

Assessment of phthalic acid ester presence in toys, children stuffs and wallpapers in Belarus

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**ИНФО
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Abstract

Plasticizers with phthalic acid ester base, so-called phthalates, have been arousing concerns of consumers all over the world for a long time, particularly those in toys and children products made of PVC. Other products are just as problematic in this respect, since these substances can be released into the environment (for example from vinyl wallpapers). Health hazard connected with the opportunity of sequential releasing of those substances eventually led to the restriction of six most widespread and most problematic phthalates in toys for children under three years old in the European Union. Despite this step toward greater safety, there are still reasonable fears that because of the great proliferation of PVC in children products, the possibility of leaking of these substances is not completely eliminated. Therefore, all sorts of organizations and information campaigns engage in safety of toys and products in general in many countries.

In Belarus, which is not a part of the European Union and where the market is connected more with Russia and other post Soviet countries, the awareness of chemical safety and safety of products among consumers in general is still at a lower level. Sources cite that European standards are stricter than standards used in Russia and Belarus. Some sources also mention bribery cases where products are marked as if they met the standards and limits.¹

This research deals with qualitative and quantitative assessment of presence of phthalic acid esters in 16 chosen products for children bought in Belarusian stores and 4 samples of vinyl wallpapers bought at the same place.

In terms of our research we had 12 samples of PVC toys and 4 samples of vinyl wallpapers tested for the presence of phthalic acid esters. Increased amount of phthalates was found in two tested toys (in the first case, it was 23% of weight of diisononyl phthalate DINP and 1.01% of weight of bis(2-ethylhexyl) phthalate DEHP; in the second case, it was 23.30% of weight of bis(2-ethylhexyl) phthalate DEHP).

In three of four tested samples of wallpapers, increased values of diisononyl phthalate DINP were noted (13.62% of weight, 4.64% of weight and 8.36% of weight). In one sample, increased value of bis(2-ethylhexyl) phthalate DEHP was also found (12.45% of weight).

Introduction

Polyvinyl chloride, better known as PVC, belongs to the most used plastic materials for several decades. It is very widely used. Most of it is used for the production of pipelines, profiles, packing materials and other consumer products. It found its place in toys and children products, too.

Despite its considerable proliferation, PVC is considered to be one of the most problematic plastic ecologically and in health point of view. One of the main disadvantages of PVC lies in its basic structural element, which is chlorine. Producing PVC or its burning causes a formation of dangerous organochlorine compounds of dioxins and furans as a by-product.

Regarding consumers, especially using a great amount of additives, which are necessary in PVC, to reach requested technological qualities, seems to be problematic. Since PVC is a very tough material in raw form, plasticizers have to be added. Spectrum of substances, which can be used for plasticizing PVC, is rather extensive, but phthalic acid esters (phthalates) are used the most often. These substances then represent even tens of percents of PVC weight

depending on required flexibility of the final product. Since these substances are not firmly chemically bound, they can successively leak from the product.

Some phthalates are provided to the market as chemical materials containing just one substance (for example bis(2-ethylhexyl) phthalate DEHP), while others are provided as complex mixture of isomers containing many different compounds with similar chemical structure (for example diisononyl phthalate DINP and diisodecyl phthalate DIDP). Phthalates today belong to the most widespread synthetic chemicals in the environment due to the fact that they are used in great extent outside of closed systems.

In addition to already mentioned function of plasticizers in PVC, they are also used in cosmetic products and personal hygiene supplies. Further, they are used in wood surface finishing supplies, cleaning and laundry detergents, glues, lubricants, medical tubes and bags for liquids, solvents and insecticides.

Using of phthalates causes their extensive leaks into the environment. It happens during using of products and during their disposal, which makes thousands of tons annually. Consequently, phthalates have been considered to be one of the most frequent and most widespread synthetic contaminants of the environment for a long time.

DEHP, which has been the most used phthalate in Europe to date, is known for being a dangerous substance for reproduction, which affects development of mammals' testicles and is classified as a reprotoxic substance in the European Union.² Its toxicity to developing male reproduction system has in fact been known for more than 50 years.³

Detected toxicity is caused mainly by mono-(2-ethylhexyl) phthalate MEHP compound, which is produced as a DEHP metabolite in the body; and it seems that it influences many aspects of liver development and functions, including hormones metabolism and immunity functions.

Because of the provable toxic properties of phthalates, it is imperative that such substances do not come into contact with the children organism. The main problem is particularly those products that children can put into their mouths. Release of phthalates from the plasticized PVC surface increases especially, when mechanical pressure and temperature increase (child chewing on a toy).

