

A Review of the Availability of Plastic Substitutes for Soft PVC in Toys

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Summary

Greenpeace commissioned this report to answer the question - Are there viable alternatives readily available that can be used as substitutes for soft PVC in toys? Our consultant utilized the expertise of polymer scientists to create this review of the available alternative materials. The question was answered definitively that substitutes exist today which are safer and cost competitive. Only lacking is the will of an individual company to accept the challenge and select appropriate materials that meet the requirements of the toy industry. This report is made available to move the debate forward constructively to ensure the safety of all children.

Summary

The current debate around soft polyvinyl chloride (PVC or vinyl) toys focuses on whether the risk to children from exposure to hazardous additives that leach during use is significant enough to warrant immediate or long-term restrictions or prohibitions of this plastic. Soft PVC contains up to 50% by weight of plasticizers, usually phthalate esters, which are not chemically bound to the plastic and therefore leach or migrate. Laboratory studies demonstrate that the phthalates may cause cancer and reproductive harm, and emerging evidence points to some phthalates as possible hormone disrupters.

Scientists know very little about how the phthalates might affect a child's health, and direct evidence proving harm as a result of exposure to phthalates in soft PVC toys is impossible to obtain without conducting controlled experiments on children and looking for adverse effects throughout their lifetimes. What is known, however, is that children are exposed to phthalates from other sources in addition to soft PVC toys.

Acknowledging this, it is important to note that there are viable alternatives to soft PVC in toys. Why take a risk at the most critical stage in a child's development? Why focus on what a "safe" level of phthalate exposure to a child might be, when this is fundamentally unknown? The terms of the debate, thus, must shift and focus not on **how** hazardous exposure to phthalates is but rather on whether there are safer substitutes for PVC and how these can be implemented.

Political Context

In the European Union (EU), the hazards of soft PVC toys were brought to the attention of the European Commission almost two years ago by Danish authorities who recommended the withdrawal of three PVC teething rings which leached phthalate softeners. Recommendations for voluntary withdrawals of soft toys containing phthalates have also been made by the Dutch, German, Belgian, Canadian, Philippines and US health or consumer protection authorities. Bans on phthalates in soft PVC toys have been initiated or are in place in Austria, Denmark, Sweden, Norway, Greece and Mexico.

In March 1998, after withdrawing several soft PVC teething rings from the market, the Spanish government requested that the Commission take EU-wide emergency action to

address the hazards from soft PVC toys. In June 1998, the European Commission's Consumer Protection Directorate put forward a proposal for a temporary, emergency ban on certain soft PVC toys for children under three, which are designed to be put in the mouth and which contain certain phthalates.

Despite agreement by the Commissioners that protective measures were necessary, they have failed to agree on a proposal for an emergency ban. The Commissioners did agree, however, on the need for long-term legislation to address the problem. Following reconfirmation by a scientific committee that soft PVC toys and childcare articles can pose a health concern, calls for an emergency ban have been renewed this year.

In the meantime, numerous companies have initiated plans to ensure that either phthalate-free or PVC-free products are available this year. While this is encouraging, concern remains that several major companies will continue to use PVC and simply replace phthalates with other additives, which could also be used in large quantities, leach out and be potentially hazardous.

A phase out of the use of PVC in the toy industry is possible in the near future. For the toy industry, PVC is not a major material. It represents only 4.5% of plastics use in toys. For the PVC industry, the use of PVC in toys represents a minute proportion of PVC product, less than 0.1% by weight of the total PVC market in Europe. The proportion of teething or articles designed to be put into a child's mouth will represent only a minor share of this 0.1%.

Alternatives to soft PVC

In the selection of alternatives for soft PVC toys, consideration must be given to environmental and health impacts of the material throughout its entire lifecycle. There are several natural materials that have traditionally been used to make toys and teething, such as wood and textiles. These materials are well tried and tested over the years, are usually durable and repairable and are used by many companies. These materials are preferred to any petrochemical-based plastics because of the global environmental impacts of the use of non-renewable fossil fuels. Given that the toy industry will continue to use soft plastic for certain items, it is necessary to identify plastics which are preferable to soft PVC.

In the long term, bio-based polymers, made from renewable sources, are preferable to any of petrochemical plastics for products which have relatively short lifecycles such as toys.

In the interim, until bio-based plastics are widely available, there are some petroleum-based plastics which are less harmful to the environment and which do not pose such a direct threat to children's health as soft PVC. Many of these plastics are already being used by toy manufacturers for certain products, such as teething rings and soft blocks.

This report examines three types of plastics as potential replacements for soft PVC in toys: Thermoplastic elastomers (TPEs), ethylene vinyl acetate (EVA) and polyolefins

(polyethylene/polypropylene), including the new metallocenes. All three materials fulfill safety requirements, ease of processing (if possible on the same equipment as PVC); aesthetic appeal, lessened environmental and health impacts; and cost competitiveness. The use of these materials to replace soft PVC is a significant improvement and represents progress toward sustainable materials. The three alternative plastics, including cost comparisons, are summarized in the table.

A summary of PVC alternatives for toys

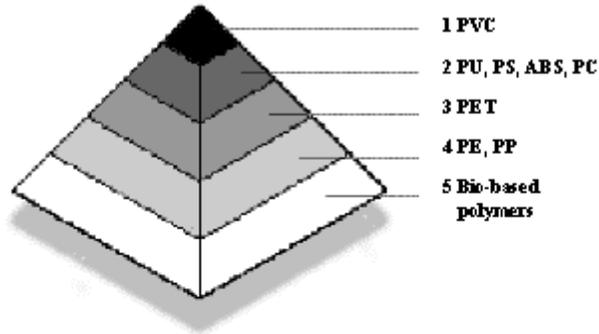
Plastic	Flexibility range	Process techniques	Replacement types	Cost/lb. (in dollars)	Environmental concerns
Thermoplastic elastomers: Styrenic Polyolefin Alloys TPUs	wide, depends on co-polymer or blend type and amounts	blow molding, extrusion, calendaring, rotational molding, thermoforming	Teethers, doll parts/figures, squeeze toys, possibly inflatable toys	0.85-1.87 depending on type and blend or co-polymer mixture	Chemicals used: styrene and polyurethane production are hazardous and both off-gas toxic chemicals in fires
EVA	wide, depends on VA content of polymer	sheet extrusion, injection molding, rotational molding	inflatable toys, teethers, possibly doll parts	0.50-0.80	chloride catalyst used in some vinyl acetate production, by-products from ethylene production
Polyethylenes, Polypropylene, blends/alloys, metallocene catalyzed polyolefins	wide, depends on chain length, co-polymer or blend	all major processing techniques	all current PVC toy applications	0.40-0.55 0.55-0.60 metallocene products	by-products from ethylene production

In addition, none of these alternatives requires phthalate plasticizers to be soft and flexible (although they could be used and care should be taken to prevent this) and all require less overall additives than PVC. When they do contain additives, these additives make up a much smaller percentage (0-2% of the polymer mixture), in comparison to up to 50% phthalate content in PVC toys. Furthermore, it appears that the alternatives are also less likely to leach than PVC as the additives are bound tighter to the polymer.

When additives are required for compounding the alternative materials, those that are non-toxic and are not endocrine disrupters should be used to reduce hazards. It is important that thorough testing of all materials to be used for toys is undertaken, and that regulations prevent the use of hazardous additives such as phthalates in any material intended for children.

