TOXICS USE REDUCTION INSTITUTE

THE MASSACHUSETTS TOXICS USE REDUCTION INSTITUTE

Massachusetts Chemical Fact Sheet

Di (1,2-Ethylhexyl) Phthalate (DEHP)

This fact sheet is part of a series of chemical fact sheets developed by TURI to help Massachusetts companies, community organizations and residents understand the chemical's use and health and environmental effects, as well as the availability of safer alternatives. Since Massachusetts companies report usage under the Toxics Use Reduction Act, readers will learn how the chemicals are being used and by which companies.

Di (2-ethylhexyl) phthalate (DEHP) is the international standard plasticizer for otherwise rigid plastics such as polyvinyl chloride (PVC). DEHP provides excellent flexibility at reasonable cost, and is found in a multitude of industrial, commercial and consumer products. Properties of other plasticizers are usually reported relative to those of DEHP. However, concerns about the human and environmental health impacts associated with the use and exposure to DEHP exist. Thus the adoption of safer alternatives that provide comparable properties should be considered where possible.

DEHP FACTS	
Synonyms	Di-octyl phthalate (DOP) Bis (sec) ethylhexyl phthalate
Chemical Formula	$C_{24}H_{38}O_4$
CAS Number	117-81-7
Vapor Pressure	1.4×10^{-6} mm Hg at 25°C
Water Solubility	0.285 mg/L at 24°C (slightly soluble in water)
Description	Colorless liquid, almost no odor

Health and Environmental Impacts

Human and environmental health impacts may result when exposure to DEHP occurs. The following is a brief summary of potential exposure routes and the associated human and environmental health impacts. As scientific research evolves new information on these impacts will likely emerge. Readers are therefore encouraged to consult the references for updates.

Exposure Routes

Human exposure to DEHP during manufacture or consumer use occurs primarily through:

- Inhalation, particularly during manufacture and processing
- Oral exposure (primarily a product-related concern), or
- Injection during medical procedures, especially when high lipid content medical fluids directly contact DEHP-containing materials.

Because DEHP has a low vapor pressure, when present in product relatively little is found in the surrounding atmosphere. However, DEHP molecules that are present in air will adsorb onto dust particles and will be deposited on surfaces through gravity or precipitation. Releases of DEHP to the air from plastic materials, coatings, and flooring in home and work environments, although small, can therefore lead to higher indoor levels than are found in the outdoor air.

DEHP is highly soluble in lipids and can result in increased potential for human health impacts when exposure occurs via certain medical procedures. Medical exposures to infants are of particular concern because of their low body weight and underdeveloped immune system. Medical procedures that can result in increased DEHP exposure in neonates include cardiac bypass procedures, total parenteral nutrition therapy, infusion of lipophilic drugs using PVC bags and tubing, and respiratory therapy.

Human Health Effects

Studies indicate that DEHP is a potential human carcinogen and that it likely impacts developmental and reproductive processes of, in particular, male infants. The oral toxicity of DEHP in humans is limited to gastrointestinal (GI) symptoms (mild abdominal pain and diarrhea.

Cancer Risk

DEHP is currently classified by the USEPA as a Class B2 (probable human) carcinogen. This determination is based entirely on liver cancer in rats and mice.

In 2000 IARC changed its classification for DEHP from "possibly carcinogenic to humans" to a Class 3 carcinogen "cannot be classified as to its carcinogenicity to humans," because of the differences in how the livers of humans and primates respond to DEHP as compared with the livers of rats and mice.

The California Occupational Health and Human Services classified DEHP as a carcinogen in 1988, and it has remained listed in the California Proposition 65 legislation as such since that time.

Reproductive/Developmental Effects

Studies in rodents exposed to doses in excess of 100 mg/kg/day of DEHP clearly indicate that the testes are a primary target organ, resulting in decreased testicular weights and tubular atrophy.

Oral exposure to DEHP also appears to negatively impact the seminal vesicles, epididymis, and prostate gland in rats and mice. When DEHP enters the human body, the compound is rapidly metabolized into various substances that are readily excreted.

