chemsec
INTERNATIONAL CHEMICAL SECRETARIAT

Replacing phthalates

Why and how to substitute this hard-to-spell chemical group

Introduction

Phthalates is certainly a complicated word to spell. It is also a group of chemicals that are hard to avoid exposure to in daily life. Phthalates are used in a wide variety of applications due to their versatility, but are mainly used as plasticisers in plastics and can be found in everything from wall coverings and furniture to electronic devices and toys. Phthalates make up two-thirds of the plasticisers market, and since plasticisers are so frequently used it means that phthalates are all around us.

What makes this concerning is that many phthalates are proven to be hazardous for human health and the environment. Although data is not available for all the substances in this large group of chemicals, studies have shown that many phthalates are toxic for reproduction, hormone-disrupting and have negative effects on the brain. What adds to the concern is that phthalates are not chemically bound to the material to which they are added. This means that they continuously leach out into the environment, increasing human and environmental exposure to them.

Although some regions have started to regulate the use of these omnipresent chemicals, other regions are lagging behind with their chemicals legislations. In the European Union, several phthalates are classified as toxic and listed as substances of concern, with a handful of them under stricter regulation. Other important regions like the United States and China lack chemicals policies to deal with the threat of hazardous phthalates at a federal level, although in recent years China has started to implement policies similar to those in the EU and is, in fact, even stricter than the EU when it comes to phthalates in food contact materials.

In several cases, it has been proven that progressive chemicals policies drive innovation, and there is no reason why the case of phthalates should be any different. But stricter regulation is not the only thing needed to speed up the phase-out of hazardous phthalates. Leading brands and companies also need to be progressive and take the lead in the transition towards safer chemical alternatives.

There are already viable safer alternatives on the market to replace hazardous phthalates in many applications. That is the most important prerequisite for a successful substitution, and it has already been achieved.

Now it is just a matter of switching to these alternatives.

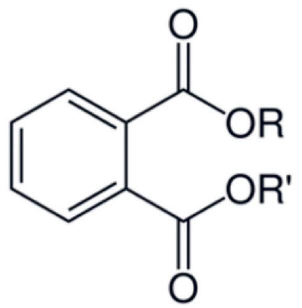
The chemical facts

Phthalates are not a single chemical substance but instead refer to a group of chemicals. Technically speaking, phthalates are esters of phthalic acid, produced as colourless, odourless, syrupy liquids with low water solubility, high oil solubility and low volatility.

They are typically divided into two groups: low molecular weight phthalates and high molecular weight phthalates. The first group to be commercialised was the former with side chains containing 3-6 carbon atoms. Further exploration of this family of substances led to the development of the latter, which have more than 6 carbon atoms in their side chains.

The most well-known phthalate is di-(2-ethylhexyl) phthalate, normally referred to as DEHP. This high molecular weight phthalate is the most used phthalate in the world today, and is also known to be among the most hazardous for human health.

The nomenclature (naming) can be a bit confusing when it comes to phthalates. Historically, the name phthalate has been used to refer only to the subgroup orthophthalates. But today the term phthalates can encompass a larger group of molecules than orthophthalates alone, such as terephthalates – which have been used as alternatives to orthophthalates. In this report, we mean orthophthalates when we just say phthalates; other subgroups of phthalates will be referred to by their full chemical family name.



The general chemical structure of a phthalate molecule. The "R" means that this part of the molecule varies between the different phthalates. The more carbon atoms here, the higher the molecular weight.

Common phthalates

Low:

BBP	(benzyl-butyl phthalate)
DBP	(di-butyl phthalate)
DCHP	(di-cyclohexyl phthalate)
DIBP	(di-isobutyl phthalate)
DIPP	(diisopentyl phthalate)

High:

DEHP	(di-(2-ethylhexyl) phthalate)
DPHP	(di-(2-propylheptyl) phthalate)
DNOP	(di-n-octyl phthalate)
DINP	(diisononyl phthalate)
DIDP	(diisodecyl phthalate)

Phthalates are widely used in plastic

Phthalates have been used since the early 1900s, and because of their versatility they are used in countless different applications. What can be said, however, is that phthalates are most commonly used as plasticisers, meaning they are added to plastics to increase flexibility, transparency, durability and longevity – most commonly in PVC plastics. Without phthalates (or other plasticisers) added to them, these plastics would be stiff and brittle.

