

Lead and cadmium are not the only toxic risks associated with PVC. PVC is the most environmentally-damaging plastic. The PVC lifecycle—its production, use and disposal—results in the release of toxic, chlorine-based chemicals. These toxins are building up in the water, air and food chain. The result: severe health problems, including cancer, immune system damage, and hormone disruption. No one can escape contamination. Everyone, everywhere, has measurable levels of chlorinated toxins in their bodies.



1436 U STREET, NW  
WASHINGTON, DC 20009  
1-800-326-0959

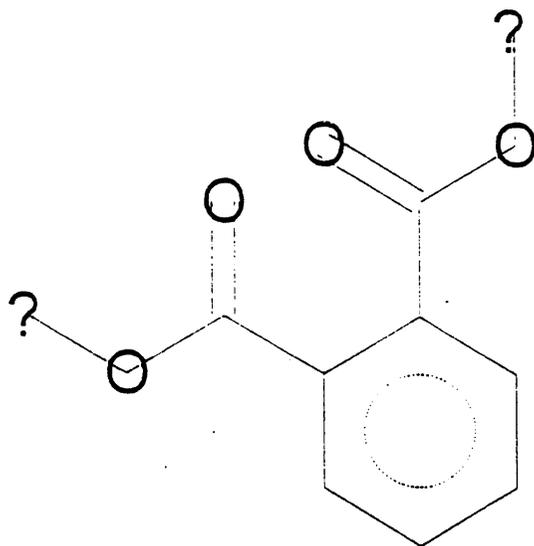
<http://www.greenpeaceusa.org>

# Determination of the Composition and Quantity of Phthalate Ester Additives in PVC Children's Toys.

Ruth Stringer  
Irina Labounskaia  
Dr David Santillo  
Dr Paul Johnston  
John Siddorn  
Angela Stephenson

Greenpeace Research Laboratories Technical Note 06/97

September 1997



Greenpeace Research Laboratories  
University of Exeter  
Department of Biological Sciences  
Prince of Wales Road  
Exeter EX4 4PS  
UK

## 1. Summary

PVC (polyvinyl chloride or vinyl) is widely used in toys and other children's products. For soft applications, such as toys designed for chewing ("teethers"), softeners or plasticisers are added to give the desired flexibility. Although a range of chemicals are used as softeners, phthalate esters (phthalates) are by far the most commonly used.

Phthalates do not bind to the PVC, remaining present as a freely mobile and leachable phase in the plastic. As a consequence, phthalates are continuously lost from soft PVC over time. Contact and pressure, such as that applied during teething or play, can increase the rates at which these chemicals leach from the plastic.

Children in contact with soft PVC toys may, therefore, ingest substantial quantities of phthalates during normal play, especially from toys specifically designed to be chewed. This is of concern as phthalates are known to present a number of hazards. Although acute toxicity appears to be low, phthalates have been shown to cause a range of adverse effects in laboratory animals following longer exposure, including damage to the liver and kidney and, in some cases, effects on the reproductive tract.

The limited research available to date on the composition of phthalates in PVC toys has raised concerns over the potential for exposure of children to these chemicals. Despite this, manufacturers do not provide information on the types or quantities of additives present in toys. Greenpeace was interested, therefore, to obtain a range of typical soft PVC toys from a number of countries, particularly those designed to be chewed, and to determine the types and quantities of plasticisers present.

A total of 71 toys were purchased, drawn from 17 countries, the majority of which (63) were PVC or had PVC sections. In almost all soft PVC toys analysed, phthalates comprised a sizeable proportion (most frequently 10-40%) of the total weight of the toy. Although historically the most commonly used phthalate was DEHP (di(2-ethylhexyl)phthalate), the most frequently identified, and generally most abundant, phthalate in the current investigation was the isomeric form DINP (diisononyl phthalate). Of the 63 PVC toys analysed, 40 contained DINP as the predominant phthalate, compared to only 8 for DEHP. DEHP was also present as a minor component of many of the toys containing DINP, perhaps as a contaminant in the DINP. Of the 8 non-PVC toys analysed, only one contained any detectable phthalate, and then only in trace quantities (possibly as a contaminant from the PVC in which it was packaged).

Although less well researched than DEHP, DINP shows similar toxicological properties in laboratory animals. Effects recorded include liver and kidney disorders, damage to the reproductive tract, increased incidence of certain forms of cancer and diverse effects on development and metabolism. More recently, research has revealed that DINP, along with some other phthalates, shows weak activity as a mimic of the hormone estrogen in human cell lines. When purchased for laboratory use, DINP is labelled with a number of hazard phrases, including "*harmful by inhalation, in contact with skin and if swallowed*", "*possible risk of irreversible effects*" and "*may cause cancer*". In contrast, toys containing up to 40% by weight DINP in a readily leachable form are frequently labelled "*non toxic*".

A number of other compounds were identified in some of the toys, generally at lower but significant concentrations. - DBP (dibutyl phthalate) and BBP (butylbenzyl

phthalate), found in several toys, are known to be particularly hazardous. The estrogenic chemical nonylphenol was isolated from 13 toys, while 2 toys were found to contain the fungicide Fungitrol 11 (Folpet).

The rates at which chemicals leach from soft PVC were not determined in this study. Nevertheless, the presence of these chemicals in such quantities in toys designed to be chewed by babies and young children, along with published evidence that such additives are hazardous and can leach from PVC toys, raises serious concerns. The Danish EPA has recently demonstrated that the leaching of phthalates, particularly DINP, from teething toys can be substantial. This has been supported by similar studies in other countries and has led, in some cases, to recommendations that certain toys be withdrawn or even that the use of soft PVC in toys for young children should be discontinued.

The study carried out by Greenpeace has demonstrated that phthalates, particularly DINP and DEHP, are widely and abundantly used in high contact children's toys. Their use represents a significant potential for exposure of children to chemical hazards, of particular concern during sensitive periods of development. Although it is practically impossible to make accurate predictions of dose, exposure to such hazards is clearly unacceptable. The only way to avoid direct intake of phthalates is to eliminate the use of PVC in all soft toy applications.

## 2. Introduction

PVC (polyvinyl chloride, or vinyl) is a widely used material, including extensive use in toys and other children's products. PVC is never formulated without a range of additives to enhance its properties (Ehrig 1992). In order to soften PVC for the manufacture of toys such as chewy teethers, soft figures and inflatable toys, softeners or plasticisers are added. A number of chemicals are used, although by far the most common are the phthalates (phthalic esters or benzenedicarboxylic acid esters). They represent 69% of plasticiser use in the USA, 92% in Western Europe and 81% in Japan. Overall, they represent 82% of the 2.5million tonnes (5400 million pounds) of plasticiser use in these three regions (Bizarri *et al.* 1996). They are moderately persistent and, as a consequence of their wide use, are the most abundant man-made chemicals in the environment (Jobling *et al.* 1995).

Phthalates in soft PVC product are not tightly bound to the plastic, but are present as mobile components of the plastic matrix. Loss of phthalates by volatilisation over time from soft PVC has long been recognised. According to Cadogan *et al.* (1993) "...because plasticisers in flexible PVC are not chemically bound to the polymer, they may be lost from the finished article during its use or after final disposal." This is acknowledged by other sources, including the UK Department of the Environment, who recognise that the widely used phthalate plasticiser DEHP (di(2-ethylhexyl) phthalate) "will also be released from plasticised products during their use and after their disposal" (DoE 1991); Phthalates can also be released from soft PVC by surface contact, especially where mechanical pressure is applied (e.g. during chewing of a PVC teether). Releases of phthalates during manufacture, use and disposal of PVC products, in addition to their use as additives in inks, lubricants, perfumes and other open-ended applications, has led to their ubiquitous distribution and abundance in the global environment.

Our exposure to phthalates is therefore twofold. We are exposed to background levels of contamination in air, food and water, but may also be exposed through direct contact with soft PVC products, particularly those intended as high contact products, such as children's toys and teethers. Although less persistent in the body and environment than many other synthetic organic compounds, the continued release of large quantities of these chemicals to the open environment ensures that concentrations and, therefore, exposures remain substantial. Moreover, recent research suggests that phthalates may persist in human body tissues for longer periods than previously assumed (Dirven *et al.* 1993).

Given the known and potential toxicity of the phthalates, individually and as a chemical class, and the ability of the phthalates to leach out of the PVC matrix through contact or volatilisation, the continued use of soft PVC as a material for children's toys raises serious concerns. This is especially true since children will receive their greatest exposure to many of these products, particularly teethers, at an early and sensitive stage of their development. It has been known since 1983 (Hanson 1983) that DEHP was present in high concentrations in children's products and could leach out under simulated dermal and oral contact. There appeared to be no consistent relationship between either the concentration of phthalate in the product or the duration of the experiments and the amount of DEHP that leached out. Nevertheless, it was apparent that DEHP would continue to leach out of a product over an extended period. Moreover, if pacifiers ("dummies") were squeezed during the leaching experiments, to imitate the action of a child chewing, the rate of release of DEHP was increased.

