



CPSC Staff Statement on the
Toxicology Excellence for Risk Assessment Report,
“Exposure Assessment: Potential for the Presence of Phthalates in Specified Materials at
Concentrations Above 0.1 Percent”
August 2016

The report, *Exposure Assessment: Potential for the Presence of Phthalates in Specified Materials at Concentrations Above 0.1 Percent*, presents the findings of research conducted by the Toxicology Excellence for Risk Assessment Center at the University of Cincinnati (TERA Center), under a contract with the U.S. Consumer Product Safety Commission (CPSC). The TERA Center performed this research to summarize available information on the production and use of specified plastics, regarding the possibility that these plastics contain certain phthalates at concentrations greater than 0.1 percent (1,000 ppm).

The 10 specified phthalates are:

- Di-(2-ethylhexyl) phthalate (DEHP);
- Dibutyl phthalate (DBP);
- Benzyl butyl phthalate (BBP);
- Diisononyl phthalate (DINP);
- Diisodecyl phthalate (DIDP);
- Di-n-octyl phthalate (DnOP);
- Diisobutyl phthalate (DIBP);
- Di-n-pentyl phthalate (DPENP);

- Di-n-hexyl phthalate (DHEP); and
- Dicyclohexyl phthalate (DCHP).

The specified plastics researched are:

- Acrylic resins: Polymethylmethacrylate (PMMA) and Polyacrylonitrile (PAN);
- Butadiene-ethylene resins (BER);
- Ethylene-butene copolymers (EBC);
- Ethylene copolymers: Ethylene vinyl acetate (EVA) and Ethylene vinyl alcohol (EVOH);
- Ethylene-propylene monomer (EPM) and Ethylene-propylene-diene monomer (EPDM);
- Ionomers (Surlyn®);
- Polycarbonate (PC);
- Polystyrene (crystal and general-purpose [GPS]), medium-impact (MIPS), and super-high-impact (SHIPS) grades; Styrene-butadiene copolymers (SBC);
- Silicone rubber (SR);
- Styrene-acrylonitrile copolymers (SAN); and
- Styrene-butadiene-styrene rubber (SBS) and styrene-butadiene rubber (SBR).

This research was completed in support of CPSC's work on third party testing burden reduction consistent with assuring compliance. CPSC staff will consider this information in evaluating whether staff could make a recommendation for a Commission determination that one or more of the specified plastics does not contain any of the 10 specified phthalates in concentrations above 0.1 percent; and thus, may not require third party testing to assure compliance with section 108 of the Consumer Product Safety Improvement Act of 2008.

This report will be posted on CPSC's website to keep stakeholders informed of the progress of technical research related to the agency's regulatory activities.



TERA

Exposure Assessment: Potential for the Presence of Phthalates in Specified Materials at Concentrations Above 0.1 Percent

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Abbreviations

3D	Three-dimensional
ABS	Acrylonitrile butadiene styrene
APR	Association of Post-consumer Plastic Recyclers
BBP	Benzyl butyl phthalate
BCUP	t-Butyl cumyl peroxide
BPA	Bisphenol A
°C	degree Celsius
CASRN	Chemical Abstracts Service Registry Number
CCOHS	Canadian Center for Occupational Health and Safety
CD	Compact disc
CDC	Centers for Disease Control and Prevention
CDR	Chemical Data Reporting
CDR-CDAT	Chemical Data Reporting-Chemical Data Access Tool
CFR	Code of Federal Regulations
CHAP	Chronic Hazard Advisory Panel
CO	Carbon monoxide
CPSA	Consumer Product Safety Act
CPSC	U.S. Consumer Product Safety Commission
CPSIA	Consumer Product Safety Improvement Act of 2008
D3	Hexamethylcyclotrisiloxane
D4	Octamethylcyclotetrasiloxane
DBP	Dibutyl phthalate
DCHP	Dicyclohexyl phthalate
DCPD	Dicyclopentadiene
DEHP	Di-(2-ethylhexyl) phthalate
DHEP	Di-n-hexyl phthalate
DHEXP	Dihexyl phthalate
DIBP	Diisobutyl phthalate
DIDP	Diisodecyl phthalate
DINP	Diisononyl phthalate
DIOP	Diisooctyl phthalate
DMC	Dimethyl carbonate
DNA	Deoxyribonucleic acid
DnOP	Di-n-octyl phthalate
DOP	Di-octyl phthalate
DPC	Diphenyl carbonate
DPENP	Di-n-pentyl phthalate
DTBP	Di- <i>tert</i> -butyl peroxide

DVD	Digital videodisc
EBC	Ethylene-butene copolymers
EBR	Butadiene-ethylene resins
ECY	Washington State Department of Ecology
ENB	Ethylidene norbornene
EPA	U.S. Environmental Protection Agency
EPDM	Ethylene-propylene-diene monomer
EPM	Ethylene-propylene monomer
E-SBR	Emulsion styrene-butadiene rubber
EVA	Ethylene vinyl acetate
EVAL	Ethylene vinyl alcohol
EVOH	Ethylene vinyl alcohol
EVOL	Ethylene vinyl alcohol
FAQ	Frequently asked questions
FDA	U.S. Food and Drug Administration
GS-MS	Gas chromatography-mass spectrometry
GMS	High-mono glycerol monostearate
GP	Green polymer additives
GPS	General-purpose polystyrene
GR-S	Government rubber-styrene
HC	Health Canada
HCR	Heat cured rubber
HD	Trans-1,4- hexadiene
HIPS	High impact polystyrene
HPD	Household Product Database
HSDB	Hazardous Substances Data Bank
IARC	International Agency for Research on Cancer
IHS	Information Handling Services
IISRP	International Institute of Synthetic Rubber Producers, Inc.
ISO	International Organization for Standardization
IV	Intravenous
LDPE	Low density polyethylene
LIM	Liquid injection molding
LLDPE	Linear low density polyethylene
LSR	Liquid silicone rubber
mg	Milligram
mg/kg	Milligram(s) per kilogram(s)
MIPS	Medium-impact polystyrene
MMA	Methyl methacrylate

MSG	Methacrylate Sector Group
NSCEP	National Service Center for Environmental Publications
Ni-PET	Nickel-polyethylene terephthalate
NIOSH	National Institute of Occupational Safety and Health
NLM	National Library of Medicine
NO	Nitric oxide
OECD	Organisation for Economic Cooperation and Development
OPPTS	U.S. EPA Office of Pollution Prevention and Toxic Substances
PAN	Polyacrylonitrile
PC	Polycarbonate
PE	Polyethylene
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
ppb	Parts per billion
ppm	Parts per million
PS	Polystyrene
PTFE	Polytetrafluoroethylene
RAPEX	European Rapid Alert System
RTV	Room temperature vulcanizing
RIVM	National Institute for Public Health and the Environment (Netherlands)
SAN	Styrene-acrylonitrile copolymers
SBC	Styrene-butadiene copolymer
SBR	Styrene-butadiene rubber
SBS	Styrene-butadiene-styrene rubber
SHIPS	Super-High-Impact Polystyrene
SPIN	Substances in Products in Nordic Countries
SR	Silicone rubber
SRNL	Savannah River National Laboratory
S-SBR	Solution styrene-butadiene rubber
TERA	Toxicology Excellence for Risk Assessment
TTDM	Tert-Dodecyl Mercaptan
UC	University of Cincinnati
µg/kg	Microgram(s) per kilogram
UL	UL LLC
U.S.	United States
UV	Ultraviolet
WEEE	Waste electric and electronic equipment

1. Introduction

The Consumer Product Safety Act (CPSA) requires third party testing of children's products for compliance with the applicable children's product safety rules. Section 108 of the Consumer Product Safety Improvement Act of 2008 (CPSIA) restricts the presence of 6 phthalates in children's toys and child care articles: Dibutyl phthalate (DBP), Benzyl butyl phthalate (BBP), and Di-(2-ethylhexyl phthalate (DEHP) may not be present in concentrations above 0.1 percent in accessible component parts of children's toys and any child care article that is designed or intended by the manufacturer to facilitate sleep or the feeding of children age 3 and younger, or to help children age 3 and younger with sucking or teething (CPSC, 2014). In addition, the CPSIA set an interim prohibition (in place until the Commission issues a final rule) regarding Diisononyl phthalate (DINP), Di-n-octyl phthalate (DnOP) and Diisodecyl phthalate (DIDP) may not be present in concentrations above 0.1 percent in any children's toy *that can be placed in a child's mouth*, and in any child care article that is designed or intended by the manufacturer to facilitate sleep or the feeding of children age 3 and younger, or to help children age 3 and younger with sucking or teething. In accordance with the CPSIA, the CPSC established a Chronic Hazard Advisory Panel (CHAP) to, among other things, make recommendations about whether the interim prohibitions should be made permanent and whether additional phthalates should be prohibited in children's products. The CHAP recommended that the interim prohibition on Diisononyl phthalate (DINP) be made permanent and four additional phthalates, Diisobutyl phthalate (DIBP), Di-n-pentyl phthalate (DPENP), Di-n-hexyl phthalate (DHEXP), and Dicyclohexyl phthalate (DCHP) be permanently banned for use in children's toys and child care articles at concentrations greater than 0.1 percent. The CHAP recommended lifting the interim ban on DnOP and DIDP. After the CHAP released its report, CPSC issued a notice of proposed rulemaking proposing most of the CHAP's recommendations regarding prohibitions on phthalates. (79 Fed. Reg. 78324 (Dec. 30, 2014)).