Once potential replacements are examined to meet toy material requirements, it is also important to consider the long-term environmental impacts of the alternatives. By ranking plastics in a pyramid, from worst to best, it is possible to evaluate materials from a lifecycle perspective, in an effort to select the most appropriate plastic.

Greenpeace has created such a pyramid with PVC at the top as the most environmentally damaging of the plastics. [1] The hierarchy is as follows:



Note: The following plastics have not been placed on the Greenpeace plastics pyramid of problems: Thermoplastic elastomers (TPEs) are copolymers or alloys of conventional plastics and therefore could fall under 2 or 4 on the pyramid, depending on which material is used to make the TPEs; Ethylene Vinyl Acetate (EVA) is ranked at 3 along with PET. Metallocenes are ranked at 4, the same as polyolefins.

The Greenpeace Plastics Pyramid of Problems

This report demonstrates that rather than spending resources on only assessing the risks of phthalate plasticizer in PVC toys, at the potential detriment to children, attention should focus on which alternatives can be developed and selected to replace PVC in toys. In the meantime, soft PVC toys should not be permitted for sale or use, in line with the precautionary principle. This states that when there is evidence of potential harm, the exposure should be eliminated despite the lack of clearly proven cause-effect relationships.

Notes:

1 See Wytze van der Naald and Beverley Thorpe, PVC Plastic: A Looming Waste Crisis, Greenpeace International, 1998.

Section 1: Introduction

The current debate around polyvinyl chloride (PVC or vinyl) toys focuses on whether the risk to children from exposure to softeners (plasticizers) known as phthalate esters which leach during use is significant enough to warrant restrictions or prohibitions of this plastic. Laboratory studies demonstrate that the phthalates may cause cancer and reproductive harm, and emerging evidence points to some phthalates as possible hormone disrupters.

Scientists know very little about how phthalates might affect a child's health, and it is virtually impossible to follow a child throughout his/her lifetime to determine whether exposure to phthalates from a toy caused harm. What is known, however, is that children are exposed to phthalates from other sources in addition to soft PVC toys, such as in food (including infant formula), dust and air.

Acknowledging this, it is important to note that there are viable alternatives to PVC in toys. Why take a risk at the most critical stage in a child's development? Why focus on what a "safe" level of phthalate exposure to a child might be when this is fundamentally unknown? The terms of the debate, thus, must focus not on **how** hazardous exposure to phthalates is but rather on whether there are safer substitutes for PVC and how these can be implemented.

Some toy companies and retailers have taken precautionary action by removing soft PVC toys from their product line. For example, the Lego company has eliminated most of its PVC products and has issued a statement of intent to eliminate those remaining. Other companies taking precautionary action include Little Tikes of the US, Ambi Toys of the Netherlands, Tolico of Denmark, Babelito of Argentina and Chicco, Prenatal and Giochi Preziosi of Italy.

This report provides an analysis of existing plastic alternatives to replace soft PVC in toys. This report does not cover PVC replacement by other materials such as cloth, wood or bio-based plastics, which may serve as better long term alternatives, nor does it examine issues of consumption or waste from the production and use of toys. Direct substitution for soft PVC toys, such as blow-up/inflatables, teethingers and pacifiers, squeeze toys, and dolls are the focus of this analysis since hard PVC applications, such as stacking blocks, are minimal and easily substituted with numerous alternatives.

Following an overview of plastics use in toys and material requirements in toy manufacture, a detailed analysis is provided of three types of plastics that have been identified which could immediately replace PVC in the majority of soft toy applications. This overview covers applications, limitations, and use of additives. Also provided is a cost-comparison and overview of environmental considerations for the alternatives.

The alternative plastics to soft PVC toys presented in this report are also applicable as replacements for other flexible PVC applications such as medical devices, packaging,

other sheeting applications, etc. The replacement of PVC in other applications will require an analysis of specific product requirements and processing needs.

Section 2: Background - Plastics Use in Toys

The era of plastics use in toy production began in 1868 when John Wesley Hyatt discovered cellulose nitrate which served as a substitute for expensive and ecologically damaging ivory billiards balls. By the turn of the century, plant based plastics were used widely in doll production. Since the 1950s petrochemical-based plastics have been increasingly used in the toy industry. Currently, plastics are used in more than 80% of all new toys made.

In many respects, plastic materials are cheaper, easier to process, and have more color possibilities than the conventional toy making materials like clay, metals, ceramic, and wood. However, with this increasing use of petroleum-based plastics in toys also comes concerns over impacts to children's health from plastics additives and environmental concerns over plastic production and disposal.

The most commonly used plastics to make both soft and rigid toys are commodity resins like High Density Polyethylene (HDPE), Polypropylene (PP), Polystyrene (PS), and Polyvinyl Chloride (PVC). Other resins like Polyamid (PA) Nylons, Acrylonitrile Butadiene Styrene (ABS), Acetal resins (Poly oxymethalate, POM), Poly Methyl Methacrylate (PMMA, or Acrylics), Polycarbonate (PC), Polyurethane (PU), are also used according to the properties required for a particular toy.

The use of PVC in toy production (only approximately 4.5% of plastics use in toys) came under scrutiny in the early 1980s due to the possible adverse health effects associated with a particular softener, Di(2-ethylhexyl) phthalate (DEHP). Following a U.S. Consumer Product Safety Commission investigation into health risks from DEHP exposure, in 1986 the Toy Manufacturers of America entered into a voluntary standard which allowed no intentional addition of DEHP into pacifiers, rattles and teethers (a maximum of 3% by weight). [2] This resulted in its replacement with other phthalate softeners, for which mounting evidence points to risks to children.

Environmental problems can be associated with all synthetic plastics, from production to disposal; however, PVC has the greatest impact on the environment and on health throughout its lifecycle. PVC is also linked to the formation of dioxins and dioxin-like compounds when short-life applications such as toys, disposable medical applications, and packaging are incinerated as a disposal method. [3] PVC production has also been identified as a large source of dioxin and other persistent organic chemicals.

The hazards posed by PVC to human health and the environment throughout its lifecycle (production, use, and disposal) necessitate the identification of safer and more environmentally preferable materials to replace the PVC fraction used in the toy industry. Lifecycle considerations of alternative plastics are discussed in Section 6 and an

evaluation of the environmental impacts of the various petrochemical plastics, which are ranked in a pyramid from worst to best, is included in Appendix B.

Notes:

- 2 Report to the U.S. Consumer Product Safety Commission by the Chronic Hazard Advisory Panel on Di(2-ethylhexyl) Phthalate (DEHP), September, 1985.
- 3 See Pat Costner, The relationship between chlorine input and to combustors and dioxin output, Annotated bibliography, Greenpeace International, April, 1997 for an overview of the scientific studies supporting a PVC/dioxin link in incineration. Available on the Greenpeace Web Page, www.greenpeace.org.

Section 3: Plastic Processing Techniques for Toys

A wide variety of processing techniques have traditionally been used in plastic toy production. Table 1 presents some of these processes, the materials used and typical uses in the toy industry. [4] As noted, while PVC use in toy production is very limited, its use has been predominant in the production of certain types flexible products (especially sheets for inflatable toys and doll's heads) because of its ease of processing using certain techniques and ability to accept additives to achieve specific qualities. The alternatives described in Section 5 can also be processed using common processing techniques, and at times on the same equipment as PVC toys, with process modifications.

