that pre-registered the substance in the largest quantities (two at >1000 tonnes, one at 100-1000 tonnes and nine at 10-100 tonnes). Apart from answers from the manufacturer mentioned in section 1.1.1., the questionnaire has only been completed by three of the companies and none of these have answered that they import the substance.

Based on the information provided by industry, it is considered to be unlikely that the substance will be imported into the EU after the beginning of 2011. As indicated above, the US manufacturer has now ceased production and there is no indication from any of the Asian companies' websites that they import into the EU.

1.1.3 Import of the substance in mixtures

DIHP has, until recently, been included in a number of marketed mixtures in concentration of 1-10%. A number of sealants manufactured outside the EU (the identified products are produced in the USA) are marketed by suppliers within the EU and it is likely that there has been some import of the substance within such mixtures in 2010, as the substance was still being produced in the USA over that period.

No data have been made available to quantify the extent of this possible import within mixtures. As mentioned above, the production in the USA was due to cease by the end of 2010 and the stocks to be consumed within a three month period. There is therefore some potential for small amount of imports of articles and mixtures containing DIHP into the EU in 2011.

1.1.4 Import of the substance in articles

The main former use of DIHP in the EU was as plasticiser in PVC and, according to the OECD SIDS, the substance was largely used in PVC flooring (OECD, 2005).

As mentioned above, DIHP was formerly produced in both Europe and the USA. As DIHP has been manufactured in the USA until 2010, it may to some extent have been imported in articles with

flexible PVC parts and import may also be possible within 2011. However, it has not been possible to quantify the extent of such import.

1.2 Uses of the substance

1.2.1 Overview

As the manufacturing of DIHP in the EU stopped some time ago, the main stocks held by manufacturers are likely to have been consumed. It cannot be excluded that the substance may still be used in small quantities for some purposes; for example, based on stocks of the substance held by downstream users or imported from the USA.

In the following, applications of the substance that took place until recently are described briefly. DIHP can still be found in a few product catalogues on the websites of some chemical suppliers, but the substance is not available on the websites of the manufacturers listed in the catalogues.

The main reported uses of DIHP were:

- Plasticiser in PVC;
- Plasticiser in sealants and printing inks.

1.2.2 Use as plasticiser in PVC

1.2.2.1 Background

According to OECD (2005), in 2005 DIHP was mainly used as an additive (plasticiser) to impart flexibility to polyvinylchloride (PVC) resins, which in turn were largely used in the manufacture of flooring products.

According to the sales specifications of the DIHP-based plasticiser Jayflex 77, DIHP was a general purpose, strongly solvating, highly compatible phthalate plasticizer which processed faster than the phthalate plasticiser DEHP (Exxon Mobil, 2003).

DIHP was introduced as a complete or partial replacement for DEHP/BBP blends in flooring and other applications (Exxon Mobil, 2006). The listed advantages of DINP were: lower plastisol viscosity at equal efficiency and improved viscosity stability; comparable or better stain resistance; lower volatility; lower migration; and volume cost savings.

The following applications were listed for the use of DIHP as a plasticiser (Exxon Mobil, 2006):

- Vinyl flooring, tile and carpet backing;
- Moulding and coating plastisols;
- Partial replacement for other low molecular weight plasticizers (e.g. DEHP) in extrusion, injection moulding and calendering applications requiring improved processability.

The SIDS Initial Assessment Report (OECD, 2005) mentions that DIHP was not used in applications such as medical devices or toys at the time of that report.

In an Austrian survey of phthalates in different products from 2010, DIHP was not found in any of the analysed products (Umweltbundesamt, 2010b).

No breakdown of the former consumption of DIHP into application areas has been identified. A major part of the DIHP seems to have been used for manufacturing of flooring. PVC flooring typically consists of several layers on top of each other. DIHP was recommended for use in the top wear layer and the chemical foam layer (Exxon Mobil, 2006). For the impregnation layer, mechanical foam layers and solid PVC, layer the phthalate DINP was recommended instead.

Whereas DINP, DIDP and DPHP are used as general plasticiser alternatives to DEHP, DIHP as a fast-fusing (gelling) plasticiser seems mainly to have been used as alternative for applications requiring improved processability. These applications are the same as applications in which DEHP was used in combination with the fast fusing co-plasticiser BBP. The main use of BBP in 2007 was production of flooring by plastisol coating which accounted for nearly 50% of the EU consumption of BBP (COWI *et al.*, 2008a). Other main uses were spread coating of leather and textiles and calendering of films for many application such as packaging, calendered flooring and wall covering. The same seems to have been the situation as regards DIHP.