The primary metabolite created is mono-ethylhexyl phthalate (MEHP), which is thought to be responsible for much of DEHP's reproductive toxicity. A review of various studies indicates that

MEHP generally produces developmental, reproductive and hepatic toxicity in laboratory animal. Because the majority of conversion of DEHP to MEHP occurs in the GI tract, exposures to DEHP by ingestion may be more hazardous than those by the intravenous route, which largely bypass the GI tract.

Based on an evaluation of multiple studies, the US National Toxicology Program (NTP) has determined that exposure of neonates to DEHP is a "serious concern". Specifically, the developing organism is more sensitive to DEHP than the juvenile or adult organism. In addition, the age at first exposure to DEHP appears to have a clear influence on the primary reproductive system effect, testicular damage. As a result of its review of associated studies, the NTP has determined that no adverse effects are observable in males at concentrations below 3.7 mg/kg bw/day.

DEHP has been listed as a developmental toxin under California Proposition 65 since 2003.

Environmental Hazards

DEHP is widespread in the environment. According to EPA, it is often found near industrial settings, landfills, and waste disposal sites.

DEHP is not chemically bound to the polymer matrix and can therefore be released throughout the lifecycle of products. DEHP enters the environment through releases from manufacturing facilities that make or use DEHP and from consumer products that contain it. Over long periods of time, it can also migrate out of plastic materials and into the environment.

When DEHP is released to soil, it usually attaches strongly to the soil and does not move very far away from where it was released. DEHP has also been found in groundwater near waste disposal facilities. When DEHP is released it dissolves very slowly into underground water or surface waters that contact it.

(For section references, see endnote #1)

Use Nationally and in Massachusetts

As a plasticizer, the primary function of DEHP used in products is to soften otherwise rigid plastics and polymers. An estimated 90% of DEHP is used as a plasticizer for PVC.

The uses of DEHP fall into two major categories: Polymer uses (e.g., consumer products such as footwear, shower curtains and toys, medical devices and commercial/industrial uses) and non-polymer uses (e.g., dielectric fluids, paints, adhesives and inks). Non-polymer uses represent less than 5% of the total DEHP used nationally.

Approximately 45% of total U.S. consumption of DEHP is for plasticizing various industrial and commercial products. Industrial and commercial uses of DEHP include resilient flooring, wall covering, roofing, aluminum foil coating/ laminating, paper coating, extrudable molds and profiles, electronic component parts and wire and cable coating and jacketing.

Medical devices comprise approximately 25% of total U.S. manufacturer use of DEHP. Medical devices that contain DEHP include PVC sheet materials such as IV bags, and tubing used in a variety of medical applications.

In 2002, U.S. manufacturers produced approximately 240 million pounds of DEHP. The annual U.S. production rate remains constant.

In 2004, Massachusetts manufacturers consumed approximately 3.75 million pounds of DEHP.

Table 1 summarizes the historical use of DEHP in Massachusetts for companies using more than 10,000 pounds (the reporting threshold) of DEHP annually. The information on chemical use is based on what has been reported to the Massachusetts Toxics Use Reduction Program for 1990 and 2004. The numbers presented do not reflect production changes in the companies over the time period.

Figure 1 illustrates the percent change in DEHP use by industry sector. As shown, five of these sectors have experienced 100% reduction in their reportable use of DEHP. While the companies in the Rubber Products sector no longer manufacture in Massachusetts, both the Footwear and Electrical Capacitors industry sectors have largely moved away from the use of DEHP towards other less toxic chemicals. The Paints and Pigments sector has also reduced all use of DEHP below reporting thresholds. Surface Coatings, of Wilmington was able to eliminate its use of DEHP in its non-acrylic paint products as well.