The CPSC is seeking information upon which to base a recommendation as to whether specific materials used for children's toys and child care articles can be determined not to contain any of the specified phthalates in concentrations above the 0.1 percent limit, and thus, would not require third party testing to assure compliance to Section 108 of the CPSIA.

This report summarizes available information on the production and use of 11 types of plastics (see Table 1) with regards to the possibility of these plastics containing certain phthalates at concentrations greater than 0.1 percent (1000 ppm) (see Table 2).

Table 1. Specified Plastics

Plastic	CASRN(s)¹
Acrylic resins: Polymethylmethacrylate (PMMA) and Polyacrylonitrile (PAN)	9011-14-7; 9008-29-1; 25014-41-9
Butadiene-ethylene resins (BER)	25068-01-3
Ethylene-butene copolymers (EBC)	25087-34-7
Ethylene copolymers: Ethylene vinyl acetate (EVA) and Ethylene vinyl alcohol (EVOH)	24937-78-8; 25067-34-9
Ethylene-propylene monomer (EPM) and Ethylene-propylene-diene monomer (EPDM)	61789-00-2; 25038-36-2; 9010-79-1; 27155-45-9
Ionomers (Surlyn [®])	9078-96-0
Polycarbonate (PC)	25037-45-0; 24936-68-3; 25971-63-5; 111211-39-3; 103598-77-2
Polystyrene (crystal and general-purpose [GPS]), medium-impact (MIPS), and super-high-impact (SHIPS) grades; Styrene-butadiene copolymers (SBC)	9003-53-6; 9003-55-8
Silicone rubber (SR)	63394-02-5
Styrene-acrylonitrile copolymers (SAN)	9003-54-7
Styrene-butadiene-styrene rubber (SBS), and styrene-butadiene rubber (SBR)	308076-28-0; 61789-96-6

¹ CASRN stands for Chemical Abstracts Service Registry Number.

Table 2. Specified Phthalates

Phthalate	CASRN(s)
Di-(2-ethylhexyl) phthalate (DEHP)	117-81-7
Dibutyl phthalate (DBP)	84-74-2
Benzyl butyl phthalate (BBP)	85-68-7
Diisononyl phthalate (DINP)	28553-12-0; 68515-48-0

Diisodecyl phthalate (DIDP)	26761-40-0; 68515-49-1
Di-n-octyl phthalate (DnOP)	117-84-0
Diisobutyl phthalate (DIBP)	84-69-5
Di-n-pentyl phthalate (DPENP)	131-18-0
Di-n-hexyl phthalate (DHEP)	84-75-3
Dicyclohexyl phthalate (DCHP)	84-61-7

The CPSC requested that Toxicology Excellence for Risk Assessment (TERA) investigate the five factors below:

- The raw materials used in the production of the specified plastics;
- The manufacturing processes used worldwide to produce the plastics;
- Typical applications for the specified plastics in consumer products, especially toys and child care articles, focusing on circumstances where the plastic could contain phthalates at concentrations greater than 0.1 percent;
- The potential use of recycled materials containing the specified phthalates in the production of the plastics; and
- The potential for phthalate contamination during packaging, storage, use, or other factors.

TERA investigated which plastics are typically used in which applications, why the specified phthalates might be used in the plastic, and the range of typical phthalate concentrations used for each plastic/application. Our investigation consisted of multiple literature research tiers. TERA did not conduct experimentation. TERA also sought and reported information on why a specific phthalate may be unlikely to be present in any of the specified plastics and explained the reasons why that given phthalate would not be present. Our research approach is described in Section 2. Our research was not exhaustive of the worldwide primary literature. We first screened secondary sources such as books and government reports for information and supplemented these data with information from the primary literature. Our focus was to identify relevant information on the 5 factors for the specified phthalates in the 11 plastics in order to address the question of whether their use in toys or child care articles may contain any of the specified phthalates in concentrations above 0.1 percent.

1.1 References

CPSC (2014). Prohibition of Children's Toys and Child Care Articles Containing Specified Phthalates. Docket No. CPSC-2014-0033, Consumer Product Safety Commission. pp. 78324-78343. Available at: <https://federalregister.gov/a/2014-29967>.

2. Literature Review Strategy

There are hundreds of thousands of factsheets, books, reports, and manuscripts on plastics, polymers, and materials. To research each of the 11 categories of plastics for each of the five factors previously given (raw materials used, manufacturing processes, typical applications, potential use of recycled materials, and the potential for phthalate contamination), a multi-tiered approach for collection, review, and compilation of the information was undertaken. The research involved the following four-tiered strategy.

Tier 1 determined the “universe” of information using secondary sources to identify the material categories and gather background information. These resources were screened for chemical name(s) and CASRN(s) to more specifically identify the subject material within each category. Tier 1 utilized the University of Cincinnati (UC) library catalog, a database called “SummonTM”, to evaluate all relevant findings for combined terms in Table 3.

Tier 2 evaluated authoritative secondary sources, primarily federal, national and international agency reports and databases. The databases searched included the National Library of Medicine’s Household Product Database (HPD), the Substances in Products in Nordic (SPIN) Countries database, and the European Rapid Alert System for dangerous non-food products (RAPEX) database.

Tier 3, or primary literature searching, was conducted for literature related to the 5 factors for the 11 subject plastics and 10 specified phthalates. Following preparation of draft sections for each material, based on the information gathered in Tiers 1-3, missing information or “gaps” were identified and targeted searches conducted for the information in Tier 4.

Tier 4 involved “gap searching”, conducting additional searching of the primary literature and the World Wide Web targeted for the specific topics with missing or little information. This tier focused primarily on gaps in information for use, recycling, and migration. The overall research approach for this project is shown in Figure 1.