In 1994 a study conducted by Health Canada reported substantial concentrations of DEHP in a number of children's product (specifically teething rings) and made the first attempts to assess the significance of such toys as point sources of exposure to phthalates (Meek and Chan 1994). While recognising the problems in arriving at reliable dose estimates, these authors concluded that: "...for infants and toddlers, the total intake [of DEHP] may be higher [than for other sectors of the population] as a result of exposure from children's products that contain DEHP..."

It should be noted that no other phthalates were analysed in this study. Indeed, to date there appear to have been few attempts to describe and quantify the distribution of phthalates other than DEHP in PVC consumer products. Both the Dutch and Danish governments have, however, recently studied the leaching of phthalates from PVC teething rings. These studies showed that, for some products, leaching rates were substantial and might lead to doses of phthalates which would exceed tolerable daily intakes agreed by the European Commission Scientific Committee for Food (McKenzie 1997, Vinkelsee *et al.* 1997, SCF 1995).

Greenpeace was interested to determine current patterns of use of phthalates as softeners in PVC toys, using analytical techniques that would yield empirical data on composition. The data from this study cannot be used to produce estimates of doses children will receive. Nevertheless, they provide a clear picture of the use of what are, essentially, hazardous chemicals in teething rings and other high contact children's products. The collection of samples from a number of countries, both in terms of country of purchase and manufacture, was designed to give an overview of global market trends, as well as local differences, in the use of PVC and phthalates in these products. In addition, some information was obtained on the presence of other chemicals as additives or contaminants in the toys.

### 3. Materials and methods

A total of 71 toys were purchased off the shelf from retail outlets in 17 countries and forwarded to the Greenpeace Research Laboratories for analysis. The distribution of toys received according to country of purchase is summarised in Figure 1 and a description of each is given in Table 1. Distribution according to country of manufacture is shown in Figure 2.

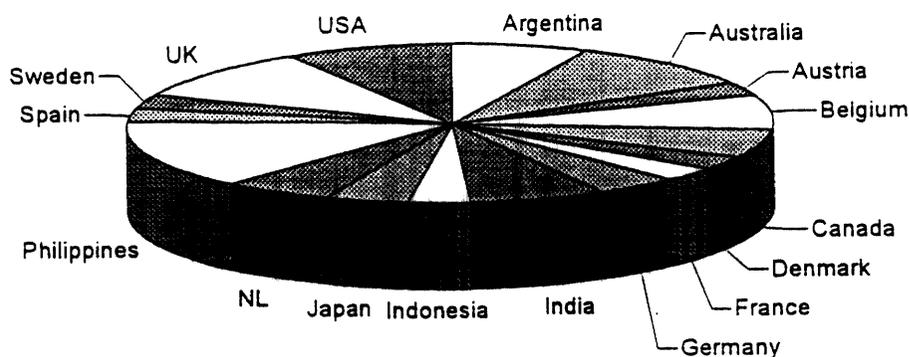
On receipt at the laboratory, samples were taken of each of the toys (samples of each section where the toys consisted of several discrete materials or textures) for determination of chlorine content as an indicator of PVC (using X-ray microanalysis; results not shown).

All PVC toys and a selection of non-PVC toys were subsequently analysed for phthalate plasticisers. Each toy, or section of toy, was frozen in liquid nitrogen for several seconds and then grated to produce a finely ground material (with a typical particle size of less than 2 mm) to ensure efficient extraction of the plasticisers.

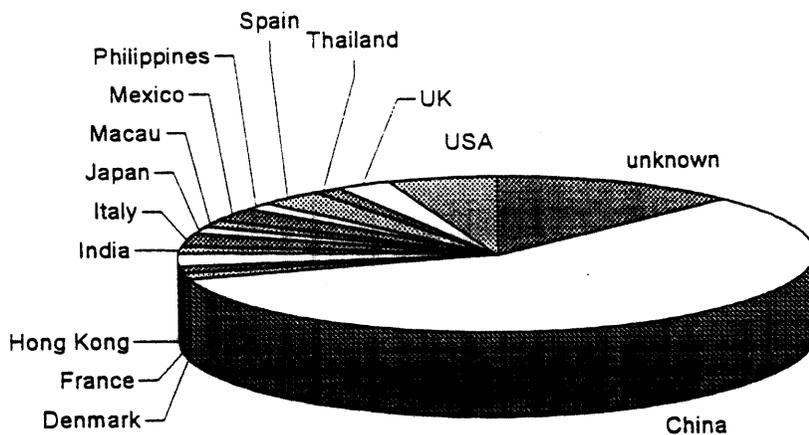
Approximately 1 g of each section (weight accurately recorded in each case) was transferred to a glass bottle and shaken with a known volume of hexane, followed by sonication for 30 minutes to improve contact between solvent and sample. The solvent fraction was decanted off, fresh solvent added and the process repeated. The two

solvent fractions were combined, evaporated or diluted to a known volume and analysed using a Hewlett Packard GC/MS (gas chromatograph/mass spectrometer), operated in scan mode. Phthalates were identified according to their retention times and mass spectra using standards obtained both from laboratory suppliers, and commercial producers/suppliers as reference. Concentrations of individual phthalates in the toys or toy sections were determined using calibrations prepared using these standards.

Extraction and analytical procedures were carefully quality controlled. QC procedures and acceptance criteria were based on USEPA method 606 for the analysis of phthalates in water samples (EPA 1984).



**Figure 1. Distribution of the toys analysed according to country of purchase**



**Figure 2. Distribution of the toys analysed according to country of manufacture**

Laboratory Code	Bought in:	Made in:	Description
6001	USA	China	Teether
6002	USA	China	Doll
6004	USA	China	Teether
6005	USA	USA	Teether
6006	Netherlands	China	Plastic duck
6008	Netherlands	China	Baby book
6013	Sweden	China	Vinyl ball
6014	Sweden	China	Vinyl ball
6015	Spain	China	Animal toy
6016	UK	China	Teether
6018	UK	USA	Teether
6020	Spain	China	Teether
6022	UK	UK	Teether
6023	Australia	China	Teether
6024	Australia	not known	Teether
6025	Australia	China	Teether
6026	Australia	China	Teether
6027	Australia	China	Teether
6028	Japan	Honk Kong	Aeroplane
6032	France	France	Bath toy
6033	Australia	China	Teether
6034	Australia	China	Teether
6035	Denmark	Macau	Doll
6036	France	Mexico	Teether
6038	Denmark	Denmark	Teether
6039	Japan	Japan	Doll
6040	Japan	China	Toy food
6041	Austria	Italy	Teether
6042	Austria	Italy	Teether
6043	UK	not known	Rings on a stick
6044	UK	China	Animal toy
6045	UK	China	Animal toys
6046a	UK	China	Gift set - star
6046b	UK	China	Gift set - head
6046c	UK	China	Gift set - squeeze bulb
6047	USA	China	Teether
6048	USA	China	Baby book
6049	Belgium	China	Teether
6050	Belgium	China	Baby book
6051	Belgium	Spain	Nasal aspirator
6052	Belgium	Spain	Teether
6053	Belgium	China	Baby book
6054	India	not known	Teether
6055	India	not known	Teether
6056	India	not known	Animal toy
6057	India	India	Doll
6061	India	not known	Inflatable toy
6063	Canada	China	Bracelet doll's house
6064	Canada	China	Inflatable toy
6065	Argentina	China	Animal toy
6067	Argentina	China	Teether
6068	Argentina	Mexico	Teether
6069	Argentina	China	Animal toy
6071	Argentina	not known	Animal toy
6072	Netherlands	China	Doll

Table 1: Description of toys analysed (continued over)

Laboratory Code	Bought in:	Made in:	Description
6073	Netherlands	Thailand	Animal toy
6078	Indonesia	China	Teether
6081	Indonesia	not known	Teether
6083	Germany	Hong Kong	Teether
6085	Germany	China	Bath toy
6086	Germany	China	Bath toy
7001	Philippines	China	Teether
7002	Philippines	USA	Teether
7005	Philippines	China	Toy food
7006a	Philippines	China	Bath toy - clam
7006b	Philippines	China	Bath toy - frog
7007	Philippines	USA	Teether
7008	Philippines	UK	Teether
7009	Philippines	not known	Teether
7010	Philippines	China	Teether
7011	Philippines	Philippines	Teether
7012	Philippines	China	Inflatable toy
7013a	Canada	China	Key teether - soft section
7013b	Canada	China	Key teether - hard section
7013c	Canada	China	Key teether - hard ring
7014	Canada	China	Animal toy

