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# Phthalates in Toys

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## 1. Pollution Monitoring Laboratory of CSE

The Centre for Science and Environment (CSE), a non-governmental organization based in New Delhi, has set up the Pollution Monitoring Laboratory (PML) to monitor environmental pollution. PML is an ISO 9001:2000 certified laboratory accredited by SWISO, CH-5610, Wohlen, Switzerland, conducting Pollution Monitoring and Scientific Studies on Environmental Samples. The Lab has highly qualified and experienced staff that exercise Analytical Quality Control (AQC) and meticulously follow what is called Good Laboratory Practices (GLP). It is equipped with most sophisticated state-of-the-art equipments for monitoring and analysis of air, water and food contamination, including Gas Chromatograph with Mass Detector (GC-MS), Gas Chromatograph (GC) with ECD, NPD, FID and other detectors, High Performance Liquid Chromatograph (HPLC), Atomic Absorption Spectrometer (AAS), UV-VIS Spectrophotometer, Mercury Analyzer, Respirable Dust Sampler etc. Its main aim is to undertake scientific studies to generate public awareness about food, water and air contamination. It provides scientific services at nominal cost to communities that cannot obtain scientific evidence against polluters in their area. This is an effort to use science to achieve ecological security.

## 2. Introduction

Phthalates or phthalate esters, are esters of phthalic acid mainly used as plasticizers (substances added to plastics to increase their flexibility) in Poly Vinyl Chloride (PVC). PVC is a widely used material, including extensive use in toys and other children's products such as chewy teethers, soft figures and inflatable toys. Phthalates represent 69% of plasticizer use in USA, 92% in Western Europe and 81% in Japan. Overall, they represent 82% of the 2.5 million tonnes (5400 million pounds) of plasticiser use in these three regions (Bizzari *et al*, 1996). Di- (2-ethylhexyl phthalate (DEHP), dibutyl phthalate (DBP), di-isononylphthalate (DINP), di-isodecyl phthalate (DIDP) , benzyl butyl phthalate (BBP) and di-n-octyl phthalate (DNOP) are phthalates mainly used in converting polyvinyl chloride (PVC) from a hard plastic to a flexible plastic.

Phthalates migrate into the air, into food and/or into people, including babies in their mother’s wombs. Phthalates have been found in indoor air and dust (Rudel *et al*, 2001), and in human urine, blood, and breast milk (Kato *et al,* 2003). Phthalates can be released from soft PVC by surface contact, especially where mechanical pressure is applied (e.g. during chewing of a PVC teether). Loss of phthalates by volatilization over time from soft PVC has long been recognized (Cadogan *et al*, 1993). 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 lead to their ubiquitous distribution and abundance in the global environment. There was concern about their effects on the environment, human reproductive system and

function of hormones in the human body. Phthalates which comprise 10-40% of the total weight of toy have been under scrutiny because of their potential health effects, particularly on reproductive development (Duty *et al*, 2003).

The EU has banned the use of DBP, DEHP, BBP from children's toys and childcare articles, and DINP, DIDP and DNOP from items that children are likely to put in their mouths. Other countries, including US, Japan, Denmark, Argentina, and Mexico, have also banned phthalates from children's toys. This has not led to a decrease in plasticizer use as a whole, but has caused a shift in the type of phthalates most commonly used. The market has undergone a shift, in that DINP and DIDP have replaced DEHP in many instances (Sources: ICB Chemical Profile, 26 February 2007. CMR Chemical Profile, 28 August 2006).

In India there are no regulations for phthalates in Toys. India has recently banned imports of several types of toys from China for six months, the ban appears to be aimed more at protecting the unorganized Indian domestic toy sector, rather than the health hazard fears .http://www.atimes.com/atimes/South_Asia/KA30Df02.html. Chinese manufacturers are known to make phthalate-free toys for half of the world and toys with phthalates for the other half of the world to save a few pennies. http://somd.com/news/headlines/2008/7247.shtml

Toys sold in the Indian market have been shown to contain shockingly high levels of lead and cadmium (Kumar and Pastore, 2007) but there are no reports of phthalates in toys from India. Phthalates like DEHP, DINP and DIDP added to PVC toys to improve flexibility in soft PVC products are not tightly bound to the plastic, but are present as mobile components of the plastic matrix. Children may be exposed to these compounds through direct contact with soft PVC products, particularly those intended as high contact products, especially where mechanical pressure is applied (e.g. during chewing of a PVC teether). Children are more vulnerable to the potential adverse effects of phthalates given their increased dosage per unit body surface area, immature metabolic system capability and developing endocrine and reproductive system. Therefore it was considered imperative to undertake a study on phthalates in children's toys and other childcare articles.

## 3. Toy Industry in India

Toy Association of India (TAI), the principal toy association, estimates that the toy market in India is about INR 20 billion at current prices; All India Toy Manufacturers association (AITMA), also estimates the size of the market at the retail level to be about INR 20 billion. As per estimates, there are more than 3000 toy makers in the country. These are a heterogeneous group - from the very small to large multinationals with an Indian presence. TAI itself has a membership of over

700 units, of which about 400 are toy manufacturers in their own right. AITMA has a significant presence across the country too, but the bulk of its members are from Western India. Toys manufactured in India can be broadly classified into the following categories- Plastic Toys include Mechanical & Activity toys, Plastic & Soft Dolls, Plush/Stuffed Toys, Board games/Puzzles, Educational Games & Toys, Wooden Toys, Metal/ Tin Toys, Electronic Toys/Games, Collectibles and Stationary items converted into playthings.

The Indian toy market can be categorized as under:

**Unorganised sector:** It consists of producers scattered across the country. It is said that 60 per cent toy factories are set up in Delhi and 30 per cent toy units are in Mumbai, while 10 per cent toy units are set up in Saharanpur, Moradabad, Mysore and Jammu and Kashmir.http://www.rediff.com/money/2006/jan/10spec1.htm. Toys made in the unorganized sector use cheap recycled plastic, which can be a source of poisoning and lack of regulatory control poses serious health risks to the children.

**Organised sector:** The large toy companies, which have a presence in India today, are the Mattel Toys, Hasbro (through Funskool) and Lego (distribution only) through the Mahindra Intertrade, a company set up by one of the country's largest business houses. www.unido-aaitpc.org/unido-aaitpc/new1/tanzania/litpp-pdf/urt024.pdf.

**Mattel-** Mattel is recognized as one of the100 Most Trustworthy U.S. Companies by Forbes Magazine. The Mattel Company is a $6 billion company and their market share in India is around 20%. Mattel Toys (India) Private Limited is a subsidiary of Mattel, Inc., the worldwide leader in the design, manufacture and marketing of toys and family products. The Mattel family is comprised of such best-selling brands as Barbie®, the most popular fashion doll ever introduced, Hot Wheels®, Matchbox®, Polly Pocket®, Radica® and Fisher-Price® brands

**Lego-**. Lego is a company based in Denmark founded in early 70's, is world's sixth-largest manufacturer of toys, very popular in Europe and North America.

**Funskool** - is the third largest producer set up in 1987. Funskool is the joint venture between the Indian tyre giant MRF, and Hasbro Inc., a leading toy company. Hasbro is a worldwide leader in children's and family leisure time entertainment products and services, including the design, manufacture and marketing of games and toys ranging from traditional to high-tech.

## 4. Phthalates

Phthalates or **phthalate esters**, are esters of phthalic acid and are mainly used as plasticizers (substances added to plastics to increase their flexibility) in Poly Vinyl Chloride (PVC). The PVC

polymer chains are attracted to one another, and therefore form a very rigid structure. The phthalate plasticizers are chiefly used to soften PVC to help the chains slide against each other. The structure of phthalate plasticizers is that of a phthalate ester, which is simply a phthalate with, an ester group ( Figure 1)

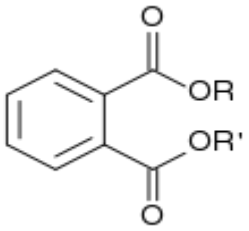



Figure 1. General chemical structure of phthalates. R and R' = $C_nH_{2n+1}$; n = 4-15

**4.1 Properties**

Phthalate esters are the dialkyl or alkyl aryl esters of phthalic acid (also called 1,2-benzenedicarboxylic acid) added to plastics. Phthalates allow the long polyvinyl molecules to slide against one another. They are colorless liquids like vegetable oil with a faint odor, low volatility and insoluble in water, highly soluble in mineral oil, hexane and most organic solvents, this makes them readily soluble in body fluids, such as plasma and saliva. http://nih.gov

**4.2 Uses**

Phthalates are used in a large variety of products, from enteric coatings of pharmaceutical pills to viscosity control agents, gelling agents, film formers, stabilizers, dispersants, lubricants, binders, emulsifying agents, and suspending agents. End applications include adhesives and glues, agricultural adjuvants, building materials, personal care products, detergents and surfactants, plastic objects, paints, printing inks and coatings, pharmaceuticals, food products and textiles. Phthalates are also frequently used in soft plastic fishing lures, adhesives, caulk, paint pigments, and nail polish. Phthalates are used in a variety of household applications (shower curtains, adhesives and perfume) modern pop-culture electronics and medical applications such as catheters.

The most widely-used phthalates are the DEHP, DIDP and DINP. DEHP is the dominant plasticizer used in PVC, due to its low cost. BBP is used in the manufacture of foamed PVC, which is mostly used as a flooring material. Table 1 gives a list of some phthalates and their structure.

