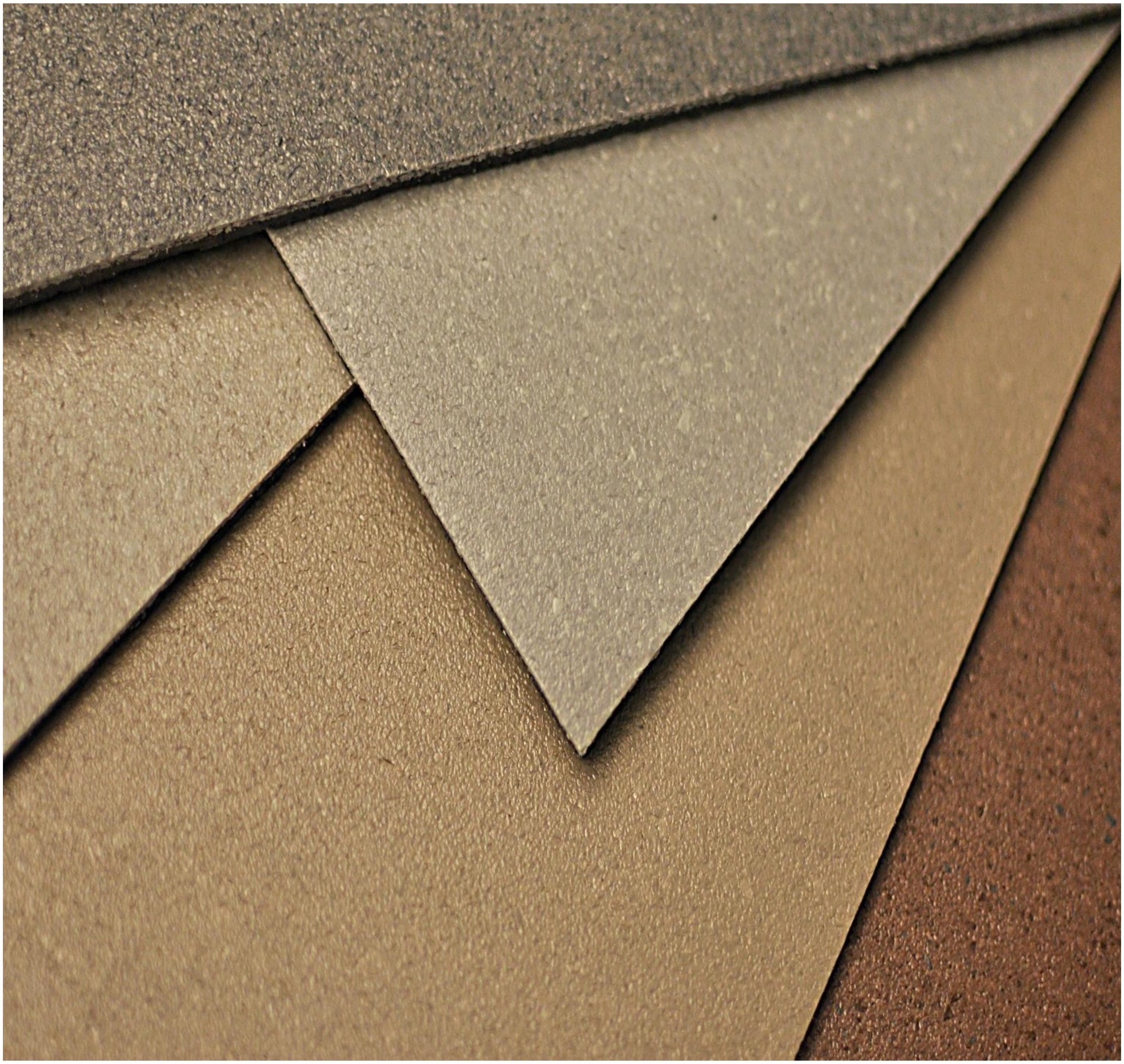
Phthalate-free Plasticizers in PVC

By Sarah Lott



Healthy Building Network

Transforming the market for building materials to advance the best environmental, health and social practices.

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Executive Summary

This Healthy Building Network (HBN) Research Brief examines replacements for phthalate plasticizers in Polyvinyl Chloride (PVC) building materials. Plasticizers are added to PVC to make it flexible, but since they are not tightly bound to the PVC molecules, they migrate from PVC products. Phthalates, the most commonly used plasticizers in PVC, are known endocrine disruptors – chemicals that interfere with hormone signaling, which is especially critical to early childhood development. Additionally, many phthalates are known carcinogens and reproductive and developmental toxicants. Exposures to these toxic plasticizers from PVC products can occur throughout their lifecycle. Therefore, it is crucial that PVC products containing phthalate plasticizers be eliminated from the built environment.

In response to consumer and regulatory pressures, PVC building products manufacturers have begun to offer phthalate-free products. This research brief takes a detailed look at the six plasticizer alternatives now in use in PVC building products. It compares what is known and unknown about these substances' human health and environmental impacts, and compares them to the known effects of a standard phthalate used in PVC building products, diisononyl phthalate (DINP).

Key Findings

- HBN identified six phthalate-free plasticizer types, three synthetic and three bio-based, in use in commercial PVC building products.

The available data suggest that non-phthalate plasticizers present fewer human health hazards than phthalates. This is not the same as saying that there are no health hazards associated with these non-phthalate plasticizers. It is important to remember that plasticizers – phthalates or not – will migrate from PVC products and building occupants will inevitably be exposed to them. However, some phthalate-free plasticizers raise fewer concerns than others. Our comprehensive review of available literature finds that:

- Two bio-based products – Grindsted Soft-n-Safe (made by Danisco/DuPont) and Polysorb ID 37 (made by Roquette) are well studied and appear to be the least toxic of the six non-phthalate plasticizers reviewed.

- Di-(2-ethylhexyl) terephthalate (DEHT), sold by Eastman Chemical under the trade name Eastman 168, fares better than DINP in most health and environmental hazard endpoints. However, further study is needed due to uncertainties surrounding endocrine disruption and reproductive toxicity.

- GreenScreen hazard assessment gives Ecolibrium, a proprietary plasticizer made by Dow, a high score (3) when it does not contain antioxidants and a lower score (2) when it does. However, the GreenScreen methodology does not account for upstream (manufacturing) impacts. Dow’s decision to keep Ecolibrium’s ingredients secret makes it impossible to fully consider its impacts.