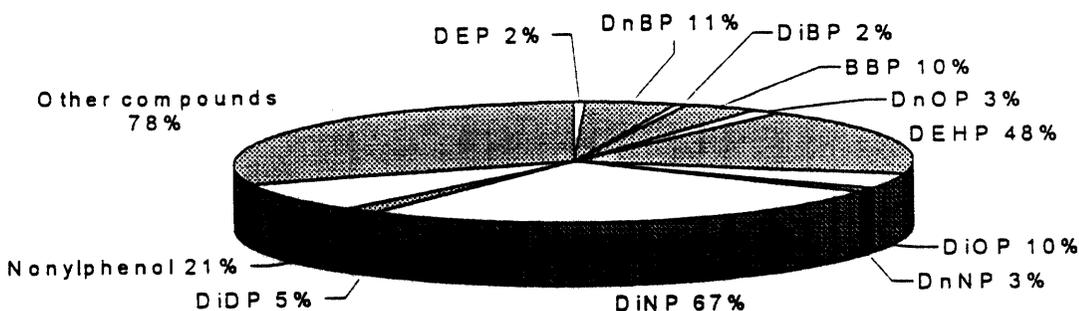
**Table 1: Description of toys analysed, with country of purchase and of origin**

During the initial phase of the survey the following phthalates were quantified: DEP (diethyl phthalate), DnBP (di-n-butyl phthalate), DiBP (diisobutyl phthalate), BBP (benzylbutyl phthalate), DEHP (di(ethylhexyl) phthalate) and DINP (diisononyl phthalate). Other phthalates and alkyl phenols were identifiable with mass spectral matching and comparison of retention times with target analytes. However, they were not quantifiable because of the non-availability of analytical standards. They are therefore reported in Table 2 as being detected but not quantified. For some samples, this precludes calculation of a figure for total phthalate concentration. Acquisition of further phthalate standards, development of methods and further Quality Control work allowed an extended range of compounds to be quantified during later analyses. Octyl and nonyl phenols were also quantified for later samples.

Sample 6044 presented difficulties for other reasons. The phthalates isolated corresponded with DINP based on retention time. However, the profile of the sample differed markedly from that of the standard, indicating a variation of composition sufficient to add a degree of uncertainty to the quantitation.

#### 4. Results.

Almost all toys, or subsections of toys, identified as PVC contained phthalate esters, with the majority in the range of 10-40% by weight (Table 2). Notable exceptions include 6068, 6078, 7008, 7009 and 7013b&c, which XRM analysis identified as PVC but did not contain phthalates. Samples 6068, 7013b and 7013c were hard, and so absence of plasticisers is understandable. Sample 7001, which contained only 0.004% phthalate was also hard PVC. Of the others, the identity of the plastic was uncertain in



**Figure 3. Frequency distribution for phthalates and other compounds in PVC toys. % indicates proportion of all PVC toys in which compound was found.**

6078, 7008 and 7009; XRM identified traces of chlorine at close to detection limits in these samples, yet their appearance and texture were more consistent with polyolefins (possibly polyethylene or polypropylene). Only one non-PVC toy contained phthalates (sample 6022). The trace concentrations of DEHP probably result from surface contamination from the packaging, a transparent plasticised PVC pouch, in which it was sold..

DINP was the phthalate most frequently found in toy samples and tended to be present in the highest concentrations. DEHP was the next most frequently found. Where present, isomeric phthalates generally comprised 10-40% of the weight of the toy, though the maximum recorded was over 50% DINP in a teether. This is in line with other studies on the phthalate content of children's products (Bragt 1997, Hanson 1983, 1985). Not infrequently, toys would contain high concentrations of DINP and traces of DEHP. This is most probably due to DEHP being present as an impurity in the DINP (Marsden 1996).

The isomeric phthalates DIOP (diisooctyl phthalate) and DIDP (diisodecyl phthalate) were found at concentrations in excess of 10 percent in a few samples and were present, but not quantified, in several others. The following phthalate esters were found at comparatively low concentrations in the toys in this study: DEP (0.16%) DnBP (0.002-0.18%), DiBP (0.45%), BBP (0.001-0.02%), DnOP (di-n-octyl phthalate, not quantified), DnNP (di-n-nonyl phthalate, not quantified). The distribution of phthalates and other compounds in the toys is shown in Figure 3.

Nonylphenol was detected in 13 toys (in both sections analysed for sample 7006), at concentrations, where quantified, of 0.009-0.36%. Octylphenol was not detected in any of the toys. A number of other compounds were isolated from some of the toys. Only a fraction of these could be identified reliably, including the fungicide Fungitrol 11 (found in samples 6069 and 6072), the antioxidant butylated hydroxytoluene (BHT, found in seven samples) and a range of long-chain paraffins (C10-C30, identified in 15 samples). More tentative identifications were obtained for esters of bis(2-ethylhexyl) adipate (DEHA, five samples), esters of phosphonic and propanoic acid, alkyl benzenes and derivatives of phenol and butyric acid. No further attempts were made to confirm identities or quantify these additional compounds.

Sample	PVC?	%DEP	%DnBP	%DiBP	%BBP	%DnOP	%DEHP	%DIOP	%DnNP	%DINP	%DiDP	Total % phthal.	% nonyl phenol
PH6001	Part	n/d	n/d	n/d	n/d	n/d	0.06	n/d	n/d	37.20	n/d	37.26	n/d
PH6002	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	8.80	n/d	8.80	n/d
PH6004	Part	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	35.67	n/d	35.67	n/d
PH6005	Part	n/d	n/d	n/d	n/d	n/q	n/d	n/d	n/q	n/d	n/d	n/q	n/d
PH6006	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	41.71	n/d	41.71	n/d
PH6008	Yes	n/d	n/d	n/d	n/d	n/d	0.16	n/d	n/d	16.36	n/d	16.52	n/d
PH6013	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	24.03	n/d	24.03	n/d
PH6014	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	24.28	n/d	24.28	n/d
PH6015	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	32.52	n/d	32.52	n/d
PH6016	Part	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	37.23	n/d	37.23	n/d
PH6018	Yes	n/d	n/d	n/d	n/d	n/q	n/d	n/d	n/q	n/d	n/d	n/q	n/d
PH6020	Part	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	36.32	n/d	36.32	n/d
PH6022	No	n/d	n/d	n/d	n/d	n/d	0.01	n/d	n/d	n/d	n/d	0.01	n/d
PH6023	No	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
PH6024	Part	n/d	n/d	n/d	n/d	n/d	n/d	n/q	n/d	n/d	n/d	n/q	n/d
PH6025	Part	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	31.69	n/d	31.69	n/d
PH6026	No	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
PH6027	No	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
PH6028	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	33.08	n/d	33.08	n/d
PH6032	Yes	n/d	n/d	n/d	n/d	n/d	35.54	n/d	n/d	n/d	n/d	35.54	n/d
PH6033	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	27.74	n/d	27.74	n/d
PH6034	No	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
PH6035	No	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
PH6036	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/q	n/d	n/d	n/d	n/q	n/d
PH6038	Yes	0.16	n/d	n/d	n/d	n/d	1.62	n/d	n/d	30.56	n/d	32.35	n/d
PH6039	Yes	n/d	n/d	n/d	n/d	n/d	15.37	n/d	n/d	n/d	n/d	15.37	n/d
PH6040	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	17.39	n/d	17.39	n/d

Table 2, page 1 of 3. Quantities of phthalate esters and alkyl phenols detected in children's toys.

