



PRESSURE ON PLASTICIZERS

TOXICITY CONCERNS prompt retailers, regulators to phase out widely used phthalates

BRITT E. ERICKSON, C&EN WASHINGTON

IN A WORLD without plasticizers, all objects made of polyvinyl chloride (PVC) would be as hard and rigid as sewer pipes. But thanks to a class of compounds called phthalates, PVC can be soft, flexible, and durable, making it attractive for use in endless applications—artificial leather, electrical wire insulation, and garden hoses, to name a few.

Phthalates provide flexibility to vinyl products, but they are also controversial. Concerns—justified or not—have been bubbling up for more than a decade over their potential to disrupt hormones and cause reproductive and developmental effects. As a result, the plasticizer industry is in a state of flux, scrambling to adapt to ever-changing demands from regulators and the marketplace.

And it's a big marketplace. The global plasticizer market was about 8 million metric tons last year, according to IHS Chemical, a market research firm. Phthalates make up about 70% of that volume, IHS says.

The plasticizers are widely used in building and construction materials to make vinyl surfaces longer-lasting and easier to

maintain. Items in which they're used most often include floor and wall coverings, roofing membranes, and cable and wire insulation. Phthalates are also used as plasticizers in automotive parts, medical goods, and synthetic leather. In rubber, inks, paints, adhesives, perfumes, hair spray, and nail polish, they act as a solvent.

The chemicals have been manufactured since the 1930s by reacting an alcohol with an acid, such as phthalic anhydride. The properties of the resulting esters depend on the specific alcohol and acid. The number of alcohol-acid combinations that are possible and their resulting properties are as endless as the number of applications.

Most phthalates, however, never make it into commercial products because of concerns about performance, cost, availability, or toxicity. The alcohols used in making phthalates typically range from one or two carbons up to 13, forming either a straight or branched alkyl chain. Phthalates that end up with three to eight carbons in their alkyl side chain have received the most scrutiny because they have been associated with reproductive and developmental effects in lab animals.

RETAILERS REACT

Major home improvement stores in the U.S. have pledged to stop selling laminate flooring that contains phthalates.

Such studies have prompted regulators around the world to impose restrictions on a handful of phthalates in toys and other children's products, as well as in cosmetics and, more recently, electronics equipment

in the European Union. But regulators are not in agreement over which phthalates and applications should be restricted.

PUBLIC HEALTH and consumer advocacy groups, meanwhile, are pushing for broader restrictions, saying phthalates should be removed from all consumer products, including the construction materials and other durable goods that make up the bulk of plasticizer use.

Major retailers in the U.S. are bowing to pressure from such advocacy groups and voluntarily removing products containing phthalates from their store shelves. Home Depot, for example, announced in April that it would stop selling vinyl flooring containing phthalates by the end of this year.

"As the world's largest home improvement retailer, Home Depot's new policy sends a strong signal to the marketplace that retailers want healthier building materials free of harmful chemicals like phthalates," says Andy Igrejas, director of Safer Chemicals, Healthy Families, a coalition of public health advocacy groups. The coalition launched a campaign two years ago called Mind the Store, which aims to encourage retailers to stop selling products that contain harmful chemicals.

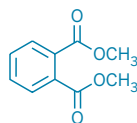
Other major home improvement retailers in the U.S., including Lowe's and Lumber Liquidators, quickly followed Home Depot's lead, also pledging to stop selling flooring that contains phthalates.

The American Chemistry Council (ACC), which represents chemical manufacturers, claims that "the science does not support the removal of phthalates from vinyl flooring." Retailers and customers should "closely examine misleading claims about phthalates used in vinyl flooring, rather than allowing scare tactics to distort the facts," the group's phthalates panel tells C&EN.

Health advocacy groups previously put pressure on retailers to stop selling food packaging, shower curtains, rubber ducks, and children's toys that contain phthalates. Mike Schade recalls working on those cam-

BIG WORLD Many phthalates and phthalate replacements jostle for use in polyvinyl chloride and other applications

Linear phthalates



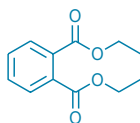
Dimethyl phthalate (DMP)

CAS: 131-11-3
Molecular weight: 194.2
NOAEL: 750 mg/kg-day^a

Used with cellulose acetate and nitrate.

No evidence of antiandrogenicity

No restrictions



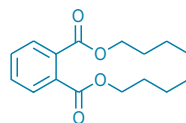
Diethyl phthalate (DEP)

CAS: 84-66-2
Molecular weight: 222.2
NOAEL: 750 mg/kg-day^a

Used in fragrance mixtures; phased out by a major producer in 2011.

No evidence of antiandrogenicity

No restrictions



Di-n-butyl phthalate (DBP)

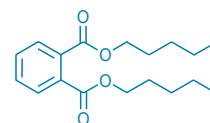
CAS: 84-74-2
Molecular weight: 278.4
NOAEL: 50 mg/kg-day^a

Used in adhesives and other applications; phased out by a major producer in 2011.

