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Inhalation and Ingestion of Phthalate Compounds from Use of Synthetic Modeling Clays

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Phthalate esters, including di-2-ethylhexyl phthalate (DEHP), benzylbutyl phthalate (BBP) and di-n-octyl phthalate (DNOP), are plasticizers used to soften polyvinyl chloride (PVC). This PVC is used for many household items such as flooring, shower curtains, medical devices, food packaging, and toys. Phthalates have been the focus of numerous studies that aim to assess their potential to cause birth defects and/or reproductive abnormalities. Animal experiments have indicated that low exposures to phthalates have the potential to alter the organs that produce and deliver sperm, and phthalates also exhibit adverse effects on other organs and systems (Raloff 2000b). Ema and Miyawaki (2002) demonstrated that the phthalate, BBP, causes adverse effects on the development of the reproductive system in male rats. Phthalates have also been shown to cause thelarche, premature breast development, in young girls aged 6 to 24 months. In a study conducted in San Juan, Puerto Rico, 41 girls with thelarche and 35 girls with normal development were tested to find possible reasons for the premature development. About 68% of the girls with thelarche had detectable phthalate levels, opposed to only 17% of the girls with normal development (Raloff 2000a). The results of studies like these prompted the Environmental Protection Agency to establish a drinking water standard for the phthalate, DEHP, of 6.0 ppb in 1994 (USEPA 2002), and DEHP has been labeled as a "probable human carcinogen" for over a decade (USEPA 1993).

Children and infants are likely to experience phthalate exposure when mouthing, sucking, or chewing on toys or other objects that contain phthalates (Shea 2003). When children suck on teethers or old pacifiers made of soft PVC, the phthalates are released from the PVC and into the child's saliva. Although the European Union put a temporary ban on phthalate softeners in baby toys, so far, no limits have been put in place for phthalate content in toys or other products in the United States (Christen 2000). However, manufacturers have reduced the DEHP levels in mouth toys to a maximum of 3%, substituting di-isononyl phthalate (DINP). This substitute is less studied than DEHP, and although its toxicity is not well understood, it now makes up 11 to 40 percent of the total weight of many soft PVC toys.

In recent years, polymer clay, also made of PVC, has become a popular modeling

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material for children, adolescents, and adult craftspeople. This material is soft at room temperature, can be molded by hand, and can be baked in a conventional oven at low heat, resulting in a permanent solid object (Bernstein 1998). Phthalates are used in these clays to keep them soft and workable before they are baked and are often present as 3.5 to 14 percent of the total mass *(Philips Service (PSC) Laboratory, Ontario).* The hardening process, usually completed in kitchen ovens, drives off the phthalates and creates a significant inhalation exposure route. The intensive direct handling involved in the molding of the material also produces the potential for ingestion exposure from hand to mouth transfer. The purpose of this investigation was to determine the potential inhalation and ingestion exposure from routine usage of these synthetic modeling clays. In this study two types of modeling material labeled "non-toxic" were tested for phthalate exposure to humans through handling and inhalation.

MATERIALS AND METHODS

Popular and widely-used polymer clays sold under the brand names Fimo and Sculpey were brought to the laboratory in their original packaging. Two basic types of exposure experiments were performed: one to determine air emissions and potential subsequent inhalation of gaseous phthalate fumes emitted during manufacturer-prescribed baking conditions, and the other to determine potential hand-to-mouth ingestion. Three phthalate compounds, butyl benzyl phthalate (BBP), diethyl hexyl phthalate (DEHP), and di-n-octyl phthalate (DOP) had been previously determined to be the three most common phthalate compounds present in these clays. However, this laboratory later determined that most of the products contained a complex mixture of phthalate compounds which often included di-n-hexyl phthalate (DHP) and several other chemically similar phthalate compounds.*(PSC Analytical Services, Organic Data Package for VPIRG, June 2001).* In addition, the phthalate terephthalic acid (DEHT) was found to be indistinguishable from DOP in terms of retention time and spectra. Both PSC and our laboratory found that the compound initially identified as DEHP could be another very chemically similar phthalate.

In the first part of the experiment, phthalate fume emissions were determined for ten synthetic clay samples. Between 1.0 mg and 7.0 mg of synthetic polymer clay of each brand and color was taken from newly opened packages and placed using metal forceps into pre-weighed 20 mL headspace vials with a sample septum built into the cap. Following clay introduction and reweighing, each vial was capped and baked using a laboratory Digiblock digestion hotblock at 132°C (270°F) for 20 minutes as per package instructions. Blank samples were prepared by similarly baking headspace vials with no clay material added. Following the baking procedure, each vial was cooled to room temperature, and 1.0 mL of gas was removed with an air sampling syringe for phthalate analysis.

All samples were analyzed for phthalate content by GC/MS (HP 5890 Series 2) using EPA method 3810 for sampling of the headspace gas after baking and EPA method

606 for the GC/MS settings and analysis. A manual headspace analysis technique was used to allow consistency with recommended baking conditions. A direct splitless injection of 1.0 mL with a He flow of 0.5mL/min and column type DB5 625 30mx.32 ID were used in the analysis. Standards were prepared using various aliquots of a 160 mg/L commercially purchased certified mixed phthalate reference standard (AcqMethod Phthalate Mix), which provided a calibration range of 8-120 μg/L.