**Table 1. Some common phthalates and their structural formulae**

| Name | Acronym | Structural formula |
|---|---|---|
| dimethyl phthalate | DMP | $C_6H_4(COOCH_3)_2$ |
| diethyl phthalate | DEP | $C_6H_4(COOC_2H_5)_2$ |
| diallyl phthalate | DAP | $C_6H_4(COOCH_2CH=CH_2)_2$ |
| di-n-propyl phthalate | DPP | $C_6H_4[COO(CH_2)_2CH_3]_2$ |
| di-n-butyl phthalate | DBP | $C_6H_4[COO(CH_2)_3CH_3]_2$ |
| diisobutyl phthalate | DIBP | $C_6H_4[COOCH_2CH(CH_3)_2]_2$ |
| di-n-pentyl phthalate | DNPP | $C_6H_4[COO(CH_2)_4CH_3]_2$ |
| dicyclohexyl phthalate | DCP | $C_6H_4[COOC_6H_{11}]_2$ |
| benzyl butyl phthalate | BBP | $CH_3(CH_2)_3OOCC_6H_4COOCH_2C_6H_5$ |
| di-n-hexyl phthalate | DNHP | $C_6H_4[COO(CH_2)_5CH_3]_2$ |
| diisohexyl phthalate | DIHxP | $C_6H_4[COO(CH_2)_3CH(CH_3)_2]_2$ |
| diisoheptyl phthalate | DIHpP | $C_6H_4[COO(CH_2)_4CH(CH_3)_2]_2$ |
| di(2-ethylhexyl) phthalate | DEHP, DOP | $C_6H_4[COOCH_2CH(C_2H_5)(CH_2)_3CH_3]_2$ |
| di(n-octyl) phthalate | DNOP | $C_6H_4[COO(CH_2)_7CH_3]_2$ |
| diisooctyl phthalate | DIOP | $C_6H_4[COO(CH_2)_5CH(CH_3)_2]_2$ |
| diisononyl phthalate | DINP | $C_6H_4[COO(CH_2)_6CH(CH_3)_2]_2$ |
| diisodecyl phthalate | DIDP | $C_6H_4[COO(CH_2)_7CH(CH_3)_2]_2$ |
| ditridecyl phthalate | DTDP | $C_6H_4[COO(CH_2)_{12}CH_3]_2$ |
| diisotridecyl phthalate | DIUP | $C_6H_4[COO(CH_2)_{10}CH(CH_3)_2]_2$ |

(Source : Heudorf *et al* 2007)

### 4.3 Labeling of phthalates

There are no labeling requirements for phthalates specifically. Usually toys are not labeled for phthalates. Infact , most toys do not use label wheter they are made from PVC. Some manufacturers are beginning to label their baby products and toys as “phthalate-free,” ostensibly giving parents the information they need to make educated purchasing decisions. There are no

standards to regulate the “phthalate-free” label or ensure that products labeled “phthalate-free” actually do not contain phthalates.

### 4.4 Phthalates and children’s toys

Global toy market is of the order of US$105.0 billion. USA is the world’s biggest importer of toys worth US$35.0 billion , Germany, 18% of the world market (US$19.0 billion), Hong Kong 13% (US$14.0 billion), Britain 7% (US$8.0 billion) France 6% (US $ 6.5 billion). http://www.who.int/ifcs/documents/forums/forum5/toying_agarwal.pdf. 70% of the toys sold in the United States and a large portion of those sold in the European Union and elsewhere come from China and remaining from Taiwan, Japan or Philippines. www.who.int/ifcs/documents/forums/forum5/03_ts_en.doc.

Many of today's toys are made of flexible plastic such as Poly Vinyl Chloride (PVC). From dolls to rubber duckies, a popular choice is PVC which is made flexible by the addition of a phthalate plasticizer during fabrication of the material. Flexible vinyl is durable and can endure years of hard play without losing its color, its flexibility. It is easily cleaned and cheap.

Two phthalates DEHP and DINP, are most commonly used as primary plasticizers in flexible vinyl products, such as soft teethers that may be mouthed by infants. However due to evidence of the toxicity of DEHP in laboratory animal studies it was replaced in children’s products with DINP. DEHP a diester of phthalic acid and the branched-chain 2-ethylhexanol has been the most commonly used phthalate, however DINP (a complex substance of branched, predominantly C-9 isomers) is currently the most common plasticizer used in children toys. Source: PVC Toy Information Center, available at http://www.pvc.toys.com/index.asp?page=2)

Phthalates are not covalently bound to the plastic matrix, but are present as mobile components of the plastic matrix and leach out of PVC when they come in contact with lipophilic substances. 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). In addition, they are released directly into the environment during production and use and after disposal of PVC and other phthalate-containing products. Phthalates bioaccumulate in invertebrates, fish, and plants but do not biomagnify, because higher animals efficiently metabolize and excrete them. They are ubiquitous contaminants in food, indoor air, soils, and sediments. Source: Department of Health and Human Services; 2000 Available at: http://cerhr.niehs.nih.gov/news/index.html

Phthalates have been shown to cross the placenta and pass into breast milk (Parmar *et al* 1985 in animal studies). So, prenatal exposure and exposure from breast feeding may occur in

humans. Infants and young children consume more calories per kilogram of body weight, consume relatively more dairy and other fatty foods, and have higher minute ventilation than do adults, so dietary exposures and exposure from indoor air would be expected to be higher in infants and young children (Etzel *et a*l, 1999).

It is estimated that the total intake of DEHP, excluding non-dietary ingestion, is higher in all children younger than 19 years than in adults (Meek and Chan 1994).

Highest estimated intakes are in children 0.5 to 4 years old. Non-dietary ingestion of phthalates can occur when children mouth, suck, or chew on phthalate-containing toys or other objects and is difficult to quantify directly(Marin *et al*, 1998; Steiner *et al* 1998).. Estimates are made by combining data on the amount of time children mouth nonfood items (Konemann, 1998) and leaching rates of DEHP and DINP from phthalate-containing objects in mouthing studies performed in adults. There are recommendations which suggest removal of DINP (and DEHP) from children's toys because exposure may be high enough to cause concern (Fiala *et al* 2000).

In the United States of America and Canada, the uncertainty in predicting exposure levels, especially in very young children and infants, has led to the removal of all phthalates from infant bottle nipples, pacifiers, teethers, and infant toys intended for mouthing.

**4.5 Safer Alternatives to Phthalate in Toys**

Safer cost-effective alternatives exist such as PVC-free toys that are manufactured without phthalates as well as phthalate-free plasticizers. Safer alternatives to PVC baby/children's products and toys include toys made out of biobased plastics, polyethylenes, polypropylenes, thermoplastic lastomers, and ethylene vinyl acetate (EVA) that are free of phthalates. These plastics do not require the use of phthalates since some are naturally softer, also pose fewer life cycle hazards because they are not chlorinated and do not release dioxins and furans during manufacture and disposal and are manufactured with chemicals that are less hazardous.

Another option is PVC with non-phthalate plasticizers that have been used to soften toys for years. For example, a Danish company Danisco, one of the largest manufacturers of food additives in the world, introduced phthalate alternatives for toys and other products that has been approved for use in both the EU and the U.S.

Two of the most common alternatives to phthalates are acetyl tributyl citrate (ATBC) and 1,2-Cyclohexanedicarboxylic acid diisononyl ester (DINCH), which is derived from DINP and has a similar chemical structure, however existing data on their chronic toxicity on humans is insufficient (Schmidt, 2008).

Mattel, Hasbro and Toys “R” Us -- US based multinational companies – announced they would meet the EU standards globally. Over the past two years, some of the United States’ largest retailers including Wal-Mart, Target, Sears Holdings (Sears and Kmart), and Toys “R” Us have announced major policies to phase out or restrict toxic chemicals such as phthalates and/or PVC in children’s toys and infant products. http://energycommerce.house.gov/cmte_mtgs/110-ctcp-hrg.061008.Lester-testimony.pdf.

## 5. Health risks associated with phthalates

Phthalates are widely believed to be harmful to human health, causing damage to the male reproductive system, on preterm breast development in females, on pulmonary function and on duration of human pregnancy. There are several studies on *in vitro* and *in vivo* effects of phthalates and evidences from human and epidemiological studies.

**Pediatric exposure**

Phthalates have been shown in animal studies to cross the placenta and pass into breast milk so prenatal exposure and exposure from breast feeding may occur in humans. A recent study found measurable levels of 9 phthalate metabolites in 163 infants who were born in 2000–2005.In most (81%) infants, 7 or more DEHP phthalate metabolites were above the limit of detection. Infant exposure to lotion, powder, and shampoo were significantly associated with increased urinary concentrations of monoethyl phthalate, monomethyl phthalate, and monoisobutyl phthalate, and associations increased with the number of products used. Levels in the urine were closely correlated with use of infant care products (lotion, powder, shampoo) within 24 hours of urine sample collection, making it clear that what goes on baby also goes into baby **(**Sathyanarayana *et al* 2008).

A study on prenatal toxicity of 3 different dozes of DINP (0, 40, 200, 1000 mg/kg bw, gestational days 5 to 15 in rats) showed fetal effects (slight increased rates of skeletal retardation and soft tissue and skeletal variations, occurrence of some soft tissue and skeletal malformations). These effects were seen with one of the types of DINP at maternal toxic doses (1000 mg/kg bw/day), but not at the two lower doses (Hellwig *et al*, 1997).

Another study investigated the possible role of DEHP exposure during pregnancy and a link between exposure to phthalates and pre term birth. DEHP and Mono Ethyl Hexyl phthalate (MEHP) levels were measured in cord blood of 84 consecutive births at the general practice Brindisi Hospital, Brindisi, Italy in 2003 were found in 77% samples. Newborns that were MEHP positive had lower gestational age as compared to MEHP negative infants. Findings suggest that exposure can begin *in utero* and that it may affect fetal development (Latini *et al*, 2003).

**Respiratory effects**

In a Swedish epidemiological study, exposure to phthalates -BBP, DEHP, and DBP via house dust, has been related to asthma and allergic symptoms in children. From the cohort, of 10,852 children, 198 cases were selected with persistent allergic symptoms and 202 controls without allergic symptoms. Higher median concentrations of BBP was found in cases with dust (0.15 vs. 0.12 mg/g dust) than among controls. Analysis of the case group by symptoms showed that BBP was associated with rhinitis ($p = 0.001$) and eczema ($p = 0.001$), whereas DEHP was associated with asthma ($p = 0.022$) ( Bornehag *et al* 2005).

Another study from Birmingham showed the role of exposure to phthalates from PVC products in the development of asthma and allergies (Table 2). It was found that high levels of phthalates from PVC products can modulate the murine immune response to a co-allergen. Heated PVC fumes possibly contribute to development of asthma in adults (Jaakkola and Knight, 2008).