Reproduction, development

U.S.: prohibited in toys, child care products

EU: prohibited in child care products, cosmetics



Di-n-pentyl phthalate (DPENP, DnPP)

CAS: 131-18-0
Molecular weight: 306.4
NOAEL: 11 mg/kg-day^a

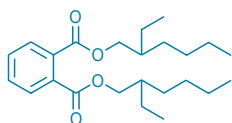
Long phased out of commercial use in PVC.

Reproduction, development

U.S.: proposed ban in toys, child care products

EU: not registered under REACH

Branched phthalates



Di(2-ethylhexyl phthalate (DEHP), dioctyl phthalate (DOP)

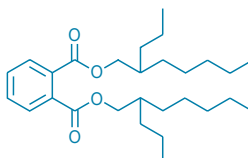
CAS: 117-81-7
Molecular weight: 390.6
NOAEL: 5 mg/kg-day^a

Largest-volume general-purpose PVC plasticizer globally; considered a benchmark for plasticizer performance.

Reproduction, development

U.S.: prohibited in toys, child care products

EU: prohibited in child care products, cosmetics



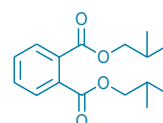
Di(2-propylheptyl) phthalate (DPHP)

CAS: 53306-54-0
Molecular weight: 446.7
NOAEL: na

Major general-purpose PVC plasticizer.

No evidence of antiandrogenicity

No restrictions



Diisobutyl phthalate (DIBP)

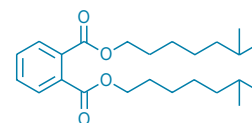
CAS: 84-69-5
Molecular weight: 278.4
NOAEL: 125 mg/kg-day^a

Used with cellulose nitrate.

Reproduction, development

U.S.: proposal to prohibit in toys, child care products

EU: not yet evaluated



Diisooctyl phthalate (DIOP)

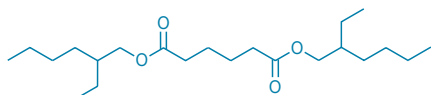
CAS: 27554-26-3
Molecular weight: 390.6
NOAEL: na

Limited commercial information.

Limited toxicity data; antiandrogenicity possible based on structure-activity relationships

No restrictions

Potential replacements

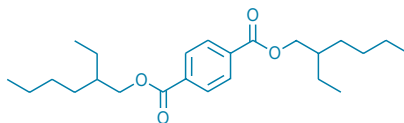


Di(2-ethylhexyl) adipate (DEHA)

CAS: 103-23-1
Molecular weight: 370.6
NOAEL: 800 mg/kg-day^a

Secondary plasticizer, low-temperature.

No evidence of antiandrogenicity

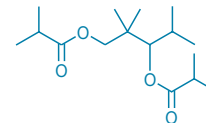


Di(2-ethylhexyl) terephthalate (DEHT)

CAS: 6422-86-2
Molecular weight: 390.6
NOAEL: 750 mg/kg-day^a

Replacement for DEHP and DINP.

No evidence of antiandrogenicity



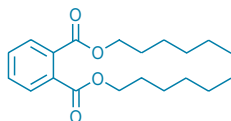
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate (TPIB)

CAS: 6846-50-0
Molecular weight: 286.4
NOAEL: 1,125 mg/kg-day^a

Secondary plasticizer.

No evidence of antiandrogenicity

NOAEL = no-observed-adverse-effect level, DINP includes isomers with C₈–C₁₀ ester groups, a = antiandrogen endpoint, DIDP includes isomers with C₉–C₁₁ ester groups, DINCH includes isomers with C₈–C₁₀ ester groups, PVC = polyvinyl chloride, na = not available, EU = European Union, REACH = Registration, Evaluation, Authorisation & Restriction of Chemicals



Di-n-hexyl phthalate (DHEXP)

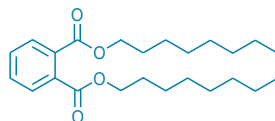
CAS: 84-75-3
Molecular weight: 334.4
NOAEL: 250 mg/kg-day^a

Limited commercial information.

⚠️ Reproduction, development

🚫 **U.S.:** proposed ban in toys, child care products

EU: not registered under REACH



Di-n-octyl phthalate (DNOP)

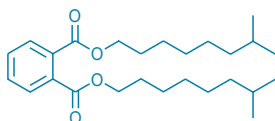
CAS: 117-84-0
Molecular weight: 390.6
NOAEL: na

Limited commercial information.