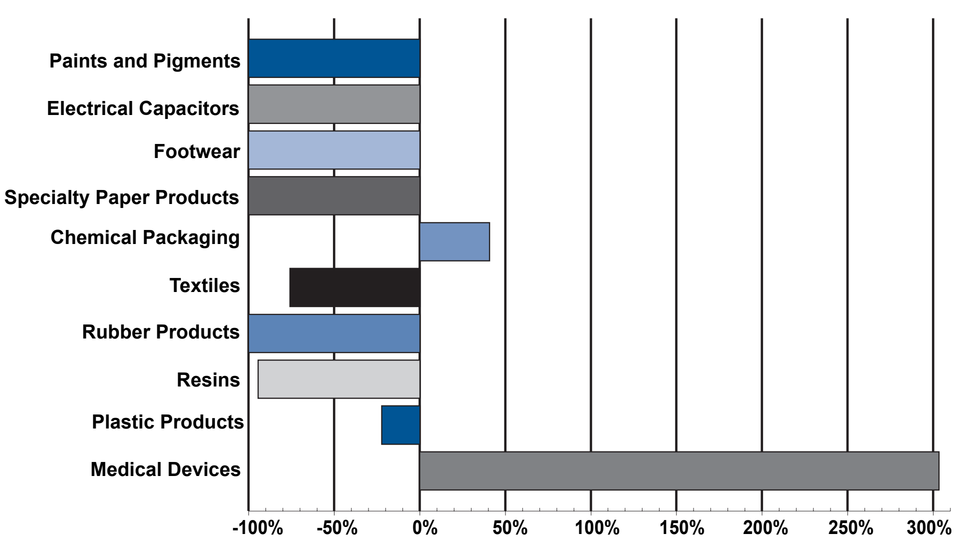
The Specialty Paper Products sector eliminated its use of DEHP in the early 1990s. Both companies still manufacture in Massachusetts (Rexam has moved its operations to South Hadley and now operates under the name Intelicoat Technologies) but have modified their processes to avoid the need for the plasticized polymer coating previously used.

Other industry sectors that experienced significant reductions in the use of DEHP from 1990 to 2004 include the Plastics Products, Textiles and Resins sectors.

- The Plastics Products sector exhibited a variety of responses to market challenges over the study period. One company, Plymouth Rubber, was able to reduce its use of DEHP below reportable amounts within two years of the implementation of the TURA program. On the other hand, two companies, Biltrite Corporation (a manufacturer of industrial grade vinyl flooring products), and Barbour Corp (a manufacturer of molded marine products) increased their production and therefore use of DEHP substantially.

Table 1. Massachusetts DEHP Consumption by Industry Sector (1990 – 2004)				
Industry Sector	*Facility Name*	*Location*	*Use (pounds)*	
			1990	*2004*
Chemical Packaging	Callahan Company	Walpole	0	32,931
	George Mann & Company Incorporated	Stoneham	23,400	0
Specialty Paper Products	Rexam DSI (now Intelicoat Technologies Inc.)	West Springfield	15,712	0
	Sullivan Paper Company	West Springfield	23,462	0
Electrical Capacitors	Aerovox Incorporated	New Bedford	594,763	0
	Cornell Dubilier Company	New Bedford	348,760	0
Footwear	Quabaug Rubber Company	North Brookfield	406,156	0
Medical Devices	Haemonetics Corporation	Braintree	0	307,553
	Filtrona Extrusion (also known as Bunzl Extrusion and Pexco Inc.)	Northborough and Athol	335,202	1,044,139
Paints and Pigments	Surface Coatings Incorporated	Wilmington	35,309	0
	Stahl USA	Peabody	43,000	0
Plastic Products	Barbour Corporation Incorporated	Brockton	116,598	798,353
	Biltrite Corporation	Chelsea	814,456	1,217,859
	Plymouth Rubber Company	Canton	251,000	0
	Regalite Plastics Corporation	Newton	1,409,103	0
Resins	AlphaGary	Leominster	0	262,699
	Berkshire Electric Cable Company	Leeds	561,187	0
	Global Products	Leominster	240,128	0
	Indusol	Sutton	145,560	0
	Lynn Plastics Corporation	Lynn	22,003	0
	Teknor Apex Company	Attleboro	3,975,485	12,300
Rubber Products	Armstrong World Industries	Braintree	45,899	0
	Polyfibron Technologies Incorporated	Adams	16,743	0
Textiles	Bradford Industries	Lowell	74,840	0
	Clark Cutler McDermott	Franklin	236,916	0
	Mykrolis Corporation (filter media)	Bedford	0	75,471
		Total DEHP Use	9,735,682	3,751,305