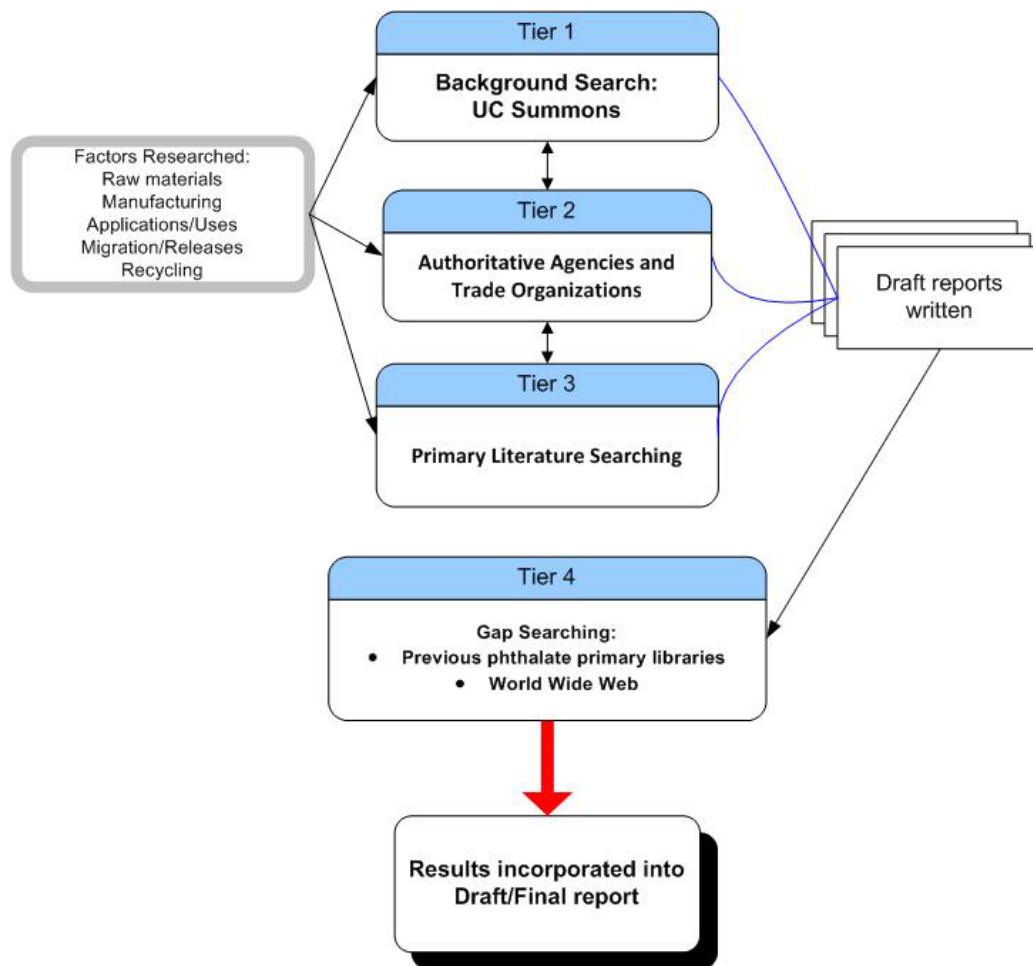


Figure 1. Research Approach for Five Factors for Subject Plastics

1.2 Tier 1. Universe of Literature

The purpose of Tier 1 was to gain an overview of the available information about the five factors and the potential presence of phthalates in the subject plastics. Later tiers would narrow the information from the universe of literature to focus specifically on the 5 factors, 10 phthalates and 11 subject plastics.

In Tier 1, compendia or reviews of literature on the materials in reference books, encyclopedias, handbooks, and dissertations were searched with the University of Cincinnati (UC) “Summon™,” resource (a Google-like search). This service allows one to quickly search, discover, and access reliable and credible library content. The search provides instant access to the breadth of library holdings in one relevancy-ranked list.

To evaluate the literature on the 11 plastics, we used the chemical name and/or CASRN. This search provided a wealth of information (see Table 3 below). As this search engine provides content based on relevance to search terms, the first 100 items in Summon™ were evaluated for content based on title, abstract, or Table of Contents. The Summon™ search was refined by limiting the search to: 1) the book catalog, and 2) content type to conference proceedings, book chapter/book/ebook, and dissertations in English. The book catalog search was not date limited; however, search for the content was limited to 2000-2015. The search was conducted in December 2015.

The number of books identified within the UC Book Catalog (via the Summon™ search engine) obtained with key chemical name or CASRNs relevant to the project and published prior to December 2015 is shown in Table 3. The identified information related to the specified plastics was then reviewed and organized according to the five factors. Relevant books were either checked out of the library or obtained through online UC library resources. Approximately 15 books were used throughout this report and are listed in Appendix A.

Table 3. Universe of Literature from Summon™ (Tier 1)

Specified Plastic	Search String	Hits^a	Relevant Downloaded and Reviewed
Acrylic Resins	(9011-14-7 OR 9008-29-1 OR Plexiglass OR 25014-41-9)	2,996	5
Acrylic Resins	(acrylic resins)	9,808	9
Butadiene ethylene resin	Butadiene ethylene resin OR 25087-34-7	6	3
Butadiene-ethylene resin	(butadiene-ethylene resin OR 25068-01-3)	719	8
Ethylene-Butene copolymers	(ethylene-butene copolymers OR 25087-34-7)	658	26
Ethylene copolymers	(ethylene vinyl acetate OR 24937-78-8)	19,916	34
Ethylene copolymers	(ethylene vinyl alcohol OR 25067-34-9)	21,909	22
Ethylene-propylene monomer	(ethylene propylene monomer OR EPM OR 61789-00-2 OR 9010-79-1)	21,701	15
Ethylene-propylene-diene monomer	(ethylene-propylene-diene monomer OR EPDM OR 25038-36-2 OR 27155-45-9)	2,746	24

Ionomers	(Surlyn [®] OR 9078-96-0)	250	10
Ionomers	(ionomers)	1,291	11
Polycarbonate	(polycarbonate OR 25037-45-0 OR 24936-68-3 OR 25971-63-5 OR 111211-39-3 OR 103598-77-2)	7,041	11
Polystyrene	(polystyrene OR 9003-53-6)	32,236	21
Silicone rubber	(Silicone rubber OR 63394-02-5)	11,281	20
Styrene-acrylonitrile copolymers	(Styrene-acrylonitrile copolymers OR SAN OR 9003-54-7)	1,216	16
Styrene-butadiene copolymers	(styrene-butadiene copolymers OR 9003-55-8)	2,012	10
Styrene-butadiene-styrene rubber	(styrene-butadiene-styrene rubber OR SBS OR 9003-55-8)	21,088	18
Styrene-butadiene rubber	(styrene-butadiene rubber OR SBR OR 308076-28-0 OR 61789-96-6)	14,122	14
Total		170,990	274
Duplicates			123
Total minus duplicates			151

^aHits are number of citations listed using search term/string (excluded newspaper articles and book reviews). Summon[™] restrictions included: limit to articles from scholarly publications, including peer review for 2000-2015, and English.

Based on professional judgment from reviews of titles and/or abstracts, 151 references were obtained from Tier 1 to develop an introduction to the literature for the 11 plastics for this project.

1.3 Tier 2. Authoritative Secondary Sources (Websites)

The purpose of Tier 2 was to identify secondary sources from websites of authoritative agencies or organizations throughout the world that could have reports or other information of relevance to this project.

In previous reports for CPSC on phthalates in consumer products, and the presence of phthalates in other plastics, TERA obtained useful information for raw materials, manufacturing, applications and potential contamination/migration from authoritative secondary sources based on a search of the World Wide Web. The 48 sites (listed in Appendix B) identified in the previous reports were pared down to 11 sites relevant to this project for the 5 factors for the 11 specified materials. In Tier 2, this subset of 11 sites, listed in Table 4, was searched for the specified materials. The 5 factors were screened from the information obtained for each material from authoritative secondary sources such as reviews, factsheets, regulatory documents, or risk

assessments. Tier 2 searches for authoritative secondary sources using chemical name, acronym and/or CASRNs were conducted on the World Wide Web for each of the specified materials. Searches were conducted during October, 2015. Table 4 shows the acronyms, chemical name, and CASRNs for materials searched in Tier 2.

Many of the sources from government regulatory agencies contained information or reports of chemical agents and were familiar to TERA. While we searched only English language sources, we identified sources from all over the world. We formed the search strategy for potentially relevant phthalate-specific information on the 5 factors that would be applied in Tier 3 based, in part, on our findings in this tier. Table 5 shows the 5 factors stratified by the subset of 11 relevant sources.

Table 4. Tier 2 Secondary Literature Search Terms

Chemical	CASRN	Abbreviation
Acrylic Resin <ul style="list-style-type: none"> • Polymethylmethacrylate • Polyacrylonitrile 	9011-14-7, 9008-29-1 , 25014-41-9	PMMA PAN
Butadiene-ethylene resins	25068-01-3	EBR
Ethylene-butene copolymers	25087-34-7	EB
Ethylene copolymers: <ul style="list-style-type: none"> • Ethylene vinyl acetate • Ethylene vinyl alcohol 	24937-78-8, 25067-34-9	EVA EVOH
Ethylene-propylene monomer Ethylene-propylene-diene monomer	61789-00-2 , 9010-79-1, 25038-36-2 , 27155-45-9	EPM EPDM
Ionomers <ul style="list-style-type: none"> • Suryln[®] 	9078-96-0	
Polycarbonate	25037-45-0 , 24936-68-3 , 25971-63-5 , 111211-39-3 103598-77-2	PC
Polystyrene <ul style="list-style-type: none"> • Crystal and general-purpose polystyrene • Medium-impact polystyrene • Super-high-impact polystyrene • Styrene-butadiene copolymers 	9003-55-8 9003-53-6	PS GPS MIPS SHIPS SBC
Styrene-acrylonitrile copolymers	9003-54-7	SAN
Styrene-butadiene-styrene rubber Styrene-butadiene rubber	308076-28-0 61789-96-6	SBS SBR
Silicone rubber	63394-02-5	SR