1.2.2.2 Involved processes and supply chain

The supply chain of DIHP consisted of the following steps (similar to other phthalates used in PVC):

- Manufacture/import of the substance.
- Formulation – preparation of compound, which is pre-mixed, extruded PVC granulate ready for production of PVC end-product (e.g. hoses or toys); or plastisol, a pasty mixture (or "paste") of constituents prepared for spread coating of textiles or other materials. Formulation would often take place by the same companies doing the processing.
- Processing – manufacturing of PVC materials/articles by processes such as spread coating, calendering, injection moulding and extrusion.
- Post-processing (for some applications) – may involve the manufacture of articles on the basis of PVC materials, e.g. manufacturing of office supplies on the basis of PVC films.
- Use phase.

Process and sector descriptors and NACE codes for main industrial processes of former uses of DIHP are listed in Table 1.

Table 7: Use descriptors and NACE codes for main industrial processes of former uses of DIHP (adjusted and updated from COWI et al., 2008a which describes the processes involving the use of BBP)

Process	Process descriptor *1		Descriptor for sector of use *1		NACE codes *2	
Synthesis of DIHP	PROC1	Use in closed process, no likelihood of exposure.	SU9	Manufacture of fine chemicals	C20.1.4	Manufacture of other organic basic chemicals
	PROC 3	Use in closed batch process (synthesis or formulation)				
Compounding of polymer	PROC5	Use in closed batch process (synthesis or formulation)	SU12	Manufacture of plastic products, including compounding and conversion	C20.1.6	Manufacture of plastics in primary forms
Formulation of sealant	PROC3,4	Use in closed batch process (synthesis or formulation) Use in batch and other process (synthesis) where opportunity for exposure arises	SU10	Formulation [mixing] of mixtures and/or re-packaging	C20.5.9	Manufacture of other chemical products n.e.c.
Formulation of printing ink	PROC3,4	Use in closed batch process (synthesis or formulation)	SU10	Formulation [mixing] of mixtures and/or re-packaging	C20.3.0	Manufacture of paints, varnishes and similar coatings, printing ink and mastics
Calendering of polymer	PROC6	Calendering operations	SU12	Manufacture of plastic products, including compounding and conversion	C22.2.1,	Manufacture of plastic plates, sheets, tubes and profiles
					C22.2.3	Manufacture of builders' ware of plastic
Spread coating (with plastisol)	PROC10	Roller application or brushing	SU5, 12	Manufacture of textiles, leather, fur	C22.2.1	Manufacture of plastic plates, sheets, tubes and profiles
				Manufacture of plastic products, including compounding and conversion	C13.9.9	Manufacture of other textiles n.e.c.

Process	Process descriptor *1		Descriptor for sector of use *1		NACE codes *2	
Application of sealant	PROC19	Hand-mixing with intimate contact and only PPE available				
Printing (application of printing ink)	PROC10	Roller application or brushing	SU6	Manufacture of pulp, paper and paper products	C17.2	Manufacture of articles of paper and paperboard

*1 Process descriptors extracted from the REACH guidance, chapter R.12: Use descriptor system (ECHA 2010)

*2 NACE codes and description extracted December 2010 from: http://ec.europa.eu/comm/competition/mergers/cases/index/nace_all.html

1.2.3 Use of DIHP in mixtures

1.2.3.1 Sealants and coatings

DIHP was used in a range of marketed sealants and coatings according to material safety data sheets (MSDSs) provided on the websites of manufacturers and suppliers in December 2010. Examples of uses are shown in the table below. The sealants are of different kinds including two-component systems, one-component polyurethanes and acrylics.

DIHP was present in the products in concentrations in the range of 1-10%. Most of the products in the table were manufactured by manufacturers outside the EU, but the products are marketed by suppliers within the EU.

Information has specifically been requested from two manufacturers in the EU with MSDSs on their websites indicating the presence of DIHP in at least one type of sealants. One of the manufacturers has answered that they have discontinued the use of DIHP. No direct alternative to DIHP was available and the manufacturer decided to carry out a total reformulation of the sealants rather than a substitution of DIHP.

1.2.4 Printing inks

According to CEPE (European Council of producers and importers of paints, printing inks and artists' colours), DIHP should not be used in printing inks according a voluntary agreement by printing ink manufacturers to not use substances toxic to reproduction Cat 1B. CEPE brings approximately 85% of this industry together in its membership together and CEPE's printing ink group, EuPIA, represents close to 90% of the printing ink manufacturers selling in Europe (www.eupia.org).