In 2005, almost 90% of the plasticisers produced in the world were phthalates. Although this figure dropped to 65% in 2017, the lion's share of the plasticisers market still belongs to phthalates. Since the market has grown during this period, the actual amount of phthalates produced has only decreased by 10% (from 5.4 to 4.9 million metric tonnes). In the future, the global demand for plasticisers is not expected to drop, instead forecasts say it will increase by around 2% per year.

Due to the overwhelming consumption of plastics in the world today, phthalates can be found almost everywhere: in cars, electric wiring, toys, wall coverings, flooring, furniture, shoes, bags, packaging, medical devices – you name it. Quite a large proportion of flexible plastic is in fact made up of plasticisers, contributing up to 50% of the final plastic's weight. One study, for example, found that flexible tubing used in medical devices can consist of up to 70% phthalates.[1]

Even though the use of phthalates as plasticisers has decreased somewhat – mainly in the European Union – due to legislative actions, phthalates such as DINP, DPHP and DIDP are still produced in the EU and used in many applications. In the rest of the world, DEHP continues to be the dominant plasticiser even though its share of the market has decreased in recent years. Even so, DEHP accounted for one third of global plasticiser production in 2017, with the bulk of production in Asia.

1. Benjamin et al, Journal of Hazardous Materials, 2017

Phthalates are also used as solvents, for example, as fragrance carriers in cosmetics.

Much of the plastic goes into packaging

Around 40% of all plastics in the world are produced for packaging, of which 60% is packaging for food or beverages.[2] When you add this to the fact that phthalates are used in nearly all plastics, it becomes clear that plastic packaging is a major application for phthalates.

Today, the majority of products are sold in some kind of plastic packaging. One example is food. Fast food wrappings and other take-away containers are common examples – even vegetables and meat nowadays tend to come in plastic packaging. Since this plastic comes in direct contact with the food and phthalates are prone to leach out from the material, many people are exposed to these hazardous chemicals.

Recently, as part of the project behind this report, a comprehensive database of chemicals associated with plastic packaging was published.[3] It identifies over 4,000 substances associated with plastic packaging. Of these, 63 were identified as very hazardous to human health based on official classification, while the corresponding number for the environment was 68 chemicals. From these, five phthalates were identified as the most urgent substances to asses in more detail regarding their impact on human health and the environment when used in plastic packaging. These five were BBP, DBP, DIBP, DEHP and DCHP. The study concludes that phthalates are still widely found in plastic packaging, which further justifies their designation as high-priority substances to substitute with safer alternatives.

Phthalates from plastic packaging end up in food

For some of these phthalates (DBP, DIBP and DEHP), food has been found to be the primary source of exposure.[4] Fatty foods have been found to be specifically associated with increased phthalate levels in humans due to the fact that phthalates dissolve easily in fats and oils. One study actually shows that people who eat a lot of fast food have 40% higher phthalate levels in their blood.[5] However, several studies have also found high phthalate levels in non-fatty food such as bread.[6,7]

Phthalates also migrate from items used in factories such as single-use gloves, conveyor belts and plastic tubing for liquids,[8] as well as from different kinds of food packaging such as plastic containers with foiled lids, paper cups with plastic laminate and plastic bags in carton boxes. In the case of oily foods in glass packaging, 25% of all products were reported to be non-compliant (non-authorised plasticiser uses or plasticiser levels above migration limits) due to the presence of plasticiser in the plastic layers of metal closures.[9]

In summary, one can conclude that plastic packaging and phthalates are closely related – regarding both use and exposure. The fact that phthalates tend to leach out from the plastic material, especially when the content is either fatty or heated, makes it a major source of phthalate exposure for humans.