As an example, inflatable toys such beach balls, wading and swimming pools, boats and floats, and stand up figures are frequently made by cutting and sealing plasticized PVC sheet. Materials like ethylene vinyl acetate (EVA) and novel metallocene catalyst based Polyethylenes, which allow simple, joining techniques like radio frequency (RF) welding represent useful substitutes to plasticized PVC sheets.

TABLE 1. Common processing techniques in the toy industry.

Technique	Typical Plastics	Typical Application
Injection molding	Polystyrene (PS), Acrylonitrile-Butadiene-Styrene (ABS), PVC and all kinds of thermoplastics	Blocks, solid parts, model kits
Blow molding	High Density Polyethylene (HDPE), PVC	Wheels, hollow parts, figures
Rotational molding	Emulsion PVC, HDPE	Doll parts, squeeze toys
Thermoforming	PS, Polyethylene (PE), Polypropylene (PP), Polyethylene Terephthalate (PET), Ethylene vinyl acetate	Playing boards, play sheets
Calendering	PVC	Sheet for inflatable toys
Sheet extrusion	PS, PVC	Sheet for thermoforming and for inflatable toys
Coated fabrics	Several plastics, usually PVC coated polyester	Cloth substitutes, soft doll bodies
Foaming	Polyurethane, polystyrene	Soft balls, surfboard filler
Biaxial orientation	XLPE, PS sheet	Shrink wrap and other items
Dipping	PVC, latex	Handle grips, balloons
Slush molding	Emulsion PVC, polyethylene	Dolls, boots and other clothing

Some of the different processing techniques are described below, the most important of which for toy production are injection molding (hollow/filled objects) and extrusion:

Injection molding: Plastic material is melted using heat and shear energy and injected under pressure into a mold to achieve the required shape. Building blocks, figurines, hard/flexible teethingers, and other types of toys are produced using this technique.

Blow molding: A continuous tube of plastic material is extruded using heat and pressure. The tube, called a 'parison', is then blown with pressurized air to achieve a shape, inside a closed mold. Most of the dolls, soft balls, and hollow toys are made using this technique.

Rotational Molding: Plastic material is heated until the particles fuse, and while this fusion takes place, the closed mold is rotated in the minor and major axes to achieve a uniform wall thickness. Toys such as plastic boats, figure busts, dolls heads, and large hollow toys are made using this technique.

Thermoforming: The plastic sheet is heated just below its softening temperature, and then pressure is placed on it with a male and/or female mold to produce a shape. Pressure and vacuum can be used to achieve maximum wall thickness, uniformity, and strength. Plastic materials are also processed in a rubbery state using this technique. This technique is used to make toy trays, cups, masks, and boards.

Sheet Extrusion: Molten plastic materials are continuously extruded through a die to form sheets. Generally this method is used for making rigid sheets used in thermoforming. Films and tubes can also be made through extrusion.

Calendering: Sheets are made using a continuous, synchronized method which converts raw materials, fuses the sheets and then passes them through the nips of a series of rolls. This process can be used with PVC and ABS (acrylonitrile-butadiene-styrene), as well as polyethylene and polypropylene. These flexible sheets are used to make toys such as inflatable beach balls. Calendering is often a second step after extrusion.

Lay-up: A liquid gel of plastics is applied on the mold surface and a number of layers of reinforcing agents, such as glass fibers, are added to form an article. This technique is used to make toys of with intricate shapes and contours which would be difficult to make using conventional techniques.

Dipping: This is a simple technique of dipping the mold into a plastic solution and fusing the coating to make the article. Soft flexible toys such as balloons, handle grips and flexible covers can be made using this technique. It is often used in latex processing.

Slush molding: This is a useful technique to produce hollow objects which involves filling a hollow mold with a solution of plastic material, exposing the mold to heat, gelling an inner layer or wall of material in the mold, inverting the mold to pour out the

excess liquid material, and heating the mold to fuse the material. The mold is then cooled and the finished part removed.

The following sections discuss the functional requirements of materials used in toys and the types of materials which could replace PVC.

Notes:

4 See Mark, et. al, Encyclopedia of Polymer Science and Engineering, John Wiley & Sons, 1989 for a detailed overview of plastics use in toys.

Section 4: Material Requirements for Toys

In general, design requirements and characteristics needed for a particular product (how it will be used, colorfastness, stability under harsh conditions) as well as ease of processing and overall cost, will drive the choice of material used in producing a particular toy. In today's competitive toy market, cost containment will often take precedent over other factors.

Nonetheless, most designers will consider a series of material requirements before designing a toy or replacing one material for another. PVC replacement in toys could be achieved by two methods: design of new products with different characteristics or substitution of PVC for other materials in the same product. Common factors to be considered in material selection are listed below.

Some of the important requirements for alternative materials include: avoidance of toxic or endocrine disrupting additives, and none or minimal leachables; safety (avoidance of chipping and breaking); strength and durability under various conditions of use; ease of processing; aesthetic appeal; cost competitiveness; and environmental and health impacts throughout the lifecycle of the alternative material.

1. **Durability/Safety/Operating Conditions:** Toys are generally expected to be strong so as to not chip, incur stress cracking, or break and resist abrasion. Alternative materials should have high strength, rigidity, and resistance to creep (deformation of the polymer).

Since a large fraction of toys are used outdoors, the material must have good weatherability (temperature and weather extremes) and ultraviolet (UV) stability. Generally, unstable chemicals and weak bonds are more prone to oxidative cleavage which initiates a chain reaction of degradation. The plastic material should thus be chemically stable to withstand degradation. The alternative should also be resistant to water, solvents, oils and chemicals which may be reactive with the plastic (with the material and/or the additives). Durable toys will last longer and will not end up as quickly in the landfill or incinerator.

2. **Avoidance of toxic or endocrine disrupting additives which might leach during use:** In addition to being non-toxic to a child when ingested or under other conditions of exposure, the material should use none or only minimal amounts of non-toxic additives, eliminating or maintaining leachability as low as possible.
3. **Flexibility/resilience:** Toys must be made flexible yet tough enough to withstand abuse and prevent breakage. Resistance to repeated flexing (fatigue resistance) and an ability to retain the product shape after repeated use may also be critical. A variety of properties combine to make a plastic flexible, such as the types of molecular bonds, crystallinity, plasticizer, humidity, and secondary attraction forces (e.g., steric hindrance and polarity).
4. **Economics:** Cost-competitive. Alternative materials should have a high strength to weight ratio, meaning that less material can be used to produce a product of similar strength. When more than one material is available for a toy, the choice of material often becomes a matter of economics. However, environmental and health and safety considerations should be paramount.
5. **Ease of processing and processing problems:** As every cent is accounted for in this competitive industry, alternative materials must be easily processed by conventional techniques with normal processing equipment or on the same equipment as PVC toy manufacture. Also, difficulties in processing of alternative materials and the ability to overcome those difficulties must be considered.
6. **Aesthetic appeal:** A major requirement for consumer products such as toys is their appearance. This is the single largest contributing factor to product survival. Materials must have a wide array of color compatibility and a rich 'feel'.
7. **Regulations and specifications:** Designers must meet international or national government regulations or industry specifications concerning the use of materials in toys. Usually considered in such regulations and specifications are additive content, flammability, food contact, and leachates.
8. **Other material/fabrication requirements:** Material properties to consider include electrical insulation properties, transparency, frictional properties, surface finish and specific gravity. Processing requirements include the need for assembly or coating, paintability/colorability, or any post molding operations required.
9. **X - ray Opacity:** Since children can ingest toys, especially if small parts are involved, plastics can be made radiopaque and x-ray visible by chemically binding barium salts to polymer chains. This aids detection if swallowed.