Sample	PVC?	% DEP	% DnBP	% DIBP	% BBP	% DnOP	% DEHP	% DiOP	% DnNP	% DINP	% DIDP	Total % phthal.	% nonyl phenol
PH6041	Yes	n/d	0.18	n/d	n/d	n/d	n/d	n/d	n/d	35.28	n/d	35.46	n/d
PH6042	Yes	n/d	0.04	n/d	n/d	n/d	n/d	n/d	n/d	34.61	n/d	34.65	n/d
PH6043	No	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
PH6044	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	31*	n/d	31*	n/q
PH6045	Part	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	30.44	n/d	30.44	n/d
PH6046a	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	30.74	n/d	30.74	n/d
PH6046b	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	23.39	n/d	23.39	n/d
PH6046c	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	13.14	n/d	13.14	n/d
PH6047	Part	n/d	n/d	n/d	n/d	n/d	n/d	n/q	n/d	n/d	n/d	n/q	n/q
PH6048	Part	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	14.75	n/d	14.75	n/d
PH6049	Part	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	29.16	n/d	29.16	n/d
PH6050	Yes	n/d	n/d	n/d	n/d	n/d	0.06	n/d	n/d	19.61	n/d	19.67	n/d
PH6051	Yes	n/d	n/d	n/d	n/d	n/d	25.66	n/d	n/d	n/d	n/d	25.66	n/d
PH6052	No	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
PH6053	Yes	n/d	n/d	n/d	n/d	n/d	0.05	n/d	n/d	23.23	n/d	23.28	n/d
PH6054	Part	n/d	n/d	n/d	n/d	n/d	0.78	n/d	n/d	n/d	n/d	0.78	n/d
PH6055	Yes	n/d	n/d	n/d	n/d	n/d	11.36	n/d	n/d	n/d	n/d	11.36	n/d
PH6056	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/q	n/d	n/d	n/q	n/q	n/d
PH6057	Yes	n/d	0.02	0.45	n/d	n/d	n/d	n/d	n/d	n/d	n/d	0.46	n/d
PH6061	Yes	n/d	n/d	n/d	n/d	n/d	13.85	n/d	n/d	n/d	n/d	13.85	n/d
PH6063	Part	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	24.35	n/d	24.35	n/d
PH6064	Yes	n/d	n/d	n/d	n/d	n/d	0.042	n/d	n/d	19.58	n/d	19.622	n/d
PH6065	Yes	n/d	n/d	n/d	n/d	n/d	0.06	n/d	n/d	33.52	n/d	33.58	0.15
PH6067	Part	n/d	n/d	n/d	n/d	n/d	0.1	n/d	n/d	n/d	20.13	20.23	n/d
PH6068	Part	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	0.009
PH6069	Yes	n/d	n/d	n/d	n/d	n/d	0.04	n/d	n/d	43.94	n/d	43.98	0.34

Table 2, page 2 of 3. Quantities of phthalate esters and alkyl phenols detected in children's toys.

Sample	PVC?	% DEP	% DnBP	% DiBP	% BBP	% DnOP	% DEHP	% DiOP	% DnNP	% DINP	% DIDP	Total % phthal.	% nonyl phenol
PH6071	Yes	n/d	n/d	n/d	n/d	n/d	0.006	n/d	n/d	37.72	n/d	37.726	n/d
PH6072	Part	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	46.34	n/d	46.34	n/d
PH6073	Yes	n/d	n/d	n/d	n/d	n/d	0.09	n/d	n/d	37.92	n/d	38.01	0.17
PH6078	Part	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
PH6081	Yes	n/d	0.003	n/d	0.01	n/d	0.03	10.23	n/d	n/d	n/d	10.273	n/d
PH6083	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	37.6	n/d	37.6	n/d
PH6085	Yes	n/d	0.004	n/d	n/d	n/d	0.02	n/d	n/d	25.51	n/d	25.534	0.07
PH6086	Yes	n/d	0.003	n/d	n/d	n/d	0.022	n/d	n/d	26.27	n/d	26.295	0.067
PH7001	Part	n/d	n/d	n/d	n/d	n/d	0.004	n/d	n/d	n/d	n/d	0.004	0.024
PH7002	Yes	n/d	n/d	n/d	0.02	n/d	0.34	17.08	n/d	n/d	n/d	17.44	0.02
PH7005	Part	n/d	n/d	n/d	n/d	n/d	0.01	n/d	n/d	44.09	n/d	44.1	0.02
PH7006A	Yes	n/d	n/d	n/d	n/d	n/d	0.003	n/d	n/d	44.75	n/d	44.753	0.36
PH7006B	Yes	n/d	n/d	n/d	n/d	n/d	0.02	n/d	n/d	43.8	n/d	43.82	0.36
PH7007	Yes	n/d	n/d	n/d	n/d	n/d	0.005	n/d	n/d	n/d	15.72	15.725	n/d
PH7008	Part	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
PH7009	Yes	n/d	n/d	n/d	0.004	n/d	0.05	n/d	n/d	50.99	n/d	51.044	n/d
PH7010	Part	n/d	0.002	n/d	0.004	n/d	0.008	n/d	n/d	37.86	n/d	37.874	n/d
PH7011	Yes	n/d	n/d	n/d	n/d	n/d	16.72	n/d	n/d	0.396	n/d	17.116	n/d
PH7012	Yes	n/d	n/d	n/d	0.004	n/d	0.238	n/d	n/d	38.09	n/d	38.332	n/d
PH7013A	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	0.021
PH7013B	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
PH7013C	Yes	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d
PH7014	Yes	n/d	n/d	n/d	0.001	n/d	0.043	n/d	n/d	35.86	n/d	35.904	n/d

Table 2, Page 3 of 3. Quantities of phthalate esters and alkyl phenols detected in children's toys. Where a toy is recorded as being part PVC, a PVC subsection was analysed. n/d : not detected. n/q : detected but not quantified. \* : uncertainty in quantification due to disparity between sample and analytical standards. abbreviations for phthalates are as follows: DEP diethyl phthalate; DnBP di-n-butyl phthalate; DiBP diisobutyl phthalate; BBP butyl benzyl phthalate; DnOP di-n-octyl phthalate; DEHP di(ethylhexyl)phthalate; DiOP diisooctyl phthalate; DnNP di-n-nonyl phthalate; DINP diisononyl phthalate; DIDP diisodecyl phthalate; Total % phthal. -- sum of all phthalates present, expressed as a percentage of the total weight of the toy; % nonylphenol -- nonylphenol concentration as a percentage of the total weight of the toy.

## 5. Discussion

This study was targeted at plasticised PVC toys and so does not cover the entire range of toys on sale. Nevertheless, some trends were evident. The majority of toys received were made wholly or partly of PVC, though the plastic was only infrequently identified on the packaging. All inflatable toys, bath toys, and baby books received consisted of phthalate-plasticised PVC. Squeeze toys, which appeared in a number of categories, were also consistently phthalate-plasticised PVC. Other categories were less consistent. One other notable fact is that most of the toys were manufactured in China. A full breakdown of the country of manufacture of toys is given in Figure 2.

Contrary to initial expectations, DEHP was not the most commonly used phthalate. In a report prepared for the US Consumer Product Safety Commission in 1983 (Hanson 1983), DEHP was the only phthalate identified in eleven of fourteen children's products analysed. It was also the focus of the study by Meek and Chan (1994). However, in the current study, DINP (diisononyl phthalate), a mixture of 30 or more isomers of dinonyl phthalate, was the most common form identified, although other, long-chain, isomeric mixtures were also isolated. This reflects a market shift away from DEHP towards the use of the much more poorly characterised isomeric phthalates. This is especially true in China, the origin of the majority of the toys analysed.

As, historically, the most commonly used phthalate in PVC was DEHP, the majority of toxicological and other research on the phthalates has been carried out on this compound. Initially assessed as having fairly low toxicity, based on acute exposure studies in laboratory animals, it is now recognised that DEHP can exert a number of chronic toxic effects following longer exposures and may be an important reproductive poison, (Life Systems, Inc., 1993). More recently concern has been raised about the ability of DEHP and some other phthalates to interact with hormone receptors in animals. Jobling and coworkers (1995) demonstrated that DEHP was able to bind to the human estrogen receptor, although it showed no significant estrogenic activity. Its potential to interfere with other aspects of the hormone system has not been fully investigated.

Concern over the toxicity of DEHP has led to its being used less frequently in food contact materials (e.g. PVC foodwrap). Nevertheless, this does not extend to consumer products in general, although direct exposure may be a very significant source. At the same time, the trend away from DEHP use appears to have led, in many cases, simply to replacement with other phthalates, including isomeric mixtures of phthalates such as DIOP, DINP, and DIDP.

The market shift to DINP may be a response to serious concerns relating to the suspected reproductive toxicity and other hazards associated with DEHP. Although less extensively studied, data currently available for DINP suggest that this isomeric phthalate may also carry many of the hazards associated with DEHP, impacting similar target organs in chronic studies (especially the liver, kidney and reproductive tracts) as DEHP. DINP, for example, has been shown to exhibit a range of toxic effects in laboratory animals. There is, therefore, little reason to assume that isomeric phthalates present less of a potential hazard.

Furthermore, the formulations of technical mixes will tend to vary in composition in a similar fashion to technical mixes of, for example, the PCBs. This will greatly complicate analytical procedures and toxicological testing. Pure standards will not be available for the individual components of these mixes for the foreseeable future, so it will not be possible to determine their relative concentrations within any product. Variation between batches and the contamination of commercial and industrial mixes with other phthalates, or even other

compounds, is frequently noted (*e.g.* see Harris *et al.* 1997). It is recognised, for example, that technical preparations of DINP may contain smaller quantities of DEHP as a contaminant of the manufacturing process (Marsden, 1996). This could account for the DEHP reported in some of the toys in this study in which DINP was the dominant phthalate. Similarly, some isomers will be expected to exhibit the greater persistence and/or toxicity than others. Until each component has been characterised, purified and tested, these isomeric mixes will continue to present an unquantifiable risk.