Table 5. Information for Five Factors Gathered from Relevant Websites in Tier 2

Database	Raw Materials	Manufacturing Process	Applications	Recycled Materials	Migration/Contamination
EPA ^{a,b,c,d} (CDR, NSCEP, OPPTS, Science Inventory)		√	√	√	
HazMap ^e			√		
Health Canada ^f (HC)			√		
HSDB ^g	√	√	√		
NIOSH ^h	√	√	√		
IARC ⁱ	√	√	√		
OECD ^j		√	√		
ECY ^k			√		
HPD ^l			√		√
RAPEX ^m			√		
SPIN ⁿ			√		√

^aEPA NSCEP

<http://www.epa.gov/nscep/>

^bEPA CDR-CDAT

http://java.epa.gov/oppt_chemical_search/

^cEPA Science Inventory

<http://cfpub.epa.gov/si/>

^dEPA OPPT

<http://iaspub.epa.gov/apex/pesticides/f?p=INERTFINDER:1:1395578990735::NO:1:>

^eHazMap

<http://hazmap.nlm.nih.gov/index.php>

^fHealth Canada

<http://www.hc-sc.gc.ca/index-eng.php>

^gHSDB

<http://toxnet.nlm.nih.gov/newtoxnet/hsdb.htm>

^hNIOSH

<http://www.cdc.gov/niosh/topics/>

ⁱIARC

<http://monographs.iarc.fr/ENG/Monographs/PDFs/index.php>

^jeChemPortal

<http://www.echemportal.org/echemportal/participant/page.action?pageID=9>

^kECY

<http://www.ecy.wa.gov/programs/hwtr/RTT/cspa/index.html>

^lHPD

<http://householdproducts.nlm.nih.gov/cgi-bin/household/searchall>

^mRAPEX

<http://ec.europa.eu/consumers/safety/rapex/alerts/main/index.cfm?event=main.listNotifications>

ⁿSPIN

<http://195.215.202.234/fmi/xsl/spin/SPIN/maininfo.xsl?-db=SPINstof&-lay=SPINnavn&-view>

All the websites investigated provided some information for use or application of the plastics.

Three to 5 sites provided information on raw materials and manufacturing; only 1 or 2 sites had information on recycling and migration/contamination for the specified materials.

1.4 Tier 3. Literature Searching

The purpose of Tier 3 was to search the worldwide primary literature to locate required information not found in the approaches used in the earlier tiers. For this tier, TERA took two approaches:

- searching the primary literature for the 11 specified plastics and phthalates with online databases that, based on previous CPSC projects, have been useful for the 5 factors; and
- searching the EndNote libraries from previous CPSC projects for the 10 phthalates for the 11 plastics specified in this project.

In the first approach, TERA searched 4 online databases: Scopus (www.scopus.com), Web of Science (www.webofscience.com), Pubmed (<http://www.ncbi.nlm.nih.gov/pubmed/>), and Toxline (<http://toxnet.nlm.nih.gov/newtoxnet/toxline.htm>) for primary literature for the 5 factors for the 11 specified plastics. No date limit was placed on the searches. An example of search results is shown in Table 6 with the keywords searched and resultant hits for each search string. If the results were too numerous, then the search was narrowed with the addition of “phthalate” as a key word. Appendix C provides the results for the four databases searched. All hits for search strings were recorded, saved, and downloaded into a raw EndNote library (the “Material Library”). After an initial prescreen to remove duplicates, extraneous, and irrelevant studies, a second, more thorough screening was performed to determine relevancy and likelihood for the research paper to contain needed information.

TERA thoroughly screened the literature search results first for relevance (removing those studies that obviously were not relevant to this research), and then reviewed the potentially relevant studies for the information still needed for the factors(s) for each material.

Screening of the literature searches focused on English language articles in accessible and reputable journals; literature in obscure journals, or in foreign language articles were not obtained for this report. Screening of patent literature was limited to patents for uses of the specified materials (*i.e.*, patents for new processing or technology were excluded).

In the second approach, EndNote libraries containing approximately 3,400 references, compiled for phthalates of interest in previous CPSC Tasks 11 and 12 (the “Phthalate Libraries”) (in Table 7 shown below), were searched. After removal of duplicates, there were 1,129 references. The specified plastics for this project that were identified in 106 relevant references are shown in Table 7. This alternate approach was performed to increase our confidence that our search approach in Tier 3 was thorough.

Table 6. Example Search Table

Name of Database		
Date Conducted		
Limits Placed on search		
Material	Second Approach for Primary Literature (search string used)	Number of Hits (The resultant number of hits would be in this column.)
Acrylic Resins	(acrylic resins AND phthalate)	
	(acrylic resins OR Plexiglas AND phthalate)	
Butadiene-ethylene resin	(butadiene-ethylene resin OR 25068-01-3)	
Ethylene-Butene copolymers	(ethylene-butene copolymers OR 25087-34-7)	
EPDM	(ethylene-propylene-diene monomer OR EPDM OR 25038-36-2 OR 27155-45-9)	
EPM	(ethylene propylene monomer OR EPM OR 61789-00-2 OR 9010-79-1)	
Ethylene copolymers	(ethylene vinyl acetate OR 24937-78-8 AND phthalate)	
	(ethylene vinyl alcohol OR 25067-34-9 AND phthalate)	
Ionomers	(Surlyn OR 9078-96-0)	
	(ionomers)	
Polycarbonate	(polycarbonate OR 25037-45-0 OR 24936-68-3 OR 25971-63-5 OR 111211-39-3 OR 103598-77-2 AND phthalate)	
Polystyrene	(polystyrene OR 9003-53-6 AND phthalate)	
Silicone rubber	(Silicone rubber OR 63394-02-5 AND phthalate)	
Styrene-acrylonitrile copolymers (SAN)	(Styrene-acrylonitrile copolymers OR 9003-54-7 AND phthalate)	
Styrene-butadiene copolymers	(styrene-butadiene copolymers OR 9003-55-8 AND phthalate)	
Styrene-butadiene-styrene rubber (SBS), and styrene-butadiene rubber (SBR)	(styrene-butadiene-styrene rubber OR SBS OR 9003-55-8 AND phthalate)	
	(styrene-butadiene rubber OR SBR OR 308076-28-0 OR 61789-96-6 AND phthalate)	
Total		
Duplicates		
Total minus duplicates		

Table 7. Searches with Previous Phthalate Libraries^a

Material	Second Approach for Primary Literature (search string used)	Number of References
Acrylic Resins	(9011-14-7 OR 9008-29-1 OR Plexiglass OR 25014-41-9)	33
Butadiene-ethylene resin	(butadiene-ethylene resin OR 25068-01-3)	0
Ethylene-Butene copolymers	(ethylene-butene copolymers OR 25087-34-7)	0
Ethylene copolymers	(ethylene vinyl acetate OR 24937-78-8)	20
Ethylene copolymers	(ethylene vinyl alcohol OR 25067-34-9)	0
Ethylene propylene monomer	(ethylene propylene monomer OR EPM OR 61789-00-2 OR 9010-79-1)	1
Ethylene-propylene-diene monomer	(ethylene-propylene-diene monomer OR EPDM OR 25038-36-2 OR 27155-45-9)	6
Ionomers	(Surlyn [®] OR 9078-96-0)	0
Ionomers	(ionomers)	1
Polycarbonate	(polycarbonate OR 25037-45-0 OR 24936-68-3 OR 25971-63-5 OR 111211-39-3 OR 103598-77-2)	0
Polystyrene	(polystyrene OR 9003-53-6)	36
Styrene-acrylonitrile copolymers (SAN)	(Styrene-acrylonitrile copolymers OR 9003-54-7)	1
Styrene-butadiene copolymers	(styrene-butadiene copolymers OR 9003-55-8)	2
Styrene-butadiene-styrene rubber (SBS), and styrene-butadiene rubber (SBR)	(styrene-butadiene-styrene rubber OR SBS OR 9003-55-8)	9
Styrene-butadiene-styrene rubber (SBS), and styrene-butadiene rubber (SBR)	(styrene-butadiene rubber OR SBR OR 308076-28-0 OR 61789-96-6)	5
Silicone rubber	(Silicone rubber OR 63394-02-5)	3
Total		118
Duplicates		10
Total minus duplicates		106

^a Search string used in search function “Abstract contains [search string] OR Title contains [search string] OR Keywords contains [search string]” in EndNote.

1.5 Tier 4. Gap Searching

Closer scrutiny of searches within the Material Library for this project was conducted by narrowing searches to include key words related to factors where there were data gaps (material, recycled materials, and phthalate migration or contamination, and uses in toys or children’s products or by a child) to be sure no literature source was overlooked (Tables 8 and 9). In addition, the same scrutiny was applied to the Phthalate Library from previous tasks.