For the period 2003-2008, a stable consumption of 0.2-0.4 tonnes DIHP for printing inks based on organic thinner was registered in the Norwegian Product Register (SPIN, 2008). This application was not registered in the product registers of the other Nordic countries. In Australia, DIHP was reportedly imported for use in screen printing inks (NICHAS, 2008).

Data from SPIN indicates that DIHP, at the least until recently, has been used in inks. The inks may have been imported from countries outside the EU or manufactured by companies that are not members of CEPE. It has not been possible to identify any marketed inks that contain DIHP based on an internet search.

Table 8: Examples of uses of sealants with DIHP according to MSDSs on supplier's web-sites

Description	**Concentration of DIHP according to MSDS**
Base component of two component system. Barrier coating for protection of metallic and non-metallic surfaces against attach from aqueous solutions. Application by brush or heated airspray (EU manufacturer)	5-10%
One component, solvent free, flexible polyurethane resin. Mainly used for wet dynamic crack and joints. Ideally suitable for water cut-off in concrete or masonry structures (EU manufacturer)	6-10%.
Acrylic caulk	5-10%
Synthetic, multipurpose, water-dispersed sealant. A multi-purpose product ideal for many interior and exterior sealing applications. Can be applied with most conventional caulking guns or pressurized flow equipment. Seals many metal, wood, painted or primed surfaces, and certain abraded plastics	1-10 %
Transparent, acrylic, solvent-based and high-gloss curing, sealing, and dustproofing compound. Recommended for exterior concrete.	1-5%

1.2.5 Spotcheck

According to a MSDS from a manufacturer in the USA, DIHP was present in concentrations of 5-15% w/w in a visible spotcheck penetrant (Magnaflux, 2008). The product was (as of December 2010) being marketed on the websites of several suppliers within the EU. The spotcheck is a red, visible, non-destructive test method, which provides for the detection of surface discontinuities (flaws) in ferrous and non-ferrous test materials. Spotcheck was, according to the manufacturer, used for crack detection results in the following applications: Automobile parts and off-road equipment, farm equipment, welds, castings, forgings, leak testing, pressure vessels, aircraft maintenance/marine construction maintenance, petroleum pipelines, power plant inspections, general metalwork.

According to the Swedish Chemicals Agency 47.1 tonnes of mixtures containing 8.98 tonnes of DIHP were imported to Sweden from other EU countries in 2009 and registered in the Swedish Product Register (KemI, 2010). The concentration varied from 4.5% to 20% DIHP by weight. Mixtures containing DIHP were registered as used in manufacture, repair and other uses for motor vehicles, metals and other products. The registered applications seem to be identical to the applications described for the spot test, but could also include sealants. This use is not registered in the SPIN database and a similar application was not registered in the product registers of the other Nordic countries. The use may be something specific used for some production processes in Sweden and the Swedish data cannot be used for extrapolation of the EU consumption, but could indicate that significant quantities of DIHP may have been used for this application.

1.2.6 Oil additive

DIHP has been used as an oil additive for engine oils. One product was, until recently, marketed as additive to improve the viscosity index. According to a MSDS (from 2009) from an EU manufacturer, the concentration of DIHP was in the range of 2.5 to 5 % w/w (Wynn's, 2007a). DIHP was present in the same concentration range in an oil additive from the same manufacturer marketed as additive that stops leaks in oil systems without the need to dismantle the system (Wynn's, 2007b). DIHP is also included in MSDSs for oil additives from manufacturers in the USA. According to the EU manufacturer, DIHP has recently been replaced by DINP (EC No. 271-090-9; CAS No. 68515-48-0).

1.2.7 Other applications

For one of the marketed alternatives to DIHP, it is mentioned that it can also substitute for DIHP in adhesives, which indicates that DIHP may have been used for adhesives. However, no information on actual use of DIHP in adhesives has been obtained.

No other former or present applications of DIHP have been identified in the available literature.

1.2.8 Possible releases and exposures

1.2.8.1 Occupational exposure and releases from formulation and application

As it seems that DIHP is no longer used in manufacturing processes within the EU (given that it is seemingly no longer manufactured or imported), occupational exposure to DIHP will be only briefly described in the following.

According to the OECD Emission Scenario Document on Plastic Additives (OECD, 2004), the major releases of phthalates from polymer conversion processes occur initially as gaseous phthalate. Some of this remains in the air as gas or aerosols (small droplets staying in the air), or adsorbs onto particles in the air. Other parts are quickly condensed to the liquid form on surfaces and will be washed off when the production equipment is cleaned periodically. There is generally no processing water, except cooling water in some cases, which is not in contact with the plastic matrix.