2. *R. Geyer et al, Sci. Adv., 2017*
3. *Groh et al, Science of the Total Environment, 2019*
4. *Wormuth et al, Risk Analysis, 2006*
5. *Zota et al, Env. Health Perspectives, pdf*
6. *Cirillo et al, J. Agric. Food, 2011*
7. *Sioen et al, Environment International, 2012*
8. *Petersen & Jensen, Food Additives and Contaminants: Part A, 2010*
9. *McCombie et al, European Food Research and Technology, 2012*

Phthalates interfere with our hormones

Phthalates have been a subject of concern for a long time, mainly because of their negative effects on reproduction. Most of the phthalates identified as toxic to reproduction have been classified as such due to their negative effects on fertility and the development of the offspring. One example is DEHP, which shows both adverse effects on testicular development in the offspring and reduced fertility in adults. Phthalates have also been linked to reduced sperm count, mobility and quality as well as low testosterone levels.[10]

In addition, phthalates are associated with negative neurological effects, including links to autism spectrum disorder and low cognitive function. They have also been found to have hormone-disrupting effects. The SIN List[11] includes eight phthalates that have been found to be endocrine disruptors, among them are DINP and DCHP.

One characteristic that makes phthalates especially concerning is the fact that they are not chemically bound to the materials they are added to. This leads to phthalates being continuously released from products, with several factors accelerating this process such as heat or light.[12] Since phthalates are present in so many products – many of them in direct contact with our skin or the food we eat – this continuous release of hazardous chemicals is a recipe for disaster. An American study from 2016 actually found that 96% of all Americans had phthalates in their blood streams.[13]

But phthalates are not only hazardous to human health, they are also hazardous to the environment. Examples of environmental effects include accumulation in the food chain and acute or chronic toxic effects on aquatic organisms.

In summary, the extensive use of phthalates in products has led to exposure becoming unavoidable since these hazardous chemicals are almost everywhere. The close-to-human uses (such as food packaging or cosmetics) further amplify the exposure and, together with the many proven hazards of phthalates, make them a group of chemicals that needs to be closely monitored as well as regulated and substituted, in order to avoid further harm.

10. Benjamin et al, Journal of Hazardous Materials, 2017; Milosevic et al, Environmental Monitoring and Assessment, 2018; Desdoits-Lethimonier et al, Human Reproduction, 2012; Huang et al, PLOS One 2012

11. The SIN List is a list of hazardous chemicals that are likely to be banned or restricted in the future. All chemicals on the SIN List meet the criteria of Substances of Very High Concern (SVHCs) as defined by REACH.

12. Benjamin et al, Journal of Hazardous Materials, 2017

13. Harley et al, Environmental Health Perspectives, 2016

So why are these chemicals allowed?

Today's chemicals regulation is mainly designed to deal with chemicals substance by substance. To classify or regulate one chemical, a lot of scientific evidence is required to prove its hazardous properties. The easiest way to replace a hazardous phthalate that has been regulated is to use another structurally similar phthalate that can provide the same technical function. The obvious risk, of course, is that when the newer chemical is studied more closely, it will show similar hazardous properties. However, performing such studies takes many years, so while regulators are catching up with new scientific evidence the chemical can continue to be used. This process of regrettable substitution can then be repeated over and over again due to the multitude of existing phthalates.

Finding better ways of dealing with chemical groups in the regulation process is currently a much-debated issue.

In the European Union

In Europe, many phthalates are classified as hazardous to human health and the environment and several phthalates are included in the EU chemicals legislation REACH. Moreover, eight phthalates have so far been placed on the Authorisation List, which means that a chemical is not allowed to be produced or imported into the EU unless a special permit has been granted.

In addition, there are further restrictions for phthalates in toys and children's products, restricting the use of BBP, DBP, DEHP, DIBP, DIDP, DINP and DNOP. For the first four of these phthalates, their use will also be restricted in other products from July 2020. Another important piece of EU legislation – the RoHS directive – regulates the use of BBP, DBP, DEHP and DIBP in electrical and electronic equipment.

Several member states of the European Union have also implemented national phthalates legislations that go beyond the EU legislation. Denmark, for example, has restricted all phthalates in toys and children's products aimed at children up to three years old.

It is concerning, however, that several phthalates that have been proven hazardous to human health are still allowed to be used in plastic food contact materials, including BBP, DBP and DEHP. This is due to the fact that chemicals in food contact materials are regulated under a different legislation than REACH.