- Hexamoll DINCH (Diisononyl cyclohexane-1,2-dicarboxylate) also compares favorably overall to DINP, including for carcinogenicity and developmental toxicity. However, DINCH uses DINP in its manufacture and DINCH is less biodegradable and more persistent in the environment than DINP.

- Eastman Chemical’s dibenzoate plasticizers, sold under the Benzoflex trade name, compare well with DINP, but contain substances that are more ecotoxic and have the potential to bioaccumulate.

Even without phthalate plasticizers, the lifecycle of PVC has inherent toxicities that cannot be avoided. At its core, PVC relies upon chlorine chemistry that forms toxic byproducts from its manufacture to its disposal. While the elimination of phthalate plasticizers from PVC does not these solve inherent problems, it does provide a specific relief to building occupants who are otherwise exposed through the everyday use of PVC products. To achieve flexibility without the use of these chemical additives, building material options other than PVC are available and should be prioritized for use over PVC.

Recommendation

Due to its overall human health and environmental impacts from manufacturing to disposal, PVC should be a choice of last resort in the selection of building materials. If the use of flexible PVC is unavoidable, two bio-based products – Grindsted Soft-n-Safe (COMGHA) and Polysorb ID 37 (Isosorbide diesters) – are well studied, appear to be the least toxic, and therefore should be preferred over the other plasticizers studied in this assessment.

Plasticizers in Context

Advocates of healthy building materials have long targeted products made with polyvinyl chloride (PVC, also sometimes referred to as "vinyl")[a] for elimination. Much of the concern arises from the way all PVC begins and ends its lifecycle. Its manufacture requires chlorine, and when PVC is in a fire or heated to high temperatures in manufacturing processes, trouble ensues, such as the release of highly toxic dioxins, vinyl chloride monomer, and hydrogen chloride.[b]

Also exacerbating PVC's toxicity throughout its lifecycle are toxic additives such as heavy metal stabilizers, which are required to keep PVC from breaking down during manufacture and use, and phthalate plasticizers, which are required to make PVC flexible. Heavy metals used in stabilizers include lead, a potent developmental toxicant; cadmium, a potent neurotoxin and carcinogen; and organotins, some of which are reproductive and developmental toxicants. Many phthalate plasticizers are known endocrine disrupting chemicals[c] - chemicals that disrupt hormone cell signal pathways – and have been known to have toxic effects on reproduction and development. Additionally, some phthalates are known carcinogens. These additives are not tightly bound to the PVC molecules and have been known to migrate from PVC products.[d]

U.S. and European manufacturers have replaced lead and cadmium stabilizers with calcium-zinc, barium-zinc, and organotin stabilizers in most applications.[1]

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[a] Note, however, that not all "vinyl" compounds are polyvinyl chloride and do not necessarily share PVC's hazardous lifecycle characteristics. See HBN's "Sorting out the Vinyls – When is "Vinyl" not PVC?"

[b] See a detailed discussion of PVC's lifecycle in HBN's 2002 report "Environmental Impacts of Polyvinyl Chloride Building Materials." A February 2014 *Environmental Building News* article written by Brent Ehrlich, "The PVC Debate: A Fresh Look," includes a more recent review of the PVC lifecycle.

[c] See the The Endocrine Disruptor Exchange (TEDX) for more details on endocrine disruptors.

[d] Numerous studies have documented alarming levels of phthalates in infants, children, breast milk, and the general population. See summary of studies by Breast Cancer Action: http://www.breastcancerfund.org/clear-science/radiation-chemicals-and-breast-cancer/phthalates.html and Biomonitoring data from the Centers for Disease Control: http://www.cdc.gov/biomonitoring/biomonitoring_summaries.html. See HBN's 2002 report "Environmental Impacts of Polyvinyl Chloride Building Materials" for previous studies on leaching of heavy metals from PVC.

They are also beginning to substitute phthalates with alternative plasticizers formulations.

These improvements don't apply to products made in China that are flooding the U.S. market. The dirtiest production of vinyl PVC has shifted overseas,[e] where toxic additives and manufacturing processes, including mercury cell technology,[f] are still used to produce PVC.

Some US and European PVC building product manufacturers are now touting the elimination of phthalate plasticizers. These formulations are given names such as "Clean Vinyl Technology"[2] and "BioVinyl"[3] suggesting that they are safe for you and the environment. This marketing is quite ahead of reality. The absence of phthalate plasticizers hardly makes PVC a clean or truly bio-based material. All of the serious toxicity problems of the chlorine lifecycle remain and other additives may still also be of concern. However, it is an important to stop bringing phthalates into buildings, where people are being exposed to these toxic chemicals.

[e] Imports of PVC flooring from Asia to the US have been on the rise over the last decade. According to the statistics from the database USA Trade Online, from 2002 to 2012, the value of plastic floor covering imports from Asia to the US rose from $145 million to $612 million. The majority of those imports are likely to contain toxic phthalates such as DEHP, which, according to the most recent estimates, still holds 60% of the plasticizer market in Asia ("Evaluation of new scientific evidence concerning DINP and DIDP in relation to entry 52 of Annex XVII to REACH Regulation (EC) No 1907/2006." *European Chemicals Agency*, August 2013. Available at: http://echa.europa.eu/documents/10162/31b4067e-de40-4044-93e8-9c9ff1960715).

[f] Mercury cell technology is a production process for chlorine which is known to generate significant mercury emissions. For a full description of this and other chlorine production processes see HBN's 2002 report "Environmental Impacts of Polyvinyl Chloride Building Materials." A recent review by Brent Ehrlich, "The PVC Debate: A Fresh Look," found that the use of this process has been minimized in the US and is no longer used for PVC. However, 75 facilities are still in use globally and, according to the International Conference on Mercury as a Global Pollutant, 63% of China's PVC production accounts for the largest consumption of mercury globally through the use of mercury catalyst, mercuric chloride, and straight mercury. Read the whole story here: http://www2.buildinggreen.com/article/pvc-debate-fresh-look

Comparing the Toxicity of Alternatives

To ensure that regrettable substitutions (trading one bad chemical for another bad chemical[g]) aren't made, HBN took a deeper look at these alternative plasticizers.

