

Phthalate Puzzle

Abhijit Ghosh

The most common plasticizer, phthalates, are facing stricter regulations due to their omnipresence and possible effects on human health, and environment. But high cost, lack of application range, and unknown long-term effects of non-phthalate alternatives make the scenario puzzling.

Waldo Semon conducted a seminal experiment in the Ohio-based laboratory of B F Goodrich Rubber Company in 1926 when he mixed vinyl polymers, an industrial waste of rubber production, with a solvent and heated. The solvent was nothing other than a plasticizer, and the result was 'plasticized polyvinyl chloride' or the commonly known PVC.

Historically, PVC was first discovered in 1838, by the French physicist and chemist Henri Victor Regnault and then in 1872, by the German chemist Eugen Baumann. But its rigid nature posed difficulties in working with it and thereby limited its applicability. Plasticized PVC, a brainchild of Waldo Semon is flexible and typically contains 40% plasticizer. Today, PVC is a major commodity polymer comprising about 13% of the total global production of synthetic plastics. This clearly indicates how widely plasticizers are used. Global consumption of plasticizers every year is estimated to be more than eight million tons. Around 1930, plasticizers were introduced into the commercial manufacturing of PVC formulations. In essence, a plasticizer is the measure of performance rather than physical properties as its incorporation increases flexibility and workability. Pure PVC [1–4] is highly rigid in nature. Hence, plasticizers are added to make the PVC, other plastics or polymers, flexible and pliable.

Among the numerous (approximately 30,000) substances that have been evaluated for their plasticizing properties, economic viability, and broad spectrum, physical properties of phthalates



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or phthalic acid esters (PAEs) make them an important class of plasticizers. According to the plasticizers.org, 63.5% of the world's plasticizer market is shared by four phthalates. Again, the extensive use of such plasticizers categorizes them as a ubiquitous group of environmental and health hazards too. Phthalates have been the subject of numerous investigations and concerns because of their widespread applications in modern plastics, medical and paramedical devices, and cosmetics [3, 4].

Since phthalates are not covalently bonded to the polymer matrices they are incorporated in; they leach out over time and under favorable conditions, such as the application of heat or through repeated contact. The route of human exposure to phthalates is mainly through ingestion, inhalation, and skin contact. Food packaging is one of the major sources of ingested phthalates. Indoor air (PVC flooring) and personal products (shampoo, nail polish, etc.) turn out to be the common sources of inhaled and dermal exposure respectively [5].

In the *Fourth National Report on Human Exposure to Environmental Chemicals*, published in 2009, the presence of many phthalate metabolites was reported in the general population of USA. Adult women had higher levels of urinary metabolites than men as phthalates are highly used in toiletries and cosmetics [6]. A biomonitoring study (2011–2012) conducted across 17 countries in Europe found that younger children are more exposed than older children to phthalates. This finding is similar to several US studies which suggest the same. Again, urinary metabolites were higher in children than mothers. Without much insight though, it is proposed that higher exposure relative to their body size may be the reason of higher phthalate concentration in young children [7].

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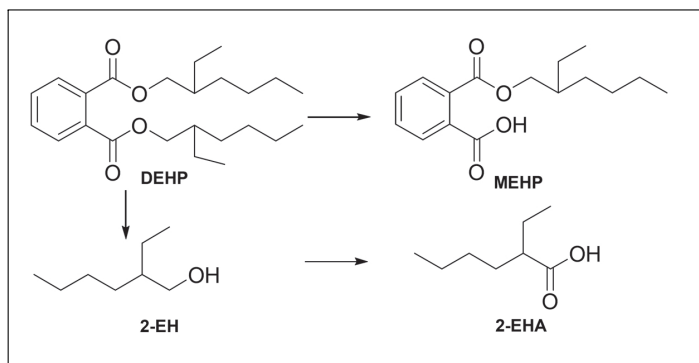