⚠️ Liver, thyroid effects; no evidence of antiandrogenicity

🚫 **U.S.:** interim ban in toys that can be placed in children's mouths, child care products; proposal to lift ban

EU: prohibited in products placed in children's mouths; not registered under REACH



Diisononyl phthalate (DINP)

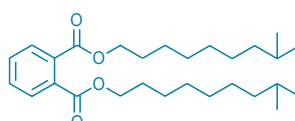
CAS: 28553-12-0
Molecular weight: 418.6
NOAEL: 300 mg/kg-day^a

Commercially important phthalate plasticizer; used in general flexible PVC applications.

⚠️ Antiandrogen, liver effects; listed by state of California as a carcinogen

🚫 **U.S.:** interim ban in toys that can be placed in children's mouths, child care products

EU: prohibited in products placed in children's mouths



Diisodecyl phthalate (DIDP)

CAS: 26761-40-0
Molecular weight: 446.7
NOAEL: 600 mg/kg-day^a

Major general-purpose PVC plasticizer with a particular use in wire and cable applications.

⚠️ Liver effects

🚫 **U.S.:** interim ban in toys that can be placed in children's mouths, child care products; proposal to lift ban

EU: prohibited in products placed in children's mouths

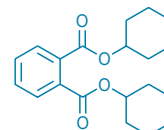


Toxicity concerns



Restrictions

Other phthalates



Dicyclohexyl phthalate (DCHP)

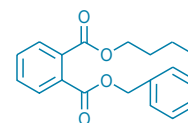
CAS: 84-61-7
Molecular weight: 330.4
NOAEL: 16 mg/kg-day^a

Secondary plasticizer for PVC and in ink and coating formulations.

⚠️ Reproduction, development

🚫 **U.S.:** proposal to prohibit in toys, child care products

EU: not yet evaluated



Butylbenzyl phthalate (BBP)

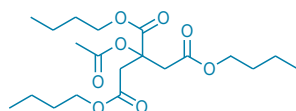
CAS: 85-68-7
Molecular weight: 312.4
NOAEL: 50 mg/kg-day^a

Important plasticizer for flooring.

⚠️ Reproduction, development

🚫 **U.S.:** prohibited in toys, child care products

EU: prohibited in child care products, cosmetics

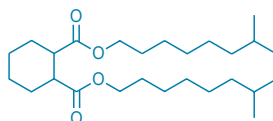


Acetyl tributyl citrate (ATBC)

CAS: 77-90-7
Molecular weight: 402.5
NOAEL: 1,000 mg/kg-day^a

Replacement for DEHP and DINP.

⚠️ No evidence of antiandrogenicity

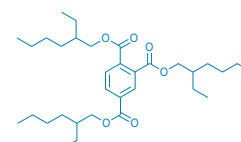


Diisononyl cyclohexane-1,2-dicarboxylate (DINCH)

CAS: 166412-78-8
Molecular weight: 424.7
NOAEL: 1,000 mg/kg-day^a

Replacement for DEHP and DINP.

⚠️ No evidence of antiandrogenicity



Tris(2-ethylhexyl) trimellitate (TOTM)

CAS: 3319-31-1
Molecular weight: 546.8
NOAEL: 100 mg/kg-day^a

Low-volatility plasticizer used in automotive interiors.

⚠️ Limited evidence of antiandrogenicity

“Approximately 90% of all phthalates are used to soften vinyl plastic products.”

paings several years ago for the Center for Health, Environment & Justice, an advocacy group. Today, as director of the Mind the Store campaign, Schade is focusing his efforts on getting retailers to stop selling phthalate-containing building materials and household products beyond vinyl flooring. His targets include adhesives, caulks and sealants, vinyl-backed carpeting and area rugs, garden hoses, mini blinds, roofing membranes, and wall coverings.

The campaign is also concerned about phthalates in “children’s back-to-school supplies, apparel—especially for children and women of child-bearing age—beauty and personal care products, and cleaning products,” Schade tells C&EN.

Consumers can avoid exposure to phthalates by not purchasing PVC products, Schade advises. “Approximately 90% of all phthalates are used to soften vinyl plastic products,” he says. Those products,

he adds, are often labeled with the word “vinyl” or a plastic recycling sign with the number 3 in the center.

Regulators are taking their own steps toward removing phthalates from the marketplace, albeit at a much slower pace than retailers. Officials in the U.S. and Europe agree on the fate of three phthalates—di(2-ethylhexyl) phthalate (DEHP), benzyl butyl phthalate (BBP), and dibutyl phthalate (DBP)—in children’s toys but are at odds about many other phthalates in myriad applications.

Over the past decade, production and use of DEHP in the U.S. and EU have decreased as a result of regulatory pressure and are likely to decline more in anticipation of new European rules. DEHP, also known as dioctyl phthalate, is currently banned at levels greater than 0.1% in toys and child care products in the U.S. and EU, as well as in cosmetics in the EU. It is still

the largest-volume general-purpose PVC plasticizer globally, however, because of its widespread use around the world in other products. BBP and DBP are also banned in toys and child care products in the U.S. and EU, as well as in cosmetics in the EU.