While multiple alternatives have been identified via various alternative assessments, HBN narrowed its review to those plasticizer alternatives that HBN has identified as in use in commercially-available phthalate-free PVC building products. Through this lens, HBN identified six alternative plasticizer types in commercial use:

- Di-(2-ethylhexyl) terephthalate (DEHT a.k.a DOTP)
- Diisononyl cyclohexane-1,2-dicarboxylate (DINCH)
- Dibenzoates [commonly Dipropylene glycol dibenzoate (DGD) or a blend of DGD, Diethylene glycol dibenzoate (DEGD), and Triethylene glycol dibenzoate (TGD)]
- Acetylated monoglycerides of fully hydrogenated castor oil (COMGHA)
- Isosorbide diesters
- Ecolibrium [a proprietary vegetable oil based blend]

Using available toxicity data on these six phthalate-free plasticizers – compiled from European Chemicals Agency (ECHA) REACH[h] registration dossiers and reports, GreenScreen hazard assessments,[i] U.S. Environmental Protection

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[g] Regrettable substitutions typically result from substituting a red listed chemical with another similar performing chemical about which less is known. Upon assessment these similar chemicals may turn out to have similar hazards.

[h] Registration, Evaluation, Authorisation and Restriction of Chemicals, more commonly known as REACH, is a European Union regulation that reviews the production and use of chemicals and their potential human and environmental health impacts. For more information on this legislation and access to the European Chemical Agency's public database of REACH data see: http://echa.europa.eu/regulations/reach

[i] The GreenScreen For Safer Chemicals is a method for comparative chemical hazard assessment that benchmarks chemicals on a 4 point scale. Alternative plasticizers should receive a benchmark 2 or higher. More information at http://greenscreenchemicals.org/

Agency (EPA) High Production Volume Challenge (HPV)[j] chemical hazard characterizations, and previously conducted journal research – HBN compared the manufacturing, human, and eco- toxicity of these phthalate-free plasticizer chemicals.

While available toxicity data suggests that at least some of the alternatives to the primary phthalates in commerce are an improvement to the status quo, manufacturer secrecy, toxicity and migration/exposure data gaps inhibit a full understanding of the relative merits of the new plasticizers.

The table below summarizes what is known and unknown about the six alternative plasticizers now in use, and the products in which they are used.

[j] The US EPA High Production Volume (HPV) Challenge Program engages with US companies to make health and environmental toxicity data on chemicals publicly available. Learn more about this program and access HPV Chemical data at: http://www.epa.gov/chemrtk/index.htm

Alternative Plasticizers in PVC Building Products

Phthalate-free plasticizers in building materials are either synthetic (made from petrochemicals) or bio-based (made from agricultural products).

Three types of synthetic alternative synthetic plasticizers are known to be used in PVC floors and other building products:

- Dibenzoate plasticizers such as dipropylene glycol dibenzoate (DGD) (alone or in a blend with other dibenzoates)
- Diisononyl cyclohexane-1,2-dicarboxylate (DINCH)
- Di-(2-ethylhexyl) terephthalate (DEHT, a/k/a DOTP).

Three bio-based alternative types are also being used in PVC flooring:

- Isosorbide diesters produced from fatty acids of vegetable origin and isosorbide derived from glucose, sold under the trade name, Polysorb ID 37™
- Acetylated monoglyceride derived from hydrogenated castor oil bio-based plasticizer (also known by its acronym, COMGHA), sold under the brand name, Grindsted Soft-n-Safe™
- Dow's Ecolibrium plasticizer

In addition to these in-commerce plasticizers, alternative assessments have identified a variety of other potential substitutes.[k] However, HBN did not find these additional alternatives in use in commercial phthalate-free PVC building products. Therefore, they were not included in the toxicological assessment for this brief.

[k] Data on these plasticizer alternatives has been captured in HBN's Pharos Project (a building materials database and transparency tool, available at https://www.pharosproject.net) via two common ingredient records: Synthetic non-phthalate plastisol plasticizers; and, Bio-based non-phthalate plastisol plasticizers. Additional alternatives will require the same scrutiny if they are considered for use in building materials in the future.

Table 1. Toxicity Comparison of Plasticizers in PVC Building Products

Identification	**Plasticizer (CAS#)**	**Diisononyl Phthalate (DINP)[a] (68515-48-0; 28553-12-0)**		**Diisononyl cyclohexane-1,2-dicarboxylate (DINCH)[b] (166412-78-8; 474919-59-0)**		**Dibenzoate blends[c] (27138-31-4; 120-55-8; and/or 120-56-9)**		**Di-(2-ethylhexyl) terephthalate (DEHT)[d] (6422-86-2)**		**Vegetable Oil based blend[e] (8013-07-8; 68082-35-9 & Antioxidant)**		**Acetylated monoglycerides of fully hydrogenated castor oil (COMGHA)[f] (736150-63-3)**		**Isosorbide diesters[g] (1215036-04-6)**
	Trade name	Jayflex (ExxonMobil Chemical); Palatinol (BASF)		Hexamoll DINCH (BASF)		Benzoflex 9-88 and Benzoflex 2088 (Eastman Chemical)		Eastman 168 (Eastman Chemical)		Ecolibrium (Dow)		Grindsted Soft-n-Safe (Danisco/DuPont)		Polysorb ID37 (Roquette)
	Use in Building Materials	Plasticizer in toys, vinyl flooring, wire and cable, wood veneer/finish, sealants, and carpet backing		Vinyl flooring & wallcovering; Len-Tex "Clean Vinyl Technology"		Vinyl flooring, adhesives and sealants; Forbo Allura LVT		Vinyl flooring & wallcovering; Len-Tex "Clean Vinyl Technology", Johnsonite Azrock VCT		PVC products including wire and cable, flooring, and fabric; Teknor Apex BioVinyl, Advanta Flooring Tuff-Seal Prime, Draper SheerWeave		PVC, polyolefin, styrene, and PET products; Tarkett IQ Naturals and UpoFloor Hovi Quartz and Podium Naturale		Plasticizer, solvent, lubricant, or surfactant in the manufacture of plastic compositions, such as vinyl flooring; Gerflor Mipolam Symbioz
	GreenScreen (GS) Benchmark (BM)[h]	BM 1[b]	+	BM 2	?	LT-P1	+	BM 3$_{DG}$	+	BM 2 (w/ antioxidant) BM3 (other forms)[i]	?	LT-U	?	LT-P1
Manufacture	**Raw Material**	Petroleum	=	Petroleum	=	Petroleum	=	Petroleum	+	Bio-based, % not reported	+	80% Bio-based	++	100% Bio-based, potential for use of cellulosic (non-food) feedstock
	Manufacturing Toxicity	High hazard: E, M, R, Rs, Ss	-	High Hazard: C, R, Ed	+ + -	High Hazard: D (one) Medium Hazard: Ed (all)	+	High Hazard: A & M	= = ?	High hazard: A, E, M, R, Si; Antioxidant lifecycle unknown	+	High Hazard: E, M, Rs, Si	+	High Hazard: E, M, Si
Human Toxicity	**Carcinogenicity**	Prop 65 listed carcinogen	+	No activity considered relevant to humans	? ? ?	Data Gap (DG), though not expected	++	No effect (NE)	+ ? +	NE for one monomer and antioxidant, DG for other monomer	?	DG, though not expected	?	DG, though not expected