**Hepatic effects**

DEHP is a well known hepatotoxin in rodents. Large amounts of specific phthalates fed to rodents have been shown to damage their liver and testes, and initial rodent studies also indicated hepato carcinogenity. Male and female rats were fed DINP at dietary levels of 0, 0.03, 0.3 or 0.6% for a period up to 2 years. Statistically significant and dose-related increases in liver and kidney weights were observed in the mid and high dose groups. Histopathologically, in the top dose centrilobular to midzonal hepatocellular enlargement was observed in kidneys. An increase in tubular cell pigment was observed. No peroxisome induction was observed in the livers of treated rats compared with controls. A slight, but statistically significant increase in mononuclear cell leukemia in the mid and high dose groups was also observed (Lington *et al*, 1997).

**Male reproductive health**

Recent studies have reported effects of phthalates on male reproductive health, such as reduced sperm production in laboratory animals. Phthalates may induce antiandrogenic or estrogenic effects in humans.

One of the first studies from Harvard School of Public Health linked phthalate exposure with harm to human reproductive health. Men who had monobutyl phthalate (MBP) or monobenzyl phthalate in their urine tended to have lower sperm counts, with the highest concentrations leading to the lowest sperm counts (Duty *et al* , 2003).

Developmental defects in male rat pups, similar to those seen in a syndrome termed testicular dysgenesis syndrome (TDS), have been documented after dosing pregnant rat dams with certain phthalates DBP, DEHP or BBP, albeit at high doses (Sharpe, 2005) .

**Table 2 Potential health effects of selected phthalates**

| S. No. | Potential health effects | Phthalate associated | Reference |
|---|---|---|---|
| 1 | **Pediatric exposure** | | |
| | Preterm birth (shorter pregnancy duration). | DEHP | Latini *et al* 2003 |
| | Prenatal toxicity (antiandrogenic in fetal life) | DINP | Hellwig *et al* 1997 |
| 2 | **Respiratory effects** | | |
| | Asthma and Allergy in children. | BBP and DEHP | Bornehag *et al* 2004 |
| | Asthma allergy persistent wheezing, persistent cough, persistent phlegm, nasal congestion, respiratory infections | DEHP | Jaakkola and Knight, 2008 |
| 3 | **Hepatic effects** | | |
| | Increased liver weights, elevated liver enzyme levels, histological changes, and, in some cases tumours. | DEHP, DINP | Albro and Lavenhar, 1989 ; McKee *et al* 2002 |
| | Peroxisomal proliferation(a process related to metabolism of cholesterol and fatty acids) | DEHP | Elcombe and Mitchell , 1986 |
| 4. | **Developmental and Reproductive effects** | | |
| | Toxic to reproduction, capable of causing changes to both male and female reproductive systems in mammals e.g. development of testis in early life. | BBP, DBP, DEHP | Gray *et al* , 2000 |
| | Reduce testosterone | DEHP | Parks *et al* 2000 |
| | Poor semen quality | DMP, DEP, DBP, BBP, DEHP and DnOP | Duty et all 2003; Rozati *et al* , 2002 |
| | Genital defects, reductions in anogenital distance (AGD) in male infants. | DEHP, | Swan *et al*, 2005 |
| | | BBP(rats) | Nagao *et al* 2000 |
| | Premature breast development in females | DBP(rats) | Barlow and Foster, 2003 |
| | | DEP, DEHP, DBP | Colon *et al* 2000 |

In a recent human US study high levels of phthalate metabolites in urine samples from pregnant women were correlated with a relatively short ano-genital distance (AGD) in their male babies. Prenatal urinary levels of phthalate metabolites were inversely related to AGD. Of the 10 boys with the highest score for phthalates, 9 had AGD below the mean. The median metabolite levels

associated with short AGD, or other signs associated with TDS, did not exceed those found among 25 % of the female US population (Swan *et al*, 2005).

A recent British study showed that the phthalate DBP or its metabolite MBP suppresses steroidogenesis by fetal-type Leydig cells in primates as in rodents (Hallmark *et al* 2007).

**Female Reproductive health**

A study conducted in Puerto Rico suggested a possible association between plasticizers with known estrogenic and antiandrogenic activity and the cause of premature breast development in a human female population with exposure to DEHP. Forty one patients with thelarche from the San Juan City Hospital's Pediatric Endocrinology Division and 35 control subjects were studied. High levels of DMP, DEP, DBP, DEHP, and MEHP in serum were detected in 28 thelarche patients (68%) compared to 1 and 5 control subjects who had detectable levels of di-isooctyl phthalate and DEHP, respectively. The largest differences between cases and controls were for DEHP where the average concentrations were 450 and 70 ng/ml (ppb), respectively ($p < 0.05$) (Colon *et al*, 2000) .Table 2

## 6. Regulations for Phthalates in Toys

### 6.1 International

Ban for phthalates in products, intended for children, exists in European nations, Argentina, Fiji and Mexico. Austria, Japan, Denmark, Finland, France, Germany, Greece, Norway, and Sweden banned the use of phthalates in manufacturing soft vinyl toys.

**European Union**

Since 1999 the European Union has prohibited the use of phthalates in children's toys. The Council Directive (1999/815/EC) which applies to toys and childcare articles made of soft PVC adopted measures prohibiting the sale of toys and childcare articles intended to be placed in the mouth by children under three years of age made of soft PVC containing one or more of the substances - DINP, DEHP, DBP, DIDP, DNOP, and BBP; importing these products is also prohibited.

Directive 2005/84/EC an amendment to Council Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations extends the ban on 6 phthalates (DINP, DEHP, DBP, DIDP DNOP, BBP) for the manufacture of toys for children under three years of age. DEHP, BBP, and DBP are restricted for all toys; DINP, DIDP, and

DNOP are restricted only in toys that can be taken into the mouth. The restriction states that the amount of phthalates may not be greater than 0.1% mass percent of the plasticized part of the toy. Such toys and childcare articles containing these phthalates in a concentration greater than the limit mentioned above shall not be placed on the market. These phthalates are allowed at any concentration in other products and other phthalates are not restricted. http://europa.eu/scadplus/leg/en/lvb/l32033.htm

**Denmark**

According to Statutory Order no. 786 of 11 July 2006 on a ban on phthalates in toys and childcare articles of the Ministry of Environment, the phthalates DEHP, DBP and BBP shall be banned from use as substances or as constituents in chemical products in concentrations exceeding 0.1% by mass of plasticized material in toys and childcare articles. Import and sale of these toys and childcare articles shall also be banned. The phthalates DINP, DIDP and DNOP shall be banned from use as substances or as constituents in chemical products in concentrations exceeding 0.1% by mass of plasticized material in toys and childcare articles which can be placed in the mouth by children. Import and sale of such toys and childcare articles shall also be banned

Other phthalates in toys for children (0-3 years old) which are intended, or normally can be expected, to be placed in the mouth, including in particular dummies, bibs, jewellery as well as bathing articles etc. shall be banned from use as substances or as constituents in chemical products or components hereof in concentrations exceeding 0.05% by mass. **http://www.mst.dk/NR/rdonlyres/29DF03C6-E815-4022-9CA2-E18A6857613D/0/StatutoryOrderno786of11July2006.pdf**

**USA**

In USA, the California Environmental Protection Agency (Cal/EPA) listed DEHP in Proposition **65** (edition September 2003) as being potentially carcinogenic and reproductive hazards. Some phthalates will be restricted in children's toys sold in California starting in 2009. Following California, the federal government restricted three types of phthalates permanently and put interim restrictions on three others, effective February 10, 2009.

The Consumer Product Safety Improvement Act (CPSIA), section 108 bans children's products that contain certain concentrations of phthalates. This interim ban is effective from February 9, 2009 , childcare products (products for children under three years of age) and children's toys (toys produced for children under twelve years of age) containing concentrations of DEHP, BBP, and DBP greater than 0.1% will be considered banned hazardous materials. DINP, DNOP, and DIDP in concentrations greater than 0.1% will be placed on a provisional ban unless there is a future determination of safety. http://www.cpsc.gov/ABOUT/Cpsia/faq/108faq.html

**Japan**

The Japanese Minister for Health, Labour and Welfare imposed a ban on PVC toys containing **DINP and DEHP** (phthalate derivates) in August 2003 in the Food Sanitation law (JFSL) - Section 4(mandatory standard) and Japan Toy Safety standard- ST 2002, Part 3 Clause 1.9 (voluntary standard). DEHP is prohibited from being used in any toy product and DINP must not be used in any toy that might be put in the mouth by a small child. **http://www.mhlw.go.jp/topics/bukyoku/iyaku/kigu/dl/11.pdf**

**China**

China's toy industry is regulated since early 2007 by China Compulsory Certification (CCC) from the nation's Certification and Accreditation Administration (CNCA). Toys are subject to inspection and certification review. Chinese toys must meet the criteria set by International standard ISO8124.1:2002 which itself is modeled on EU's standard for toys (EN71 Safety of Toys - Safety aspects related to mechanical and physical properties). But there are no standards for phthalates.

**6.2 India**

**Bureau of Indian Standard**

With regard to safety guideline for toys, Bureau of Indian Standards (BIS) has published three standards

1. IS 9873 (Part 1): 2001/ISO 8124 –1:2001 covers Safety Requirements of Toys, Safety Aspects related to mechanical and physical properties.

2. IS 9873 (Part 2): 1999/ISO 8124 –2:1994 covers Safety Requirements of Toys, Flammability requirements; and ,

3. IS 9873 (Part 3): 1999/ISO 8124 –3:1997 covers Safety Requirements of Toys; Migration of certain elements (has limits for heavy metals).

None of these standards give limit for phthalates in children's toys and childcare articles. The BIS guideline with regard to toy production is self-regulatory and not mandatory. Toy manufacturers don't register for the ISI mark for their products and therefore do not follow even the voluntary standard.