In the United States

Phthalates are not as regulated in the United States as they are in the European Union. A number of phthalates that are regulated in the EU are, for example, approved by the Food and Drug Administration (FDA) for use in food applications – including process equipment and packaging – and medical devices. Eight phthalates[14] are, however, restricted in toys. The Toxic Substances Control Act (TSCA) also includes five phthalates[15] in a priority list for risk evaluation. In cosmetics, no phthalates are restricted at the moment.

In China

China – where the regulation of phthalates has been lagging behind for some time – has in recent years identified a need to restrict this group of substances. A restriction – similar to the one in the EU – concerning phthalates in toys has been in force since 2013, and since 2017, phthalates are no longer allowed in plastic food packaging. Restrictions on other types of plastic packaging (i.e. non-food) are also being considered. Furthermore, in the recent five-year plan from the Chinese government a need to replace phthalate plasticisers with new, preferably bio-based, alternatives was identified.

In summary, the fact that regulation of phthalates is increasing is a positive sign, and it is now therefore crucial to find safer alternatives to replace phthalates in all their different applications.

14. DEHP, DBP, BBP, DINP, DPENP, DHEXP, DCHP, DIBP
15. DBP, BBP, DEHP, DIBP, DCHP

Alternatives to phthalates

Understanding the function

The use of a specific phthalate in a certain product or material is not a coincidence. It has probably been carefully selected to provide a specific function. It is therefore not possible to provide a simple and universal way to substitute phthalates. An alternative that can substitute phthalates in one application is not necessarily fit to do the same in another application. Instead, a wide variety of alternatives are required to replace phthalates and cover all their specific functions.

This is why it is important to understand the *function* that a phthalate serves when it is added. Taking this function as a basis one can list solutions to achieve the same function. If the desired function is to make PVC flexible for use in a shower curtain, then a non-phthalate plasticiser might do the trick. But using another type of plastic, for example polyethylene (PE), would remove the need for phthalate plasticisers entirely, as would a switch to a completely different material such as textile. In some cases, it might turn out that the function is not so important. Take a scented product for example. Perhaps it would be just as attractive without perfume.

In fact, substituting PVC for another material has become a common way to avoid phthalates entirely, and as there are also other problems associated with PVC (the production and waste phase) this is probably a preferable strategy when possible.

Choosing a drop-in substitute might seem to be the easiest solution, but in this case process changes may also be needed to optimise the function of the new substitute.

It should be noted, however, that in the case of phthalates as plasticisers, there are a vast number of possible molecules that plasticise a polymer. The function is not dependent on a specific chemical bonding but rather on other characteristics. This has also led to quite a variety of existing alternatives.

Analysing alternatives

The act of substituting one hazardous chemical for another one that is equally hazardous is known as regrettable substitution. One example of this phenomenon is the substitution of the hormone-disrupting chemical Bisphenol A with its equally hazardous cousins Bisphenol S or F.

3-step guide to substituting phthatalates

1 Scope

Understand the function of the added phthalates in the relevant products and processes.

2 Criteria

Decide which physical and functional properties the alternative must have in order to match all functions within the scope.

Decide upon criteria for hazard properties.

3 Assessment

Investigate which alternatives have viable properties according to the criteria. Include external variables in the investigation – for example availability – in order to decide which would be the most suitable alternative.

To avoid this, it is necessary to know that the alternative is safer than what has been used before. This requires in-depth knowledge of the alternative.

One recommended method for assessing alternatives is the GreenScreen for Safer Chemicals from the NGO Clean Production Action. In this methodology, 18 hazard endpoints are assessed and summarised in a table. An algorithm is applied to the hazard classifications to calculate an overall benchmark (BM) score, ranging from BM1 to BM4:

- BM 1: Avoid – chemical of high concern
- BM 2: Use – but search for safer substitutes
- BM 3: Use – but there is still opportunity for improvement
- BM 4: Prefer – safer chemical
- BM U: Unspecified due to insufficient data (data gaps for key hazard endpoints)

An important feature of the GreenScreen methodology is that it also considers data gaps in order to avoid regrettable substitution, this means that less investigated alternatives cannot be given a good benchmark score.