In the end, cost will be the determining factor in choosing between two similar materials, if other considerations such as environmental, health and safety are equal. Cost considerations, however, need to include both actual material cost on a per weight basis in addition to gains from material conservation and process conditions.

Section 5: A Comparison of Various Plastic Alternatives to PVC

Based on the requirements for specific toys, various materials can be selected as potential alternatives to PVC. The materials listed below represent three types of readily available plastic alternatives which fulfill the material considerations listed in the previous section. Some of these alternative materials are currently being widely used, while some are newly developed with advance technology, and are only now entering the market. None of the three alternative plastics require the large quantity of additives required to soften PVC. Nonetheless, toy manufacturers should undergo a detailed examination of alternative materials for their health and safety and environmental impacts before selecting a new plastic.

All of the alternative plastic materials addressed (in fact the vast majority of plastics on the market today) are petrochemical based and thus cannot be considered sustainable in the long term due to limits in resources and the contribution that petrochemical production makes to global climate change. Substitutes have been chosen to address immediate concerns of children's health and safety and minimizing product lifecycle environmental impacts.

The question of additives

All plastics, including bio-based plastics, require the use of additives to aid processing, enhance material properties (reinforce), reduce material costs (fillers) and impart specific characteristics such as stability (heat and light), flexibility, flame resistance, provide color and aesthetics, etc. Because of its brittle nature and heat sensitivity, PVC by far uses the greatest amount of additives of any commercial resin. For example, the vast majority of all stabilizers are used in PVC (because of its susceptibility to dehydrochlorination) as well as 90% of global plasticizer use and 95% of all phthalate use (some 1.4 billion lbs. per year).

When plastics are used, there is always a possibility that incorporated additives may migrate in small amounts to product surfaces, and into the surrounding media. Thus migration may lead to some human exposure to additives. This migration or leaching from the polymer molecules to the surface, may vary widely depending upon: type of plastic matrix; diffusion properties of the additive in the plastic matrix; contact environment, time, and temperature; interaction between different additives, and concentration of additives.

Below is a short generic summary of plastics additives. These are described in greater detail in Appendix A. External paints, pigments, and adhesives are not considered. It is important to note when additives are required for compounding the alternative materials (specific characteristics cannot be achieved through polymer modification), non-toxic alternatives should be used to reduce risks to children. Also, plastics additives may affect

polymer properties, so when possible, it is useful to minimize their use, as well as eliminate those that are toxic or endocrine disrupting.

Table 2: Additives used in plastic production

Additive type	Reason for use	Chemical(s) used	% by weight of polymer	Main plastics using additive
Plasticizers	Soften/add flexibility	phthalates, adipates epoxidized soy oil, phosphates, trimellitates	depends on flexibility needed, up to 60% or more	PVC, sometimes used but not required with other polymers and thermoset rubbers
Fillers/ Reinforcements	lower cost/ enhance mechanical properties	wood flour, kaolin, cotton, glass, carbon, mica	low to high, depending on application	mainly used in rigid plastics
Pigments	allows wide range of colors	carbon black, titanium dioxide, lead compounds	>1-4%	polystyrene, polypropylene, PVC
Flame Retardants	slow the burning rate of plastics/inhibit volatilization of combustible gases	halogenated hydrocarbons, antimony oxide, phosphorous compounds, alumina trihydrate	Depends on type of application, flammability of resin, and presence of other additives	all types
Antioxidants	retard oxidative degradation	hindered phenols thioesters, organophosphite	0.05-1.0%	polyolefins, styrenics
Blowing agents	create foaming, softness	hydrazine derivatives, citric acid/sodium bicarbonate, nitrogen, air	depends on qualities needed	polyurethane, PVC, styrenics, low density polyethylene
Lubricants	improve processing	fatty amides, PTFE wax, fatty acids, esters, waxes, metal stearates	depends on plastic/ processing technique	primarily PVC, also polyolefins
Heat Stabilizers	protection from thermal degradation	mixed metals salts, organotin lead compounds	depends on conditions	primarily PVC
UV Stabilizers	to avoid UV degradation	pigments and carbon black, benzophenones, amine light stabilizers	0.05-2%	polyolefins and other plastics used mainly outdoors
Impact modifiers/ Processing aids	improve resistance to stress	thermoplastic elastomers	depends on product use	mainly PVC, also polyolefins

The types and amounts of additives used depend on the particular product and its use; therefore formulations of additives vary widely. For example, the use of several types of additives, such as flame retardants and blowing agents depends on the type of use for the toy (e.g., a flame retardant might be used on a play tent but not a teether).

In general, none of the alternatives requires the use of phthalate softeners and all contain less total additives than PVC. When they do contain additives, these make up only a very

small percentage (0-2% each of the polymer mixture), compared to up to 50% phthalate content in PVC toys (without considering the many other additives PVC requires). [5] For example, ethylene vinyl acetate (EVA) plastics can contain additives (UV stabilizers, antioxidants and pigments). The alternatives also appear to have less leachables than PVC, meaning that it is more likely that additives will be bound to the plastic polymer or retained by the polymer matrix. It is well known that the phthalates are not chemically bound to PVC, so that they can easily leach out during normal use.

Description of substitutes for PVC in toys

- **Thermoplastic elastomers: (TPE)**

TPE is a material that combines the processability of a thermoplastic with the functional performance and properties of a conventional thermoset rubber. This allows processing of flexible, rubbery articles with speed, efficiency and at low cost. These materials can match or better the characteristics of flexible PVC in terms of strength, appearance and performance. The TPEs have the highest growth rate among materials at 8-9%, as newer applications come up replacing conventional flexible materials, one of which is PVC.

Many TPEs are on the market today, and are being widely used for applications where PVC or rubber was used. Many of the TPEs are copolymers or alloys of conventional plastics. A co-polymer is two or more different polymers chemically linked together, while an alloy or blend is a physical mixture of two or more polymers. Copolymers and polymer blends allow tailoring of product qualities through variation in the quantity of each polymer involved.

TPEs can be processed into a wide range of flexibilities, strength properties, and are easily colored, and are easily processed with conventional equipment. They also have high temperature range without degradation and have good resistance to a wide variety of environments. Finally, TPEs have a rich, tactile 'feel' adding to their aesthetic qualities.

Two most important fabrication methods for TPEs are extrusion and injection molding. Both the equipment and methods normally used for the extrusion or injection molding of a conventional thermoplastic are generally suitable. Materials such as olefinic TPEs can be blow molded on standard equipment to produce figurines and hollow parts. They can also be calendered like PVC for flexible sheet manufacture and post form heat-welded to produce inflatable toys. These materials can also be thermoformed and foamed using chemical and mechanical blowing agents. TPEs are currently used in the automotive, medical, food, construction, industrial, business machines and consumer applications.

Most of the TPEs can be produced in a wide hardness range (from 30 Shore A up to 75 Shore D) without the use of additives by controlling the hard matrix phase and soft domains interspersed in the hard matrix. This would greatly reduce the possibility of any additives leaching post-processing and use.