The important factors determining the amount of phthalate released to the working environment and the wider environment are:

- The volatility of the phthalate.
- The working temperatures during processing. Higher temperatures imply higher releases due to evaporation.
- The surface area of the PVC exposed to air.
- Existence of exhaust air cleaning system.
- For the working environment only: Closed or open production processes, existence of air suction systems.

Occupational exposure to phthalates has been described in the Risk Assessment Reports (RAR) for the three phthalates DEHP, BBP and DBP. The same exposure routes are expected for DIHP. The RAR for BBP (EC, 2007) discusses occupational exposure in some detail. Generally, the main routes of occupational exposure are anticipated to be inhalation of BBP gas and, if formed, liquid aerosol, and by dermal uptake of liquid BBP, especially in processes performed at elevated temperatures, and in cases of direct contact during manual loading into process equipment, product sampling and cleaning of the process equipment. Calendering of PVC flooring is given as an example of higher exposure due to elevated temperatures in an open process. As described in detail for DEHP (EC, 2008), much of the gas emitted in cases of hot processes with phthalates will likely rapidly condense to form an aerosol with the consequence that workers will be exposed to both gas and aerosol.

The exposure of workers in the further processes depends on the phthalate concentrations generated in the working environment air (exposure via inhalation), on the direct skin contact with surfaces with the phthalate present (dermal exposure) and in both cases the time span of the exposures.

Exposure to DIHP in the occupational setting has, according to the OECD (2005), not been extensively measured but is expected to be low. Area monitoring and personal sampling data have been collected for airborne exposure to two other phthalates, BBP and DINP, at two flooring manufacturers. The data show that, at typical customer sites, measured airborne levels ranged from 0.01 to 1 mg/m^3. As a very conservative approach, assuming exposure at 1 mg/m^3 for 8 hours, 10m^3 inhaled during a working day and complete absorption of inhaled materials, this equates to an internal dose of 10 mg. Assuming that the typical worker weights 70 kg, this equates to a dose expressed on a body weight basis of 0.14 mg/kg/day (OECD, 2005).

At the later stages of the product cycle, the occupational exposure is expected to be low as the articles in which phthalates are contained are, in general, not handled at elevated temperatures. Workers laying imported vinyl with DIHP may be exposed to DIHP gases, but it is expected that all import of DIHP with flooring and other articles will cease in 2011.

1.2.8.2 Exposure to DIHP in articles and mixtures

According to the OECD SIDS (2005), the majority of phthalate esters found in the environment are likely to come from the slow release of these chemicals from polymer products as a result of weathering processes. Indeed, once phthalate esters are produced and used in various products, emissions may occur during the end-use of a wide range of these products. However, since most phthalate esters are contained within a polymer matrix, emissions are retarded during the life of the polymer product. There have not been any quantitative estimates of DIHP exposure in the general population, but according to OECD (2005), it is expected to be low.

In general, very limited information on DIHP releases from articles and mixtures is available, but the release routes are expected to be the same as for other phthalates used for similar applications. The application pattern for DIHP seems to have been quite similar to the application pattern for BBP.

For BBP, the main releases from articles and mixtures are releases to air and waste water from flooring and, to a smaller extent, releases from coated fabric, upholstery and other end-products from plastisol processing. The total releases of BBP from the entire life cycle in 2007 were estimated to be about 5% of the total consumption to waste water (in particularly from flooring), 0.1% to soil and 0.6% to air (COWI *et al.*, 2008a). Releases to soil are very dependent on whether the articles that contain the phthalates are used outdoors and the extent to which parts of the

products are released by abrasion. For DEHP, such releases are significant and about 3% of the total consumption in 2007 was released by this pathway. For DIHP, outdoor applications do not seem to have been significant and the release rate by this pathway is likely to be lower and comparable to the release rate for BBP by this release pathway (0.1% from above).

As the major use of DIHP has been in flooring, and in particular in the upper layer of the flooring, it is assumed that releases from flooring will also be the major release pathway for DIHP. Manufacturers have indicated that one of the advantages of DIHP as compared to the BBP/DEHP blend is lower volatility, indicating that the releases to the air would be lower from DIHP as compared to BBP and DEHP.