Figure 1. Percent Change in DEHP Use (1990 to 2004) by Industry Sector



- The Textiles sector includes two companies (Bradford Industries and Clark Cutler McDermott) manufacturing fabric for a variety of uses. Each of these companies reduced their use of DEHP below reportable amounts in the early 1990s. The third company, Mykrolis, a division of Millipore Corporation, has reported relatively constant manufacturing of flat sheet hollow fiber filter membranes.
- The Resins sector has also had a variety of responses to market pressures over the course of the TURA program. Two companies in the coated wire and cable industry (Berkshire Electric Cable and Global Products) reduced their use of DEHP below reportable amounts. Two polymer resin compounders, AlphaGary and Teknor Apex, continue to use DEHP in certain flexible

products, though the trend is toward significantly reduced DEHP use as this industry develops other viable plasticizer alternatives.

Data from two industry sectors show increases in the use of DEHP from 1990 to 2004. The Medical Device sector has experienced the most dramatic increase in the use of DEHP along with significant increases in production over that time period. Both Filtrona and Haemonetics primarily manufacture flexible tubing for the health care industry, though they also manufacture bags and sheet materials for health care applications.

Massachusetts Inputs and Outputs

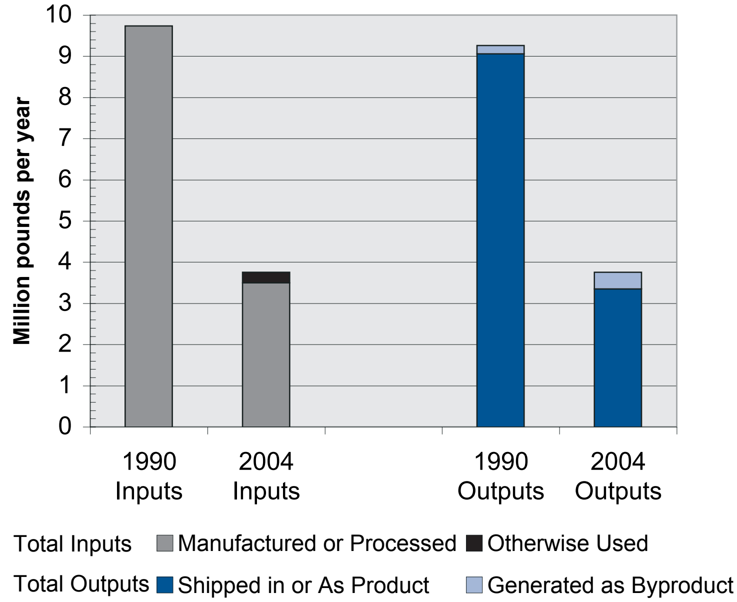
The change from 1990 to 2004 in absolute amount of inputs and outputs in Massachusetts is shown in Figure 2. Inputs include DEHP that is manufactured or processed, as well as DEHP that is "otherwise used" – ancillary uses that do not become incorporated into the final product. Outputs include DEHP that is generated as byproduct (i.e., all non-product material created by a process line prior to release, on-site treatment, or transfer) and the amount of DEHP that is shipped in or as product. As shown, the majority of DEHP used is manufactured or processed and subsequently shipped in product.

As shown in Figure 2, both inputs and outputs have been significantly reduced overall in the Commonwealth from 1990 to 2004. Specifically, from 1990 to 2004 the amount of DEHP manufactured or processed was reduced by 64%, while the amount shipped in product over the same time period was reduced by 63%.

(For section references, see endnote #2)

Overall, Massachusetts has experienced a 61% reduction in the use of DEHP since 1990.

Figure 2.
Inputs and Outputs of DEHP in Massachusetts



In medical device applications there are additional performance criteria for the plasticized polymer. Important considerations include the tendency of plasticizers to migrate out of the polymer matrix, and the ability of the plasticized polymer to be sterilized by different methods. Additional concerns include:

- For sheet applications – tensile strength, cold flexibility (because solutions must be cold-storable) and clarity.
- For tubing applications – elastic recovery must be optimized to assure that tubing does not kink during use.