Much of the existing data on the toxicity of DINP has been collated by the Swedish National Chemicals Inspectorate (KEMI 1994) and by the European Commission under the IUCLID initiative (European Chemicals Bureau 1996). Additional data is available from the US EPA (Myers 1991, USEPA 1991 & 1992) and from the Aristech Chemical Safety Information Database (Aristech 1995).

A wide range of toxic effects has been recorded in mammals following acute and chronic laboratory exposures (KEMI 1994). Some, such as stress and damage to the liver, kidney, stomach and other organs and effects on blood and urine biochemistry (European Chemicals Bureau 1996, Myers 1991, USEPA 1991 & 1992), appear to be characteristic of many of the phthalates tested to date. Long-term exposure to DINP has been linked to gross changes in organ and body development in rodents. In addition, exposure to DINP appears to increase the incidence of certain cancers in rats, including liver, testicular and endometrial tumours, and lead to reduced survival from mononuclear cell leukaemia (MCL) (Aristech 1995, KEMI 1994). Structural and functional changes in development of reproductive organs have also been reported following chronic exposure to DINP (European Chemicals Bureau 1996, Myers 1991, USEPA 1991), as well as some evidence for an increase in frequency of deformed and non-motile sperm in rats (USEPA 1992).

In some of the studies described above, a No-Observed-Effect-Concentration of DINP could not be determined, *i.e.* significant toxicological or developmental effects were observed even at the lowest doses used (Myers 1991). In addition, it is worth noting that the relatively low acute and chronic toxicity often reported for DINP to aquatic organisms (Adams *et al.* 1995, Rhodes *et al.* 1995) may simply result from the poor water solubility of the compound.

As for DEHP, the ability of DINP and other isomeric phthalates, or their metabolites, to interact with hormone systems has not been properly investigated. Nevertheless, recent research by Harris *et al.* (1997) demonstrated that DINP can show weak estrogenic activity in the human breast cancer cell line ZR-75, although inconclusive results were obtained from yeast screen assays.

Understandably, as for most chemicals, very little information exists on the effects of DINP on humans. Nevertheless, a single case study (attributed to BASF) refers to chronic skin irritation in a child exposed to DINP. Further details, including the route of exposure, are not available (European Chemicals Bureau 1996).

Despite the recognised hazards associated with DINP and, indeed, with the other phthalates identified in this study, children's toys that contain high percentage compositions of phthalates are not labelled accordingly. The information available on packaging of PVC toys which may comprise more than 40% phthalate by weight is in stark contrast to that supplied when phthalates are purchased as chemicals for laboratory use. This is illustrated by the contrast between the risk and safety information that must be followed when handling DINP in the laboratory and the labelling on a toy. A typical toy comprising 41% by weight DINP (6006) was simply labelled "non-toxic". However, under EU legislation (directive 67/548 As amended) DINP purchased for laboratory use bears the following risk and safety phrases:

*R45 – may cause cancer*

*R20/21/22 - harmful by inhalation, in contact with skin and if swallowed*

*R40 - possible risk of irreversible effects*

*S53 - avoid exposure, obtain special instructions before use*

*S45 - in case of accident, or if you feel unwell, seek medical advice immediately*

*S36/37/39 - wear suitable protective clothing, gloves and eye/face protection*

*S3/7 - keep container tightly closed in a cool place*

Furthermore, DINP purchased in the USA must be accompanied by a material safety data sheet carrying the following warnings (Aristech 1995):

*SKIN CONTACT - excessive contact may produce mild irritation. Persons with pre-existing skin disorders may be more susceptible to dermatitis. Remove contaminated clothing. Wash skin thoroughly with soap and plenty of water. Call a physician.*

*INGESTION - may cause nausea, vomiting and diarrhea. The chronic health effects of this product have not been fully determined. Give 1-2 glasses of milk or water. Induce vomiting by sticking finger down the back of throat. Call a physician.*

The data from this investigation do not allow us to estimate the dose to which a child playing with any one toy will be exposed. As mentioned above, it is well recognised that DINP and other phthalates leach from PVC to the air, in to liquid solvents and on to the skin. The dose received by an individual child playing with a certain toy will depend on many factors, including phthalate composition and concentration, toy design and purpose, exposure time, method of play and degree of mouthing and chewing activity. Any estimates of dose would, therefore, be highly subjective. This was acknowledged by Meek and Chan (1994). These authors analysed teethers for DEHP and estimated exposure based on assumed leaching rates. They estimated that exposure to PVC teethers in children up to 4 years old could boost exposure of the average child to around 50% of the maximum tolerable daily intake for DEHP in Canada, but recognised that the range of individual exposures is probably extremely wide.

However, research carried out for the US Consumer Product Safety Commission (CPSC) in the early 1980s (US Directorate for Health Sciences, 1983) did attempt to estimate exposure through direct measurement of phthalate leaching under simulated use conditions. They estimated that a child could ingest 66-1055mg (milligrammes) of phthalates from toys, teethers and pacifiers. This was a total dose based on use of these products over 1-3 years. Exposure via skin contact with vinyl pants and playpen liners was also thought to contribute a significant dose; a further dose of over 200mg over two years according to one scenario.

More recently, a study carried out by the Danish EPA (Vinkelsoe *et al.* 1997) reported substantial leaching of a range of phthalates (including DEHP, DINP, BBP, DnBP and DnOP) from some PVC teethers, even under chemical and mechanical conditions which may be much milder than those to which the products are subjected under normal use. Since this study measured actual leaching rates, their dose estimates have greater precision than do those of Meek and Chan (1994). The Danish EPA concluded that the worst teether, soft vinyl sweets produced by Chicco, would give a child a dose of 2219ug (microgrammes) phthalates/kg body weight through chewing for three hours. This is more than 40 times the tolerable daily intake agreed for DINP by the European Commission's Scientific Committee for Food (SCF 1995). Over the same period, a second teether would provide a dose of 1044ug/kg of phthalates and a third 9ug/kg. The Danish EPA recommends that even the teether releasing 9ug/kg should be removed from the market as a precaution since a child actively chewing a teether would

extract more phthalates from the teether than the baths of artificial saliva used in the tests (MacKenzie 1997).

The Dutch government has also conducted similar tests (Bragt 1997), estimating that children sucking or biting toys over 4 months could be exposed to 1-2mg phthalate (DINP plus DIDP) per day. This compares with maximum background exposure from food sources of 0.18mg/day. The Dutch Institute for Public Health and Environment (RIVM) recommend a tolerable daily intake (TDI) of 0.15mg/kg body weight for DINP and 0.18mg/kg body weight for DIDP. Consequently, it is estimated that between 5% and 50% of babies chewing PVC teethers exceed the Dutch TDI for DINP. None exceeded the Dutch TDI for DIDP. The EC Scientific Committee on Foods (SCF 1995), however, has assigned temporary tolerable daily intakes (t-TDIs) to DINP and DIDP at lower levels (0.03 and 0.05mg/kg body weight respectively). Clearly, a greater proportion of children will be ingesting phthalates in excess of these t-TDIs. A full listing of the TDIs and t-TDIs published by the EC Scientific Committee for Foods are given in Table 3 below.

On the basis of their study, RIVM concluded that, although exposure presented no immediate danger to babies, negative effects could not be excluded. The Dutch Ministry of Health therefore asked that toy manufacturers and distributors make efforts to prevent unnecessary and undesirable exposure of babies to phthalates (Bragt 1997).

Whilst attention naturally focuses on those components which are present in, and leachable from, toys in the largest quantities, some of the minor components have also shown toxic effects in experimental systems.

DnBP was found in seven samples at a concentration range of 0.002-0.18%. It affects the liver and kidneys (Chan & Meek 1994 Life Systems, Inc. 1990) and the male and female reproductive systems in laboratory animals (Wine *et al.* 1997, Chan and Meek 1994). Reproductive success can be impaired (Wine *et al.* 1997, Chan & Meek 1994, Ema *et al.* 1995, Life Systems, Inc. 1990). Offspring may be malformed (Chan & Meek 1994, Ema *et al.* 1993, Ema *et al.* 1995), with reproductive function in male offspring compromised. DnBP has also been reported to mimic the hormone estrogen (Jobling *et al.* 1995).

BBP, which was found in six samples (concentration 0.001-0.02%), is also estrogenic (Jobling *et al.* 1995) and can reduce testicle size and sperm production in rats (Sharpe *et al.* 1995). It can have adverse effects on the female reproductive system (Ema *et al.* 1994) and may have the capacity to induce birth defects in animals (Chan & Meek 1994, Ema *et al.* 1993, Ema *et al.* 1995).