## 7. Review of Literature

Health Canada analyzed 41 children's products made in the US, China, and Thailand for the presence of DINP and DEHP. DINP was detectable in 27 of the 41 products in concentrations that ranged from 3.9 to 44% dry weight. Criteria for the selection of products were not discussed in any of these surveys. No information on market share, length of availability on the market, or estimates of the numbers of products in circulation was noted in any study. Only Health Canada listed the product number, country of origin, manufacturer/distributor, and brand (Health Canada, 1998).

Chen measured DINP in 31 of 35 toys and found a concentration range of 15.1–54.4 % dry weight as reported by the Consumer Product Safety Commission (CPSC, 1998).

A study from Spain in which 15 toy samples were analysed for phthalate concentrations by soxhlet and supercritical fluid extraction showed that the PVC products contained high DOP concentrations (Marin *et al*, 1998).

Forty-two plastic products intended for mouthing, or with a high potential for mouthing, by children of age group 0.5-3 years were analyzed for total and leachable phthalate contents. DINP was found in 64% of the products tested and its concentration ranged from 3.9 to 44%. Migration of DINP from PVC products into saliva stimulant was studied using simulated chewing activity and an Instron Universal Testing Machine. Under the conditions used in this study, the DINP migration rates from teethers and squeeze toys were found to vary from 0.04 to 1.29 µg/10 $cm^2$ /h. The migration rates show a 40-fold variation within the plastic products tested. However, 83% of the products showed a migration rate of <0.32 µg/10 $cm^2$/h. The mean value was found to be 0.3 µg/10 $cm^2$/h with a distribution median of 0.23 µg/10 $cm^2$/h (Gill *et al*, 1999).

A total of 72 toys most of which were PVC or had PVC sections purchased in 17 countries were analysed for phthalates. In almost all the soft PVC toys analysed, phthalates comprised a sizeable proportion (most frequently 10-40%) by weight. The predominant phthalates detected were DINP and DEHP. Other phthalates identified in high concentrations in some toys include isomeric mixes of DIOP and DIDP. The estrogenic chemical nonylphenol was isolated from 13 toys, while 2 toys were found to contain the fungicide Fungitrol 11 (Folpet). 78% of PVC toys contained one or more extractable organic compounds in addition to those reported above (Stringer *et al ,* 2000).

In February 2001, market surveillance was performed in the Netherlands and 62 soft toys were sampled. Forty-seven of these toys contained plasticized PVC. DINP and DEHP were the predominant plasticizers and were usually found in concentrations between 30 and 45% by

weight. One teething ring was made of PVC plasticized with 45% by weight of DINP and was not in compliance with Directive 1999/815/EC. The DINP and DEHP migration was determined in saliva simulant using the 'Head over Heels' agitation method. All toys complied with the Scientific Committee on Toxicity, Ecotoxicity and the Environment (SCTEE) guidance release value of 6.7 $\mu g\ min^{-1}$ 10 $cm^{-2}$. The DEHP migration of six toys exceeded the SCTEE guidance release value of 1.7 $\mu g\ min^{-1}$ 10 $cm^{-2}$(Bouma and Schakel, 2002).

The presence of plasticizers in PVC toys obtained in October 1998 was investigated. DINP, DEHP, DBP, DNP, DHP and di-2-ethylhexyl adipate (DEHA) were detected. The phthalates were found in all of the 68 samples. The principal phthalate found in toys was DINP, which was present in 48 of 68 samples. The DINP content ranged from 15 mg/g to 580 mg/g, and mean content was 308 mg/g. The highest content was found in a pacifier toy. DEHP was present in 20 of 68 samples and the content ranged from 2.0 mg/g to 380 mg/g. The mean content was 162 mg/g. It was found in 60% of domestic toys (Sugita *et al*, 2001).

An HPLC method using a UV detector for the determination of phthalate ester plasticizers (PAEs) in PVC children's toys showed DINP and DEHP at the levels of 196-449mg/g (7 toys) and 63-453 mg/g (5 toys), respectively. DBP and DEHA were also detected in the range of 39-118 mg/g (3 toys) and 63-254 mg/g (3 toys), respectively. No PAEs were found in 11 toys which were manufactured from an infant chewing point of view (Niinoa *et al* 2001).

Another study conducted on testing of phthalates in toys and other articles for children upto 3 years of age showed that out of the 15 products investigated, one or more of the phthalates were found in 10 products. Among the investigated phthalates, BBP (<0.005-0.019%) was present in three samples, DIBP (<0.005-0.226%) in three samples, DBP (<0.005-0.463%) in six samples**,** DEHP (0.037-28.976%) in four samples, DINP+DIDP (1.200-37.290%) was present in three samples (of which DIDP was present in only one sample). The content of one or more phthalates in 8 of the investigated products was found to be higher than the maximum allowed concentration, 0.05% (Rastogi *et al*, 2003).

In a recent study of phthalates in toys in which 20 easily available PVC toys were purchased in Washington and Michigan at retailers including Fred Meyer, Toys"R" Us, Target, Kmart , Walmart, Rite Aid, Bartell Drugs, toy stores and dollar store and tested for 17 phthalates using GC/MS . 5 different phthalates including DEHP, DBP, DIDP, DINP and an unidentified octyl phthalate, DINP and DIDP most were commonly identified. Six of the toys tested had phthalate content between 28 to 47%. A green ball purchased at Toys "R" Us contained the highest amount of phthalates with more than 47% of the ball made up of phthalates. Several squeeze toys, including a rubber ducky purchased at Fred Meyer and a Target brand penguin had more than 30% phthalate. A

Target-brand “Baby I’m Yours” doll contained more than 30% total phthalates. A dinosaur figurine purchased at Wal-Mart contained more than 28% total phthalates (Schreder, 2007).

A report on Toy safety in US found that two toys with phthalate levels that far exceed limits allowed by the Consumer Product Safety Improvement Act38 scheduled to take effect in February 2009. Laboratory tests found DINP at an estimated concentration of 400, 000 parts per million (40%) and DIDP at an estimated concentration of 64, 000 parts per million (6.4%) in one toy. Another toy was found to have an estimated concentration of 95, 000 parts per million (9.5%) DINP (Hitchcock, 2008).

## 8. Objectives of the Study

The main objective of this study was to assess the phthalate content of toys and other child care articles used by children.

## 9. Materials and Methods

### 9.1 Sampling methodology

24 Toy samples of major brands from organized and unorganized sector were purchased randomly from various markets in Delhi in the month of October 2008. Soxhlet extraction was carried out at the PML during the same month. Each samples was analyzed in triplicate for 8 phthalates by USEPA method 8061A. Details of the samples purchased are in given in Annexure I.

### 9.2 Equipments

Thermoquest-Trace GC with the $^{63}$ Ni selective Electron-Capture Detector and advanced software (Chromcard-32 bit Ver 1.06 October 98), DB-5 capillary column, Rotary evaporator (Buchi type) and a 10-μl syringe from Hamilton Co. were employed.

### 9.3 Glassware

All the glassware used was properly cleaned including treatment in muffle furnace at 400$^0$C for 2-4 hours and thorough rinsing with solvent, prior to use.

**9.4 Chemicals**

All the solvents acetone, methylene chloride, hexane (HPLC) grade used for the analysis were purchased from E-Merck. Each lot of reagents used for the study was checked for phthalate contamination.

**9.5 Standards**

Phthalate reference standards were obtained mostly from Sigma Chemicals, USA. The products were analysed for the content of following phthalates: -dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), benzylbutyl phthalate (BBP), di-*n*-octyl phthalate (DNOP), diethylhexyl phthalate (DEHP), diisononylphthalate (DINP), diisodecylphthalate (DIDP). Anhydrous sodium sulfate, sodium chloride was purchased from s. d. Fine Chem Ltd.

**9.6 Sample extraction**

E***xtraction*** –Method by Rastogi (1998) was followed, 5 g sample was soxhlet extracted in 100mL dichloromethane for 16 h at 60°C. 90 ml of the extract was concentrated under vacuum using a rotary evaporator at 30°C. 1µl of the appropriately diluted extract was analysed by GC-ECD. All samples were analysed in triplicate for phthalates.

**9.6 Sample analysis**

The samples were analysed by using EPA method 8061A for Phthalates by Gas Chromatograph (Thermoquest-Trace GC) with the $^{63}$ Ni selective electron-capture detector.

**GC Conditions**

| | |
|---|---|
| **GC Column** | Capillary column DB- 5 (5%-phenyl)-methyl polysiloxane (length 30m, ID 0.25 mm and film 0.25µm). |
| **Carrier gas** | Nitrogen, 0.5 ml/min flow |
| **Injector** | Split less mode 250$^0$C Injection Volume 1.0µl |
| **Temperature Programme** | Start temperature 150$^0$C with a hold time of 1 minute, then from 150$^0$C to 200$^0$C at a rate of 5$^0$ C/minute with a hold time of 1 minute and finally from 200$^0$C to 280$^0$C at a rate of 3$^0$ C / minute with a hold time of 14 min. The total run length was 50 minutes. |
| **Detector** | ECD , 300 $^0$C make up gas Nitrogen 30 ml/min |

Peak identification was performed by the GC software (Chromcard-32 bit Ver 1.06 October 98). Calibration curves for all of the phthalates were linear (R2 ≥0.999) in the investigated concentration range 0.1 - 2.0 μg/ml and for DINP 1.0 - 5.0 μg/ml. Calibration curve for DIDP was not prepared as DIDP was determined as DINP due to overlap of GC peaks of these phthalates. The samples were calibrated (retention time, area count) against standard mixture of known concentration of 8 phthalates. See Table 2. Identification of phthalates was performed by comparing the retention time (Rt) of the samples GC-peaks with the Rt of the phthalate standards. No phthalates were detected in reagent blanks. The phthalates present in high concentrations were analyzed after appropriate dilution of the sample extracts with hexane. Phthalates identified in the toy samples are shown in Figure 2.

**9.7 Calculations**

The contents of phthalates in a sample extract were calculated using the calibration standard closest to the sample extract. The identification of phthalates was performed by comparing the GC retention times of the sample peaks with the retention times of phthalate standards. GC chromatograms of DINP and DIDP overlap partly, the chromatographic pattern of isomeric DINP and DIDP was considered for the identification of these phthalates. When a product contained DINP as well as DIDP, the content of both of these phthalates in the product was determined together as DINP (DINP is currently the most common plasticizer used in children toys). When a product contains both DNOP and DINP, DNOP in such a product could not be determined by the present method because of interference by isomeric GC peak(s) of DINP. The GC separation of the phthalates under study as well as chromatographic pattern of DINP and DIDP is shown in Figure 4A and phthalates detected in toy samples in Figure 4B, 5A and 5B.

