Why do we worry about phthalates?

What are they?

Phthalate esters (PEs) are a group of man-made organic chemicals produced by the reaction of an alcohol with phthalic anhydride. Various alcohols are used, typically, having a carbon chain length in the range C_8 – C_{10} although alcohols with chain lengths of C_4, C_7, C_{11} and C_{13} are also used for specialist applications. The most commonly used *phthalate esters* (PEs) are di-2-ethylhexyl phthalate (DEHP) also referred to as DOP or DNOP (di-octyl phthalate), di-isodecyl phthalate (DIDP) and di-isononyl phthalate (DINP). PEs are clear liquids, with little or no smell and are of low volatility. They do not readily dissolve in water and are not persistent in the environment.

Uses

The most important use of PEs - more than 90% of European production - is as plasticisers for polyvinyl chloride (PVC) which they turn into a material which is soft, flexible, resilient and easier to handle. PVC consumes the largest volume of plasticisers since its molecular structure - more than that of any other polymer - allows it to have its properties modified by the incorporation of plasticisers. PEs are not just additives (like colourants or stabilisers) but are important components which largely determine the mechanical performance of polymers.

Applications of flexible PVC include a wide range of products from medical devices, such as tubing and blood bags, to the manufacture of clothing and footwear, electrical cable insulation, packaging, stationery, toys and baby care items, wall and floor coverings, roofing and automotive parts. In Europe, DEHP is the only plasticiser permitted for use in blood bags by the European Pharmacopoeia.

PEs have also been used to help prevent nail varnish from chipping, make perfume last longer and make tool handles stronger and more resistant to breaking. Others help adhesives, sealants, paints and many other products to be more effective.

How do they work?

PVC is a polar polymer with strong attractive and repulsive charges. Plasticisers also have strong polar bonds as well as long non-polar hydrocarbon chains. So when a plasticiser is added to PVC before it is processed, it is held in the polymer matrix by attractive forces between its polar bonds and those in the polymer. At the same time, the non-polar chains in the plasticiser interpose themselves between the polymer chains, attenuating the PVC/PVC attractive forces and resulting in a far less rigid material.

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Benefits

PEs have proved popular because different levels and types of PEs confer properties required by a wide variety of PVC products. Their use results in benefits such as ease of processing, flexibility, durability and low cost in applications such as cable insulation and sheathing, floor coverings, wall coverings and synthetic leather.

Risks Associated with Manufacture, Use and Disposal

As PEs are so widely used, they have been subjected to extensive testing to determine their impact on health and the environment. Some, including DBP (di-butyl phthalate), BBP (butyl benzyl phthalate) and DEHP, have been found, at high dose levels, to cause reproductive effects in rodents and have therefore been classified under the Classifcation, Labelling and Packaging Regulation (Regulation (EC) No 1272/2008), as Toxic to Reproduction Category 1B. It is evident that not all PEs have the same effects on rodents and so others, including DINP, DIDP and the higher molecular weight PEs, have not been classified or labelled.

For this reason DBP, BBP, DIBP (di-isobutyl phthalate) and DEHP have been added to the list of substances subject to Authorisation (Annex XIV) for specific uses under REACH. Thus, any company wishing to market or use these substances after the "Sunset Date" of 21st February 2015 must submit an application to the European Chemicals Agency (ECHA) for an authorisation by the 21st August 2013, otherwise continued use after the Sunset Date will not be allowed. Authorisations can be granted if the applicant demonstrates that the risk from the use of the substance is adequately controlled or, in some cases, if the applicant shows that the socio-economic benefits of using the substance outweigh the risks and there are no suitable alternative substances or technologies. Uses of DEHP, BBP and DBP in medical products are not subject to authorisation under REACH and use of phthalates in food contact materials is also outside the scope of the REACH authorisation procedure (see below).

The REACH Regulation also places responsibilities on industry to provide information in response to requests from consumers (usually in the form of safety data sheets) on the safe use of these substances on their own or in preparations and in articles.

Risk assessments, conducted under the EU Existing Substances Regulation (793/93/EEC) have been published for the five major PEs (BBP, DBP, DEHP, DIDP and DINP) currently in use. No risks have been identified for any of the applications in which DINP and DIDP are used. However, occupational exposure limits have been defined to control emissions of BBP and DEHP from processing plants. In addition, for DEHP, it was proposed that consideration should be given to restricting its use in food contact materials and some medical applications. The risk reduction strategies also proposed that, for precautionary reasons, the use of PEs in toys and child care articles should be limited.

These risk reduction proposals have been met via the following legislation:

- Regulation (EC) No 1272/2008 (Plastics materials intended to come into contact with food) sets legal migration limits for phthalates into various food types. In addition, the use of several PEs is restricted to specific applications.
- Directive 2007/47/EC, amends three earlier directives concerning medical devices. It relates to devices intended to store or transport substances to or from the body. It states that such devices containing PEs classified as carcinogenic, mutagenic or toxic to reproduction, of category 1A or 1B must be labelled that they contain such phthalates. Also the manufacturer must provide a specific

justification for the use of these devices for the treatment of pregnant or nursing women and children.

- Annex XVII of the REACH Regulation states that DBP, BBP and DEHP may not be used in any toys and childcare articles and that DINP, DIDP and DNOP may not be used in toys that can be placed in the mouth.

PEs have been shown not to accumulate in humans or animals. In the body, they are rapidly metabolised and the products excreted. Also, they are readily biodegradable and have been shown not to persist in the environment. PEs have not been shown to cause cancer in humans; no PEs have been classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC) or under the EU's CLP (Classification, Labelling and Packaging) Regulation and associated legislation.

The hazard classification and risk assessment of the PEs has been based on effects seen in rodents. At this time, there is insufficient scientific evidence to conclude that any PEs are endocrine disruptors in humans. Some PEs cause reproductive effects at high doses in rats and mice, by a process which involves the endocrine system. However, these effects have only been seen at exposure levels many times higher than those experienced by humans. One possibility is that DEHP can also cause toxicity to the male reproductive system in animals by a non-endocrine mechanism – by zinc depletion - in testicular sertoli cells.

Exposure Routes

The amount of PEs found in finished products has little to do with potential exposure, since that depends on whether the substances can migrate from the articles and that is determined by the way they were manufactured.
Contrary to public concerns, PEs cannot leach out of bottles containing drinking water or carbonated drinks as such bottles do not contain PEs. Most of these bottles are made of polyethylene terephthalate (PET) which, despite its similarity in name, is very different, chemically, from phthalate esters.

Control Measures

People most likely to be exposed to PEs are those involved in the manufacture and processing of polymers. Possible exposure to PEs is controlled by the principles laid down in the Control of Substances Hazardous to Health (COSHH) Regulations in the UK. This entails, as a priority, control of emissions at source, by the application of engineering controls, ventilation, where necessary, and the wearing of personal protective equipment.

Alternatives

Different plasticisers are used to produce materials with different properties through variations in plasticiser structure that result from the particular acid and alcohol used in their formation. Adipate esters such as diethylhexyl adipate (DEHA) are also used as plasticisers. Other substances include polyesters, trimellitates, citrates, benzoates, phosphates and alkyl sulphonates. However, phthalate esters remain the most popular choice because of their best all-round performance.

Key to phthalates included in this paper:

BBP	Butyl benzyl phthalate
DBP	Di-butyl phthalate
DEHP	Di (2-ethylhexyl) phthalate
DIBP	Di-isobutyl phthalate
DIDP	Di-isodecyl phthalate
DINP	Di-isononyl phthalate
DNOP/DOP	Di-octyl phthalate

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