There are numerous TPEs available on the market. Some of the most applicable as substitutes for PVC toys include:

1. **Styrenic block copolymers:** These TPEs have a low cycle time, and can be processed by conventional molding techniques. The combination of styrenic TPEs can be controlled during manufacture to give a wide range of properties like strength, flexibility, tack, and softening temperatures. Styrenic TPEs offer high surface quality, durability, and lack of crumbling. Styrenic TPEs include styrene/butadiene/styrene (SBS) block copolymers, styrene/isoprene/styrene block copolymers, styrene/ethylene-butylene/styrene (SEBS) block copolymers, and styrene/ethylene-propylene/styrene block copolymers. SEBS is already used in the production of toys (teething rings by Tolico in Denmark) and can replace PVC for the production of dolls heads (with hair) using rotational molding techniques, one of the most difficult PVC substitutions.
2. **Polyolefin blends:** Olefinic TPEs are blends of olefinic thermoplastics (mainly polypropylene) and elastomers, also generally olefinic. These also can be controlled to give a wide range of properties ranging from flexible elastomeric to tough, rigid materials, for use in a range of applications. These TPEs have excellent weathering properties and resistance to environmental conditions and chemicals. They also have easy coloring characteristics.
3. **Elastomeric alloys:** This category of TPEs (also known as synthetic rubber) can successfully replace rubber because of its processing ease as compared to rubbers. An example of an elastomeric alloy is a mixture of polypropylene-ethylene-propylene-diene-terpolymer (PP-EPDM). These TPEs can be processed with conventional machinery capable of heat and shear melting of materials, similar to those used for polypropylene, polyethylene and PVC.

Given the various types of TPEs on the market, custom compounding is conducted for TPE materials to suit wide performance capabilities from flexible films to rigid applications. A more extensive analysis of TPEs is justified to better understand the characteristics of various TPE grades and types that could replace different PVC applications. One type of TPE, thermoplastic polyurethane, uses significant quantities of chlorine, and therefore would not be considered a suitable substitute for PVC. TPE polymers that appear lower on the pyramid of plastics such as polyolefins, are preferable to those higher up the pyramid, such as styrenes.

Commercial information:

TPEs are produced by companies such as DuPont, Monsanto, Eastman Chemicals, Shell, Hoechst Celanese, GE Plastics, Himont, Exxon, Mytex, CFT and various companies like M. A. Hanna, Tecknor Apex, which can custom compound the material according to specific performance requirements.

- **Ethylene vinyl acetate: (EVA)**

Like PVC, EVA can range from thermoplastic to elastomeric state, depending upon the vinyl acetate (VA) content of the copolymer. [6] Vinyl acetate is produced by one of three methods: by reacting acetylene and acetic acid; by passing mixed vapors (acetylene gas with acetic acid vapor) over a catalyst of zinc acetate; or by reacting ethylene with acetic acid and oxygen in the presence a catalyst.

EVA is made by the co-polymerization of ethylene and VA by free radical polymerization initiated either by a peroxide or perester. With the increase in VA content (5-50%), the molecular crystallinity is reduced and material properties are affected. Properties like clarity, low temperature flexibility, heat sealability, and impact strength improve with increased VA content, without the use of leachable plasticizers or other additives. These properties are retained over time unlike plasticized PVC, which would lose its plasticizer and other additives and become hard, especially when exposed to harsh weather conditions.

Some polyethylene/EVA copolymers has been shown to contain additives, including phthalates, which could be present deliberately or as a result of contamination in the process technology. However, EVA does not require phthalate additives to achieve flexibility and direct use of phthalates or contamination sources should be eliminated, along with other toxic additives, if EVA is to be a viable PVC substitute.

Sealing temperatures are reduced with EVA, leading to a reduction in the fabrication time for flexible sheets and films, increased efficiency and lower production cost. EVA copolymers can accept high degrees of filler loading without serious degradation of their physical properties.

EVA can be used in toy manufacture to achieve a broad range of toy properties including: flexibility, toughness and resilience. EVA has a good stress cracking resistance for toys which would require periodic washing and cleaning with chemical or physical agents.

EVA processing techniques are similar to those used with low-density polyethylene. It can be processed on standard processing equipment by major plastics processing techniques such as injection molding and virtually all extrusion processes (such as sheet extrusion). Because EVA is more polar than polyolefins, it can also be radio frequency welded for flexible sheeting and film applications. However, due to high surface tack and friction, processing EVA films may require special attention (such as anti-statics or anti-blocking agents). Tack refers to the stickiness that EVA possesses, which may cause the plastic melt to stick to the metal walls of the processing equipment.

There is a large market for EVA, particularly for flexible film and sheeting, which is mainly used in packaging. It is currently available in the market in the form of films (60%), extruded forms (6%), and color coatings (can be very important for toys), injection and blow molded applications (5%). Some toy manufacturers such as Baby Vision, Early Start, Learning Curve, and International Playthings are already using EVA

in the production of teething rings and other soft infant toys. Because of its ability to be heat and radio frequency welded, EVA could also be an excellent candidate to replace PVC in inflatable toys. EVA could also be used in rotational molding to produce dolls heads and other parts.

A multitude of other types of vinyl acetate co-polymers are available, many of them being used in packaging and coating applications. Also, by increasing the VA content of the co-polymer (over 40%-50%), additional ethylene-vinyl acetate copolymers are formed. These have either thermoplastic properties, elastomeric properties, or thermoset (vulcanized rubber) properties. Vinyl acetate-ethylene elastomers have a wide colorability, color retention, and good age stability.

Lastly, polyvinyl alcohol (PVOH) is commonly produced through the transformation of EVA. PVOH is a water soluble material with wide application in the adhesive area.

Commercial information:

EVA is produced by DuPont Co., Exxon Chemicals, Union Carbide Corp., Quantum Chemicals, Bayer Corp., Chevron Chemicals, Elf Atochem and Millenium Petrochemicals Inc.

- **Polyolefins**

Polyolefins have been used for decades in the toy industry and are a preferred plastic for many applications because of their ease of processing by injection, blow and extrusion molding; their durability, colorability, and cost-effectiveness. Polyolefins are extremely versatile, with differing properties being achieved without the use of plasticizers or other additives. For example, the polyethylenes can be made from hard to soft by modifying hydrocarbon chain length or cross-linking. In general, increasing the density of the polyolefins increases stiffness, hardness, heat and chemical resistance, but reduces impact strength and stress-crack resistance. Polyolefins are also popular due to their low energy demand during melt processing. Polyolefins can be considered among the least dangerous petrochemical plastics in terms of their environmental impacts through production, use, and disposal.

Instead of developing new thermoplastic materials, companies are more and more concentrating their efforts on the development of new blends of polyolefins and other existing polymers, which can be tailored to suit various applications and performance characteristics. A large variety of polyolefins are can be used directly or blended with other materials to suit particular needs. Some of these polyolefins surpass PVC in strength, clarity, flexibility and other related properties.

Examples of some polyolefin replacements are provided in the following paragraphs. Companies such as Mattel are already producing soft children's toys, such as soft blocks, out of polyethylene.