The second phase of the research involved the determination of handling residues for each of the ten brands and colors of synthetic clay. One hundred grams of each material was handled and worked into the form of a crude bowl for five minutes by subjects wearing standard disposable medical laboratory gloves. After handling, subjects washed their gloved hands under warm running water for 30 seconds with vigorous rubbings, but no soap use. Following this, the gloved hands were dipped into a shallow metal pan containing 100 mL of methanol, and any remaining residues were rubbed off and dissolved into the methanol using a procedure of redipping the gloves and rinsing for one minute. Blank samples were produced by rinsing gloved hands that had not touched the synthetic clay in methanol.

Phthalate compounds were quantified in the methanol rinse solutions by GC/MS using similar methods as described above for the inhalation studies, with the exception that 1 μL liquid samples and standards were direct injected rather than gaseous samples. Standards for this phase of the experiment were again prepared using the 160 mg/L certified mixed phthalate reference standard (AcqMethod Phthalate Mix). Further dilutions were required for some samples.

RESULTS AND DISCUSSION

Exposure to phthalate compounds could occur either from the inhalation of fumes during and after baking or from inadvertent hand-to-mouth ingestion of residues left on the hands after working with these synthetic polymer clays.

Table 1 shows calculated exposures from inhalation of baking emissions as well as the average predicted kitchen air concentrations over the 20-minute prescribed baking period. One observation from these studies was that typically the mass of each gaseous phthalate emission was on the order of between about 0.001 percent and 0.4 percent of the total mass of the clay sample used. Because the direct compositional analysis of these clays previously found that individual phthalate compounds commonly comprised several percent of the total clay mass, these data indicate that only a small fraction of the total phthalate compounds present was volatilized by the 20-minute baking process at 270° F.

From Table 1 it can be seen that actual predicted exposures to the three individual phthalate compounds ranged from non-detectable (< 1 μg) to a high of 1,869 μg for DOP/DEHT in lavender-colored Fimo. Blank samples showed nondetectable limits of all three phthalates, while 5 of the 10 product samples tested were found to give a predicted inhalation exposure of more than 100 μg of at least one of the phthalates. As seen from Table 1, there was a great variation in gaseous phthalate emissions between samples of different colors. It can also be seen that, for most of the samples, the Fimo clays emitted much more DEHP/analogs and DOP/DEHT than BBP, while in the Sculpey clay emissions, the BBP compound was more dominant, with DOP/DEHT being generally much lower.

Table 1 also shows the calculated average phthalate kitchen air concentrations over the 20-minute baking period. Inhalation exposure would be greater if a person stayed in the kitchen beyond the 20-minute baking period, but with a 1.0 air exchange/hour convection factor, the first 20 minutes represents the majority of the total potential inhalation exposure.

It is difficult to determine the exact health implications of these results. Almost no human data exists for BBP or DOP/DEHT. There is an eight-hour OSHA standard for DEHP of 5.0 mg/m^3 (USDL, 1989), a level that was reached only by the Fimo lavender clay. Most of the Fimo DEHP/analogs concentrations were 10 to 100 times lower than this standard. It should be noted, however, that the users would be exposed to all three phthalates simultaneously. The OSHA standard has been in effect for many years and thus has not been reevaluated in the light of recent studies. It is also not intended to be applicable to young children.

The EPA drinking water standard of 6.0 μg/L for DEHP (USEPA, 2002) raises greater concern. Based on interpretation of a multitude of recent animal and human health effects studies with a margin of safety for children and other more susceptible individuals, the EPA assumes a two-liter per day average water intake, which translates to an ingestion of 12 μg/day of DEHP. From Table 1 it can be seen that the Fimo lavender would expose an individual making one 100-gram clay object to over 100 times this much DEHP and/or chemically similar analogs. Assuming that a child perhaps engaged in this activity only twice per month, then total inhalation of DEHP would still be about seven times greater than exposure from water at the proposed EPA upper limit. Overall, seven of the 10 products tested are predicted to expose the user to more than 12 μg of DEHP through inhalation, most of these by a substantial margin.

The potential exposure from hand-to-mouth transfer after working with these clays appears to be a far greater exposure route than inhalation during baking. As previously noted, in these experiments the test subjects washed, rubbed, and rinsed their hands vigorously with distilled water after clay handling before the remaining phthalate residues were quantified. This procedure probably represents an intermediate exposure case. Clearly, some children would wash their hands more thoroughly than this and with soap after using these polymer clays, but others would probably perform a less vigorous perfunctory rinse or even a simple wipe on clothing or towel.

Table 1. Calculated phthalate air emissions and inhalation exposure from polymer clay products.