TURI conducted an assessment of various plasticizer and polymer alternatives associated with DEHP in its 2006 study for the Commonwealth, entitled "Five Chemicals Alternatives Assessment Study". As part of that study, several alternative plasticizers and polymers were identified. Alternative plasticizers include other phthalates (DINP, DIDP, DIHP, BBP, DBP, and BOP), di (2-ethylhexyl) terephthalate (DEHT), dibenzoates (DGD, DEGDB, and TEGDB), adipates (DEHA and polymeric adipates), phosphates (DEHPA and TCP), citrates (ATBC and BTHC), and sebacates (DEHS and DBS).

In addition to alternative plasticizers, alternative materials can be used. As with plasticizers, appropriate alternative materials differ depending on the application.

(For section references, see endnote #3)

Alternatives

Alternative manufacturing processes to create flexible polymers can involve the replacement of DEHP with another plasticizer, or the use of a polymer or other material that does not require the use of a plasticizer to achieve the same characteristics and performance.

In general, desirable performance criteria for flexible PVC include compatibility, processability and hardness. Compatibility with PVC and any other additives present (i.e., the ability to create a stable single phase compound) is a critical factor when considering alternative plasticizers. Known as processability, PVC resin, plasticizer(s), stabilizers and lubricants should blend together readily using common plastics processing methods. In addition, the alternative plasticizer should achieve the required level of flexibility (measured as hardness) at a cost that is comparable to that of DEHP-plasticized PVC.

Alternatives for Consumer Products

DEHP has historically been used in a number of consumer products, ranging from toys to footwear to household products such as wall coverings and resilient flooring. However, the use of DEHP in these products has decreased in the past decade, largely due to increased consumer demand, as well as in response to international restrictions. DEHP has largely been eliminated from the footwear and toy industries in favor of other plasticizers or polymer matrices.

However, footwear products and toys manufactured in other parts of the world, in particular Asia, may still have DEHP and other phthalate plasticizers present.

Consumer products where DEHP may still be found include other flexible vinyl products such as rain gear, shower curtains, vinyl flooring and wall coverings. Of these, the most significant uses are in resilient flooring and in wall coverings.

Resilient Flooring

TURI focused on resilient flooring as a priority use in its 2006 study. Resilient flooring uses include residential flooring as well as commercial and high-traffic industrial applications. TURI identified several plasticizer alternatives for resilient flooring, including di (2-ethylhexyl) terephthalate (DEHT), di isononyl phthalate (DINP), dipropylene glycol dibenzoate (DGD) and di (2-ethylhexyl) adipate (DEHA).

In general, these alternative plasticizers offer similar or improved technical/performance, cost, and environmental and human health benefits to DEHP. Use of alternative plasticizers often does, however, require modifications to processing equipment and practices and there has been little incentive for resilient flooring manufacturers to pursue alternatives except in higher priced products.

Alternative materials that do not require the use of plasticizers are also available for resilient flooring applications. Performance issues that must be considered when assessing alternative materials for resilient flooring include installation, cleaning and maintenance, cost, end of life and other environmental and human health concerns. The most promising alternatives identified by TURI include linoleum (made from linseed oil, wood flour, resin, jute and limestone), cork and polyolefin co-polymers with limestone. While linoleum and cork tend to be more appropriate for residential uses, the polyolefin co-polymer flooring is designed for large high-traffic commercial areas such as in health care facilities, ships, shopping centers and airports.

In general, each of these material alternatives exhibit equal or improved performance, cost and EH&S characteristics over DEHP-plasticized vinyl flooring. As with alternative plasticizers, however, use of alternative materials for flooring is largely dictated by costs. With little external incentive to manufacture or use alternative materials the adoption rate of these alternatives has been slow, especially in the residential market. However, many health care facilities are moving towards alternative materials and polymer formulations for their resilient flooring needs. As the trend towards green building expands in the US, it is expected that the market for natural resilient flooring materials will also grow.