Key: A = Aquatic toxicity, C = cancer, D = Developmental toxicity, DG = Data gap, E = eye irritation, Ed = Endocrine disruption, M = Mammalian toxicity, NE = No effect, PBT = Persistent Bioaccumulative Toxicant, R = Reproductive toxicity, Rs = Respiratory sensitization, Si = Skin irritation, Ss = Skin sensitization

Identification	Plasticizer (CAS#)	Diisononyl Phthalate (DINP)[a] (68515-48-0; 28553-12-0)			Diisononyl cyclohexane-1,2-dicarboxylate (DINCH)[b] (166412-78-8; 474919-59-0)		Dibenzoate blends[c] (27138-31-4; 120-55-8; and/or 120-56-9)		Di-(2-ethylhexyl) terephthalate (DEHT)[d] (6422-86-2)		Vegetable Oil based blend[e] (8013-07-8; 68082-35-9 & Antioxidant)		Acetylated monoglycerides of fully hydrogenated castor oil (COMGHA)[f] (736150-63-3)		Isosorbide diesters[g] (1215036-04-6)
	Mutagenicity/ Genotoxicity	NE		=	NE	= = =	NE	=	NE	= ? =	NE for one monomer and antioxidant, DG for other monomer	=	NE	=	NE
	Reproductive/ Developmental Toxicity	Affected sperm, ovaries, and skeletal development, High doses caused decreased birth weights and infant death. High GS bench-marks for both R & D.		+	No activity considered relevant to humans	+ + +	NE other than increases in cervical ribs and potential for delayed skeletal growth	+	NE, but low confidence for reproductive toxicity	+ ? +	NE for one monomer, DG for other monomer. Low & Moderate Antioxidant GS bench-mark for R & D, respective-ly. Reduced litter sizes, body weight & skeletal development.	++	NE	+	NE other than slight reduction in bone tissue development
	Endocrine Activity	Evidence of Ed in animals and humans		?	Ed in animals, but unclear if relevant to humans	+ + +	NE in animal studies, though potential predicted for one	+	NE, but DG for thyroid effects	+ ? ?	No in-vivo testing, in-vitro found NE in one, but DG for other monomer and Antioxidant	+	NE, but DG for thyroid effects	?	DG, though in-vitro testing on other isosorbide esters had NE

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Identification	Dermal Irritation/ Sensitization	Slight Si and E; potential for Ss		+	NE in all, but one study w/ Si	+ + ?	NE for Ss in all and Si for two, slight E for one, and DGs for Si and E for one	+	NE in all, but one study w/ E	= ? =	Slight Si and E and NE for Ss for one monomer and Antioxidant; DGs for other monomer	++	NE	+	NE in all, but one study with slight Si and another study with slight E
	Respiratory Irritation/ Sensitization	NE for Rs		?	DG	? ? ?	DG for all	?	DG	? ? ?	DG for all	?	DG	?	DG
	Acute/ Chronic Toxicity (systemic)	Chronic liver and kidney toxicity, unclear if relevant to humans		+	Thyroid toxicity at high doses only, unclear if relevant to humans	+ + +	Blood pathology and motor effects at high doses, with recovery following cessation	++	NE	+ ? =	NE for one monomer, DG for other monomer, Chronic liver toxicity from Antioxidant	++	NE	++	NE
	Exposures/ Migratory behavior	Migrates from PVC, exposures expected		=	Migrates from PVC, exposures expected	= = =	Similar volatility, but DG on migration behavior	+	low potential for migration	+ ? ?	Low volatility for one monomer, DG for others	+	low potential for migration	?	DG
Ecotoxicity	Ecotoxicity	NE		=	NE	- - -	A	=	NE	= - =	A for one monomer, NE for others	=	NE	=	NE

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Bioaccumulation	NE	=	NE	- - =	While not classified as PBTs, two potentially have moderately bioaccumulative properties while the other has low estimated potential	=	NE	= - =	One monomer is expected to bioaccumulate, NE for others	=	NE	=	NE
Persistence	NE	-	Moderate persistence	= = =	NE for all	=	NE	= = -	Antioxidant is predicted to persist for ±60 days in soil and water, while others readily biodegrade	=	NE	=	NE
Biodegradability	Yes	-	No	= = =	Yes	=	Yes	= = -	Monomers are readily bio-degradable while the antioxidant is not.	=	Yes	=	Yes

? Unclear	- Worse than DINP	= Similar to DINP	+ Better than DINP	++ Best

a. DINP sources: [4,5,6,7,8]
b. DINCH sources: [9,10,11,12,13,14,15,16,17]
c. Dibenzoate sources: [18,19,20,21,22,23,24,25,26] Toxicity comparisons for individual chemical ingredients of a blend are shown in the order as listed in the header
d. DEHT sources: [27,28,29,30,31]
e. Vegetable Oil based blend (Ecolibrium) sources: [32,33,34,35,36,37] Toxicity comparisons for individual chemical ingredients of a blend are shown in the order as listed in the header.