Compound name and abbreviation	TDI or t-TDI	mg/kg body wt.
diethyl phthalate (DEP)	t-TDI	0.2
dibutyl phthalate (DBP)	t-TDI	0.05
butyl benzyl phthalate (BBP)	t-TDI	0.1
di(2-ethylhexyl phthalate (DEHP)	TDI	0.025
diisononyl phthalate (DINP)	t-TDI	0.03
diisodecyl phthalate (DIDP)	t-TDI	0.05
discyclohexyl phthalate	t-TDI	0.1
phthalic acid diesters with hexadecanol and/or octadecanol	t-TDI	0.15

Table 3. EC tolerable daily intakes (TDIs) and temporary tolerable daily intakes (t-TDIs) for phthalates (SCF 1995)

DEP was found in one sample (6038; a teether from Denmark) at a concentration of 0.16% by weight. Under laws that relate to Superfund sites, the USEPA has identified DEP as a hazardous substance (Sciences International Incorporated 1995). It can damage the male reproductive system, reduce reproductive success and cause malformation of offspring. Effects on the liver and irritation of the eye have also been reported in laboratory studies (Sciences International Incorporated 1995).

Nonylphenol (NP) is a persistent chemical that has been found to mimic the hormone estrogen and impair sperm production in fish (Jobling *et al.* 1996). Its presence in the freshwater environment results principally from the breakdown of nonylphenol polyethoxylates (NPEs), still used as industrial detergents and as spreading agents in pesticides. Nevertheless, the direct use of nonylphenol as an additive in PVC (possibly as a stabiliser in phthalate formulations), could account for further releases, and may be of particular significance as a source of exposure in children. The toxicity of nonylphenol and related compounds led to a recommendation by the Paris Commission to phase out the use of NPEs in household and industrial detergents (PARCOM 1992). Sweden is expected to call for a binding decision to phase out all uses of NPEs which result in contamination of the environment (ENDS 1996), citing in particular the known estrogenicity of nonylphenol. With this in mind, applications that could lead to ingestion by children should clearly be a priority.

As noted above, a number of other compounds were isolated from some of the toys, many of which were identified only tentatively or not at all. Of those which were identified reliably, the fungicide Fungitrol 11 (samples 6069 and 6072) deserves further consideration. Fungitrol 11, also sold as Folpet, is a phthalimide fungicide. It is recognised as a skin irritant (Royal Society of Chemistry 1987) and is highly toxic to fish and aquatic invertebrates (Royal Society of Chemistry 1987; USEPA 1987b). It can also cause tumours in mice (USEPA 1987a&b), but not rats (USEPA 1987b). Teratogenicity has been reported for rats and rabbits (USEPA 1986, 1987b). Folpet is no longer sold in the United States (Thomson 1990).

PVC resin itself is not usually vulnerable to microbiological attack. However, the phthalate plasticisers may be more susceptible. As the fungicide was found in toys with over 40% by weight phthalate content, it could well be added with the intention of preventing microbiological attack on the plasticisers or other additives.

As the identities of the majority of other compounds isolated could not be confirmed, their toxicological significance cannot be determined. Nevertheless, it is probable that a proportion of these compounds will also leach from the toys as a result of chewing or other contact and could, therefore, add to the overall burden of chemicals to which children playing with PVC toys will be exposed.

## 6. Conclusions

The current survey is the widest conducted to date on the presence of phthalate esters and other components in children's toys. Despite the fact that children have been known to be exposed to phthalate from PVC toys for some years, and the continuing concern surrounding the toxicity of phthalate esters, PVC toys still routinely contain a significant proportion of phthalates. The observed market shift from DEHP to DINP and other high molecular weight isomeric phthalates is not reassuring.

Recent research, particularly that carried out by the Danish and Dutch governments, has heightened concerns about the exposure of children to phthalates leaching from toys. As a result of the concern these studies have generated, a number of PVC products have been

withdrawn from the market in Denmark, Sweden, Italy, Spain and Greece (ENDS 1997, Mackenzie 1997). Some toys have also been removed from sale in Argentina and the Netherlands. The results presented here indicate that the majority of soft PVC toys contain substantial proportions of phthalate esters that have the potential to leach out during use and therefore present an exposure risk to infants.

Given the vulnerability of the developing child to toxic insults, exposure to all toxic chemicals should be minimised. The results of this study indicate the potential for significant exposure to toxic chemicals from PVC toys. This must be regarded as an unacceptable risk and it is recommended that plasticised PVC and alkyl phenols should be withdrawn from use in all toys.

## 7. References

- Adams, W.J., Biddinger, G.R., Robillard, K.A. & Gorsuch, J.W. (1995) A summary of the acute toxicity of 14 phthalate esters to representative aquatic organisms. *Environ. Toxicol. Chem.* 14(9): 1569-1574
- Aristech (1995) Aristech Chemical Corporation Material Safety Data sheet C1084E. Product code 1564: Diisononyl phthalate.
- Bizarri, S.N., Jaeckel, M. & Yoshida, Y. (1996) Plasticizers. CEH Marketing Research Report. Publ: SRI International.
- Bragt, P.C. (1997) Personal communication.
- Cadogan, D.F., Papez, M., Poppe, A.C., Pugh, D.M. & Scheubel, J. (1993) IN: PVC 93: The Future. Publ: The Institute of Materials; pp260-274
- Chan, P.K.L. & Meek, M.E. (1994) Di-n-butyl phthalate: Evaluation of risks to health from environmental exposure in Canada. *Environ. Carcino. & Ecotox. Revs.* C12(2): 257-268
- Dirven, H.A.A.M., van den Broek, P.H.H., Arends, A.M.M., Nordkamp, H.H., de Lepper, A.J.G.M., Henderson, P.Th. & Jongeneelen, F.J. (1993) Metabolites of the plasticizer di(2-ethylhexyl)phthalate in urine samples of workers in polyvinylchloride processing industries. *Int. Arch. Occup. Environ. Health* 64: 549-554
- DoE (1991) Environmental hazard assessment: Di(2-ethylhexyl)phthalate. Report TSD/2 Publ: United Kingdom Department of the Environment Toxic Substances Division. 51pp.
- Eberle, S. (1983) Di(2-ethylhexyl)phthalate: An assessment of the risk of cancer due to exposure from children's products. U.S. Consumer Product Safety Commission.
- ENDS (1996) Sweden pushes for phase-out of oestrogens in pesticides. ENDS Report 260, September 1996, P 40.
- ENDS (1997) Fresh squeeze on PVC industry over phthalates in baby products. ENDS Report 268. May 1997, p 30.
- European Chemicals Bureau (1996) IUCLID: International Uniform Chemical Information Database. Existing Chemicals- 1996. Edition 1.
- Ehrig, R.J. (Ed.) (1992) *Plastics recycling. Products and Processes.* Publ: Hanser Publishers, Munich, 289pp.
- Ema, M., Itami, T. & Kawasaki, H. (1993) Teratogenic phase specificity of butyl benzyl phthalate in rats. *Toxicology* 79: 11-19