Manufacturer	*Color*	*Type of Phthalate* *	*Kitchen Air Conc. (µg/m³)*	*Calculated*□ *Inhalation Exposure (µg)*
Fimo	Yellow	BBP	115.5	9.29
		DEHP	400.3	32.2
		DOP	333.2	26.8
Fimo	Lavender	BBP	163.8	45.9
		DEHP	4993	1399
		DOP	6670	1869
Fimo	Turquoise	BBP	32.3	9.04
		DEHP	637	178.3
		DOP	689	192.8
Fimo	Green	BBP	69.9	18.6
		DEHP	40.2	10.7
		DOP	18.9	5.04
Fimo	White	BBP	41.9	27.2
		DEHP	15.1	15.1
		DOP	16.2	16.2
Sculpey	Sweet Potato	BBP	326.0	91.3
		DEHP	338.5	94.8
		DOP	22.5	6.23
Sculpey	Terra Cotta	BBP	183.7	51.4
		DEHP	398.7	111.2
		DOP	6.22	1.74
Sculpey	Pearl	BBP	777.8	217.8
		DEHP	61.1	17.1
		DOP	ND	ND
Sculpey	Lilac Pearl	BBP	214.9	60.2
		DEHP	6.05	1.69
		DOP	ND	ND
Sculpey	Leaf Green	BBP	2667	746.7
		DEHP	37.3	10.45
		DOP	996.1	278.9

*BBP = butyl benzyl phthalate
DEHP = A mixture of diethyl hexyl phthalate [bix(2-ethyl hexyl) phthalate] and/or very chemically similar analogs.
DOP = di-n-octyl phthalate/DEHT (terephthalic acid)
□Assumes a 3m x 5m x 3m kitchen with a 1.0 air exchange rate/hour with inhalation occurring over the 20-minute baking period.

Table 2. Phthalate residues left on hands from normal polymer clay use.

Manufacturer	*Color*	*Type of Phthalate* *	*Amount Left on Hands (mg)*	*Predicted*□ *Child Ingestion (mg)*
Fimo	Yellow	BBP DEHP DOP	3.13 13.4 17.2	1.56 6.70 8.6
Fimo	Lavender	BBP DEHP DOP	0.83 4.42 5.87	0.42 2.21 2.93
Fimo	Soft Green	BBP DEHP DOP	1.24 5.84 7.54	0.62 2.92 3.77
Fimo	Soft White	BBP DEHP DOP	1.33 6.63 8.45	0.66 3.31 4.22
Fimo	Turquoise	BBP DEHP DOP	1.29 6.11 8.39	0.64 3.05 4.19
Sculpey	Sweet Potato	BBP DEHP DOP	2.98 ND 1.61	1.49 ND 0.80
Sculpey	Terra Cotta	BBP DEHP DOP	8.22 ND 0.51	4.11 ND 0.25
Sculpey	Pearl	BBP DEHP DOP	5.35 ND 3.38	2.67 ND 1.69
Sculpey	Lilac Pearl	BBP DEHP DOP	10.4 ND 6.48	5.2 ND 3.24
Sculpey	Leaf Green	BBP DEHP DOP	6.30 ND 3.28	3.15 ND 1.64

*BBP = butyl benzyl phthalate
DEHP = A mixture of diethyl hexyl phthalate [bix(2-ethyl hexyl) phthalate] and/or very chemically similar analogs.
DOP = di-n-octyl phthalate/DEHT (terephthalic acid)
□Assumes a 50 percent hand-to-mouth ingestion factor as used by the US Consumer Products Safety Commission for young children.

The amounts of hand residue observed from each of the three phthalates, along with the predicted associated ingestion (based on a 50 percent hand-to-mouth transfer factor (CPSC 1997)) are shown in Table 2. Again, the chronic, low-level health effects of DEHP have been more thoroughly studied than the other two phthalate compounds, and thus, are emphasized for this discussion. We found virtually no DEHP/analogs on hand residues from the Sculpey products, but BBP and DOP residues were approximately equal for both Sculpey and Fimo products. Blank samples once again showed nondetectable levels of all three phthalates.

For the various colored Fimo products, the calculated DEHP/analogs ingestion amounts from a single usage ranged from 2.21 mg to 6.70 mg with a mean of 3.64 mg (i.e., 3,640 μg). This ingestion exposure would be the equivalent of 303 times the amount of DEHP that would be consumed in two liters of water containing 6.0 μg/L of DEHP. Thus, one would have to consume this water for nearly a full year to get the DEHP/analogs ingestion equivalent of one such polymer clay use.

From further examination of the eight-hour 5.0 mg/m^3 OSHA standard for phthalate inhalation exposure, it can be calculated that, with a standard average breathing rate of 20 m^3/day, total phthalate inhalation mass at this maximum permissible level would be 33 mg over an eight-hour workday, about nine times greater than the mean of the predicted exposure from a single use of polymer clay. Again, however, it should be noted that the OSHA standard is based on very limited chronic human health effect data and was developed for healthy adults. It is increasingly recognized that the main effect of DEHP is probably on endocrine systems, in turn affecting reproductive system development (Kim, et al. 2002), and thus, children are probably orders of magnitude more susceptible to DEHP exposures than healthy adults. These safety factors for sensitive segments of the population such as young children are probably much better represented by the proposed EPA drinking water standard.

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