**Table 3: Phthalates investigated in the toy samples by GC-ECD**

| S. No | Phthalate | Acronym | CAS | Molecular Weight | Retention Time (minutes) |
|---|---|---|---|---|---|
| 1 | dimethyl phthalate | DMP | 131-11-3 | 194.19 | 7.97 |
| 2 | diethyl phthalate | DEP | 84-66-2 | 222.24 | 10.40 |
| 3 | di-n-butyl phthalate | DBP | 84-74-2 | 278.34 | 17.48 |
| 4 | benzyl butyl phthalate | BBP | 85-68-7 | 312.35 | 26.50 |
| 5 | di(2-ethylhexyl) phthalate | DEHP, DOP | 117-81-7 | 390.54 | 31.04 |
| 6 | di-n-octyl phthalate | DNOP | 117-84-0 | 390.56 | 35.34 |
| 7 | diisononyl phthalate | DINP | 68515-48-0 | 418.60 | 36.06 |
| 8 | diisodecyl phthalate | DIDP | 26761-400 | 446.68 | 40.35 |

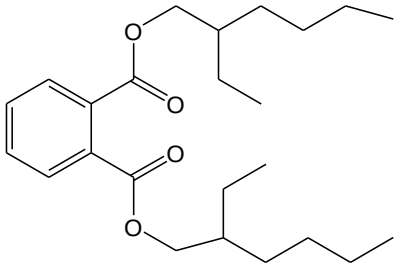
The determinations were performed in triplicate samples using external standard technique with a calibration standard close to the estimated concentrations of phthalates in the sample extract. The recovery of all of the investigated phthalates under the experimental conditions was 85-105%. The relative standard deviation (RSD) for the determination of most of the phthalates was within 10%.The reliability of the method (stability of the GC-retention time, calibration range, recovery, repeatability of determination, etc.) was checked for the present investigation, and was found to be satisfactory for the analysis of phthalate content in toys. The GC retention times (Rt) of the investigated phthalates were stable throughout the study, with a maximum variation <1% and the chromatographic pattern of DINP and DIDP were considered for the presence of these phthalates in the sample extracts.

**9.8. Confirmation by GC-MS**

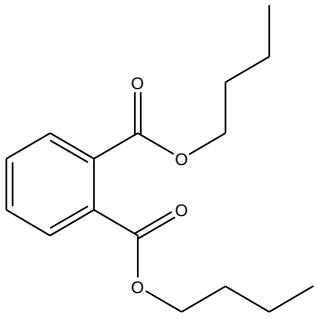
The presence of phthalates detected in the samples by GC-ECD was confirmed by GC-MS, Model Finnigan Polaris Q Ion trap GC/$MS^n$ with EI ionization (70eV), in Full Scan mode. The analytes were identified by their a) characteristic retention time b) primary ion. c) secondary ions to increase specificity.

G**C Conditions**

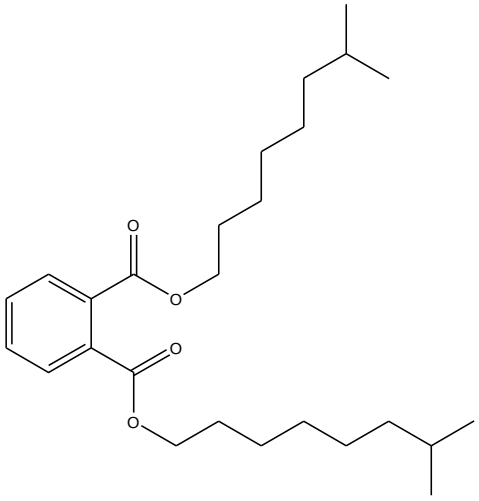
| | |
|---|---|
| **GC Column** | Capillary column DB- 5MS (5%-phenyl)-methylpolysiloxane (length 30m, ID 0.25 mm and film 0.25μm). |
| **Carrier gas** | Helium, 0.5 ml/min flow |
| **Injector** | Split less mode $250^0$C Injection Volume 1.0μl |
| **Temperature Programme** | Start temperature $150^0$C with a hold time of 1 minute, then from $150^0$C to $200^0$C at a rate of $5^0$ C/minute with a hold time of 1 minute and finally from $200^0$C to $280^0$C at a rate of $3^0$ C / minute with a hold time of 14 min. The total run length was 50 minutes. |
| **Ion source** | at 230 $^0$C; Multiplier:1100 VoltsAGC:50, 3 microscan |



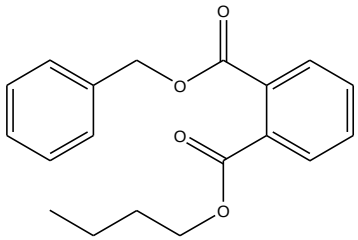
DEHP



DBP



DINP



BBP

**Figure 2: The phthalates identified in toy samples**

## 10. Results and Discussion

In the present study 24 toys and other childcare articles(teethers) used by children, manufactured in India, Taiwan, China and Thailand were analyzed for 8 phthalates- dimethyl phthalate(DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), benzyl butyl phthalate (BBP), di (2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), diisononyl phthalate (DINP), and diisodecyl phthalate (DIDP) by GC-ECD and confirmation by GC-MS. The results are presented in Annexure II.

### 10.1 All toys contain phthalates

One or more phthalates mainly DEHP, DBP, BBP and DINP were found in all the 24 toy samples (Figure 3). Phthalate concentration in 24 samples ranged from <0.1% to 16.22%. Maximum value is 162 times higher than the EU limit for phthalates of 0.1% percent of the plasticized part of the toy.

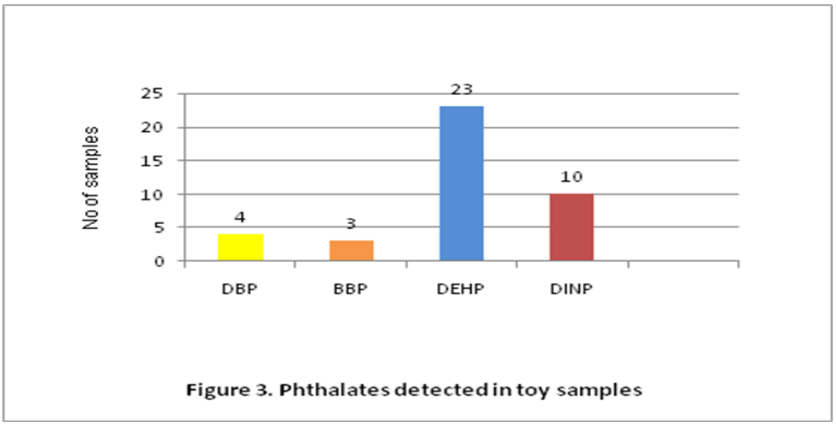



Figure 3. Phthalates detected in toy samples

DEHP was detected in 96 percent (23 out of 24) of the samples at low concentrations, ranging from <0.1 - 2.6%. DINP was detected in 42 percent (10 out of 24) of the samples ranging from <0.1 - 16.2%. DBP and BBP were detected in 4 and 3 toys out of 24 toys analysed respectively and concentrations were < 0.1-0.2%; too low to have plasticizing function and could be present as a contaminant of another phthalate; constituent of ink or paint used in toys.DEHP, DBP, BBP and DINP have been found to reduce testosterone production by the fetus which can result in off target reproductive development and abnormal genitals. DINP may be a risk for young children who routinely mouth DINP plasticized toys for seventy five minutes per day or more (CPSC, 2001).

### 10.2 High level of phthalates in toys & child care articles

Phthalates were detected in all the categories of toys however the phthalate content exceeded the EU limit in the – mouthable (29%), soft squeeze (67%) and other miscellaneous toys (60%), but was found to be within limit in hard rattle toys which is understandable (Table 4).

DEHP which is restricted in all toys was detected in 96% of the toys but in low concentrations (<0.1%) except three products. It was detected in - Inflatable Bop bag Dinosaur (Toy No 23) and Bath Duck (Toy No 24 at a concentration of 0.2 and 2.6%. DEHP was also detected in baby teethers (Toy No 7) made from non-toxic food grade silicone rubber intended to be placed in mouth that were manufactured in Taiwan at a concentration of 0.3% which is 3 times higher than the EU limit.

DINP which is restricted in toys that can be taken in mouth was found in very high concentration in many toys, especially in Chinese toys; which reflects a marked shift away from DEHP towards the use of the poorly characterized isomeric phthalates. Pip squeak toy (Toy No. 5) from India manufactured by Funskool (Branded player) contained more than 16.2 % of total phthalates (162 times higher the EU limit). Majority of the toys which contained high levels of phthalates were manufactured in China. Squeeze toys (Toy No. 6, 16, 17, 18, 21, 22, 23, 24) from China, manufactured mostly by Lovely Collections contained phthalates at a concentration ranging from 4.4-8%. DBP was detected in soft and hard biter (Toy No. 8) at a concentration of 0.2%, twice the EU limit. (Annexure II)

**Table 4: Presence of phthalates in different categories of toys**

| **Category of Toys** | **Total No. of Samples** | **Percentage exceeding 0.1% individual phthalate limit** |
|---|---|---|
| Mouthable | 7 | 29 (2) |
| Soft squeeze toys | 9 | 67 (6) |
| Hard rattle toys | 3 | 0 (0) |
| Miscellaneous(dolls, pony) | 5 | 60 (3) |

On the basis of country of origin, China leads the countries in which phthalate content exceeds the EU limit; 57% of toys manufactured in China exceeded the EU limit then came India (14%) & Taiwan (100%), only toys manufactured in Thailand were within the EU limit

**Table 5: Presence of phthalates in toys from different countries**

| Country of Manufacture | Number of Samples | Percentage exceeding individual 0.1% phthalate limit |
|---|---|---|
| China | 14 | 57 (8) |
| India | 7 | 14 (1) |
| Taiwan | 2 | 100(2) |
| Thailand | 1 | 0(0) |

The samples containing higher quantities of DINP contained smaller quantities of DEHP, perhaps as a contaminant in the manufacturing process.