- Ema, M., Kurosaka, R., Amano, H. & Ogawa, Y. (1994) Embryo lethality of butyl benzyl phthalate during early pregnancy in rats. *Reprod. Toxicol.* 8(3): 231-236
- Ema, M., Kurosaka, R., Amano, H. & Ogawa, Y. (1995) Comparative developmental toxicity of n-butyl benzyl phthalate and di-n-butyl phthalate in rats. *Arch Environ. Contam. Toxicol.* 28: 223-228
- EPA (1984) Method 606- Phthalate ester. *Federal Register* 49(209): 73-80
- Hanson, R.L. (1983) Phthalate ester migration from polyvinyl chloride consumer products. Phase I final report. Report prepared for the US Consumer Product Safety Commission, 51pp
- Hanson, R.L. (1985) Phthalate ester migration from polyvinyl chloride consumer products. Task II final report. Report prepared for the US Consumer Product Safety Commission, 51pp
- Harris, C.A., Henttu, P., Parker, M.G., & Sumpter, J.P. (1997). The estrogenic activity of phthalate esters *in vitro*. *Environmental Health Perspectives* 105(8):
- Jobling, S., Reynolds, T., White, R., Parker, M.G. & Sumpter, J.P. (1995) A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic. *Environmental Health Perspectives* 103(6): 582-587
- Jobling, S., Sheahan, D., Osborne, J.A., Matthiessen, P. & Sumpter, J.P. (1996) Inhibition of testicular growth in rainbow trout (*Oncorhynchus mykiss*) exposed to estrogenic alkylphenolic chemicals. *Environ. Toxicol. Chem.* 15(2): 194-202
- Kemi (1994) Phthalic acid esters used as plastic additives. Publ: Swedish National Chemicals Inspectorate; report 12/94, ISSN 0248-1185
- Life Systems, Inc. (1990) Di-n-butylphthalate. Publ: US DEPARTMENT OF HEALTH AND HUMAN SERVICES Public Health Service Agency for Toxic Substances and Disease Registry
- Life Systems, Inc. (1993) Di (2-ethylhexyl) phthalate. Publ: US DEPARTMENT OF HEALTH AND HUMAN SERVICES Public Health Service Agency for Toxic Substances and Disease Registry
- MacKenzie, D. (1997) Alarm sounds over toxic teething rings. *New Scientist* Vol 154, No. 2086, 14 June 1997, p10.
- Marsden, D. (Aldrich chemical company) (1996) Personal Communication.
- Meek, M.E. & Chan, P.K.L. (1994) bis(2-ethylhexyl)phthalate: Evaluation of risks to health from environmental exposure in Canada. *Environ. Carcin. & Ecotox. Revs.* C12(2): 179-194
- Myers, B.A. (1991) 13-week subchronic dietary oral toxicity study with di(isononyl)phthalate in Fischer 344 rats (final report) with cover letter dated 05-20-92: Supplemental information. Hazelton Laboratories, Washington. EPA/OTS Doc # 89-920000224.
- PARCOM (1992) Recommendation 92/8 on Nonylphenol-Ethoxylates. Paris Commission, September 1992.
- Rhodes, J.E., Adams, W.E., Biddinger, G.R., Robillard, K.A. & Gorsuch, J.W. (1995) Chronic acute toxicity of 14 phthalate esters to *Daphnia magna* and rainbow trout (*Oncorhynchus mykiss*). *Environ. Toxicol. Chem.* 14(11): 1967-1976
- Royal Society of Chemistry (1987) *The Agrochemicals Handbook*. Second Edition. Publ: Royal Society of Chemistry, Nottingham UK.
- SCF (1995) First report of the Scientific Committee for Food on certain additives used in the manufacture of plastic materials intended to come into contact with foodstuffs. (Opinions expressed until 3 May 1992). European Commission. Food Science and Techniques. Reports of the Scientific Committee for Food (33<sup>rd</sup> Series). Directorate-General for Industry.
- Sciences International Incorporated (1995) Diethyl phthalate Publ: U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICE Public Health Service Agency for Toxic Substances and Disease Registry

Sharman, M., Read, W.A., Castle, L. & Gilbert, J. (1994) Levels of di-(2-ethylhexyl)phthalate and total phthalate esters in milk, cream, butter and cheese. *Food Additives and Contaminants* 11(3): 375-385

Sharpe, R.M., Fisher, J.S., Millar, M.M., Jobling, S. & Sumpter, J.P. (1995) Gestational and lactational exposure of rats to xenoestrogens results in reduced testicular size and sperm production. *Environmental Health Perspectives* 103(12): 1136-1143

Thomson, W.T. (1990) *Agricultural Chemicals. Book IV: Fungicides.* Thomson Publications, Fresno, CA.

US Directorate of Health Sciences (1983) *Children's chemical hazards: carcinogenic risk assessment from consumer exposure to di(2-ethylhexyl)phthalate (DEHP)*

USEPA (1986) *TOX One-liners* USEPA Office of Pesticides

USEPA (1987a) *Guidance for the reregistration of pesticide products containing folpet as the active ingredient.* USEPA Office of Pesticide Programs, Washington DC.

USEPA (1987b) *Pesticide Factsheet number 215: Folpet.* USEPA Office of Pesticide Programs, Washington DC.

USEPA (1991) *Subchronic (4-week) dietary oral toxicity study of di(isononyl)phthalate in B6C3F1 mice (final report) with cover sheet dated 05-29-91.* Hazelton Laboratories, Washington. EPA/OTS Doc # 86-910000793

USEPA (1992) *13-week subchronic dietary oral toxicity study with di(isononyl)phthalate in mice, with cover letter dated 07-06-92 and attachments: supplement.* American College of Veterinary Pathology. EPA/OTS Doc # 89-920000303.

Vinkelsoe, K., Jensen, G.H., Johansen, E., Carlsen, L. & Rastogi, S.C. (1997) *Migration of phthalates from teething rings.* Danish EPA, 15-4-97.

Wine, R.N., Li, L.-H., Barnes, L.H., Gulati, D.K. & Chapin, R.E. (1997) *Reproductive toxicity of di-n-butylphthalate in a continuous breeding protocol in Sprague-Dawley rats.* *Environ. Health Persp.* 105(1): 102-107

## DETAILS OF TOYS TESTED BY GREENPEACE

Laboratory code	Bought in:	Made in:	Manufacturer/distributor	Product name	Product number	Description
6001	USA	China	Safety 1st Inc	Soft'n Munch Dessert Teether	-	Teether
6002	USA	China	Child Dimension/Hasbro	Barney Fun Time Baby Bop	-	Doll
6004	USA	China	Safety 1st Inc	Sof'Sport Teether	-	Teether
6005	USA	USA	Safety 1st Inc	Sports Fun Water Teether	-	Teether
6006	Netherlands	China	ToysWorld/CE Family Shop	Plastic Bath Ducks	-	Plastic duck
6008	Netherlands	China	CE Family Shop	Baby's First Picture Book	635	Baby book
6013	Sweden	China	CE Toyman AB	Vinyl Leksak (yellow)	01-001	Vinyl ball
6014	Sweden	China	CE Toyman AB	Vinyl Leksak (orange)	01-007	Vinyl ball
6015	Spain	China	Chicco/Artisana S.p.A.	Soft Animals (bear)	-	Animal toy
6016	UK	China	The First Years/Kiddies Products	Hard'n Soft fruits	2028	Teether
6018	UK	USA	The First Years/Kiddies Products	Cool Animal Teether	1412	Teether
6020	Spain	China	Chicco/Artisana S.p.A.	Greedy Teething Ring	65338	Teether
6022	UK	UK	The Boots Co PLC	Dolphin Cooling Teether	16-21-017	Teether
6023	Australia	China	Rainsfords Ply Ltd	Cooling Gum Soother	4531	Teether
6024	Australia	not known	Playskool Baby Inc/Hasbro	Teething Ring	-	Teether
6025	Australia	China	Safety 1st Inc	SoiKey Teething Ring	-	Teether
6026	Australia	China	Tommee Tippee/Jackel Int Ltd	Rattle Teether	-	Teether
6027	Australia	China	Remco Baby, Azrak-Hamway Int'l	Infant Play Teething Toy	-	Teether
6028	Japan	Honk Kong	Combi Co. Ltd	not known	-	Aeroplane
6032	France	France	CE Vullfi SA	Bath Toys (Fish)	523200	Bath toy
6033	Australia	China	Tommee Tippee/Int'l Brands Ltd	Squeakee-Teether	405259	Teether
6034	Australia	China	Tommee Tippee/Int'l Brands Ltd	Cooling Teether	403159	Teether
6035	Denmark	Macau	AS Mega Trading/Mentorn films	Space Precinct - Officer Took	-	Doll
6036	France	Mexico	Playskool Baby Inc/Hasbro	Animo Dentition	-	Teether
6038	Denmark	Denmark	Top-Toy AS	Hand og Fod Baby	143 103	Teether
6039	Japan	Japan	Bandai Co. Ltd	not known	-	Doll
6040	Japan	China	Toyroyal/Royal Co Ltd	Plastic Cream Cake	-	Toy food
6041	Austria	Italy	Chicco/Artisana Spa	Golosoni Teething Toys	64160.0	Teether
6042	Austria	Italy	Chicco	Baby Fruits	63151	Teether
6043	UK	not known	Fisher-Price/Mattel	Stack Rings	-	Rings on a stick
6044	UK	China	Disney/Arco Toys/Mattel	Silbiditos Tiger ("Tigger")	66600	Animal toy

Full details of toys analysed, with country of purchase and country of origin, Page 1 of 3