Table 8. Search Results for Migration, Contamination, and Recycling from Phthalate Library

Gap Searching	Number of Hits Identified	Number Relevant
Contamin* OR Migrat* AND phthalate	454	68
Evaporat*	5	0
Leach	67	4
Migration AND Phthalate NOT PVC	94	5
Movement AND Phthalate	2	10
Recycl* OR Reus* OR Reconstit*	70	7
Thermoplastics	38	10
Toy OR children's product OR child	43	17
Total	773	121

Table 9. Search Results for Migration, Contamination, and Recycling from Material Library

Search Term	Tier 1 library	Tier 3 library
Contaminat*	68	215
Evaporat*	18	54
Leach	47	126
Migrat*	48	185
Movement	16	36
Reus*	30	78
Reconstit*	5	17
Recycl*	46	86
Toy OR children's product OR child	84	197
Total	362	994

As a final step, TERA conducted searches on the World Wide Web to fill any remaining data gaps, primarily through Google (www.google.com) and Google Scholar (www.scholar.google.com). Based on the material, phthalate, and type of information still needed, these searches were performed using CASRNs, chemical names, and keywords. In addition, www.Amazon.com was also searched for chemical name (CASRNs were not used).

From these results, products in specific departments (for example, “toys and games”) were evaluated as to whether the products include the type of material in the product description. If the results were reasonable upon visualization of the items, they were included in this report. For example, a basketball backboard is described as “acrylic fusion back board with black slam-it rim and all-weather net” and it was included as a consumer product made of acrylic.

3. Acrylic Resin [Polymethylmethacrylate (PMMA) and Polyacrylonitrile (PAN)] CASRNs: 9011-14-7; 9008-29-1; 25014-41-9

Acrylic plastic is a family of synthetic plastic materials containing one or more derivatives of acrylic acid (Acrylic Plastic Forum, 2016). The family includes a range of polyacrylates, polymethacrylates and polyacrylonitrile (Brydson, 1999). Poly(methyl methacrylate) (PMMA) [or poly(methyl 2-methylpropenoate)], also known as acrylic or acrylic glass, is commercially the most important member of this family of acrylic polymers (Brydson, 1999). PMMA (for example, Plexiglass, CASRN 9008-29-1) and many other acrylic polymers are the synthetic polymers of methyl methacrylate. Plexiglass is a transparent, amorphous thermoplastic that is often used in sheet form as a lightweight or shatter-resistant alternative to glass. It is a tough, highly transparent material with excellent resistance to ultraviolet (UV) radiation and weathering, and it can be colored, molded, cut, drilled, and formed. Polyacrylonitrile (PAN) is a thermoplastic material made from polymerization of the monomer, acrylonitrile; however, almost all PAN resins are produced from mixtures of monomers with acrylonitrile as the main component (Qin, 2016). PAN is a hard, rigid thermoplastic material that is resistant to most solvents and chemicals, is slow to burn, and is of low permeability to gases (Encyclopaedia Britannica, 2016). PAN is the most popular acrylic precursor, which is used widely to produce carbon fibers (containing 85 percent or more of PAN) (Park and Heo, 2014; Encyclopaedia Britannica, 2016). Although PAN is a thermoplastic, it does not melt under normal conditions, but degrades between 251-351°C (Beyler and Hirschler, 2002).

1.6 Raw Materials Used in Production of Acrylic Resin

Several additives may be blended with PMMA and PAN. Brydson (1999) reported that plasticizers are sometimes added to PMMA with DBP as the commonly used plasticizer in quantities of approximately 5 percent. Plasticizers, including the phthalate DnOP and dioctyl adipate are reportedly used in the production of PAN (Drobny, 2007), but the author did not report the amounts that are incorporated into the polymer.

1.6.1 Raw Materials Used in Making PMMA and PAN

The raw materials used in making PMMA and PAN (Brydson, 1999; Fink, 2013; Drobny, 2007; Kirk-Othmer, 2014) include:

- *Monomers*: methyl methacrylate (MMA); acrylonitrile; methyl acrylate; vinyl acetate
- *Solvents*: water; sulfuric acid; straight chain ethers (not specified); tetrahydrofuran; toluene; hexane; N,N-dimethylacetamide; dimethylformamide
- *Emulsifier(s)*: sodium lauryl sulfate

- *Initiators/catalysts/reaction accelerators/redox systems*: benzoyl peroxide; azobis-type catalysts (2,2'-azobis (isobutyronitrile), 2',2'-azobis (2,4-dimethylvaleronitrile); diacylperoxide-type catalysts (such as lauroyl peroxide, dibenzoyl peroxide, bis[3,5,5-trimethylhexanoyl]peroxide); perester-type catalysts (such as tert-amylperoxy-2-ethylhexanoate, tert-butylperoxy-2-ethylhexanoate); percarbonate-type catalysts (such as bis(4-tert-butylcyclohexyl)peroxydicarbonate); UV curing catalysts (such as 2,2-dimethoxy-2-phenylacetophenone, benzophenone, and methyldiethanolamine, acylphosphine oxide); pentavalent vanadyl ion-thiourea combination; sodium metabisulfite; potassium persulfate; ferrous sulfate
- *Initiator/promoter systems for cold curing of acrylic resins*: zinc 2-ethylhexanoate solution; cobalt 2-ethylhexanoate; tert-butylperoxybenzoate as peroxide source
- *Molecular weight modifier/chain transfer agents*: lauryl mercaptan
- *Chain length inhibitor*: hydroquinone
- *Stabilizer*: UV absorbers: phenyl salicylate; 2,4-dihydroxybenzophenone; resorcinol monobenzoate; methyl salicylate; stilbene; benzotriazole; 2-hydroxybenzophenone; salicylic acid phenyl ester UV absorbers
- *Plasticizers*: DBP (5 percent); DnOP; dioctyl adipate
- *Suspension agents/dispersants*: talc; kaolin; gelatin; magnesium carbonate; aluminum oxide
- *Buffering agents*: sodium hydrogen phosphates
- *Lubricants*: stearic or stearyl acid; lauryl alcohol; cetyl alcohol
- *Cross-linkers*: di- or trivinyl benzene; diallyl esters of dibasic acids; glycol dimethacrylates
- *Colorants*: dyes and pigments (not specified)
- *Flame retardants*: phosphoric acid esters; chlorinated polyphosphates; halogenated polyphosphonate; ammonium polyphosphonate; carbon nanotubes; alkyl acid phosphate; zirconium phosphate; tetrabromobisphenol; tri(acryloyloxyethyl)phosphate; 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane; tricresyl phosphate; tris(2-chloroethyl)phosphate; antimony trioxide; zirconium hydroxide; barium metaborate; tin oxide; montmorillonite; butyl acrylate
- *Antistatic agents* (antistats): a surfactant (unspecified); a vinyl polymer (unspecified) having a poly(oxyethylene) chain and a sulfonate (unspecified); carboxylate or quaternary ammonium salt structure (unspecified); a polyether-ester amide (unspecified) with a methyl methacrylate-butadiene-styrene copolymer; a functional polyamide elastomer (unspecified) or a polyamide-imide elastomer (unspecified) having a low content of hard segments

1.7 Manufacturing Processes used Worldwide to Produce Acrylic Resin

1.7.1 PMMA

PMMA is routinely produced by emulsion polymerization, solution polymerization, and bulk polymerization. Generally, radical initiation is used (including living polymerization methods), but anionic polymerization of PMMA can also be performed. PMMA is commercially produced by free-radical polymerization that involves the use of peroxides or azodiisobutyronitrile at temperatures up to about 100 °C (Brydson, 1999). Free-radical polymerizations can be performed homogeneously, by bulk or solution polymerization, or heterogeneously, by suspension or emulsion polymerization.

1.7.1.1 Bulk Polymerization

This type of polymerization is extensively used in the production of PMMA sheet and to a lesser extent rod and tube (Brydson, 1999). A prepolymer is first prepared, typically by heating the monomer, methyl methacrylate, freed from inhibitor, and a catalyst (benzoyl peroxide) in a mold. The liquid prepolymer syrup, consisting of a solution of polymer in monomer, is then cooled to room temperature. Some manufacturers may incorporate a plasticizer, coloring agents and UV light absorbers at this stage (Brydson, 1999). An alternative approach to preparing prepolymer syrup involves dissolving some polymer in the monomer and adding some peroxide to the mixture. Fink (2013) reports that traditional initiators and UV curing catalysts are also used (see list in Section 3.1.1). For cold curing, an initiator/promoter system consisting of a zinc 2-ethylhexanoate solution, a cobalt 2-ethylhexanoate, and, as peroxide source, *tert*-butylperoxybenzoate, can be used (Fink, 2013).