### 10.3 Soft toys contain higher levels of phthalates

Interestingly all the toys in which high amounts of phthalates were detected are soft in nature. In the soft toy category 2 out of 9 toys and in hard toys category 9 out of 15 samples exceeded the EU limit for phthalates. Absence of plasticizer is understandable. Phthalates in soft toys are not tightly bound to the plastic**,** but are present as mobile components of the plastic matrix. They can be released from soft PVC by surface contact, especially where mechanical pressure is applied (eg. during chewing, sucking). Phthalate concentration exceeded the EU limit of 0.1% mass percent of the plasticized part of the toy in more than 45 percent of the samples analyzed (11 out of 24 toys)(Table 6)

**Table 6 Presence of phthalates among hard and soft toys**

| **Category of Toys** | **Number of Samples** | **Percentage exceeding 0.1% individual phthalate limit** |
|---|---|---|
| **Hard** | 9 | 22.22(2) |
| **Soft** | 15 | 60(9) |
| **Total** | **24** | **45.83(11)** |

### 10.4 GC-MS confirmation of phthalates detected in toys

The phthalates- BBP, DBP, DEHP and DINP detected in toy samples were confirmed by GC-MS. The dominant fragment of all phthalates measured in electron impact ionization MS is at m/z149

this is a result of the loss of the alkyl ester groups and the formation of protonated phthalic anhydride moiety. Characteristic ions – primary and secondary ions and the retention time for major phthalates detected in toy samples are given in Table 7. Mass spectra are given in Figure 6A, B and 7A, B.

**Table 7. Characteristic ions for major phthalates detected in toy samples**

| S. No. | Phthalate. | CAS | Retention time (minutes) | Primary ion | Secondary Ions |
|---|---|---|---|---|---|
| 1 | di-n-butyl phthalate | 84-74-2 | 13.99 | 149 | 205, 223 |
| 2 | benzylbutyl phthalate | 85-68-7 | 22.19 | 149 | 91, 206 |
| 3 | di-2-ethyl hexyl phthalate | 117-81-7 | 26.37 | 149 | 167, 279 |
| 4 | diisononyl phthalate | 68515-48-0 | 32.13 | 149 | 167, 293 |

### 10.5 Some manufacturers are making toys without phthalates

Manufacturers do not provide any information on the toxic chemicals used in the products on the label. None of the phthalate containing toys was labeled as such. Only one manufacturer Chicco from China (softy soft) keys<0.1%) states on the label “NO PVC or Phthalate”.

It is pertinent to mention that one of the manufacturers namely Lovely Collection did not find it worthwhile to mention on the package either an address for the manufacturer or the date of manufacture.

### 10.6 Labeling on toys

The BIS has provided safety labeling guidelines for toys in its standard - IS 9873 (Part 1): 2001/ISO 8124 –1:2001 covers Safety Requirements of Toys, Safety Aspects related to mechanical and physical properties. The packaging for toys and games intended for use by children from 3 to 6 years old and containing small parts, balloons, small balls or marbles must contain a cautionary statement regarding choking hazards.

All the Manufacturers do not provide details on the label regarding age and the indications of specific hazard(s) like “Warning! Not suitable for children under 3 years”, “Contains small parts” should appear on the label or in the instructions for the use of all the toys.

## 11. Conclusions

- Young children (below 3 years) suck and chew on toys, they extract and ingest certain quantities of the plasticizers. Some phthalates are suspected to cause allergy, asthma and affect the kidneys and liver, also cause testicular damage.

- DEHP, BBP, and DBP are restricted for all toys; DINP, DIDP, and DNOP are restricted only in toys that can be taken into the mouth. **The restriction states that the amount of phthalates may not be greater than 0.1% mass percent of the plasticized part of the toy.**

- 24 products (toys and other articles) used by children, available in the local markets, manufactured in India, Taiwan, China and Thailand were analyzed for 8 phthalates –DMP, DEP, DEHP, BBP, DBP DINP, DIDP, and DNOP by GC-ECD as soft PVC children's products are plasticized with phthalates. The phthalates detected were confirmed by GC-MS.

- One or more of the phthalates mainly DEHP, DBP, BBP and DINP were found in all the 24 samples tested. DEHP was detected at levels from <0.1- 2.6%; DINP was present in high concentrations at a level of 0.1 - 16.2%. DBP and BBP were detected at low concentrations of < 0.1-0.2%. The identity of the phthalates detected was confirmed by GC-MS.

- DINP was the major phthalate detected and was found in very high concentration which reflects a shift away from DEHP towards the use of the poorly characterized isomeric phthalates especially in Chinese toys.

- DEHP was also detected in baby teethers (Toy No 7) made from non-toxic food grade silicone rubber intended to be placed in mouth that were manufactured in Taiwan at a concentration of 0.3% which is 3 times higher than the EU limit. DBP was detected in soft and hard biter (Toy No. 8) at a concentration of 0.2%, twice the EU limit.

- Soft toys contain higher levels of phthalates as compared to hard toys like rattles, which is understandable as primary function of phthalates is softening of hard plastic materiel.

- There are no regulations for phthalates in toys in India. Children may be at higher risk of adverse effects of phthalates because of anticipated higher exposures during a time of developmental and physiologic immaturity. Phthalates have been banned in the EU, United States and Canada and several other countries, from toys intended for mouthing.

- Manufacturers should give details on the label regarding age and indicate specific hazards from the toy; if any & Parents should read the labels of toys and avoid purchase of products made of PVC plastic; which often contains phthalate softeners.

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## Annexure I: Baby toys purchased in the local market in Delhi

| Toy No. | Type | Brand | Manufacturer/Importer | Place of Manufacture | Date of Manufacture | Remarks |
|---|---|---|---|---|---|---|
| 1 | Teether | Flo-Rite | Flo-Rite Baby Product Pvt. Ltd.;Gala No.2, 1st Floor, Hindustan Biscuit Compound, Pipe Road, Kurla (W), Mumbai-400070 | India | Nov-07 | Made from non-toxic food grade silicone rubber. |
| 2 | Gum Soother | HelloBaby | Hello Baby Pvt. Ltd.11, Laxmi Ind. Estate, M.G. Road, Goregaon (W), Mumbai-40009 | India | Jun-08 | Non toxic, water filled-Food grade with fragrance |
| 3 | Gum Soother | Mr. Toothy | Arihant Industries; 57 (2A) 1, Ground Floor, Bhenslor Ind. Estate, Kunta Road, Village Dunetha, Nani Daman, Daman-396210 (UT) **Mktd by:** Shadilal & Sons, Mumbai-400003 | India | Jul-08 | Non toxic, durable, contents safe for drinking |
| 4 | Animal Figurine-Bear | Ashu A.R.P. | Ashu A.R.P. Toys & Dolls, **Mktd. By:** Ashok Toys, Delhi-6 | India | Jun-05 | * |
| 5 | Pip Squeaks Toy | Funskool | Funskool (India) Ltd., 826, Tarapore Towers, Mount Road, Chennai-600002 | India | May-03 | Non-Toxic.<br>Age: 3-18 months |
| 6 | Squeeze Toy -Donald duck | Lovely Collection | * | China | * | Small parts, Not for children under 3 years |
| 7 | Teether | Piyo Piyo | Tung Ling Industrial Co. Ltd. **Imported By:** VPN Tradelinks, A-17 Mukherjee Nagar Comm. Complex, Delhi-110009 | Taiwan | Nov-07 | Food gradable silicone; Designed for babies six month old and up. |
| 8 | Soft & Hard Biter | Piyo Piyo | Tung Ling Industrial Co. Ltd. **Imported By:** VPN Tradelinks, A-17 Mukherjee Nagar Comm. Complex, Delhi-110009 | Taiwan | Sep-07 | T.P.E. & P.P.; Designed for babies six month old and up. |
| 9 | Toy-ball | Xin Fei Toy | * | China | * | Choking Hazards: small parts, not for children under 3 years. |

| Toy No. | Type | Brand | Manufacturer/Importer | Place of Manufacture | Date of Manufacture | Remarks |
|---|---|---|---|---|---|---|
| 10 | Baby Rattle | Disney Baby | **Imported & Mktd By:** SUN BABY, (Unit of Krona Uquatec Ltd.), FA-308, Mansarovar Garden, New Delhi-110015 | Thailand | Nov-07 | * |
| 11 | Softy-Soft Keys | Chicco | Imported & Mktd By: Gayatri Imports & Exports Pvt. Ltd. B-2/15A, Model Town-1, Delhi-110009 | China | Imported on: Jan.2008 | No PVC & Phthalate For Age: 3-18 months |
| 12 | Bath Fish | * | * | China | * | * |
| 13 | Baby Rattle | HelloBaby | Venus Industries, Bhatiya Glass Compound, Vakola Pipe Line Road, Santacruz (E), Mumbai-400055; **Mktd By:** Shadilal & Sons, Mumbai-400003 | India | Feb-06 | * |
| 14 | Baby Rattle | Baby Lovely | * | China | * | 3-24 Months; Small parts, Not for children under 3 years |
| 15 | Rattle & Teether | Good Cutely | * | China | * | Age: 3+ |
| 16 | Squeeze Toys-Mickey mouse | Lovely Collection | * | China | * | Not suitable for children under 3 years due to small parts |
| 17 | Inflatable (Soft Whale) | Puff 'N' Play | Intex Development Co. Ltd., 8th Floor, Dah Sing Financial Centre, 108 Gloucester Road, Wanchai, Hong Kong | China | * | Age: 2+ |
| 18 | Doll | Fashion Doll | * | China | * | Age: 3+ |
| 19 | Doll | Barbie Fashion Fever | Fancy Fittings Ltd., 259/145, Minerva Indl. Estate, 2nd Floor, Sewri Bunder Road, Sewri (E), Mumbai-400015; **Mktd By**: Mattel Toys (India) Pvt.Ltd, 4th Floor, 'B' Wing, Phoenix House, 462, Senapati Bapat Marg, Lower Parel, Mumbai-400013 | India | Sep-08 | Small parts. Not for children under 3 years |

| Toy No. | Type | Brand | Manufacturer/Importer | Place of Manufacture | Date of Manufacture | Remarks |
|---|---|---|---|---|---|---|
| 20 | Toy (My Little Pony) | Funskool | Hasbro Far East Ltd, RM 1106-7, World Commerce Centre, Harbour City, Tsim Sha Tsui, Hong Kong; **Imported & Marketed by**: Funskool (India) Ltd. Tarapore Towers, VI Floor, 826, Anna Salai, Chennai-600002 | China | May- 07 | Ages 3+ |
| 21 | Squeeze Toys- Doll | Lovely Collection | * | China | * | Small parts. Not for children under 3 years |
| 22 | Squeeze Toys- Mickey mouse | Lovely Collection | * | China | * | Small parts. Not for children under 3 years |
| 23 | Inflatable- Bop Bag (Dino) | Champ | * | China | * | Ages 3+ |
| 24 | Bath Duck | * | * | China | * | * |