Estimates of releases of DEHP and BBP from flooring show that the major release pathway is to waste water (COWI *et al.*, 2008a,b). Whereas the emission of DEHP from flooring to the air is estimated at 12 t/year, the release to wastewater is estimated at 942 t/year. For DEHP it is assumed that 0.3% of the DEHP of the flooring is removed every year by abrasion, half of it removed by washing and half of it removed as dust. The release by leaching and washing is estimated at 26 mg/m^3/year. As DIHP is mainly present in the upper layers of the flooring, the release rates for DIHP expressed in percentage of the total content are probably larger for DIHP than for DEHP, but no data have been identified on the actual release rates.

An Austrian investigation of phthalates in 10 house dust samples found DIHP concentrations in the range of 1-120 mg/kg in the dust, with a median concentration of 8 mg/kg. For comparison, the concentration of DEHP ranged from 60 to 3,269 mg/kg with a median of 231 mg/kg while the median for BBP was 35 mg/kg (Umweltbundesamt, 2010a). The assessment report does not indicate the extent to which the houses were equipped with PVC flooring and the actual phthalate content of the flooring.

1.2.9 Conclusions on manufacture, uses and exposure

Based on the reported information below, the following conclusions have been reached:

- No registration dossier has been submitted for DIHP, indicating that DIHP is not manufactured within the EU and not imported as a pure substance or in mixtures in any significant amount.
- Manufacturers of phthalates in the EU have confirmed that DIHP is not produced within the EU.
- Until recently, DIHP was manufactured by one company in the EU but the manufacture has been discontinued because of the classification of DIHP and the availability of suitable alternatives. Manufacture of DIHP in the USA was understood to have stopped by the end of 2010.
- The recent discontinuation of the manufacture in the EU and the USA means that even recent data cannot be used for indicating the use of the substance in 2011.
- Mixtures with DIHP produced outside the EU (in the USA), have been marketed to some extent within the EU. However, data indicating the associated quantities have not been identified. The application of the mixtures, including sealants and fillers is expected to have been by both professionals and consumers. The import of mixtures with DIHP from the USA is expected to have ceased as no registration for import of the substance in mixtures

has been submitted and the manufacturing of DIHP in the USA reportedly ceased by the end of 2010, based on information from industry consultation.

- DIHP may have been imported in PVC articles, but no information confirming actual import within articles has been obtained. The import of articles with DIHP from the USA (if any) is expected to cease within the first half of 2011. Whilst it cannot be ruled out that articles containing DIHP will be imported from other markets outside the EU, there is no information available to suggest that this occurs in practice.

- As the manufacture of DIHP has ceased, the main exposure to DIHP today is expected to be exposure to DIHP released from articles. DIHP has been used in PVC flooring and coatings and these applications are estimated to represent the main source of exposure of consumers and the environment today. The main route for releases to the environment is likely to be releases to waste water, in particularly from the use of DIHP in flooring.

- To the knowledge of the former manufacturer of DIHP in Europe and the USA, DIHP has never been marketed by Asian manufacturers. It has not been possible to identify any marketing of DIHP by Asian manufacturers. On this basis, it is considered unlikely that DIHP would be present in mixtures and articles imported from Asia.

2 CURRENT KNOWLEDGE ON ALTERNATIVES

2.1 Alternatives to DIHP in PVC

2.1.1 Overview

DIHP is characterised as high-solvating and fast fusing compared to common general plasticisers such as DEHP, DINP and DIDP. It has been marketed as a substitute for a blend of BBP and DEHP used for vinyl flooring and a range of other applications.

Plasticisers in PVC are often used in blends with a primary plasticiser and one or more secondary plasticisers in order to obtain the desired processing properties.

Two alternative plasticiser systems are marketed explicitly by plasticiser manufacturers as substitutes for DIHP in key applications such as flooring and other plastisol applications:

- A blend of DINP and isodecyl benzoate (IDB).
- A blend of the terephthalates DEHT and DBT.

Substituting DINP or DEHT for DIHP with no use of a secondary (additional) plasticiser is also a possibility, but this imposes slightly altered production conditions (time and temperature, among others), as DINP has lower solvency for PVC than DIHP.

Other plasticiser systems may also be used as alternatives to DIHP, including other systems that have been marketed as alternatives to the DEHP/BBP blend.

2.1.2 IDB and DINP

A mix of di-isononyl phthalate (DINP) and isodecyl benzoate (IDB, CAS No. 131298-44-7; EC No. not assigned) is specifically marketed as an alternative to DIHP (Jayflex 77). IDB is marketed under the trade name Jayflex MB10 plasticizer which is indicated as a mono ester of benzoic acid and isodecyl alcohol.