Production and use of diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), and di(2-propylheptyl) phthalate, on the other hand, are on the rise in the U.S. and EU.

In the U.S., the Consumer Product Safety Commission (CPSC) is proposing to expand the number of phthalates subject to restrictions in toys and child care products. In addition to the three phthalates already banned, DINP, diisobutyl phthalate (DIBP), di-*n*-pentyl phthalate (DPENP), di-*n*-hexyl phthalate (DHEXP), and dicyclohexyl phthalate (DCHP) would be prohibited. The proposal would, however, lift interim bans on DIDP and di-*n*-octyl phthalate (DNOP).

DINP, DIDP, and DNOP are currently prohibited in toys and child care products sold in the EU that can be placed in the mouth by children.



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CPSC's proposal to permanently ban DINP in children's products has generated a lot of debate because DINP is number two on the list of most-used phthalates by volume. Many health advocacy groups support the ban, claiming DINP can disrupt androgen hormone pathways in lab animals. Chemical manufacturers, however, say the proposal is based on an unproven process and outdated exposure data.

"Exposures to DINP are many times below the concentrations that induce adverse effects in rats," the ACC's phthalates panel says. But CPSC's proposed rule relies on a cumulative risk assessment for all phthalates that have antiandrogenic effects. So even if exposure to a particular phthalate is below the level of concern, it contributes to the overall risk from all antiandrogenic phthalates. ACC, however, argues that this cumulative risk assessment is unproven.

Exposures to DIBP, DPENP, DHEXP, and DCHP are also expected to be below levels of concern, but they too contribute to the cumulative risk from antiandrogenic phthalates.

ACC points out that CPSC's proposed

rule relies on biomonitoring data from 2005–2006. More recent data from 2009–2010 and 2011–2012 show a marked decrease in overall phthalate exposure compared with that older data, the industry group contends.

IN A LETTER SENT TO CPSC earlier this year, the EU also raises concerns about the proposed restrictions on DINP, DIBP, DPENP, DHEXP, and DCHP, saying they "would be substantially different from the current rules applicable in the EU." The biggest difference is that in the EU, each phthalate is assessed individually. In the U.S., the proposed rule is based on the combined risk of all phthalates.

The European Chemicals Agency (ECHA) evaluated the risks of DINP, DIBP, and DNOP in 2010 and concluded that, unless people put a product containing the substances in their mouth, the chemicals do not present a health risk. CPSC, however, reached a different conclusion for DINP because it considered cumulative risk from all antiandrogenic phthalates. ECHA did not assess

combined exposure to DINP with other phthalates.

The U.S. and EU agree on restrictions on DEHP, BBP, and DBP in children's toys. But EU officials are planning to completely phase out the three phthalates, along with DIBP, in all but a few authorized applications.


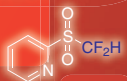
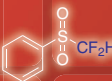
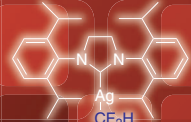


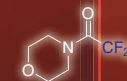





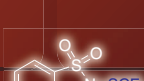

Earlier this month, the EU announced a ban on these four phthalates in electrical equipment, effective 2019. ECHA is currently seeking information to identify what other products contain the four phthalates, what the levels are, and how much migrates out of the products. Nine other phthalates are widely expected to be phased out in the EU.

It will likely be several more years before regulators completely remove these phthalates from the market and evaluate the safety of alternatives. In the meantime, retailers will face continued pressure from advocacy groups to pull phthalate-laden products off the market. And chemical manufacturers, even as they defend phthalates, are racing to develop the next best plasticizer. ■

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(1) Hu, J. et al. Chem. Rev. 2015, 115, 765. (2) Shen, Q. et al. Nature Comm. 2014, 5, 5405. (3) a) Hartwig, J. et al. J. Am. Chem. Soc. 2012, 134, 5524; b) Hu, J. et al. Org. Lett. 2011, 13, 5342. (4) Hu, J. et al. Angew. Chem. Int. Ed. 2013, 52, 12390. (5) Zhang, X. et al. Angew. Chem. Int. Ed. 2014, 53, 1669. (6) Umemoto, T. et al. J. Am. Chem. Soc. 2010, 132, 18199. (7) a) Hartwig, J. et al. Angew. Chem. Int. Ed. 2011, 50, 3793; b) Hartwig, J. et al. Org. Lett. 2014, 16, 1744. (8) Hartwig, J. et al. Angew. Chem. Int. Ed. 2012, 51, 536. (9) Weng, Z. et al. Angew. Chem. Int. Ed. 2013, 52, 1548. (10) Shen, Q. et al. Angew. Chem. Int. Ed. 2014, 53, 9316.



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