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f. COMGHA sources: [38], [39], [40], [41]

g. Isosorbide diester sources: [42], [43], [44]

h. The GreenScreen for Safer Chemicals is a method for comparative chemical hazard assessment, developed by Clean Production Action (CPA), which benchmarks chemicals on a 4 point scale with Benchmark 1 being the most hazardous and warranting immediate replacement and Benchmark 4 being the least hazardous. While the GreenScreen method is open and transparent, assessments should be verified through the GreenScreen Verification Process. Alternative plasticizers should receive a benchmark 2 or higher. In the absence of full assessments, an abbreviated automated method called the GreenScreen List Translator is used to rule out chemicals of concern. This method only uses hazard lists that inform the full GreenScreen method and matches them to hazard classifications to identify Benchmark 1 (LT-1) and possible Benchmark 1 (LT-P1) chemicals. Those chemicals with insufficient information to apply this method, such as those not currently on any hazard lists, are scored as "unspecified Benchmark" (LT-U). HBN, with the help of CPA, integrated the GreenScreen List Translator into the Pharos Chemical and Materials Library, from which list translator scores were generated. More on the GreenScreen methods and scoring descriptions can be found at http://greenscreenchemicals.org/.

i. Based on an unverified full GreenScreen assessment. Antioxidant only used in one out of four possible commercial formulations for Dow Ecolibrium: LPLAS-1101 EXP4.

Data Gaps

Data gaps represent lapses in current knowledge due to lack of testing or disclosure. They may also represent where further testing is needed due to uncertainty or low confidence in current conclusions, which is often likely to occur with new chemical formulations. Data gaps are noted in the table above with a question mark. Data gaps are important to note as they provide a reality check for how much is known about a substance and provide direction for future research. Therefore, data gaps determine the level of confidence in conclusions.

The least is known about Dow Chemical's plasticizer, Ecolibrium. While, Ecolibrium did undergo a GreenScreen assessment[l] by ToxServices in 2011, Dow did not provide complete versions of toxicological studies for the antioxidant used in one formulation and no toxicological data was available for a monomer used in all formulations of Ecolibrium. Additionally, the draft GreenScreen, while made public, was redacted, keeping its ingredients undisclosed. However, HBN was able to identify two likely ingredients. A Dow Chemical patent[45] names epoxidized soybean oil (ESBO) and epoxidized soybean oil methyl ester (soy eFAME) as the main ingredients of Ecolibrium. However, the antioxidant, which was shown to be of most concern via the GreenScreen assessment, remains undisclosed.

Another plasticizer with multiple data gaps is DEHT, which lacks testing on neurotoxicity, immunotoxicity, respiratory sensitization, in-vivo genotoxicity and needs further testing on reproductive toxicity and endocrine activity due to uncertainties in current data.

DINCH and COMGHA had the fewest remaining data gaps.

For most plasticizers, data gaps exist for respiratory irritation and sensitization. Data gaps in these areas are cause for concern as incidences of respiratory disease such as asthma are on the rise.[m] Furthermore, lack of data on migratory behavior and exposures exists to justify claims that the plasticizers are of no concern to building occupants and users of PVC products.

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[l] See the full draft GreenScreen assessment at: http://www.greenchemistryandcommerce.org/documents/DOWECOLIBRIUMPoylmerReportFinal3.12.12.pdf

[m] For more information on asthma and how chemicals in building materials can contribute to its development, see HBN's report "Full Disclosure Required: A strategy to Prevent Asthma Through Building Product Selection," Available at: http://healthybuilding.net/reports/asthmagens/

Manufacturing Toxicity and Exposures

Manufacturing toxicity refers to the toxicity of chemicals used to synthesize a product from cradle to gate. It is important to recognize toxicity in manufacturing as it corresponds to potential toxic exposures to workers on site and the nearby communities and ecosystem.

HBN reviewed how these plasticizer alternatives were manufactured using information collected in the Chemical and Material Library (CML) in HBN's Pharos Project.[n] In the CML, hazard warnings for specific chemicals on various chemical hazard and restricted substance lists are associated with listed chemicals and color coded for prioritization of concern, with purple and red being of greatest concern.[o] Our review found that approximately half had red-flagged chemicals involved in the manufacturing processes of these chemicals: DINCH, TGD (a component of a dibenzoate blend), Isosorbide diesters, and Ecolibrium. DINCH's manufacturing process was of greatest concern due to its use of DINP as its major ingredient, a phthalate known as a carcinogen and reproductive toxicant. It's unclear to what extent workers or end users could be exposed to DINP, but a BASF patent[46] for DINCH claims 100% conversion of the DINP. Similarly, the manufacture of TGD requires Triethylene glycol, a developmental toxicant. However, TGD makes up less than 25% of the Dibenzoate plasticizer blend, Benzoflex 2088.

Isosorbide diesters and Dow's Ecolibrium may also have red-flagged chemicals in their lifecycles. Roquette Freres, the manufacturer of the Isosorbide plasticizer Polysorb ID37, alludes to the use of the reproductive toxicant xylene in the manufacture in their patent.[47] However, according to the patent, this formulation avoids this toxic catalyst and other toxic organic solvents, thus Polysorb ID37 is free from any red-flagged ingredients. In a Dow Chemical patent[48] for vegetable-oil derived plasticizers, such as Ecolibrium, the reactive additive methanol – a developmental and reproductive toxicant – is key to the manufacture of these plasticizers.

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[n] Pharos is a project of the Healthy Building Network. To learn more about the project see: https://www.pharosproject.net/about/index/

[o] Find more information on the Pharos CML at: https://www.pharosproject.net/material/

Another consideration for manufacturing is the use of bio-based feedstocks. Three of the plasticizer alternatives discussed are bio-based: COMGHA, Isosorbide diesters, and Ecolibrium. Danisco's Soft-n-Safe, is 80% bio-based, made with castor oil, glycerol, and acetic acid. Roquette's Polysorb ID37 has the highest bio-based content at 100%, made with Isosorbide, which is derived from glucose, and vegetable fatty acids. Dow's Ecolibrium is made with soybean oil derivatives; however, it is unclear what percentage of their product is bio-based.

Bio-based products have the potential for healthier lifecycles in terms of environmental and toxic burdens, but the prefix bio- does not always mean that it's inherently sustainable.[p]

Although the current market for bio-based chemicals is a small fraction of overall agricultural production, it is important to consider sourcing of the feedstock, avoiding industrial monocultures which degrade the soil and use tons of chemicals via fertilizers and pesticides. Certificate programs are available to ensure sustainable feedstock sourcing such as International Sustainability and Carbon Certification (ISCC)'s "ISCC Plus" certificate[q] and the Institute for Agriculture and Trade Policy's Working Landscapes Certificate (WLC)[r] program. No bio-based plasticizer manufacturer yet holds one of these certificates.