Since 1983 it has been known that DEHP, which is contained in children products in high concentrations, can be released by means of simulated dermal and oral contact. It turned out that there is no direct proportionality between phthalate concentration in the product or experiment duration and amount of leaked DEHP. Nevertheless, it was clearly proven that DEHP can leak from the product for a long time and when increased pressure is applied the amount of leaked substance is further increasing.⁴

Increasing fears connected with the danger of increased phthalates exposition led some countries of European Union to the steps leading to their restriction in children products. This trend ended up in temporary ban of six most common phthalates (DEHP, DBP, BBP, DINP, DIDP and DNOP) in toys for children under three years old and was accepted from 1999/815/ES decision of European Commission. In the Czech legislation, this requirement is stated in 521/2005 regulation.

The ban was definitely confirmed by 2005/84 European Union directive concerning the ban of phthalates in children toys and goods, which states that:

“The use of certain phthalates in toys and childcare articles made of plasticised material or including parts made of plasticised material should be prohibited as the presence of certain phthalates presents or could potentially present risks related to the health of children. Toys and childcare articles which, although not intended for that purpose, can be put in the mouth, may under certain circumstances present a risk to the health of small children if they are made of plasticised material, or include parts made of plasticised material, which contains certain phthalates.”

In the Czech Republic, 284/2006 regulation lists banned phthalic acid esters (DEHP, DBP, BBP, DINP, DIDP and DNOP) and says that:

“They cannot be used as substances or components of products in concentration higher than 0.1% of weight in plasticized plastic materials used for children toys and products for children care since 16 January 2007. Toys and products for children care which contain these phthalates in higher concentration than the above stated value cannot be introduced to the market. Product for children care is any product intended for facilitation of falling asleep, calming, hygiene, children feeding or for sucking by children.”

TP TC 008/2011 Regulation, which is valid in Belarus, Russia, Kazakhstan and Estonia states limits for chosen phthalic acid esters (DBP, DMP, DOP and DEP):

“Toxicological and hygienic characteristics of hygienic safety of toys must meet the requirements specified in Annex 2 to this technical regulation of the Customs Union.”

In Annex 2, limits for migration of particular phthalates from toys are stated:

“dibutyl phthalate cannot be released from toys at all, dimethyl phthalate is restricted to 0.3 mg/dm³ in the water and 0.007 mg/m³ in the air, dioctyl phthalate is restricted to 2 mg/dm³ in the water and 0.02 mg/m³ in the air, diethyl phthalate is restricted to 3 mg/m³ in the water and 0.01 mg/m³ in the air.”

Labeling of toys and limits for content of phthalates in toys and other products in Belarus

1. Label of inappropriate products for children under 3 years old



The products can be inappropriate for children under 3 years old for several reasons: a danger of releasing of small parts and their consequent breathing in or for example the product consists of sharp parts or projections which can inflict a wound to a child. The labeling does not show unambiguously what risk the product represents.

Overview of analyzed samples and used methods

Total amount of 20 products of PVC was tested for the presence of phthalic acid esters (16 toys, 4 samples of wallpapers). More parts of some toys were tested (for example the valve of inflatable toys). List of pictures, including description, information about producer, country of origin and place of purchase are stated below. Testing was done by Institute for testing and certification, Inc. in Zlín.

Number of sample	Description	Country of origin, producer	Parts tested for content of phthalates
001	Set of rubber, plastic and inflatable animals for use in water (pool) 	China	Material of the pool and of valve
002	Beach ball for use in water (pool) 	China (Disney)	Material of the ball and of the valve
003	Squeaky bath book with the sun for toddlers 	Poland (Canpol)	Material of the book
006	Beach ball for use in water (pool) Johny Eagle 	China	Material of the ball
007	Nasal aspirator with two ends – hard and soft 	Taiwan, (Canpol company)	Squeezable blue bulb
008	Inflatable swim ring Cindy Star	China	Material of the ring and of the valve



Four yellow rubber duck for use in bath tub

009



China

Material of the toy

Small book with the sun and tulips

011



Russia

Material of the book

Yellow and white squeaky rubber pony

012



origin unknown

Material of the toy

Inflatable swim ring

014



China (INTEX)

Material of the ring and of the valve

Set of green, yellow and pink squeaky rubber animals for use in bath tub

017



China

Material of the toy – pink kitty

Yellow and orange squeaky rubber ball

018



origin unknown

Material of the toy – orange ball

Number of sample	Description	Country of origin
001	Decori – Exclusive, sand	Italy
002	ART - En Flor, light blue	Russia
003	Sintra, white with flowers	Ukraine
004	ART – Indigo, architectonic patterns	Russia

Within the scope of testing, content of extractable substances according to ČSN EN ISO 6427 was set and consequently, the presence of phthalic acid esters according to ČSN EN 14372 was set, which was expressed as a percentage by weight in the material of the whole product. Identification of organic substances in samples was done by means of gas chromatography with weight detector.