Laboratory code	Bought in:	Made in:	Manufacturer/distributor	Product name	Product number	Description
6045	UK	China	Hasbro	Pig and Cow Weebles	12084	Animal toys
6046a	UK	China	Disney/Arco Toys Ltd/Mattel	Infant Gift Set (star)	-	Gift set
6046b	UK	China	Disney/Arco Toys Ltd/Mattel	Infant Gift Set (head)	-	Gift set
6046c	UK	China	Disney/Arco Toys Ltd/Mattel	Infant Gift Set (squeeze bulb)	-	Gift set
6047	USA	China	Playskool Baby Inc/Hasbro	Funny Face Teether Rattle, Disney Babies Mickey Coll.	-	Teether
6048	USA	China	Playskool Baby Inc/Hasbro	Teether Album, Disney Babies Mickey Coll.	-	Baby book
6049	Belgium	China	Luv n'Care Ltd	Disney Babies Chew Pal	-	Teether
6050	Belgium	China	Luv n'Care Ltd	Disney Babies Play Book	201	Baby book
6051	Belgium	Spain	Kyko	Baby Nasal Aspirator	-	Nasal aspirator
6052	Belgium	Spain	Kyko	Educational Teething Rattle	-	Teether
6053	Belgium	China	De Ballon Oostmalle/Almere Haven	De Ballon Mijn Badvriendjes	-	Baby book
6054	India	not known	Shishu Products	Water Teether	-	Teether
6055	India	not known	Shishu Products	First Fruit Teether	-	Teether
6056	India	not known	Funskool Baby Toys/Hasbro	Sporty Squeaks	-	Animal toy
6057	India	India	Rajesh Toys	Vinyl Doll	-	Doll
6061	India	not known	Not known	not known	-	Inflatable toy
6063	Canada	China	Polly Pocket/Mattel	Polly Loves Puppy	14499	Bracelet doll's house
6064	Canada	China	Child Dimension	Peek'n Play Barrel (Barney)	29730	Inflatable toy
6065	Argentina	China	Disney/Mattel	Baby Donald Squeak'n Fun	66997, Ast 65363	Animal toy
6067	Argentina	China	Babelito	Mordillo Osito (red bear)	37133	Teether
6068	Argentina	Mexico	Disney/Playskool/Hasbro	First Rattle	5106	Teether
6069	Argentina	China	Disney/Mattel	Squirt'n Splash Elephant Lion King, Jungle Friend Babies	11676	Animal toy
6071	Argentina	not known	not known	Vinyl Toy (duck)	-	Animal toy
6072	Netherlands	China	Barbie/Mattel	Barbie	15611	Doll
6073	Netherlands	Thailand	Dick Bruna/Sega Preschool	Miffy Squeak	2019	Animal toy
6078	Indonesia	China	Chicco	Orange Teether	64970	Teether
6081	Indonesia	not known	Disney	Gum Cooler	5085	Teether
6083	Germany	Hong Kong	Disney/Luv'n'Care	Teether	-	Teether

Full details of toys analysed, with country of purchase and country of origin, Page 2 of 3

Laboratory code	Bought in:	Made in:	Manufacturer/distributor	Product name	Product number	Description
6085	Germany	China	Shelcore	Vinyl Duck (small)	-	Bath toy
6086	Germany	China	Shelcore	Vinyl Duck (large)	-	Bath toy
7001	Philippines	China	Disney/Luv'n'Care	Coolbite Teether	301WD, 961223	Teether
7002	Philippines	USA	Baby World	Orthodontic Pacifiers	-	Teether
7005	Philippines	China	Shelcore	Cool Cone Teether	02306	Toy food
7006a	Philippines	China	Shelcore	Bathtime Squirties (clam)	72036	Bath toy
7006b	Philippines	China	Shelcore	Bathtime Squirties (frog)	72036	Bath toy
7007	Philippines	USA	Safety 1st Inc	Sports Fun Water Teether	286	Teether
7008	Philippines	UK	Tomme Tippee/Jackel Int'l	Cooling Teether	436003	Teether
7009	Philippines	not known	Tomme Tippee/Jackel Int'l	Cooling Teether	-	Teether
7010	Philippines	China	Safety 1st Inc	Teethersaurus	144	Teether
7011	Philippines	Philippines	Evenflo/Sahara Corp	Soothing Teether	-	Teether
7012	Philippines	China	Not known	Bananas in Pyjamas	-	Inflatable toy
7013a	Canada	China	Nursery Needs/Sanitoy	Soft Teether Keys (soft)	173-Z	Teether
7013b	Canada	China	Nursery Needs/Sanitoy	Soft Teether Keys (hard)	173-Z	Teether
7013c	Canada	China	Nursery Needs/Sanitoy	Soft Teether Keys (ring)	173-Z	Teether
7014	Canada	China	Gerber	Squeeze Toy (rabbit)	46207	Animal toy

Full details of toys analysed, with country of purchase and country of origin, Page 3 of 3

**National Environmental Trust**  
1200 18th St. NW • Suite 500 • Washington, DC 20036

Office of the Secretary  
Consumer Product Safety Commission  
4330 East West Highway  
Bethesda, MD 20899

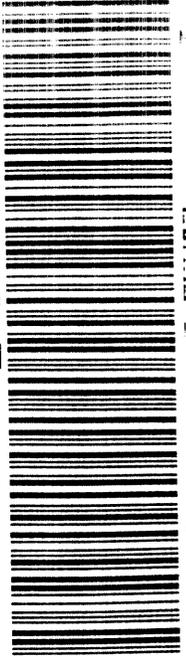
FedEx

TRK# 8043 5096 3168  
FORM 0210

20 NOV 97

IAD

20814 -MD-US  
19 GAIA



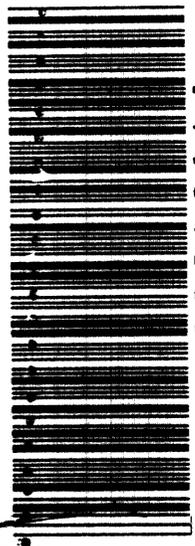
00130  
01000

**FedEx USA Airbill** Tracking Number **804350963168**

**1 From**  
Date 11/19/98  
Sender's Name J. J. V. Phone (202) 527-8800  
Company NATIONAL ENVIRONMENTAL TRUST  
Address 1200 18TH ST NW 5TH FLR Dept./Floor/Suite/Room  
City WASHINGTON State DC ZIP 20036

**2 Your Internal Billing Reference Information**  
**3 To**  
Recipient's Name Environmental Trust Phone 202-527-8800  
Company Environmental Trust  
Address 1200 18th St NW 5th Flr Dept./Floor/Suite/Room  
City Washington State DC ZIP 20036

**For HOLD at FedEx location, print address here**  
City \_\_\_\_\_ State \_\_\_\_\_ ZIP \_\_\_\_\_  
**For Saturday Delivery check here**  
Hold Saturday (Not available at all locations)  
Hold Monday (Available for FedEx Priority Overnight and FedEx 2Day only)  
Hold Wednesday (Available for FedEx Priority Overnight and FedEx 2Day only)



8 0 4 3 5 0 9 6 3 1 6 8

Form No. **0210** Recipient's Copy

**4a Express Package Service Packages under 150 lbs.** Delivery commitment may be later in some areas.  
 FedEx Priority Overnight (Next business morning)  
 FedEx Standard Overnight (Next business afternoon)  
 FedEx First Overnight (Delivers next business morning delivery to select locations) (Higher rates apply)  
 FedEx 2Day (Second business day)  
 FedEx Express Saver (Third business day)  
FedEx Letter Rate not available. Minimum charge. One pound rate.

**4b Express Freight Service Packages over 150 lbs.** Delivery commitment may be later in some areas.  
 FedEx Overnight Freight (Next business day)  
 FedEx 2Day Freight (Second business day)  
 FedEx Express Saver Freight (Up to 3 business days)  
(Call for delivery schedule. See back for detailed descriptions of freight services.)

**5 Packaging**  
 FedEx Letter  
 FedEx Tube  
 FedEx Box  
 FedEx Pkg  
 Other (Declare value and weight)

**6 Special Handling** (One box must be checked)  
Does this shipment contain dangerous goods?  No  Yes (Declaration not required)  
 Dry Ice (UN 1845)  CA  Cargo Aircraft Only  
Dangerous Goods cannot be shipped in FedEx packaging.

**7 Payment**  
Bill to:  Sender (Account no. in section 1 will be billed)  Recipient  Third Party  Credit Card  Cash/Check  
Obtain Recipient FEDEX Account No.

**Total Packages** \_\_\_\_\_ **Total Weight** \_\_\_\_\_ **Total Declared Value\*** \_\_\_\_\_ **Total Charges** \_\_\_\_\_  
\*When declaring a value higher than \$50 per shipment, you may an additional charge. See SERVICE CONDITIONS, EXCLUDED VALUE, AND LIMIT OF LIABILITY section for further information.  
**8 Release Signature**  
Your signature authorizes the carrier to deliver the shipment without obtaining a signature and agrees to indemnify and hold harmless Federal Express from any resulting claims.

**Questions?**  
Call 1-800-Go-FedEx (800)463-3339  
WCS: 129  
Rev. Date: 10/97  
Part #151557  
©1997 FedEx  
PRINTED IN USA

320

004529745 B