Human Toxicity and User Exposures

Building occupants are exposed to toxic chemicals in building materials through numerous pathways. For example, phthalates, as semi-volatile organic compounds, can migrate from PVC into the air as a gas, but more often attach to dust particles which in turn can be inhaled, ingested, or absorbed into the body through skin contact. Once exposed, chemicals can lead to a variety adverse health effects.

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[p] See for example: "Bio-based plastics: Steps towards a sustainable industry," Pharos Signal, May 6, 2013. Available at: http://www.pharosproject.net/blog/detail/id/161/bioplastics-and-sustainable-feedstock-sourcing.

[q] Find more information on this program at: http://www.iscc-system.org/en/iscc-system/iscc-plus/

[r] Find more information on this program at: http://www.iatp.org/working-landscapes

Based upon currently available data, all six of the plasticizers found in building materials appear to be an improvement from phthalate plasticizers such as DEHP and DINP.[s] COMGHA and the isosorbide diesters appear to be the least toxic plasticizers, though isosorbide diesters still need testing for endocrine activity and respiratory sensitization; both are bio-based chemicals.

DEHT[t] and Ecolibrium also appear to be of low toxicity to human health; however, toxicity data gaps exist for DEHT, and manufacturing secrecy inhibits a full understanding of Ecolibrium.

Human toxicity appears to be low for DINCH and Dibenzoates as well, with no adverse effects for multiple toxicity endpoints. However, DINCH and DGD (a dibenzoate used alone or in a blend with other plasticizers) are of greater concern due to reproductive/developmental effects and potential endocrine activity. Additionally, DINCH has potential for skin irritation and human exposures. Multiple studies have shown that DINCH, like phthalates, can migrate from PVC products and accumulate in dust particles.[49] Biomonitoring data have found evidence of DINCH exposures/metabolites in humans.[50]

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[s] According to the draft GreenScreen assessment by ToxServices, DINP is a Benchmark 1 chemical. Meaning it should be prioritized for avoidance. See the full draft assessment here: http://www.greenchemistryandcommerce.org/documents/DINPver.2-2.13.12.pdf

[t] The presence of the word "phthalate", which we have come to associate with toxic health impacts, in "terephthalate" have led some to believe that DEHT and other terephthalates share the toxic health impacts as the chemically related phthalates. However, toxicological research has not found this to be the case: no reproductive or developmental toxicity or endocrine disrupting effects have been observed in studies on DEHT. However, more studies are needed to confirm these findings. One study theorized that, "the lack of effects reported with the para-constituent (DEHT) is due most likely to differences in metabolism and the formation of the stable monoester, mono-2-ethylhexyl phthalate (MEHP) (http://www.pharosproject.net/material_chm/show/materialId/4376-20-9) from the DEHP moiety," while DEHT metabolizes into 2-ethylhexanol (http://www.pharosproject.net/material_chm/show/materialId/104-76-7) and terephthalic acid (http://www.pharosproject.net/material_chm/show/materialId/100-21-0) (Faber, Willem D., James A. Deyo, Donald G. Stump, Lisa Navarro, Karen Ruble, and John Knapp. "Developmental Toxicity and Uterotrophic Studies with Di-2-Ethylhexyl Terephthalate." Birth Defects Research 80, (2007): 396-405.).

Ecotoxicity

Ecotoxicity refers to adverse effects on the environment, including toxicity to aquatic and terrestrial organisms along with a substance's ability to biodegrade or persist in the environment and bioaccumulate in living tissues. Persistence and bioaccumulation impacts in the environment can also lead to exposures to humans.

Available data shows that all six alternative plasticizers generally have low ecotoxicty. All except DINCH are considered readily biodegradable and only DINCH and the antioxidant[u] in one formulation of DOW's Ecolibrium are expected to be persistent. Dibenzoates are considered toxic to aquatic organisms. Ecotoxicity testing is still needed for soy-eFAME, it is also considered toxic to aquatic organisms, as seen on the Canadian government's Domestic Substances List (DSL), and is expected to bioaccumulate. Overall, the least toxic plasticizer alternatives in terms of with lowest ecotoxicity are COMGHA, Isosorbide diesters, and DEHT.

[u] Antioxidant only used in one out of four possible commercial formulations for Dow Ecolibrium: LPLAS-1101 EXP4. See the full draft GreenScreen assessment at: http://www.greenchemistryandcommerce.org/documents/DOWECOLIBRIUMPoylmerReportFinal3.12.12.pdf

Conclusions

Many of these plasticizer alternatives are an improvement on phthalate plasticizers. Overall, COMGHA and Isosorbide Esters appear to be the best with few data gaps and low toxicity during manufacture and in use. Potential toxicity and data gaps surrounding DINCH, Dibenzoates and DEHT make them less desirable alternatives, while Ecolibrium, which has potential as a promising alternative, is locked behind industry secrecy and therefore cannot be fully assessed for its toxicity.

While the replacement of toxic phthalate plasticizers is a necessary step for PVC, this should not distract from the intractable environmental health issues that plague the PVC lifecycle and still necessitate its avoidance in the built environment. PVC-free materials which avoid the use of plasticizers are available commercially and, while still needing full assessment, the weight of evidence suggests that other choices such as linoleum flooring and bio-based polyethylene wallcoverings, remain superior options to PVC from an environmental and human health perspective.[v]

[v] HBN's collaborative study of resilient floorings in 2009 found that linoleum scored better than PVC for most of its lifecycle. Report available at: http://www.healthybuilding.net/docs/HBN-ResilientFlooring&ChemicalHazards-Report.pdf. Appendix A of that report also reviews other comparative studies, many of which also found linoleum flooring to have a preferable lifecycle to PVC flooring. Additionally, testing done by HealthyStuff.org in 2009 found linoleum flooring to be free of hazardous phthalates and heavy metals while detecting them in PVC flooring and wallcoverings: http://pharosproject.net/blog/detail/id/79/chemicals-of-concern-found-in-floorings-wallcoverings. Bio-based polyethylene wall coverings by Carnegie Fabrics have been found to be red-list free by Declare: http://www.declareproducts.com/node/125.