Results of testing

Increased amount of phthalates was found only in two tested toys of all children toys (in sample no. 12 – yellow and white whistle pony, namely 23.88% of weight of diisononyl phthalate DINP and 1.01% of weight of bis(2-ethylhexyl) phthalate DEHP).

In sample no. 17 – set of green, yellow and pink squeaky rubber animals for use in bath tub, the pink kitty consisted of 23.30% of weight of bis(2-ethylhexyl) phthalate DEHP.

In three of four samples of wallpapers, increased values of diisononyl phthalate DINP were detected, namely in sample 001 Decori Exclusive (13.62% of weight, 002 ART En Flor (4.64% of weight DINP), 004 ART - Indigo (8.36 % of weight DINP). In sample 003 Sintra, increased value of bis(2-ethylhexyl) phthalate DEHP was detected (12.45 % of weight DEHP).

In other products, the amount of phthalic acid esters did not exceed detection limit of 0.1% of weight for diisononyl phthalate DINP, diisodecyl phthalate DIDP, di-n-octyl phthalate DNOP, butyl benzyl phthalate BBP, dibutyl phthalate DBP and bis(2-ethylhexyl) phthalate DEHP.

Tabular results of the analysis of content of phthalates in toys are stated in table 1. Tabular results of the analysis of content of phthalates in samples of wallpapers are stated in table 2.

Sample	Value	Substance
sample no. 13 – yellow and white squeaky pony	23.88 % of weight	diisononyl phthalate DINP
sample no. 13 – yellow and white squeaky pony	1.01 % of weight	bis(2-ethylhexyl) phthalate DEHP
sample no. 15 – set of green, yellow and pink squeaky rubber animals for use in bath tub, tested subject: pink kitty	23.30 % of weight	bis(2-ethylhexyl) phthalate DEHP

Table 1: Results of the analysis for the presence of phthalic acid esters.

Sample	Value	Substance
Sample 001 Decori – Exclusive, sand	13.62% of weight	diisononyl phthalate DINP
Sample 002 ART - En Flor, light blue	4.64% of weight	diisononyl phthalate DINP
Sample 003 Sintra, white with flowers	12.45 % of weight	bis(2-ethylhexyl) phthalate DEHP
Sample 004 ART – Indigo, architectonic patterns	8.36 % of weight DINP	diisononyl phthalate DINP

Table 2: Results of the analysis of samples of wallpapers for the presence of phthalic acid esters.

Discussion and conclusion

In two toys, significant amount of phthalic acid esters was found hence there is still a potential risk that children, who come into contact with them, will be exposed to higher exposition of those substances.

Yellow and white pony which consisted of increased amount of DINP and DEHP was not labeled considering suitability of the toy for toddlers and small children. Any label of the producer or the origin of the product is also missing. It is again shown how inappropriate it is to buy children's toys without proper labeling or the origin of the toy.

Set of toys for use in bath tub, where the tested pink kitty with increased content of DEHP was found, is according to producer labeling appropriate for children over 3 years old.

Since both toys are made of rubber, they are rather suitable for smaller children and with the toy with the label for children over 3 years old it can happen that parents will ignore such warning. There is a good possibility that these toys can also be put into mouths by small children. Therefore, contained amount of phthalates in both toys is entirely inappropriate in such amount.

Even though vinyl wallpapers are not such a risk that they would be put into mouth or come into contact with the body surface directly, the plasticizers from wallpapers can be released into the air in the room and cause health problems, for example when inhaling.

To sum it up, the proportion of toys with unsatisfactory content of phthalates represents 1/6 of total amount of tested toys (that is circa 16%) according to the European standards. Belarus detection standards for phthalates do not yet exist hence it is possible to sell mentioned products on the market.

Sources

- 1) http://elfik.bygirl.net/index.php?page=n_1174762298&art=1&storyid=112
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- 3) Hale, R. C.; La Guardia, M. J.; Harvey, E.; Gaylor, M. O.; Mainor, T. M. Chemosphere 2006
- 4) Hanson, R.L. (1983) Phthalate ester migration from polyvinyl chloride consumer products. Phase 1 final report. Report prepared for the US Consumer Product Safety Commission, 51pp