Due to the interest in alternatives to phthalates, several initiatives have already investigated how safe some of the alternatives are. We will summarise some of the findings, but for more details we suggest you consult the original sources:

- Alternatives to Five Phthalates of Concern to Puget Sound from Northwest Green Chemistry
- Phthalates and Their Alternatives: Health and Environmental Concerns from the Lowell Centre
- Identification and assessment of alternatives to selected phthalates from the Danish EPA
- TCO Certified Accepted Substance List from TCO Certified

DEHT/DOTP and DINCH

The most popular non-phthalate plasticisers are DEHT and DINCH. DEHT is more widely used in the United States while DINCH is more frequently used in Europe. Both can replace phthalates, often DEHP and DINP, in almost all plasticiser applications.

Terephthalates, the group to which DEHT (sometimes called DOTP) belongs, represent 42% of the market for alternative plasticisers. DEHT has been assessed as GreenScreen Benchmark 3.

Of the aliphatics and cyclohexanoates, which represent about 14% of the alternatives market, DINCH makes up 70-80%. DINCH has been assessed as GreenScreen Benchmark 2.

Even if DEHT and DINCH are versatile alternatives, they might not be direct drop-in replacements in many applications since additional changes are needed. Chemical manufacturers therefore offer advice and expertise to optimise the process. Both DINCH and DEHT may require the addition of fast fusers and, in some cases, compatibilisation additives as well, which can lead to other problems.

DEHT is, for example, approved for food contact in the United States – so is DINCH in the EU – but the additional additives needed to optimise the specific process might not be. And neither DINCH nor DEHT pass the requirements for cables and wires as they are not suitable for high temperatures.

Epoxidised soybean oil (ESBO)

Epoxidised soybean oil (ESBO) holds about 20% of the market share for alternatives to phthalates. These alternatives can be used as plasticisers but also as compatibilisers, and are, for example, used together with DEHP in PVC. ESBO is used as a plasticiser in seals for glass jars and as a stabiliser to minimise UV degradation of PVC. It has been assessed as a GreenScreen Benchmark 3 chemical.

Trimellitates (TOTM)

Trimellitates make up about 8% of the market for alternatives to phthalates. They pass heat requirements for wires and cables and are primarily used when heat resistance is required because they are expensive compared to DEHP. In addition to cables and wires, they are also used in flooring, packaging and wall coverings. TOTMs have been assigned a GreenScreen Benchmark 2.

Acetyl tributyl citrate (ATBC)

Acetyl tributyl citrate (ATBC) is used as a plasticiser in cosmetic products and in PVC applications. However, the use in PVC is limited due to them having a comparably high water solubility. It has been assigned a GreenScreen Benchmark 3.

Some initiatives – like ChemSec's Marketplace – aim to make safer alternatives more visible by gathering them in a global database so that companies can find them more easily. The database is connected to a business-to-business platform where potential buyers can connect directly with the supplier of an alternative.

On the next page is a table summarising alternative plasticisers including, when available, a GreenScreen Benchmark score and information on alternatives on the ChemSec Marketplace.

ALTERNATIVE NAME	CAS	GREENSCREEN BM SCORE	AVAILABLE ON CHEMSEC MARKETPLACE
bis(2-ethylhexyl) adipate (DEHA)	103–23–1	2	No
acetyl tri-butyl citrate (ATBC)	77–90–7	3	Yes
diisononyl adipate (DINA)	33703–08–1	2	No
di-(2-ethylhexyl) terephthalate (DEHT)	6422–86–2	3	Yes
epoxidised soya bean oil (ESBO)	8013–07–08	3	Yes
diisononyl cyclohexanedicarboxylate (DINCH)	166412–78–8 / 474919–59–0	2	No
2-ethyl-1-hexanol	104–76–7	2	No
dimethyl phthalate (DMP)	131–11–3	2	No
white mineral oil	8042–47–5	2	No
tris(2-ethylhexyl) trimellitate (TEHTM, TOTM)	3319–31–1	2	Yes
bis(2-propylheptyl) phthalate (DPHP)	53306–54–0	2	No
oxydipropyl dibenzoate	27138–31–4	2	No
diisooctyl adipate	1330–86–5	2	No
pentaerythritol tetravalerate	15834–04–5	N.A.	Yes
alkylsulphonic phenyl ester	91082–17–6	N.A.	No

What needs to be done

Due to the rampant consumption of plastics in the world today, and the fact that phthalates are the go-to chemicals when it comes to plasticisers for this material, phthalates are present almost everywhere. It is overwhelming to think that these chemicals, which are proven to be hazardous for us and our environment, penetrate every nook and cranny of our daily lives. Phthalates are present in the most basic things, they are in our walls, our floors, our furniture, our children's toys, our groceries – everywhere. And the fact that phthalates are not chemically bound to the materials in which they are added – meaning that these hazardous chemicals continuously leach out into our environment – makes this quite alarming.