Endnotes

[1] Ehrlich, Brent. "The PVC Debate: A Fresh Look." Environmental Building News. February 2014. http://www2.buildinggreen.com/article/pvc-debate-fresh-look (Brent 2014) and "Stabilisers." PVC Europe. Accessed May 2014. http://www.pvc.org/en/p/stabilisers.

[2] "Sustainability and Product Transparency." Len-Tex Corporation. Accessed May 2014. Available at: http://www.lentexcorp.com/clean-vinyl-technology

[3] "Presenting BioVinyl." Teknor Apex. Accessed May 2014. Available at: http://www.biovinyl.com/

[4] Tomar, Rajpal S., John D. Budroe, and Rose Cendak. "Evidence on the Carcinogenicity of Diisononyl Phthalate (DINP)." The California Environmental Protection Agency Office of Environmental Health Hazard Assessment (OEHHA) Reproductive and Cancer Hazard Assessment Branch. October 2013. Available: http://www.oehha.ca.gov/Prop65/hazard_ident/pdf_zip/DINP_HID100413.pdf

[5] "Evaluation of new scientific evidence concerning DINP and DIDP in relation to entry 52 of Annex XVII to REACH Regulation (EC) No 1907/2006." European Chemicals Agency. August 2013. Available: http://echa.europa.eu/documents/10162/31b4067e-de40-4044-93e8-9c9ff1960715

[6] ToxServices LLC. "GreenScreen Assessment for Diisononyl phthalate (DINP) (CAS #28553-12-0)." Clean Production Action. February 2012. Available: http://www.greenchemistryandcommerce.org/documents/DINPver.2-2.13.12.pdf

[7] Online substance information for di-"isononyl" phthalate. European Chemicals Agency (ECHA). September 2, 2013. Available: http://apps.echa.europa.eu/registered/data/dossiers/DISS-828e025b-9dd6-1b22-e044-00144fd73934/DISS-828e025b-9dd6-1b22-e044-00144fd73934_DISS-828e025b-9dd6-1b22-e044-00144fd73934.html

[8] TURI (2006). "DEHP". In "Five Chemicals Alternatives Assessment Study" (7). Toxics Use Reduction Institute (TURI), University of Massachusetts Lowell, for the Commonwealth of Massachusetts. Available at: http://www.turi.org/TURI_Publications/TURI_Methods_Policy_Reports/Five_Chemicals_Alternatives_Assessment_Study._2006/Full_Report (TURI 2006)

[9] ToxServices LLC. "GreenScreen Assessment for Hexamoll® DINCH® (Diisononyl cyclohexanedicarboxylate) (CAS #166412-78-8, 474919-59-0)." Clean Production Action. May 2013. Available: http://www.greenchemistryandcommerce.org/documents/Hexamoll-DINCHGS5.28.13.pdf

[10] Böttcher, Arnd, Dominic Vanoppen, Jan-Dirk Arndt, Jochem Henkelmann, and Konrad Knoll. Method for Hydrogenating Organic Compounds by Means of Ru/SiO2 Catalysts. Basf Aktiengesellschaft, assignee. Patent US7355084 B2. 8 Apr. 2008. Available at: https://www.google.com/patents/US7355084. (Basf Aktiengesellschaft 2008)

[11] Online substance information for Hexamoll® DINCH. European Chemicals Agency (ECHA). April 9, 2014. Available: http://apps.echa.europa.eu/registered/data/dossiers/DISS-bead5478-f3f2-1ea2-e044-00144f67d031/DISS-bead5478-f3f2-1ea2-e044-00144f67d031_DISS-bead5478-f3f2-1ea2-e044-00144f67d031.html.

[12] *Nielsen, Brian S., Dorthe N. Andersen, Estelle Giovalle, Morten Morten Bjergstrøm, and Poul B. Larsen, eds. Alternatives to Classified Phthalates in Medical Devices. Danish Environmental Protection Agency, 2014. Available at: http://www2.mst.dk/Udgiv/publications/2014/03/978-87-93178-27-4.pdf. (Nielsen et al 2014).*

[13] *Nagorka, Regine, André Conrad, Christiane Scheller, Bettina Süßenbach, and Heinz- Jörn Moriske. "Diisononyl 1,2-cyclohexanedicarboxylic acid (DINCH) and Di(2-ethylhexyl) terephthalate (DEHT) in indoor dust samples: Concentration and analytical problems." International Journal of Hygiene and Environmental Health 214, (2011): 26-35. (Nagorka et al 2011)*

[14] *Schossler, Patricia, Tobias Schripp, Tunga Salthammer, and Müfit Bahadir. "Beyond phthalates: Gas phase concentrations and modeled gas/particle distribution of modern plasticizers." Science of the Total Environment 409, (2011): 4031-4038. (Schossler et al 2011)*

[15] *Schütze, André, Claudia Pälmke, Jürgen Angerer, Tobias Weiss, Thomas Brüning, Holger M. Koch. "Quantification of biomarkers of environmental exposure to di(isononyl)cyclohexane-1,2-dicarboxylate (DINCH) in urine via HPLC–MS/MS." Journal of Chromatography B 895-896, (2012): 123-130. (Schütze et al. 2012)*

[16] *Silvia et al. "Identification of potential biomarkers of exposure to di(isononyl)cyclohexane-1,2-dicarboxylate (DINCH), an alternative for phthalate plasticizers." Journal of Exposure Science and Environmental Epidemiology 22, (2012): 204-211. (Silvia et al. 2012)*

[17] *Maag, Jacob, Carsten Lassen, Ulla Kristine Brandt, Jesper Kjølholt, Lise Molander, and Sonja Hagen Mikkelsen. "Identification and assessment of alternatives to selected phthalates." Danish Environmental Protection Agency. Environmental Project No. 1341 (2010). Available: http://www2.mst.dk/udgiv/publications/2010/978-87-92708-00-7/pdf/978-87-92708-01-4.pdf (Maag et al. 2010)*

[18] *Vesicol Chemical Corporation. "Dipropylene Glycol Dibenzoate Robust Summary." US Environmental Protection Agency HPV Challenge Program. June 1, 2001. Available: http://www.epa.gov/hpv/pubs/summaries/diglybnz/c13057.pdf*