Figure 1. Metabolites of DEHP

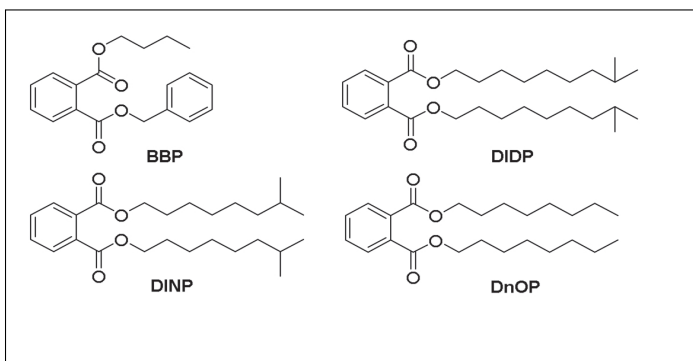
more sensitive than adult animals. While the testicular effects on animals have been known for more than three decades, recent research has been focused on phthalates' ability to affect reproductive development after utero exposure. Phthalates have been associated with malformation of the epididymis, vas deferens, seminal vesicles, prostate, external genitalia, feminization, sexually dimorphic structures in rodents, etc. The possible threat to infants and children led to a temporary ban of phthalate use in toys (excessive mouthing) and baby products such as pacifiers and teething rings across America and Europe in the late 1990s. A permanent ban followed later [7–9].

Di (2-ethylhexyl) phthalate, known as DEHP, is currently the most widely used phthalate. Pediatric exposure to DEHP through various medical devices in hospitals has been indicated by metabolic byproducts. Mammalian metabolism (*Figure 1*) of DEHP results in the formation of mono-2-ethylhexyl phthalate and 2-ethylhexanol (2-EH). 2-ethylhexanol is further metabolized to 2-ethylhexanoic acid (2-EHA) [10]. DEHP, 2-EH, and 2-EHA were found to act as peroxisome proliferators that is believed to have a strong correlation to liver carcinogenesis [11]. Moreover, phthalates have been associated with numerous health hazards ranging from hepatotoxicity, carcinogenicity, and endocrine disruption to neurotoxicity. Other than DEHP, di-isononyl phthalate (DINP), dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), di-n-octyl phthalate (DnOP), and 1, 2-diisodecyl ester (DIDP) are banned in the production of toys for children (*Figure 2*) [12–15].

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Figure 2. Phthalates banned in toys.



While phthalates are banned in children's toys, they continue to be approved for other uses. For example, phthalates are still widely popular in the manufacture of tubings used in medical applications (where it is important that the tubing stays flexible and not kink), in intravenous blood bags, etc. But a major debate that was absent for a while surfaced again in 2015. It started with the findings by the NGO, Ecology Center that most vinyl tiles contain phthalate plasticizers that are banned in children's toys. In response to the findings, world's largest home improvement retailer, Home Depot, took prompt action and pledged to eliminate certain phthalates. Similar steps were followed by some other retailers in USA [16–18].

Meanwhile, the search for alternatives to phthalate plasticizers has identified chemicals like citrates, adipates, phosphates, etc. However, the 2011 report by Lowell Center for Sustainable Production, cautions about these phthalate alternatives. Like phthalates, these alternatives do not strongly bind to the polymer either. Therefore, possible leaching out is foreseen as a concern. There are not many studies that clearly indicate the consequences of repeated exposure to these alternatives; however, these so-called safer alternatives have been shown to possess multiple health and environmental concerns [5].

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much more expensive than phthalates which do not appeal to the customers [19].

Another key challenge in the worldwide reduction of toxic phthalates arises from the lack of strong regulations in the developing and underdeveloped countries. A significant portion of manufacturing in these countries comprise unorganized sectors that rely upon cheap plastics.

An appreciable number of people from multiple corners of the world – both civic and scientific society – are still debating on the phthalate issue. For that matter, phthalates will remain a subject of concern and debates, and will be closely monitored. However, while phthalates are banned in products with a high potential for leaching, leading to human exposure (such as toys that are chewed by children), there isn't sufficient concern (or data) to warrant banning the use of all phthalates outright in other applications. Therefore, it is expected that phthalates are 'here to stay', unless suitable, reasonably priced, and safer alternatives are found.

Suggested Reading

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