There are two methods of bulk polymerization: batch cell or continuous. Batch cell bulk polymerization is the most common for making acrylic sheets although it may also be used to form rods and tubes (Acrylic Plastic Forum, 2016). The continuous method is similar to the batch method but the sheets are thinner and of smaller widths (Acrylic Plastic Forum, 2016).

1.7.1.2 Suspension Polymerization

Suspension polymerization is used to manufacture molding powders of acrylic plastics and ion-exchange resins (Kirk-Othmer, 2014). In this process, the polymerization reaction takes place between tiny droplets of the monomer suspended in a solution of water and catalyst (benzoyl peroxide). This results in polymer grains with tightly controlled molecular weights that are suitable for molding or as extrusion catalyst. Suspending agents or dispersants, lubricants and cross-linkers (see Section 3.1.1) are added to improve bead uniformity and bead performance properties (Kirk-Othmer, 2014).

After polymerization, the beads are filtered from the aqueous phase, washed, dried and may be supplied as injection molding material without further treatment; or the beads may be compounded with additives and granulated (Brydson, 1999).

1.7.1.3 Solution Polymerization

Solution polymerizations of acrylic ester monomers including PMMA employ a co-solvent (not specified) to aid in minimizing reaction viscosity and controlling polymer molecular weight (Kirk-Othmer, 2014). For solution polymerization of methyl methacrylate, acceptable solvents include N,N-dimethylacetamide and dimethylformamide. Initiators most commonly employed in solution polymerization include organic peroxides, hydroperoxides, and azo compounds (Kirk-Othmer, 2014). Chain transfer agents such as chlorinated aliphatic compounds and thiols and a chemical inhibitor (such as a hydroquinone) can be added to slow the rate of polymerization (Kirk-Othmer, 2014).

1.7.1.4 Emulsion Polymerization

This type of polymerization also involves free-radical polymerization of monomers and is used to make colloidal dispersions of PMMA. Emulsion polymerization is the most frequently used method in industry to polymerize acrylic ester monomers including MMA (Kirk-Othmer, 2014). Water, MMA, and water-soluble or free-radical initiator(s) are the principal ingredients in emulsion polymerization (Kirk-Othmer, 2014). The products of emulsion polymerizations of methyl methacrylate include paint resins, paper coating agents and paper processing agents, textile binders, and additives.

1.7.2 Polyacrylonitrile (PAN)

Acrylonitrile is the main raw material for the manufacture of PAN. Pure acrylonitrile can only be polymerized in the presence of initiators or light (Olabisi, 1997). Almost all acrylic fibers are made from acrylonitrile combined with at least one other monomer (commonly methyl acrylate and vinyl acetate) (Park and Heo, 2014; Textile Library, 2015; Kirk-Othmer, 2014).

Acrylonitrile and its comonomers can readily polymerize in the presence of free-radicals or anionic initiators and by radiation with light (Olabisi, 1997; Kirk-Othmer, 2014). Conventional or other initiators and redox systems are used for the free-radical polymerization of acrylonitrile (Olabisi, 1997).

Acrylonitrile can also be polymerized using anionic polymerization (Olabisi, 1997). This type of polymerization results in the production of yellow products; the process is less widely used compared to the free-radical polymerization.

Bulk, solution, suspension, slurry, or emulsion processes may be used to polymerize acrylonitrile. Bulk polymerization, which can either be batch cell or continuous process, is used to produce PAN because it is not soluble in its monomer, acrylonitrile, and therefore can be precipitated during the bulk polymerization. Viscosity increases during the batch polymerization; therefore, continuous bulk process is preferred over the batch process, and it is the typical method used in the industry (Olabisi, 1997).

In a continuous slurry process, dimethylformamide is commonly used as the solvent. In this process, the monomer is isolated as small suspended droplets in an aqueous medium (Olabisi, 1997). A redox system is used in the emulsion process to carry out the polymerization at lower temperatures.

1.7.3 Processing

Pure PMMA or PAN homopolymers are not optimized for most applications. Both polymers are difficult to process, for example, into filters. As such, they are compounded with comonomers such as vinyl esters (Park and Heo, 2014). PMMA and PAN are rarely sold as an end product. For uses where specific properties are required, modified formulations are created using varying amounts of other comonomers, additives, and fillers. For example, PMMA may be blended with a number of additives, with the most important being dyes and pigments (unspecified) (Drobny, 2007). Plasticizers are also sometimes added to the polymer. The most commonly employed plasticizer is DBP up to approximately 5 percent (Brydson, 1999). Drobny (2007) reported that other plasticizers such as the phthalate DnOP and dioctyl adipate are also used in PAN production, but the amounts that are incorporated into the polymer were not reported. Small amounts of UV light stabilizers may be added to improve light stability (Brydson, 1999).

Several benzotriazole, 2-hydroxybenzophenone, and salicylic acid phenyl ester UV absorbers are also used in acrylic resins (Fink, 2013). Flame retardants (do not include phthalates) and antistatic agents (antistats) used during acrylic resin processing (including PMMA) (Fink, 2013) are listed above (Section 3.1.1.)

All common molding processes are used in processing PMMA. These include:

- Injection molding;
- Compression molding; and

- Extrusion.

Processing in the melt state is accomplished by injection molding and extrusion. A large number of PMMA products are produced by manipulating the sheet, rod and tube (Brydson, 1999).

Based on the available information, DBP may be a component of PMMA at concentrations that may exceed 0.1 percent. DnOP is also reported to be used in the manufacture of PAN but the literature researched did not identify DnOP concentrations in PAN polymer.

1.8 Applications for Acrylic Resin in Consumer Products

Acrylic plastics have a wide range of uses because of high durability, UV resistance, impact strength and low weight. Acrylic has many optical uses because of its transparency (Brydson, 1999).

1.8.1 Toys and Child Care Articles

Children’s products made from acrylic include baby incubators, bath or wash-basins, knobs, and small furniture (IARC, 1979). Toys that are made from acrylic include dollhouse miniature food items. Acrylics are also used in textile fiber for baby blankets; acrylic used in apparel is often blended with wool or other fibers (Amazon.com, Inc., 2016; HSDB, 2015). Table 10 lists the number of additional uses identified on Amazon.com for toys and child care articles.

Table 10. Acrylic Resin Uses in Toys and Child Care Articles

Toys and Games	Number	Baby and Toddler Toys	Number
Hobby Tool Paints	1600	Rattles	135
Grown-Up Toys	5995	Bath Toys	51
Sports	608	Mirrors	28
Paints	730	Music & Sound	10
Science	476	Toy Gift Sets	58
Airplane Model Kits	29	Activity Play Centers	9
Accessories	450	Balls	85
Action Figures & Statues	4347	Blocks	11
Arts & Crafts	7445	Car Seat & Stroller Toys	66
Baby & Toddler Toys	874	Hammering & Pounding Toys	1
Building Toys	51	Indoor Climbers & Play Structures	3
Dolls & Accessories	2778	Push & Pull Toys	1
Dress Up & Pretend Play	2208	Rocking & Spring Ride-Ons	7

Electronics for Kids	111	Shape Sorters	3
Games	848	Stacking & Nesting Toys	10
Hobbies	3686	Stick Horses	2
Kids' Furniture, Décor & Storage	2940	Baby Teethers	4
Learning & Education	1012		
Novelty & Gag Toys	16754		
Party Supplies	1117		
Puppets	178		
Puzzles	835		
Sports & Outdoor Play	1052		
Stuffed Animals & Plush Toys	2341		
Toy Remote Control & Play Vehicles	424		
Tricycles, Scooters & Wagons	41		

A common use of acrylic copolymer is as a quality paint binder, and this is used in numerous liquid and spray paints for children’s hobbies and crafts. Specific toys were identified from a product search of Amazon.com for those made using acrylic, including gemstones and beads used to make children’s jewelry, felt stickers, doll eyes, display cases for action figures, coatings for wooden toys, toy mirrors, balls, magnets, and kids cups (Amazon.com, Inc., 2016). In the European RAPEX database for 2005-2015, two products (both nail polishes) were reported to contain acrylic with DBP at 4.7 percent and 8.9 percent (RAPEX, 2016).