*Note**No information provided by the manufacturer

**ANNEXURE II. Phthalates detected in Baby toy samples (Percent (%) by mass)**

| Sl No. | Toy No. | Manufacturer/ Brand | Country | Soft/ Hard | DMP | DEP | DBP | BBP | DEHP | DNOP | DINP | DIDP | No of times the EU Limit of 0.1% by mass percent or 1000 ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Teether | Flo-Rite | India | Soft | ND | ND | <0.1 | ND | <0.1 | ND | ND | ND | within limit |
| 2 | Gum Soother | HelloBaby | India | Soft | ND | ND | <0.1 | ND | <0.1 | ND | ND | ND | within limit |
| 3 | Gum Soother | Mr. Toothy | India | Soft | ND | ND | ND | ND | <0.1 | ND | ND | ND | within limit |
| 4 | Animal Figurine -Bear | Ashu A.R.P. | India | Soft | ND | ND | ND | ND | 0.1 | ND | ND | ND | within limit |
| 5 | Pip Squeaks Toy | Funskool | India | Soft | ND | ND | ND | ND | <0.1 | ND | 16.2* | ND | 162* |
| 6 | Squeeze Toy - Donald duck | Lovely Collection | China | Soft | ND | ND | ND | ND | <0.1 | ND | 6.0* | ND | 60* |
| 7 | Teether | Piyo Piyo | Taiwan | Soft | ND | ND | <0.1 | ND | 0.3* | ND | ND | ND | 3* |
| 8 | Soft & Hard Biter | Piyo Piyo | Taiwan | Hard | ND | ND | 0.2 | ND | <0.1 | ND | <0.1 | ND | 2* |
| 9 | Toy-ball | Xin Fei Toy | China | Soft | ND | ND | ND | ND | <0.1 | ND | ND | ND | within limit |
| 10 | Baby Rattle | Disney Baby | Thailand | Hard | ND | ND | ND | <0.1 | <0.1 | ND | ND | ND | within limit |
| 11 | Softy-Soft Keys | Chicco | China | Hard | ND | ND | ND | ND | <0.1 | ND | ND | ND | within limit |
| 12 | Bath Fish | ** | China | Soft | ND | ND | ND | ND | 0.1 | ND | ND | ND | within limit |
| 13 | Baby Rattle | HelloBaby | Mumbai | Hard | ND | ND | ND | ND | <0.1 | ND | ND | ND | within limit |
| 14 | Baby Rattle | Baby Lovely | China | Hard | ND | ND | ND | ND | <0.1 | ND | ND | ND | within limit |
| 15 | Rattle & Teether | Good Cutely | China | Hard | ND | ND | ND | ND | <0.1 | ND | ND | ND | within limit |
| 16 | Squeeze Toys- | Lovely Collection | China | Soft | ND | ND | ND | ND | <0.1 | ND | 7.1* | ND | 71* |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mickey mouse | | | | | | | | | | | | |
| **Sl No.** | **Toy No.** | **Manufacturer/ Brand** | **Country** | **Soft/ Hard** | **DMP** | **DEP** | **DBP** | **BBP** | **DEHP** | **DNOP** | **DINP** | **DIDP** | **No of times the EU Limit of 0.1% by mass percent or 1000 ppm** |
| | | | | | | | | | | | | | |
| 17 | Inflatable (Soft Whale) | Puff 'N' Play | China | Soft | ND | ND | ND | ND | <0.1 | ND | 4.4* | ND | 44* |
| 18 | Doll | Fashion doll | China | Hard | ND | ND | ND | ND | ND | ND | 4.5* | ND | 45* |
| 19 | Barbie Doll Fashion Fever | Mattel Toys | India | Hard | ND | ND | ND | <0.1 | <0.1 | ND | <0.1 | ND | within limit |
| 20 | Toy -My Little Pony | Funskool | China | Hard | ND | ND | ND | <0.1 | <0.1 | ND | <0.1 | ND | within limit |
| 20 | Toy -My Little Pony | Funskool | China | Hard | ND | ND | ND | <0.1 | <0.1 | ND | <0.1 | ND | within limit |
| 21 | Squeeze Toys-Doll | Lovely Collection | China | Soft | ND | ND | ND | ND | <0.1 | ND | 6.2* | ND | 62* |
| 22 | Squeeze Toys-Mickey mouse | Lovely Collection | China | Soft | ND | ND | ND | ND | <0.1 | ND | 8.0* | ND | 80* |
| 23 | Inflatable-Bop Bag Dinosaur | Champ | China | Soft | ND | ND | ND | ND | 2.6* | ND | ND | ND | 26* |
| *24* | Bath Duck | ** | China | *Soft* | ND | ND | ND | ND | 0.2* | ND | ND | ND | 2* |

Note 1. DEHP, BBP, and DBP are restricted for all toys in EU; DINP, DIDP, and DNOP are restricted only in toys that can be taken into mouth.

2.The restriction states that the amount of individual phthalates may not be greater than 0.1% mass percent of the plasticized part of the toy. 3.*Values are average of triplicate*

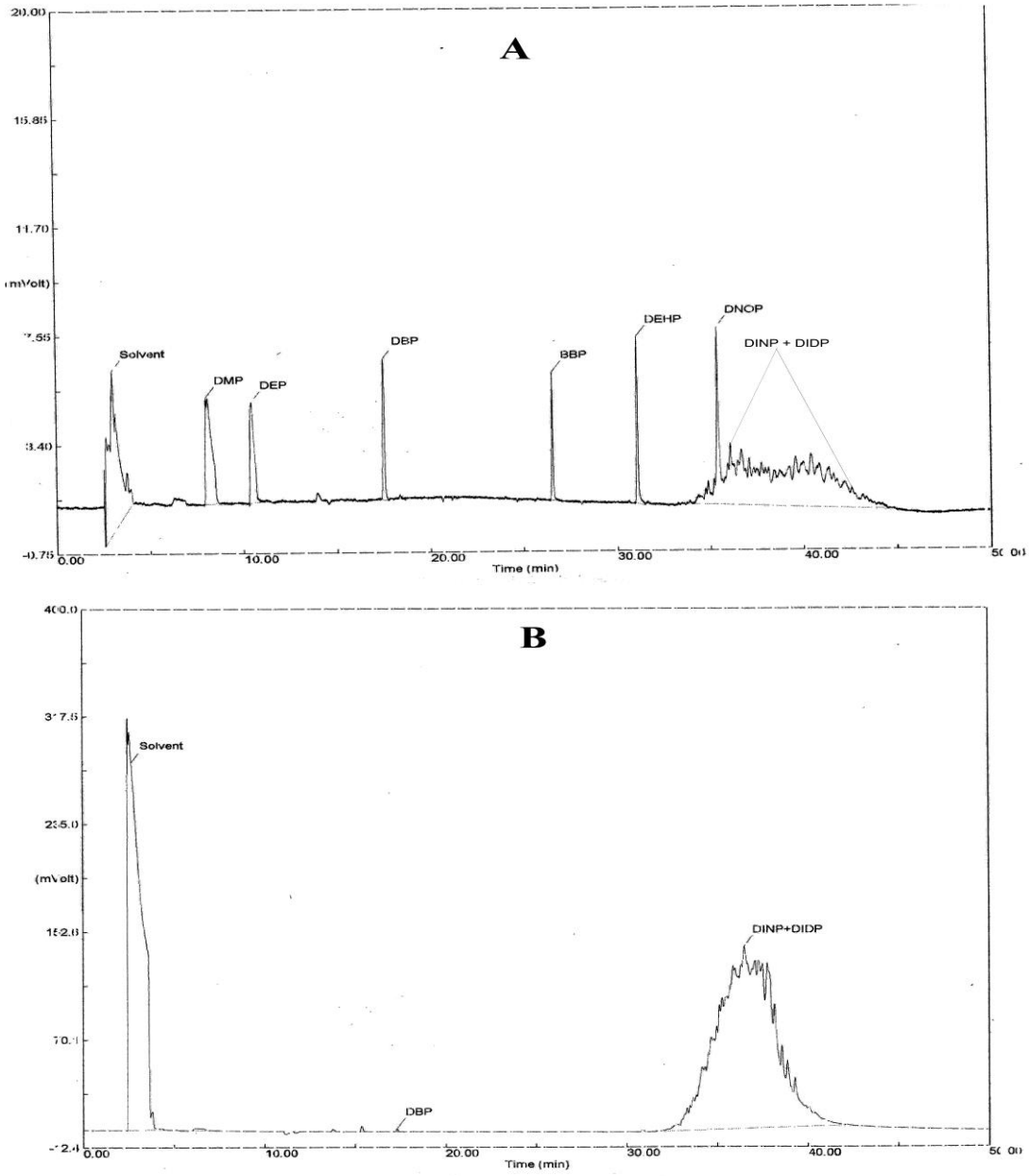


Figure 4: GC –ECD Chromatograms of – A. Standard mixture of phthalates B.. Sample extract of Toy No. 18