The characteristics and applications of IDB are described as follows by the manufacturer (ExxonMobil, 2010):

- “Fast-fusing capability, improving PVC processability.
- High efficiency for excellent performance at low temperatures.
- Balanced volatility with very low viscosity.
- Reduced volatile organic compounds (VOCs).
- Improved flexible PVC resistance to stains.
- Contribution to good foam structure and increased foaming rate”.

IDB is intended for use in a blend with DINP as the main constituent.

According to the manufacturer, IDB/DINP can substitute for DIHP in essentially all PVC plastisol applications such as flooring, wall coverings, UBC (car underbody coating) and synthetic leather, as well as in adhesives and industrial coatings.

Exact data on the price of IDB/DINP as compared to DIHP have not been identified. IDB is produced by the esterification of benzoic acid with a high molecular weight alcohol (isodecyl alcohol). IDB is a specialty plasticizer and, according to the manufacturer, it is more expensive to produce than general purpose plasticizers such as DINP or DIDP.

The following information has been obtained from the manufacturer:

- IDB has been commercialized since 2008 and the replacement of DIHP by customers which used DIHP is now complete (DIHP has been completely de-commercialized).
- Regarding technical constraints on use of the alternative, it is understood from industry that it is necessary to use IDB in combination with a high molecular weight, general purpose plasticizer like DINP for optimum performance and cost. IDB has not, on its own, replaced DIHP.
- For all flexible PVC applications, careful selection of the plasticizers is key. Formulations need to be fine-tuned to meet industrial process performance and end-use product specifications. The introduction of IDB has required extensive re-formulation work and formulation and process optimization.
- The change of plasticisers may result in some changes in the quality of the final products and, plasticiser users have to re-qualify their finished articles down the supply chain with their customers.
- The replacement of DIHP by IDB (in combination with DINP) has involved the manufacturer working for up to a full year with each customer, depending upon the application, to support the replacement.

2.1.3 DBT and DEHT

According to the manufacturer, a blend of EastmanTM DBT and Eastman 168TM non-phthalate plasticizers provides the user with a plasticiser system that has similar performance to Jayflex 77 (DIHP) (Eastman, 2010).

EastmanTM DBT consists of di-butyl terephthalate (EC No. 217-803-9; CAS No. 1962-75-0) and is commonly referred to as DBT.

Eastman 168TM consists of >98% bis(2-ethylhexyl)-1,4-benzenedicarboxylate (EC No. 229-176-9; CAS No. 6422-86-2). Synonyms are di-(2-ethyl-hexyl)terephthalate, referred to by the abbreviations DEHT, DOPT and DEHPT.

Eastman DBT plasticizer, is according to the manufacturer, a high solvating non-phthalate plasticizer that provides lower plastisol viscosity, excellent low temperature flexibility and fusion rates similar to typical high solvating plasticizers in vinyl formulations (Eastman, 2010a). As a non-phthalate plasticizer for waterborne adhesives, it reportedly provides comparable viscosity response to currently used plasticizers. Applications of DBT mentioned by the manufacturer are: adhesives for paper, packaging, vinyl flooring, wallpaper, textile coatings and woodworking.

According to the manufacturer, DEHT has performance equal to or better than most ortho-phthalate plasticizers. It reportedly offers good performance properties, excellent low temperature flexibility, resistance to extraction by soapy water and excellent non-migration properties. Applications mentioned are bottle caps and closures, coatings, coatings for cloth, electric connectors, flexible film, medical devices, pavement striping compounds, sheet vinyl flooring, toys, traffic cones, vinyl compounding, vinyl gloves, vinyl water stops and walk-off mats.

In an investigation of alternatives to phthalates in toys, the manufacturers and suppliers of toys contacted in Denmark all indicated that DEHT has been used as alternative to restricted phthalates in toys (Maag et al., 2010). One manufacturer stated that the replacement of the restricted phthalates had been a complex process, but the experience showed that DEHT and two other plasticisers, ATBC and DINCH, could be blended in a variety of combinations to achieve softened PVC that performed to the required standards with the existing production setup.

Further information on the experience with substitution of DBT and DEHT for DIHP has been requested from the manufacturer, but no information has been obtained.

2.1.4 Dibenzoates

As mentioned above, DIHP has been used as alternative to DEHP/BBP in flooring among other applications. Other alternatives to DEHP/BBP that are used for flooring may likely be used as alternatives to DIHP as well, although they may not be specifically marketed as such.

According to industry (quoted in COWI et al., 2008a), BBP has mainly been replaced by benzoates (note that IDB mentioned above is a benzoate as well). Many dibenzoate plasticisers are marketed as substance blends.