Wall Covering

Vinyl wall coverings are used in both commercial and residential settings for decorative as well as protective purposes. According to industry representatives, the majority of US wall covering manufacturers do not use DEHP. DEHP is used by some international manufacturers, and therefore may still enter the US market in their products. Alternatives to DEHP are readily available. The two most widely recognized alternatives to DEHP for wall coverings are DEHA and DINP. These alternative plasticizers present similar or improved cost, and environmental and human health characteristics. While DINP also represents a potential direct replacement for DEHP from a technical/performance standpoint, DEHA presents some challenges with respect to PVC compatibility and emissions during processing and use.

A number of alternative materials to DEHP-plasticized vinyl wall coverings have been developed. These range from polymers, to polymer/natural fiber (e.g., wood or cellulose) blends, to inorganic based textiles. The majority of alternative materials exhibit similar or improved performance, cost, and environmental and human health characteristics. However most of the alternatives are not currently available in similar color and pattern choices, which may limit their acceptance in certain applications. As with resilient flooring however, there is a move toward alternative materials for wall coverings used in health care facilities as well as in residential and commercial applications, largely in association with the increased emphasis on green building in the US.

(For section references, see endnote #4)

Alternatives for Medical Devices

PVC is widely used as a plastic in medical sheet and tubing type devices. Studies suggest that as much as 25% of all plastics used in hospital environments are PVC-based. These devices include bags used to store a variety of medical solutions and tubing used in the transfer of those solutions to the patient.

The most commonly used alternative plasticizers in medical device applications include trioctyl trimellitate (TOTM), DEHA and butyryl trihexyl citrate (BTHC). In addition, a newer plasticizer currently approved in the EU for food applications, di isononyl cyclohexane-1,2-dicarboxylate (DINCH) is being evaluated for use in medical devices in the US.

In general each of these plasticizer alternatives may provide equal or improved performance, cost and environmental and human health characteristics over DEHP. Adoption of alternatives is happening across the health care industry, though rather slowly. In part this is due to the relative lack of information about the health effects of the alternatives and their metabolites and the industry's need to protect the health of its patients.

Materials that are either inherently flexible, or that fulfill the function of the DEHP/PVC material without being plasticized are also available. One of the key concerns for these materials is their shelf life in a medical setting – that is their ability to retain flexible characteristics without leaching harmful chemicals.

Materials that have been found to be appropriate alternatives to DEHP/PVC for medical bag devices include:

- Ethylene vinyl acetate (EVA), a copolymer used in medical film applications such as for parenteral and enteral solutions, and for custom mixing of pharmaceuticals.

- Polyolefins such as polyethylene and polypropylene – stable and inert polymers which are widely used in medical device applications due to their flexibility, transparency and toughness.
- Glass, which was historically used for solution storage purposes, though is now less commonly used due to handling concerns and cost.

Materials used in medical tubing applications must be able to be formed in a variety of configurations, have thin inner walls, be durable and strong with low coefficients of friction, be highly resistant to chemicals and to temperature variations, be inert and be weldable to other components of the medical device. Appropriate alternative medical tubing materials include EVA, polyolefins and glass, as well as:

- Silicone, a naturally translucent, odorless and tasteless synthetic rubber.
- Thermoplastic polyurethane (TPU), formed by reacting alcohols with a diisocyanate or polymeric isocyanate.

In general, these materials exhibit equal or improved performance and environmental and human health characteristics over DEHP/PVC. The cost of the alternative materials tends to be greater than that of the DEHP/PVC. In addition, gas permeability of EVA and polyolefins and manufacturability of silicone and TPU are worse than DEHP/PVC. There is an environmental and human health concern associated with the manufacture of TPU, potentially making it less favorable as an alternative from that perspective.

(For section references, see endnote #5)

Regulatory Context

The US Occupational Safety and Health Administration (OSHA), the US Environmental Protection Agency (EPA) and the US Food and Drug Administration (FDA) regulate DEHP. In addition, several states have specific restrictions on DEHP.

The OSHA permissible exposure limit (PEL) for DEHP is 5 mg/m3 8-hour time weighted average.

The US EPA regulates DEHP in a number of ways:

- A maximum contaminant level for ingestion of water and contaminated aquatic organisms (such as fish and shellfish) = 6 parts of DEHP per billion parts of water.
- Health based limits for exclusion of waste-derived residues = 30 mg/kg.
- As a hazardous constituent of wastes from cleaning equipment and tanks used in paint manufacturing – hazardous waste number U028.