1. **Polyethylene:** Very low density polyethylene (VLDPE) can also be used as a PVC replacement, as it has better environmental stress cracking resistance, improved toughness, a higher softening temperature, and good low temperature impact properties. VLDPE does not have any volatiles or extractable plasticizers, nor the tack associated with EVA. Linear low density polyethylene (LLDPE) offers good stiffness and impact strength/toughness, excellent environmental stress crack and warp resistance. Ultra-low density polyethylene (ULDPE) is an ethylene copolymer with excellent environmental stress crack resistance, outstanding flex-life and flex-crack resistance, toughness and good sealability.
2. **Polypropylene:** Polypropylene offers similar properties as polyethylene including low density, good mechanical, temperature, flexing/fatigue, and stress crack resistance and rigidity. It also has excellent colorability and is easily pigmented. Polypropylene is often manufactured as a copolymer to impart different characteristics, such as flexibility and rubbery texture.

New developments in polyolefin technology

Advancements in catalyst research has led to the development of metallocene polyolefins. The metallocene catalysts allow greater process control, stereospecific molecular structures and a narrow molecular weight distribution in the polymer main chain, maximizing the uniformity of polymer physical properties. Because of this narrow molecular weight distribution, there are few low molecular weight chains, leading to low extractables and leachates. In essence, the metallocene catalysts allow the precise and predictable tailoring of process chains to impart a range of qualities on the polymer, with minimal use of additives. This technology is also being applied to polyolefin alloys such as EPDM.

Metallocenes have a good ability to incorporate different comonomers, including higher alpha olefins, such as octene into the polymer. When ethylene is co-polymerized with up to 20% of higher α -olefins, new materials called plastomers are produced. Plastomers are flexible and thermoplastic and have better properties than conventional polyolefins, at much lower densities. Copolymers containing more than 20% of comonomer are called polyolefin elastomers. These polyolefin elastomers have better flexibility, clarity, and tensile strength. This would allow them to replace PVC in applications such as inflatable toys with better mechanical properties and a thinner and lighter film, reducing the amount of material and waste generated.

Syndiotactic Polypropylene (sPP), meaning that the polymer molecules are arranged in a highly regular manner, has flexibility, clarity, and tensile strength as well as low heat seal temperatures, enabling it to be used in place of materials such as PVC, EVA, and linear low density polyethylene (LLDPE) in films, foil for decoration or stickers, and toys that need to be extruded.

Metallocene products have a significant advantage over PVC in that their low density allows as much as a 40% reduction in weight per part. They have a lower melt

processing temperature and much lower injection molding cycle times (25% less) than PVC. The resins are also more thermally stable than PVC. It has been estimated that the savings for metallocene products in terms of cost per part over PVC are in the range of 25-30%. [7]

Metallocene polyolefins can be processed using conventional techniques such as injection molding and in some instances products can be produced on the same equipment as PVC. Due to their wide range of properties and process control, the metallocene polyolefins are expected to take over a large percentage of the flexible PVC market in the coming years. Nonetheless, while these polyolefins are currently being produced by several manufacturers, wide-scale production capacity could take time to develop.

Developments in polymerization techniques also allows the production of various alloys and blends in the reactor itself. A series of polymerization reactors facilitates the production of blends. A combination of various polyolefins with an ethylene-propylene elastomer (which introduces flexibility into the blend) allows the synthesis of a broad range of materials having medium to very high strength, particularly impact strength, since a soft, rubbery phase is introduced in a base polymer. Blending of these special reactor blends with LLDPE produces a material that can be used to replace PVC in most flexible applications.

Emerging technology in polyolefin production provides greater control over molecular structure and composition, as well as polymerization and blending, resulting in materials with a broad range of characteristics that can replace virtually all soft PVC use in toys.

Commercial Information:

Polyolefins are produced by numerous companies throughout the world. Dow Chemicals (Plastics group), Exxon Chemicals, Huntsman Corporation are initiating commodity production of metallocene polyolefins. [8]

Notes:

- 5 see Ruth Stringer, I. Labounskaia, D. Santillo, P. Johnston, J. Siddorn and A. Stephenson, Determination of the Composition and Quantity of Phthalate Ester Additives in PVC Children's Toys, Greenpeace Research Laboratories Technical Note 06/97, September 1997 and Joseph Di Gangi, PhD, Warning: Children at Risk, Toxic Chemicals Found in Vinyl Children's Products, Greenpeace USA, November, 1998 and Greenpeace China, Greenpeace Study on Hazardous Additives in PVC Toys Sold in Hong Kong, October, 1998, Testing by the Hong Kong Standards and Testing Centre Ltd.
- 6 Though vinyl acetate is also a "vinyl", this refers to the chemical structure of the monomer and not to the presence of chlorine, which makes PVC a problem plastic.
- 7 Robert Wilson, Jr. The Impact of Metallocenes on PVC. SRI International, 1997, presented at the World Vinyl Forum, Akron, OH.
- 8 See David Rothman, Metallocene Polyolefins, in Chemical Week, May 21, 1997 for an overview of metallocene production capacity and benefits.

Section 6: Lifecycle Considerations for Alternative Plastics

In addition to considering the health hazards of plastic toys during use, manufacturers need to consider the impacts of their choice of material throughout the product lifecycle. It is important that manufacturers take responsibility for the environmental and health impacts caused by the production and disposal of the materials they use, constantly attempting to identify alternatives that reduce those impacts. Key environmental issues that need to be considered in material selection include:

Production: toxic emissions from production, potentially exposing workers, surrounding communities, and distant communities. Emissions from subsidiary manufacture (compounding, product production) and associated manufacture (additives) must also be considered.

Use: exposure to additives during product use, toxic chemicals generated in accidental fires.

Disposal: by-product creation during combustion, impacts in landfills, recyclability. Most plastic recycling is not true recycling (producing the same product) but rather downcycling (producing different, lower grade products). Bio-based plastics offer the best opportunity for recyclability and are preferred to any petroleum-based plastic.

There are clearly some plastics that are better from an environmental standpoint than others. See Appendix B for information on the environmental impacts of various plastics, which are ranked in a pyramid, from worst to best, with PVC as the worst.

Section 7: Cost Analysis of Alternatives

The cost of a toy or any article can be broken into direct and indirect costs. The direct costs are raw material costs, processing, labor, equipment and associated costs. The indirect costs (often called external costs) which are difficult to calculate, can be greater than direct costs, and are often incurred by workers, communities, and consumers. These include: environmental impacts, impacts to health, hazardous material handling costs, waste disposal, damage to production or recycling equipment, and costs associated with product replacement (when products are not durable).

Costs which should be considered when examining alternative materials include:

1. Superior material properties of the alternative over PVC.
2. The extremely rapid processing of alternative materials using conventional and the same equipment as PVC.
3. The amount of waste and scrap generation in the process and the reprocessability of that waste.
4. Alternative materials may have simpler processing operations and conditions, including shorter downtimes and more economical purging requirements.
5. Increased life of the expensive equipment and tooling due to lack of corrosive hydrochloric acid gas emitted during the processing of PVC. All molds, screws, barrel walls, and parts coming in contact in direct contact with PVC melt must be chrome plated to avoid corrosion, which is an expensive process.
6. Alternative materials can be used for producing thinner parts which can match or better PVC's performance. This reduces the cost per unit area by lessening product weight. For example, due to their improved strength qualities, thinner metallocene polyolefin films can be used in applications where PVC films were conventionally used. This offsets the additional cost of metallocene polyolefins.
7. Advances in technology such as thin wall injection molding can also help offset the expensive rotational molding cost by producing thinner, lighter, and stronger toys.
8. Thinner, less bulky toys can save on transportation and shipping costs and reduces material use.
9. Despite the cost justification factors listed above, given that a conventional toy weighs only a few hundred grams, final product costs would only vary slightly for most of the alternatives listed in this report. This assumes that product weight stays the same, which may not be the case for new polyolefin production techniques.