Dibenzoates particularly suitable as alternatives to BBP, according to one manufacturer, are shown in Table 3.

Table 9: Applications of dibenzoate systems from Genovique (now Eastman) as alternatives to BBP (Genovique 2008 as cited by COWI et al., 2008a)

Applications	Genovique Product 1	Genovique Product 2	Bulk Pricing compared to BBP
Flooring	Benzoflex 2088	Benzoflex 9-88	Equivalent
Calendered Film	Benzoflex 9-88	Benzoflex 2088	Equivalent
Spread Coated Fabric	Benzoflex 2088	Benzoflex 50	Equivalent
Adhesives	Benzoflex LA-705	Benzoflex 2088	Equivalent
Paint/lacquers	Velate 375	Benzoflex 9-88	Equivalent
Sealants - Glass	Benzoflex 2088	Benzoflex 9-88	Equivalent
Sealants - Construction	Benzoflex 2088	Benzoflex 9-88	Equivalent

Benzoflex 2088: Diethylene glycol dibenzoate (61-69%), dipropylene glycol dibenzoate, triethylene glycol dibenzoate

Benzoflex 9-88: Dipropylene glycol dibenzoate (89%), propenyl propyl benzoate, dipropylene glycol monobenzoate, propylene glycol dibenzoate, propylene glycol dibenzoate

Benzoflex LA-705: Proprietary benzoate esters (76-80%), dipropylene glycol dibenzoate

Benzoflex 50: Diethylene glycol dibenzoate (45%), dipropylene glycol dibenzoate (45%), , diethylene glycol monobenzoate, dipropylene glycol monobenzoate, propenyl propyl benzoate, propylene glycol dibenzoate.

Velate 375: Proprietary benzoate esters (76-82%), dipropylene glycol dibenzoate

The applied dibenzoates mentioned above have the following CAS Numbers and EC Numbers:

Diethylene glycol dibenzoate (DEGD): CAS No. 120-55-8; EC No. 204-407-6.

Dipropylene glycol dibenzoate (DGD): CAS No. 27138-31-4; EC No. 248-258-5.

Triethylene glycol dibenzoate: CAS No. 120-56-9; EC No. 204-408-1.

Propenyl propyl benzoate: CAS No. 197178-94-2; EC No. not assigned.

Dipropylene glycol monobenzoate: CAS No. 32686-95-6; EC No. not assigned.

Propylene glycol dibenzoate: CAS No. 19224-26-1; EC No. 242-894-7.

A study on alternatives to restricted phthalates in toys concluded that the fact that DGD has been a well known and much-used competitor to BBP for many years, especially in PVC flooring and in PVA adhesives, which indicates a clear potential for substituting DGD for BBP, from a technical point of view (Maag et al, 2010). This may also imply potential to replace DIHP.

Further information on the experience with the substitution of DIHP has been requested from the manufacturer of the dibenzoates, but no information has been obtained.

2.1.5 Other alternatives

A number of plasticisers are marketed as alternatives to phthalates (see e.g. Maag et al., 2010). The plasticisers are often used in blends and more plasticizers may probably be used in blends that may substitute for DIHP in some applications. Apart from the plasticizers mentioned above, no plasticizers specifically marketed as alternatives to DIHP has been identified.

2.2 Alternatives to DIHP in mixtures

A large number of plasticisers are used in mixtures such as sealants, adhesives, paints and printing inks. The plasticiser is selected in order to obtain very specific properties of the mixtures during

application and during service life. Often it may be difficult to find a like-for-like substitute for a specific plasticiser and it will be necessary to reformulate the mixture, which may require the user to accept small differences in technical properties of the mixture. According to the only former manufacturer of sealant containing DIHP from which information has been obtained, no direct substitute for DIHP was available for the specific sealant and the sealant was totally reformulated.

It has not been possible to identify any use of DIHP in mixtures where the user has indicated that it has been particularly difficult to replace DIHP.

It has been indicated by the manufacturer of oil additives (see Section 2.2.6) that DIHP used in oil additives has been replaced by DINP (EC No. 271-090-9; CAS No. 68515-48-0).

Several of the plasticisers substituting for DIHP in PVC can also be used for mixtures.

According to the manufacturer of IDB, the IDB/DINP blend can also substitute for DIHP in adhesives. According to a supplier of IBD, the plasticizer is applied in polyurethane sealants, acrylic based adhesives, MS-polymer based (silyl-terminated polyether) and silane-terminated systems and is used as an alternative for critical short-chained esters such as DIBP, DBP, BBP (Krahn, 2010). DIHP is not specifically mentioned in the technical description.