The US FDA regulates the chemical as an unintentional food additive.

Clean Water Act related regulatory restrictions in New England states include:

- Massachusetts: Reference dose = 2x10-2 mg/kg/day, oral slope factor = 1.4x10-2 mg/kg/day
- New Hampshire: Regulated toxic air pollutant = OEL 5 mg/m3
- Maine: Drinking water guideline 25 μg/L
- Rhode Island and Vermont: Groundwater quality standard = 6 μg/L, Preventive action limit = 3 μg/L
- Connecticut: Direct exposure criteria for soil, residential = 44 mg/kg, industrial/commercial = 410 mg/kg

Finally, DEHP is regulated as a carcinogen (since 1988) and a developmental toxicant (since 2003) under the California State Proposition 65. This regulation requires businesses to provide a "clear and reasonable" warning before knowingly and intentionally exposing anyone to DEHP.

(For section references, see endnote #6)

Endnotes

1. Agency for Toxic Substances and Disease Registry "Toxicological Profile for Di (2-ethylhexyl) phthalate (Update)" 2002; Børnehag et al. "The Association between Asthma and Allergic Symptoms in Children and Phthalates in House Dust: A Nested Case-Control Study" Environmental Health Perspectives 2004; Børnehag et al "Phthalates in Indoor Dust and Their Association with Building Characteristics" Environmental Health Perspectives 2003; Gray and Butterworth "Testicular atrophy produced by phthalate esters" Archives of Toxicology 1980; Lamb et al "Reproductive effects of four phthalic acid esters in the mouse" Toxicology and Applied Pharmacology 1987; National Toxicology Program Center for the Evaluation of Risks to Human Reproduction: Expert Panel Update on the Reproductive and Developmental Toxicity of Di (2-Ethylhexyl) Phthalate" 2005; USEPA "Technical Factsheet on: Di (2-ethylhexyl) phthalate (DEHP)" 2005

2. Bizzari et al "Plasticizers" Chemical Economics Handbook 2002; Toxics Use Reduction Institute "Toxics Use Reduction Act data release for reporting year 2004" 2005, see webpage: http://turadata.turi.org

3. Danish Environmental Protection Agency "Environmental and Health Assessment of Alternatives to Phthalates and to flexible PVC" 2003; Toxics Use Reduction Institute "Five Chemicals Alternatives Assessment Study" 2006 – see webpage: http://www.turi.org/industry/research/five_chemicals_study

4. EU Marketing and Use Directive 76/769/EEC; Fischer "Floorward thinking" Environmental Health Perspectives 1999; Hileman "Panel Ranks Risks of Common Phthalate: Additional research underscores concerns about DEHP that were first expressed in 2000 report" Chemical & Engineering News 2005; Marshall "Letter to TURI from OMNOVA Solutions Inc" 2007; Toxics Use Reduction Institute "Five Chemicals Alternatives Assessment Study" 2006– see webpage: http://www.turi.org/industry/research/five_chemicals_study

5. Rossi "Neonatal Exposure to DEHP and Opportunities for Prevention" 2002; Schaefer "Personal communication with Marketing Manager Specialty Plasticizers BASF Corporation" 2006; Tickner "The Use of Di-2-Ethylhexyl Phthalate in PVC Medical Devices: Exposure, Toxicity and Alternatives" 2000; Toxics Use Reduction Institute "Five Chemicals Alternatives Assessment Study" 2006– see webpage: http://www.turi.org/industry/research/five_chemicals_study

6. Bureau of National Affairs "Environmental Reporter" 2001; California Safe Drinking Water and Toxic Enforcement Act of 1986 (Chapter 6.6 added by Proposition 65 1986 General Election) Section 25249.5; EPA 2001 40 CFR 141.32(e)(62), 40 CFR 266 Appendix VII, 40 CFR 261.33 and 40 CFR 302.4; Hazardous Substance Data Bank 2000, see webpage: http://www.toxnet.nlm.nih.gov; OSHA 2001b (29 CFR 1910.1000)