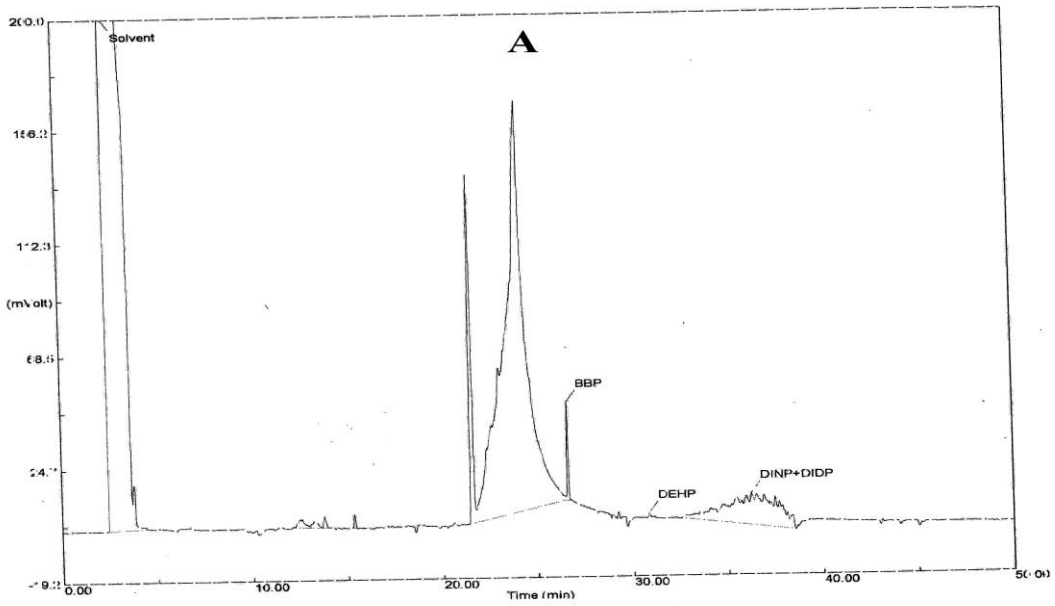


Figure 5: GC –ECD Chromatograms of – A. Sample extract of Toy No. 19 B. Sample extract of Toy No. 22

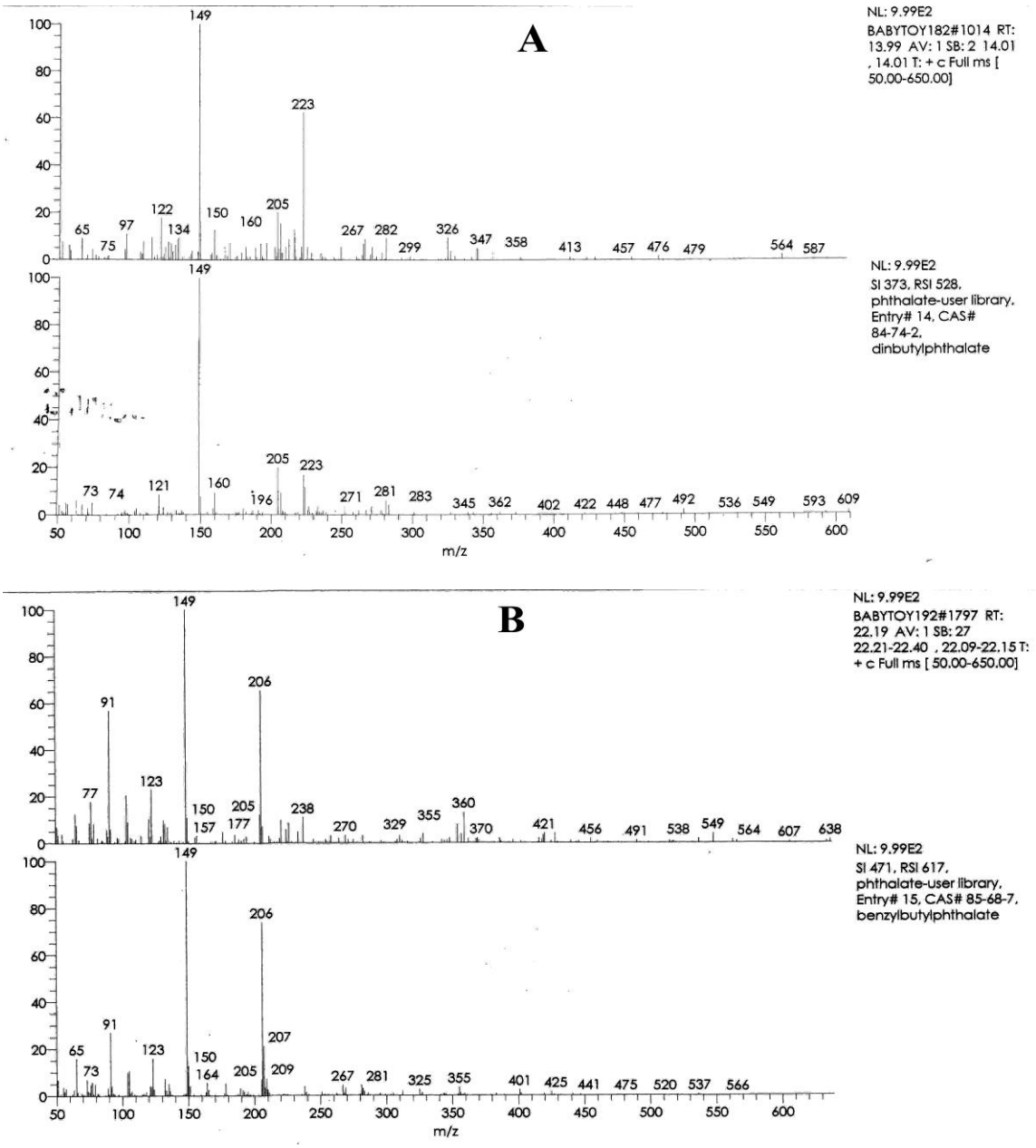


Figure 6: Mass Spectra of A. Sample extract of Toy No. 18(DBP) B. Sample extract of Toy No. 19(BBP)

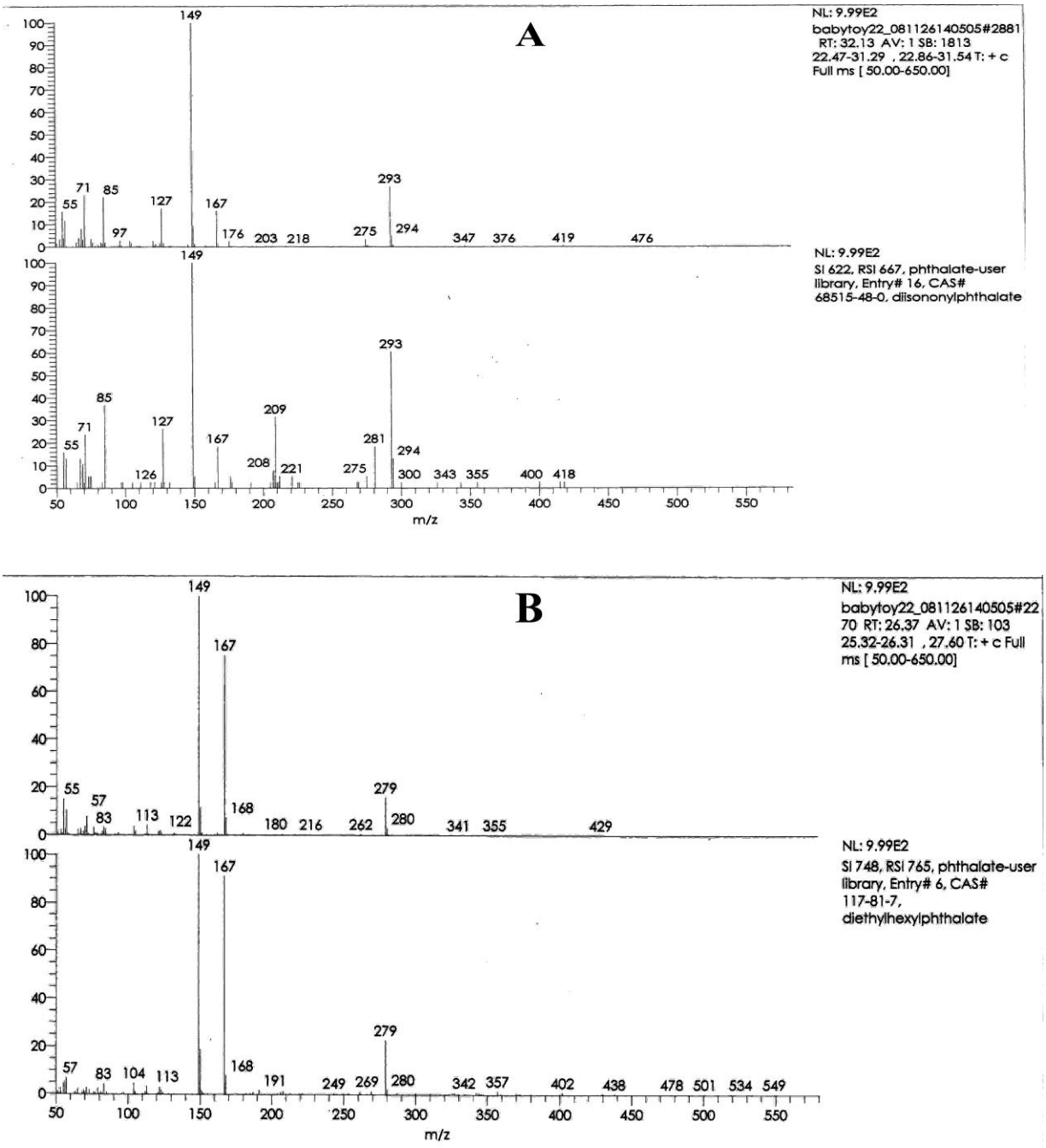


Figure 7: Mass Spectra of A. Sample extract of Toy No. 22(DINP) B. Sample extract of Toy No. 22(DEHP)