While many uses of acrylic are found in children’s toys and child care articles, a lack of labeling or identification of materials tested preclude information regarding phthalates in these items. It is stated for many articles that they are tested and have phthalates or elements, but it is not specified what the toy is made from. Other consumer product uses for acrylic are discussed in Appendix D.

1.9 Potential Use of Recycled Materials Containing Phthalate in Production of Acrylic Resin

To determine if phthalates could be introduced into acrylic resin through recycled materials used to make the acrylic resin, TERA considered whether phthalates are present in virgin plastic that may be recycled, and if so, how the acrylic plastic is being recycled. Appendix E presents an overview of plastics recycling.

While no information on measurements or concentrations of phthalates in acrylic plastic or in plastic made from recycled acrylic was found in the literature researched (as discussed above in

Section 3.1). DBP in quantities of the order of 5 percent are sometimes added to PMMA (Brydson, 1999). In addition, phthalates such as DnOP are reportedly used in the production of PAN, although the amount was not provided (Drobny, 2007).

Because phthalates are sometimes used to make acrylic resins, if the resin containing the phthalates were recycled to make new acrylic, then the phthalates might also be present in the new acrylic. Therefore, we explored whether acrylic plastic is being recycled to make new acrylic plastic.

In the United States, acrylic plastic is labeled with resin identification code (also called plastic recycling code) #7 (“Other”), and there are no standard reuse and recycling protocols for this category (Eartheasy, 2012). However, PMMA can be, and is, recycled. The Methacrylate Sector Group (MSG), which represents manufacturers of methacrylic acid and PMMA in Europe notes that PMMA is recycled by grinding, melting, and extrusion and can be made into new products, with the MMA recycled from PMMA depolymerization having high purity levels (MSG, 2016). Others report that recycling PMMA is difficult, citing high energy usage and potential environmental hazards, but noting that current recycling methods include pyrolysis as well as recovery of the monomer using depolymerization (Azo Materials, 2016a; Plastic Experts, 2016).

A search of the World Wide Web finds companies and websites that offer to sell or purchase recycled PMMA, including post commercial, post consumer, post industrial film, non-bottle containers, sheeting, manufacturing scrap, purges, and construction and demolition scrap (*e.g.*, Phoenix Recycling, 2016; Plasticsmarkets, 2016; RecPlas Ltd., 2016). In particular, used signage, display hardware and automobile light covers are being recycled (*e.g.*, RecPlas Ltd., 2016). Recycled cast acrylic and products such as signage and display racks made from the recycled plastic are available for purchase (*e.g.*, G J Plastics Ltd, 2016). These products are made from cast acrylic sheets made of recycled scrap PMMA that has been depolymerized to a liquid, which is distilled to remove impurities and made into MMA monomer (Madreperla, 2016).

In summary, the research found that DBP (at concentrations as high as 5 percent) is sometimes used as a plasticizer additive in manufacturing acrylic plastics. Recycled PMMA is being used to manufacture new acrylic sheet. If phthalates were present in the acrylic being recycled, depending on the depolymerization process, the phthalates could possibly be separated from the MMA monomer, making new recycled acrylic free of the phthalates from the original material. Therefore, recycling of acrylic using a depolymerization method (depending on the specific process) would offer the possibility of removing the phthalates from new acrylic resin made from the recycled monomer.

However, if acrylic plastic were mechanically recycled and new acrylic resin made from the recycle, then any phthalates present in the original acrylic could be present in the plastic made

with the recycle. Data to indicate how much or how often acrylic is recycled using mechanical methods, or if the resulting acrylic is used to make toys or child care articles, were not found in the literature researched for this project.

1.10 Potential Phthalate Contamination/Migration

The plasticizers that are reportedly used in the manufacture or processing of acrylic resins include DBP (5 percent), dioctyl phthalate (DnOP), and dioctyl adipate. Of these, DBP and DnOP are specified phthalates for the current project. However, no migration studies were identified that evaluated the potential for DBP or DnOP to leach out or migrate from acrylic resins, which would indicate indirectly the presence of phthalates.

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4. Butadiene – Ethylene Resins (EBR) CASRN: 25068-01-3

Butadiene-ethylene (or ethylene-butadiene) resins (EBR) are manufactured by copolymerizing ethylene and butadiene using specialized catalysts. As one of α -olefin-diene copolymers, EBR are regarded as new vulcanizable elastomers for the tire industry (Cortial et al., 2010).

1.12 Raw Materials Used in Production of EBRs

No information was identified that indicated that phthalates are used as additives in the manufacture of EBR. However, heterogeneous Ziegler-Natta catalysts have phthalates such as DIBP or DEHP as internal donors (Borealis, 2014). These catalysts may survive the polymerization process, with the potential for DIBP, DBP and DEHP to theoretically be present in concentrations of about 1 mg/kg (1 ppm, or 0.0001 percent) in the final resins (Borealis, 2014). No studies were identified that measured the phthalates in EBRs.

1.12.1 Raw Materials Used in Making EBR

The raw materials used in making EBR include:

- *Monomers*: ethylene; 1,3-butadiene
- *Catalysts*: vanadium or titanium based catalysts; homogenous vanadium based systems or heterogeneous Ziegler-Natta catalysts; Group IV metallocenes; lanthanide-based organometallic complexes; neodymocene complexes with alkylating/chain transfer agents
- *Solvents*: toluene

1.13 Manufacturing Processes used Worldwide to Produce EBR

Copolymerization of olefins, such as ethylene, and conjugated dienes, such as butadiene, is reported to be very difficult to perform because each monomer requires different polymerization conditions, such as polymerization catalysts (Nsiri et al., 2016; Monteil et al., 2004; Barbotin et al., 2000). Little information was identified regarding the manufacturing processes of EBR on a commercial scale. This report focuses on what has been identified in the open literature. Most of the information relates to the types of catalysts that have been reported to be used in copolymerizing these resins.

Several catalytic systems have been developed for use in the manufacture of EBR. The copolymerization of the monomers has been obtained using:

- (a) vanadium- or titanium-based catalysts at very low temperatures that result in alternating copolymers (Monteil et al., 2004);

- (b) homogenous vanadium-based systems or heterogeneous Ziegler-Natta catalysts at higher temperature to produce EBR with a multiblock structure in which the butadiene is essentially *trans*-1,4-inserted (Nsiri et al., 2016; Monteil et al., 2004);
- (c) Group IV metallocenes (in toluene) that produce copolymers with small amounts of inserted butadiene (1,2- and 1,4-butadiene units), with cyclopentane (or cyclopropane) rings being formed in various amounts (Choo and Waymouth, 2003; Monteil et al., 2004; Cortial et al., 2010; Nsiri et al., 2016);
- (d) lanthanide-based organometallic complexes that have been reported to be promising (Cordial et al., 2010; Nsiri et al., 2016), but result in the synthesis of butadiene-ethylene copolymer with small amounts of inserted ethylene (Monteil et al., 2004); or
- (e) Neodymocene complexes with alkylating/chain transfer agents (as coactivators) that produce copolymers with high butadiene contents (up to 60 mol percent) and with six-member rings (1,2-cyclohexane) and unsaturations (1,2- and *trans*-1,4 butadiene units) along the polymer chain (Monteil et al., 2004). Other investigators have reported the use of dimethylsilylene-bridged *ansa*-bis(fluorenyl) neodymium borohydride complexes and alkylating agents such as dialkylmagnesium compound that form cyclohexane units in the polymer chain (Cortial et al., 2010).

No additional information was identified on the other raw materials used in the copolymerization reaction(s) for EBR.

1.13.1 Processing

No information was identified in the literature researched for this project regarding how EBR resins are processed.

In summary, very little information was available on the manufacturing methods and processing of EBR. Although heterogeneous Ziegler-Natta catalysts used in the manufacturing of EBR have phthalates such as DIBP or DEHP as internal donors, their concentrations in the final resins are not likely to be greater than 0.1 percent.

1.14 Applications for EBR in Consumer Products

1.14.1 Toys and Child Care Articles

EBR was not identified in any toy or children's products from searching consumer use databases (RAPEX, 2016; ECY, 2016a,b; HPD, 2015; SPIN, 2015) by chemical name or by CASRN. No items made of EBR were identified in a search of Amazon.com (Amazon.com, Inc., 2016).