[19] *Online substance information for oxydipropyl dibenzoate. European Chemicals Agency (ECHA). September 27, 2013. Available: http://apps.echa.europa.eu/registered/data/dossiers/DISS-9ebde37c-77fe-7020-e044-00144f67d031/DISS-9ebde37c-77fe-7020-e044-00144f67d031_DISS-9ebde37c-77fe-7020-e044-00144f67d031.html*

[20] *Vesicol Chemical Corporation. "Diethylene Glycol Dibenzoate Robust Summary." US Environmental Protection Agency HPV Challenge Program. October 22, 2001. Available: http://www.epa.gov/hpv/pubs/summaries/diglydib/c13271.pdf*

[21] *Online substance information for oxydiethylene dibenzoate. European Chemicals Agency (ECHA). September 27, 2013. Available: http://apps.echa.europa.eu/registered/data/dossiers/DISS-9d8920c9-6c71-3444-e044-00144f67d249/AGGR-a357b1a0-33c8-43a7-ad50-f76580bf9c46_DISS-9d8920c9-6c71-3444-e044-00144f67d249.html#AGGR-a357b1a0-33c8-43a7-ad50-f76580bf9c46*

[22] *Vesicol Chemical Corporation. "Triethylene Glycol Dibenzoate Robust Summary." US Environmental Protection Agency HPV Challenge Program. November 16, 2001. Available: http://www.epa.gov/chemrtk/pubs/summaries/triglydb/c13309.pdf*

[23] *TURI 2006.*

[24] *Maag et al, 2010.*

[26] *Veld, Marcel G.R. Ter, Bastiaan Schouten, Jochem Louisse, Daan S. Van ES, Paul T. Van Der Saag, Ivonne M. C. M. Rietjens, and Albertinka J. Murk. "Estrogenic Potential of Food-Packaging-Associated Plasticizers and Antioxidants as Detected in ERα and ERβ Reporter Gene Cell Lines." Journal of Agricultural and Food Chemistry 54, (2006): 4407-4416. (Veld et al. 2006)*

[27] *ToxServices LLC. "Di(2-ethylhexyl) terephthalate (DEHT) (CAS #6422-86-2) GreenScreen™ Assessment ." Clean Production Action. October 11, 2012. Available: http://www.greenchemistryandcommerce.org/documents/DEHTVERIFIEDASSESSMENT_final.pdf*

[28] *Online substance information for bis(2-ethylhexyl) terephthalate. European Chemicals Agency (ECHA). April 9, 2014. Available: http://apps.echa.europa.eu/registered/data/dossiers/DISS-9eb0e894-2a52-5415-e044-00144f67d031/DISS-9eb0e894-2a52-5415-e044-00144f67d031_DISS-9eb0e894-2a52-5415-e044-00144f67d031.html*

[29] *TURI 2006.*

[30] *Maag et al, 2010.*

[31] *Nielsen et al 2014.*

[32] *ToxServices LLC. "GreenScreen™ Assessment for Dow's Ecolibrium™ Bio-Based Plasticizers." Clean Production Action. March 2012. Available: http://www.greenchemistryandcommerce.org/documents/DOWECOLIBRIUMPoylmerReportFinal3.12.12.pdf*

[33] *Organization for Economic Cooperation and Development (OECD). "Epoxidized Oils And Derivatives." United Nations Environment Programme. April 2006. Available: http://www.chem.unep.ch/irptc/sids/OECDSIDS/Epoxidized-oils.pdf*

[34] *Online substance information for soybean oil, epoxidized. European Chemicals Agency (ECHA). March 11, 2014. Available: http://apps.echa.europa.eu/registered/data/dossiers/DISS-9eba7e32-77de-006e-e044-00144f67d031/DISS-9eba7e32-77de-006e-e044-00144f67d031_DISS-9eba7e32-77de-006e-e044-00144f67d031.html*

[35] *"Fatty acids, soya, epoxidized, Me esters" CASRN 68082-35-9. US EPA Aggregated Computational Toxicology Resource (ACTOR). Accessed May 2014. Available: http://actor.epa.gov/actor/GenericChemical?casrn=68082-35-9*

[36] *Veld et al. 2006.*

[37] *Nielsen et al 2014.*

[38] *Online substance information for Grindsted Soft-N-Safe. European Chemicals Agency (ECHA). March 11, 2014. Available: http://apps.echa.europa.eu/registered/data/dossiers/DISS-a64fd6e2-81ea-7046-e044-00144f67d249/DISS-a64fd6e2-81ea-7046-e044-00144f67d249_DISS-a64fd6e2-81ea-7046-e044-00144f67d249.html*

[39] *"GRINDSTED® SOFT-N-SAFE: The safe and sustainable plasticiser for PVC." Danisco A/S. Accessed May 2014. Available: http://www.danisco.com/softnsafe/doc/snsbrochure.pdf*

[40] Maag et al. 2010.

[41] Nielsen et al 2014.

[42] Online substance information for Isosorbide Diesters. European Chemicals Agency (ECHA). November 20, 2013. Available: http://apps.echa.europa.eu/registered/data/dossiers/DISS-a21659eb-f229-54ee-e044-00144f67d031/AGGR-498ba696-432e-44ea-912c-2a772f47f015_DISS-a21659eb-f229-54ee-e044-00144f67d031.html#section_1.1

[43] Veld et al. 2006.
[44] Fuertes, Patrick and Hervé Wyart. Method for preparing diahydrohexitol diester compositions. Roquette Freres, assignee. Patent US8609872 B2. 17 Dec. 2013. Available at: http://https//www.google.com/patents/US8609872 (Roquette Freres 2013)

[45] Ghosh-Dastidar, Abhuijit, Robert F. Eaton, Antoni Adamczyk, Bruce M. Bell, and Robert M. Campbell. Vegetable-oil Derived Plasticizer. Dow Global Technologies LLC, assignee. Patent WO2013003225 A2. 3 Jan. 2013. Available: http://www.google.com/patents/WO2013003225A2. (Dow Global Technologies 2013)

[46] Basf Aktiengesellschaft 2008.

[47] Roquette Freres 2013.

[48] Dow Global Technologies 2013.

[49] Nagorka et al 2011 and Schossler et al 2011.

[50] Schütze et al. 2012 and Silvia et al. 2012.

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