Eastman DBT plasticizer is indicated by the manufacturer as a non-phthalate plasticizer for waterborne adhesives and it provides comparable viscosity response to currently used plasticizers.

As shown in Table 3, the blends of dibenzoates are marketed as substitutes for BBP in sealants for both glassing and construction.

2.3 Harmonised classification of alternatives

None of the identified alternative substances are listed in Annex VI of Regulation (EC) No 1272/2008, as amended by Commission Regulation (EC) No 790/2009 of 10 August 2009 (see Table 4).

For one of the substances (DINP), a finished Risk Assessment Report is available. The substance is not classified but, according to Annex XVII of the REACH Regulation (entry 52), DINP shall not be used as substance or in mixtures, in concentrations greater than 0.1% by weight of the plasticised material, in toys and childcare articles which can be placed in the mouth by children.

Three of the other substances have been included in previous environmental and health assessments of alternatives to classified phthalates: DEHT, DEGD and DGD (COWI *et al.*, 2008a; Maag *et al.*, 2010). None of these substances were considered to be CMR or PBT substances in any of these assessments. However, in general, data for some endpoints have been missing, affecting the ability to draw a firm conclusion.

Table 10: Harmonised classification of the identified alternative substances according to Regulation (EC) No 1272/2008 as amended by Commission Regulation (EC) No 790/2009 of 10 August 2009 (1st ATP).

Substance name	Abb.	EC No.	Cas No.	Harmonised Classification	Other information
Isodecyl benzoate	IDB	n.a.	131298-44-7	Not listed	
Di-isononyl phthalate	DINP	249-079-5	28553-12-0	Not listed	Risk Assessment Report (EC, 2003) i available Shall not be used as substance or in mixtures, in concentrations greater than 0,1% by weight of the plasticised material, in toys and childcare articles which can be placed in the mouth by children (REACH Annex XVII). COWI *et al.* (2008a) concluded that it would be reasonable to conclude that use of DINP as an alternative would not introduce significant new risks to the environment.
Di-butyl terephthalate	DBT	217-803-9	1962-75-0	Not listed	
Di (2-ethyl-hexyl) terephthalate	DEHT	229-176-9	6422-86-2	Not listed	An assessment of Maag *et al.* (2010) concluded that DEHT is not easily biodegradable and is bioaccumulative, but its aquatic toxicity could not be fully evaluated based on the data available. COWI *et al.* (2008a) concluded that no firm conclusions on the relative hazards or risks could be drawn for DEHT.
Diethylene glycol dibenzoate	DEGD	204-407-6	120-55-8	Not listed	An assessment of Maag *et al.* (2010) concluded the DEGD and DGD came out rather favourable in the environmental assessment. No studies on carcinogenicity were available for the assessment. COWI *et al.* (2008a) concluded for DGD that the substance is not a PBT substance, but does have moderately bioaccumulative properties.
Dipropylene glycol dibenzoate	DGD	248-258-5	27138-31-4	Not listed	
Triethylene glycol dibenzoate		204-408-1	120-56-9	Not listed	
Propenyl propyl benzoate		n.a.	197178-94-2	Not listed	
Dipropylene glycol monobenzoate		n.a.	32686-95-6	Not listed	
Propylene glycol dibenzoate		242-894-7	19224-26-1	Not listed	

n.a.: EC Number not assigned

2.4 Conclusions for alternatives

From the information provided above, the following conclusions have been reached:

- An alternative that is considered suitable is manufactured by the former manufacturer of DIHP and, according to the manufacturer, the replacement of DIHP by customers that previously used DIHP is now complete.
- The introduction of alternatives has required extensive re-formulation work and formulation and process optimization. The replacement has required the manufacturer to work for up to a full year with each customer, depending upon the application, to support the replacement.
- Other alternatives to DIHP are also commercially available and the alternatives seem to have substituted for DIHP in EU production already.
- The price of alternatives is reportedly slightly higher than the price of DIHP, but no exact data on the price gap has been identified. However, the price differences have reportedly not been a constraint for the replacement of DIHP.
- None of the alternatives are listed in Annex VI of Regulation (EC) No 1272/2008 as amended by Commission Regulation (EC) No 790/2009 of 10 August 2009 in relation to hazardous properties. None of these potential alternatives were considered to be CMR or PBT substances in any of the reviewed previous assessments in which they have been considered. However, in general, data for some endpoints have been missing, affecting the ability to draw a firm conclusion.

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