A per pound price list for various plastic materials is listed below. Several of the alternative materials listed in this report are currently cost-competitive with PVC. However, since parts are usually made by volume and not weight, a simple comparison of the price per unit weight (e.g. U.S. dollars/lb) would be misleading. Figures of comparative volume cost are an important issue to consider. It may also be the case that with two alternative materials, the one with a higher volume cost may prove to be more economical. One reason for this may be that the more expensive material is stiffer and can thus be used in thinner section moldings.

Table 3: Costs of PVC and various alternative materials

Material	Cost per pound (US dollars)
PVC	0.35-0.70 depending on the grade
Polyethylenes	0.40-0.55 depending on the grade 0.55-0.60 metallocene products
TPE	
Polyester	2.12-2.70
Olefinic	0.85-1.41
Styrenic	0.85-1.87
EVA	0.50-0.80 depending on grade, VA content
Polypropylene	0.30-0.50 depending on the grade

Section 8: Conclusions

The debate over the hazards of PVC toys must move away from a discussion about risk, which is almost impossible to calculate and will vary from individual to individual, to one based on the availability of safer alternatives. This report has described three alternative types of plastics that can replace PVC in all of its toy applications (there are many other plastic and non-plastic materials that could replace PVC applications). While most of these alternatives represent drop-in substitutes with minimal processing change required, some PVC applications, such as dolls heads, may require research and development prior to their effective replacement. In general, alternatives are cost-effective, often more easily processed, offer better physical qualities (increasing toy safety), avoid the use of phthalate plasticizers and use minimal additives, and have reduced environmental and health impacts throughout their lifecycle. It should be ensured that any additives are minimal and non-toxic.

Materials such as the metallocene polyolefins, thermoplastic elastomers, EVA and other olefin blends can be considered the best currently available plastic alternatives from a safety and lifecycle perspective for replacing soft PVC applications today. New technologies can also play an important role in justifying PVC replacement with these materials. Designers are pushing the limits of thin wall injection moldings using polyolefins, reducing material use in toy production. New processing techniques such as gas assisted injection molding can be used to produce toys which appear bulky from the outside but which are actually hollow on the inside. These advancements, particularly in polyolefin technologies, will lead to alternatives with superior polymer strength (allowing thinner polymers to be produced) and variability in characteristics using minimal amounts of additives, while reducing waste generation and materials use. Advancements in biodegradable plastics also hold hope for the future production of toys that are more sustainable through their lifecycle.

Table 4: A summary of PVC alternatives for Toys

Plastic	Flexibility range	Process techniques	Replacement types	Cost/lb. (in dollars)	Environmental concerns
Thermoplastic elastomers: Styrenic, Polyolefin, Alloys, TPUs	wide, depends on co-polymer or blend type and amounts	blow molding, extrusion, calendering, rotational molding, thermoforming	teethers, doll parts/figures, squeeze toys, possibly inflatable toys	0.85-1.87 depending on type and blend or co- polymer mixture	Chemicals used: styrene and polyurethane production are hazardous and both off-gas toxic chemicals in fires
EVA	wide, depends on VA content of polymer	sheet extrusion, injection molding, rotational molding	inflatable toys, teethers, possibly doll parts	0.50-0.80	chloride catalyst used in some vinyl acetate production; by products from ethylene production
Polyethylenes, Polypropylene, blends/alloys, metallocene catalyzed polyolefins	wide, depends on chain length, co-polymer or blend	all major processing techniques	all current PVC toy applications	0.40-0.55 0.55-0.60 metallocene products	by-products from ethylene production

No plastics expert will dispute the fact that PVC toys contain large amounts of phthalate plasticizers and that these additives to some degree leach. They will also not dispute the fact that other plastics do not require the large amount of additives required by PVC. Scientists agree the phthalates do have demonstrated toxic effects in laboratory experiments and that that little is known about how toxic chemicals in any amount can affect the developing child.

In the meantime, the current debate in the EU and the US focuses on whether "safe" levels of phthalate exposure can be found. Instead, policymakers should acknowledge the legitimate debate on the hazards of phthalates and the near impossibility of estimating risk of harm to children and prioritize the health of small children over the likely minimal costs to a multi-billion dollar industry of using substitute materials.

In the end, given the mounting evidence of the potential hazards that PVC toys pose to children, and the wide availability of cost-effective, safer alternatives, there appears to be no compelling reason for the toy industry to continue using PVC in its production processes. With the large amount of additives required for PVC, and its lifecycle hazards, switching from one additive to another (which may create new risks) is an unacceptable solution.

Government agencies entrusted with protecting children's health should require the substitution of PVC as the only measure which will adequately protect children's health from the hazards of PVC.

Appendix A - Plastics additives used in toys

Below is a short description of some of the main additives used in plastic toys.

Antioxidants: Virtually all plastic materials undergo reaction with oxygen. Oxidation induces breaking of long chain plastic molecules, which are responsible for its properties, into smaller low molecular weight entities. This causes a loss in plastic qualities. Addition of antioxidants, retards oxidation and thus the aging of the polymer. Antioxidants are usually used in a concentration of a fraction of one percent so leaching is very limited. Commonly used primary antioxidants are phenols and amines, phosphites, and sulfur containing compounds.

Lubricants: In polyolefin processing, lubricants are used to reduce friction between the metallic walls of a screw and barrel by forming a release film. When the lubricant is used to reduce processing difficulties, it can be classified as an internal or external lubricant. An external lubricant is on the surface of the polymer while an internal lubricant is soluble in the polymer molecules.

Stabilizers: These are primarily used in PVC processing, to allow processing and use of rigid PVC at elevated temperatures without degradation. Stabilizers retard aging and degradation by preventing the formation of hydrochloric acid gas (dehydrochlorination), avoiding oxidative degradation. Sometimes, in PVC formulations, costabilizers are used. Costabilizers do not possess thermostability ability as such, but improve the effectiveness of stabilizer systems. For example esters of phosphorus acid, epoxy compounds, polyols, and phenolic antioxidants are used as costabilizers.

UV Stabilizers: Light and oxygen may induce degradation (photo or oxidative degradation) reactions in plastics that may change the clarity and lower the physical strength of the material. Light stabilizers and UV stabilizers are used to retard this degradation. Light stabilizers are chemical compounds capable of interfering with the chemical and physical process of light induced degradation.

Fillers/Reinforcing Agents: Inorganic materials are frequently used to reduce cost, increase low cost bulk and/or improve some specific material property. When property enhancement is done, a filler is also referred to as a reinforcing filler. Since fillers are either chemically bound to the molecule, or embedded in the polymer matrix, there may be a low incidence of leaching on the surface by molecular movements.