Because of the many different functions of phthalates and the many different applications for them, there is no universal one-size-fits-all process to follow when substituting them. Each substitution requires a unique solution. However, many processes are similar – sometimes even identical – and can therefore be copied to a certain extent. But knowledge of these processes is frequently regarded as confidential business information and not shared with competitors. Companies would benefit greatly from a sharing of information connected to successful substitution and the processes involved in it, especially since cost is the primary reason for companies to hesitate when considering if and how to substitute hazardous chemicals.

Even though the situation might look grim and hopeless, there are ways to improve it. What follows are some recommendations from a policy perspective as well as from a business perspective.

Policy

Regulating phthalates has been a slow process and it is still lagging behind. Even if the production and use of phthalates has dropped significantly over the last decade in Europe, it is still extensive on a global scale.

In order to reduce impacts on human health and the environment caused by exposure to phthalates, chemicals regulations need to be stricter. Studies have shown the positive effects of regulating hazardous chemicals.[16] This is both the easiest and most effective way to mitigate the problem of hazardous phthalates, but further regulation – especially in the United States and Asia – is needed to achieve a global effect.

Stricter regulation – in combination with progressive companies phasing out phthalates from their products – would be the most efficient way to speed up the transition from these hazardous substances to safer alternatives. The availability of safer alternatives on the market is not an issue since there is an abundance of alternatives for different applications already available. What is needed instead is a regulatory push in the right direction to get things moving.

Business

Substitution of phthalates has been on the agenda for many companies for some time, and some have already phased them out – or are in the process of phasing them out – of their products by using restricted substances lists (RSLs). H&M and Marks & Spencer, for example, phased out phthalates several years ago, and earlier this year, Kingfisher announced its intention to phase out phthalates as well as additional chemicals of concern. Initiatives from leading brands such as these are an inspiration for other companies to follow suit.

Being a progressive company ahead of regulation is positive in many different ways. An improved sustainability profile could, for example, lead to an improved image and increased brand value, which in turn, could benefit a company economically by increasing sales. Furthermore, regulation-related costs – such as costs for compliance and authorisation – would be reduced.

The table on next page lists some of the companies that have taken action on phthalates.

COMPANY	ACTION
COOP Denmark	In 2016, Coop Denmark decided to phase out 12 groups of chemicals, including phthalates, from its own-label products by the end of 2017.
Walgreens Boots Alliance	In November 2018, Boots announced a restricted substance list (RSL) to be phased out by 2021. This includes groups such as phthalates.
Kingfisher	In January 2019, Kingfisher announced that it will phase out three chemical families, including phthalates, from its own brand products.
Apple	Every Apple product is free from phthalates, except some products in India and South Korea due to governmental restrictions.
IKEA	Since 2015, IKEA has removed all phthalates in food contact materials and children's products.
H&M	Phthalates are not allowed to be used in H&M production lines. These substances will be phased out from the entire production by 2020.

A push from top retailers – like the examples mentioned above – increases the need to investigate alternatives down the supply chain. This then also boosts the availability of safer solutions and lowers the costs.

In summary, there is no reason to wait any longer, safer alternatives already exist. Companies should start replacing hazardous phthalates immediately and not wait for regulation to set the pace.

16. *Report from Austrian Federal Ministry of Agriculture, Forestry, Environment and Water, 2015*

This report has been written to provide an overview of a group of chemicals that is gaining more and more attention – phthalates. Without drowning you in details, it describes why, where and how phthalates are used and offers guidance on how to substitute them for safer alternatives.

The hazardous properties of phthalates have led to public debate and, in some cases, regulation. Because of this, alternatives to phthalates are becoming more available. This report summarises current studies on alternatives to phthalates and offers a simplified approach to looking at how to substitute them.

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