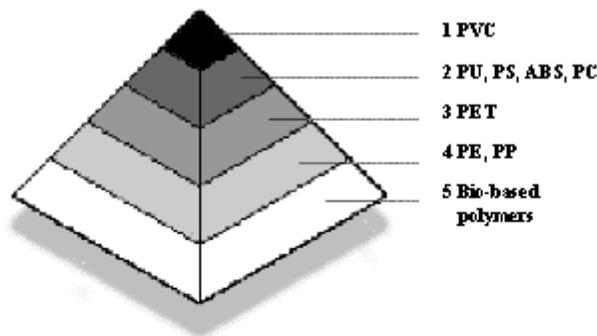
Colorants: For aesthetic purposes, toys make extensive use of colorants. These are classified as pigments, which are virtually insoluble in plastics and dyes, which are soluble. Pigments are normally melt mixed with the plastic and are known as dispersion colorants, while dyes are dissolved in the plastic and are present in a molecular solution. The colorants have to be thermally stable and resistant to weathering and must not fade out with time. However, migration of colorants as a result of partial solubility in a plastic may be seen as a problem.

Flame-retardants: Flame retardants are used to fulfill flame retardancy requirements laid down in regulations and for safety reasons. This is accomplished by inhibiting or suppressing the combustion process. Flame retardants used as additives, can either chemically or physically lower the combustibility of plastic materials. Flame retardants impede and stop the propagation at any stage of combustion.

Blowing agents: These are chemical agents which produce gases through reactions and help in the manufacture of foams. Azo compounds, which give off nitrogen gas, are widely used as blowing agents.

Processing aids: These are high polymeric materials added in small quantities to thermoplastic resins that are difficult to process. Processing aids help to accelerate the melting process, and improve the flow properties of the plastic material during processing. These also contribute towards improving the mechanical properties, unlike simple additives like plasticizers.

Appendix B: The Hierarchy of Plastics



Note : The following plastics have not been placed on the Greenpeace plastics pyramid of problems: Thermoplastic elastomers (TPEs) are copolymers or alloys of conventional plastics and therefore could fall under 2 or 4 on the pyramid, depending on which material is used to make the TPEs; Ethylene Vinyl Acetate (EVA) is ranked at 3 along with PET. Metallocenes are ranked at 4, the same as polyolefins.

The Greenpeace Plastics Pyramid of Problems

The following is an attempt to "rank" the most common plastics. Environmental and human health problems related to production, additives, product emissions, disposal and fires are considered. The aim is to provide a basis for choosing and developing alternatives for PVC. The list is ranked from the worst to the best.

1. **Polyvinyl Chloride (PVC)** - PVC has been identified as the worst plastic from a lifecycle perspective because of the creation of dioxin and other persistent organochlorines during its production, use, and disposal; hazards posed by its cancer-causing monomer, vinyl chloride; its lack of recyclability; [9] and its heavy use of dangerous additives such as lead, cadmium and the phthalate esters which can leach out during use. [10] These lifecycle hazards have led to several European nations, local governments, manufacturers, scientific and public health organizations to scrutinize and/or pass restrictions on PVC use.

2 A. **Polyurethane (PU)** - PU production and its intermediate products consume about 11% of worldwide chlorine production. Polyurethane production uses several very hazardous intermediates and creates numerous hazardous by-products. PU production has been linked to numerous occupational health problems including heart disease, asthma, and reduced sperm quality. Toluene diisocyanate, used in PU production, is a strong respiratory sensitizer. The burning of PU releases numerous hazardous chemicals including isocyanates and hydrogen cyanide. PU is potentially more hazardous in the work environment than PVC and is thus likely not an acceptable alternative, without substantial process change to reduce exposures and chlorine use.

2 B. **Polystyrene (PS)** - PS is made from benzene and ethylene raw materials. It is widely used for foamed insulation and also for hard applications (e.g., cups, some toys). Polymerized with other materials, it becomes a thermoplastic elastomer (styrene-ethylene-butylene-styrene). Other materials used in its production include butadiene and ethyl benzene. Benzene is a known human carcinogen. Butadiene and styrene (the basic building block of the plastic) are suspect carcinogens. Styrenics generally require far fewer additives than PVC and are inert in final form. However, though the lifecycle of PS appears to have less impacts than that of PVC, styrenics may not be an adequate long-term substitute for PVC for several reasons: the hazards of its raw materials, which are especially dangerous to workers; fire hazards; high energy consumption; the need for CFCs for foaming; and poor recycling.

2 C. **Acrylonitrile-butadiene-styrene (ABS)** - ABS is used as a hard plastic in many applications like pipes, car bumpers and toys (hard building blocks). ABS uses a number of hazardous chemicals. These include butadiene, styrene and acrylonitrile. Acrylonitrile is highly toxic and readily absorbed by humans by inhalation and directly through the skin. It is classified as a probable human carcinogen as are styrene and butadiene. Additives used include antioxidants and light stabilizers. ABS is extremely difficult to recycle, similar to PVC.

2 D. **Polycarbonate (PC)** - PC is used for products like CDs and refillable milk bottles and is usually made using the highly toxic phosgene derived from chlorine gas. PC does not need additives but does need solvents for its production, such as methylene chloride, a carcinogen. A number of processes have been developed to reclaim polycarbonate from CDs, milk and water bottles, but only for downcycling into lower quality products.

3 A. Polyethylene-terephthalate (PET) - PET is made from ethylene glycol and dimethyl terephthalate. PET is generally used in packaging and often contain additives such as UV stabilizers and flame retardants. In production, PET uses a number of substances irritating to the eyes and respiratory tract. PET recycling rates are high compared to other plastics.

4. Polyolefins

4 A. and B. Polyethylene and polypropylene (PE and PP) - PE and PP belong to the polyolefin family, as do metallocenes, and are completely petroleum based. It is important to note, however, that polypropylene is often made using a chlorine intermediate process though a viable non-chlorine alternative exists. The raw materials used in these plastics are relatively harmless, but can be flammable or explosive. Also, the cracking of hydrocarbon feedstocks generates persistent organic substances, such as polyaromatic hydrocarbons (PAHs). Petroleum production also generates dioxins due to the use of chlorine catalysts. Finally, the burning of these plastics can generate many volatile compounds, including formaldehyde and acetaldehyde, both identified as probable carcinogens.

Despite hazards from polyolefin production, these can be considered the least harmful of plastics production.

5. Biodegradable and bio-based plastics - Polyolefin plastics can be made biodegradable by creating weak links in the polymer chain so that bacteria and other microorganisms can break it down. While this is an important first step towards more environmentally friendly plastics, biodegradable, petroleum-based plastics cannot be considered an environmentally safe, sustainable replacements for PVC in the long run. The future lies in what are called bio-based plastics.

Bio-based plastics are created from plant materials (starch, cellulose), lactic acid, or bacteria (bacteria are fed sugars and create the polymer as a waste product). Major corporations including ICI, Monsanto, and Cargill are currently making these plastics. It is essential that the production of bio-based plastics does not involve the use and release of genetically modified organisms or allow the patenting of life.

They are currently used in packaging applications and researchers are working on bio-based plastics for medical uses. Weaknesses of bio-based plastics are: cost and production size (economies of scale have not been achieved); material properties (they can be used only for relatively short lived products right now); and a lack of composting infrastructure for their disposal.

Notes:

9 PVC Plastic: A Looming Waste Crisis, Greenpeace International, 1998.

10 See Danish Environmental Protection Agency, PVC and Alternative Materials, 1993 and Danish Technical Institute, Environmental aspects of PVC, 1995 for a detailed overview of PVC lifecycle hazards.