1.15 Potential Use of Recycled Materials Containing Phthalate in Production of EBR

No applications or uses specific for EBR or recycled EBR were identified. However, an estimated one-third of the thermoplastic elastomers cannot be recycled due to the nature of their applications (oil modifiers, adhesives or bitumen modification) (Drobny, 2007). The remaining two-thirds of the thermoplastic elastomers can be recycled using an approach similar to that of plastics such as polystyrene (Drobny, 2007). In a search of the World Wide Web, no information was found regarding EBR recycling. General information regarding plastics recycling is presented in Appendix E.

1.16 Potential Phthalate Contamination/Migration

No migration studies were identified that evaluated the potential for any of the specified phthalates to leach out or migrate from EBR resins.

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5. Ethylene-butene (EB) Copolymers CASRN: 25087-34-7, 9019-29-8

Ethylene-butene (EB) copolymer is described as 1-butene, polymer with ethylene; ethylene polymer with 1-butene; or poly(ethylene-co-1-butene) polymer. The polymer is made from the monomers, (poly)ethylene and 1-butene. Both monomers can be used to manufacture high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) (TERA, 2015). EB is reported to exhibit plastic and elastic properties (Sigma-Aldrich, 2016). It is also described as a low temperature impact modifier, with high clarity, stress cracking reduction and low temperature heat sealability (Sigma-Aldrich, 2016).

1.18 Raw Materials Used in Production of EB Copolymers

Ethylene and 1-butene can be used to manufacture HDPE and LLDPE, but no phthalates are reportedly used as additives in the manufacture of HDPE or LLDPE (TERA, 2015). However, Ziegler-Natta catalysts are used in the production of polyethylene (PE) polymers. In preparing these catalysts, phthalates such as DIBP or DHEP are often used as internal donors (Borealis, 2014). The catalysts may survive the polymerization process, such that the phthalates may theoretically be present in concentrations of approximately 1 mg/kg (1 ppm, or 0.0001 percent) in the final pellets (Borealis, 2014). No data or studies were identified in the literature researched that estimated the phthalate levels in PE plastics (TERA, 2015). Wypych (2012) cites specialized uses of DOP (isomer not specified) in PE, although relevance of these uses to the children's products is not clear.

1.18.1 Raw Materials in Making EB Copolymers

Monomers: ethylene, 1-butene

Because both ethylene and 1-butene can be used as raw materials for the production of HDPE and LLDPE, the other raw materials used in the manufacturing of EB copolymers are not expected to differ from those used in the production of HDPE and LLDPE, which did not include phthalates (TERA, 2015).

1.19 Manufacturing Processes used Worldwide to Produce EB Copolymers

Butene/ethylene copolymers are produced by the catalytic polymerization of 1-butene liquid monomer in the presence of small amounts of ethylene monomer (U.S. FDA, 2010). This yields no higher than 6 weight percent concentration of polymer units derived from ethylene in the copolymer. Polyethylene polymers such as HDPE and LLDPE are manufactured from ethylene or ethylene and 1-butene (or other alpha olefin monomers such as propylene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, 1-tetradecen, or methyl-4-pentene-1) (TERA, 2015).

There is no additional information regarding the manufacturing of EB copolymers and readers are referred to TERA (2015) for information regarding the manufacture and processing of PE polymers.

1.19.1 Processing

No information was identified regarding the processing of ethylene-butene copolymers and readers are referred to TERA (2015) for information regarding the manufacture and processing of PE polymers.

In summary, DIBP or DEHP are used as components of Ziegler-Natta catalysts. By analogy to PE, it is unlikely these phthalates would remain in the EB copolymer at concentrations greater than 0.1 percent. Based on patents for specialized materials, DOP (isomer not specified) might be used in manufacturing EB copolymers, although the relevance to children's products is not known.

1.20 Applications for EB Copolymers in Consumer Products

The only use found in the literature researched for EB is for four-gallon size plastic bags (HPD, 2015); information on other size bags was not reported. EB is permitted for use in non-food pesticide products as an inert ingredient (HazMap, 2016).

1.21 Potential Use of Recycled Materials Containing Phthalate in Production of EB Copolymers

No information on recycling of EB copolymers was found in our tiered search or in the secondary sources. A search of the World Wide Web did not identify any companies seeking to buy, or offering to sell, recycled EB copolymers.

Appendix E presents an overview of plastics recycling.

1.22 Potential Phthalate Contamination/Migration

No studies for migration of the specified phthalates from EB were located in the literature consulted for this research.

1.23 References

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6. Ethylene Copolymers [Ethylene Vinyl Acetate (EVA) CASRN 24937-78-8 and Ethylene Vinyl Alcohol (EVOH) CASRN 25067-34-9]

Ethylene vinyl acetate (EVA) copolymer is a thermoplastic polymer and consists of the monomers, ethylene and vinyl acetate. The copolymers are flexible, tough materials and have good adhesion properties and high melt strength (Campo, 2008). The vinyl content in commercial grades ranges from 1 to 10 percent. Grades with more than 20 percent vinyl acetate are called high EVAs (Campo, 2008).

Ethylene vinyl alcohol (EVOH, sometimes abbreviated as EVAL or EVOL), is a thermoplastic polymer consisting of the monomers, ethylene and vinyl alcohol. Grades of EVOH copolymers are available, with the grades being identified by the mol percent of ethylene content. EVOH has excellent gas barrier properties, high water absorption, flavor (fragrance) preservation and organoleptic properties (Salamone, 1996; Armstrong, 2004; Robertson, 2013). The vinyl alcohol content in commercial grades of EVOH typically ranges from 56 to 71 percent (Brydson, 1999).

1.24 Raw Materials Used in Production of Ethylene Copolymers

Several additives may be blended with EVA or EVOH copolymers. Generally, plasticizers are not used in EVA grades with low viscosity. However, plasticizers, for example, paraffinic mineral oils, are used in high viscosity EVA grades (Klingender, 2008). Additionally, synthetic plasticizers such as adipate- and sebacate-type plasticizers can be used to improve the cold flexibility of high vinyl acetate containing grades (Klingender, 2008). Available information does not indicate that phthalates are used as plasticizers in the production of EVA or EVOH copolymers.

1.24.1 Raw Materials Used in Making EVA and EVOH Copolymers

The raw materials used in making EVA or EVOH include (Klingender, 2008; Nagao, 2003):

- *Monomers*: ethylene and vinyl acetate, vinyl alcohol
- *Solvents*: water; methanol; methanolic potassium hydroxide in benzene; toluene; benzene; heptane; tertiary butanol
- *Emulsifiers*: sodium alkanesulfonate; dodecyl benzene sulfate; or polyorganosiloxanes and polyethylene oxide grafted with maleic anhydride and vinyl acetate
- *Initiators/catalysts/reaction accelerators*: sodium hydroxide; azo compounds such as 2,2'-azobis-(2,4-dimethylvaleronitrile), 2,2'-azobis-(2,4,4-trimethylvaleronitrile), 2,2'-

azobisisobutyronitrile, and 2,2'-azobis-(4-methoxy-2,4-dimethylvaleronitrile); peroxyesters such as t-butyl peroxyneodecanoate, t-hexyl peroxyneodecanoate, t-amyl peroxyneodecanoate, 1,1,3,3-tetramethylbutyl peroxyneodecanoate and t-butylperpivalate; peroxy-di-carbonates such as bis-(4-t-butylcyclohexyl)peroxy-di-carbonate, di-cyclohexylperoxy-di-carbonate, bis(2-ethylhexyl)di-sec-butylperoxy-di-carbonate and di-isopropylperoxy-di-carbonate; and diacylperoxides such as acetylperoxide, benzoylperoxide, di-lauroylperoxide, di-decanoylperoxide, di-octanoylperoxide and di-propylperoxide.

- *Molecular weight modifier or chain termination agents*: vinyl acetate
- *Activators*: triallyl cyanurate; triallyl isocyanurate; trimethylol propane trimethacrylate; ethylene dimethylacrylate; 1,4-bis(tertiary butyl peroxy isopropyl) benzene; 2,5-dimethyl-2,5-bis(tertiary butylperoxy) hexane; dicumyl peroxide; zinc oxide
- *Antioxidants*: styrenated or octylated diphenylamine; aralylated phenols (unspecified); polycarbodiimide (e.g., Rhenogram P 50)
- *Fillers*: carbon black, talcum (microtalcum); neutral clay; silica; vinyl silane
- *Flame retardants*: aluminum trihydrate with a vinyl silane; zinc borate; magnesium carbonate
- *Other additives/release agents/processing aids/coloring agents*: stearic acid, zinc stearate, vinyl silane, paraffin wax, or commercial internal lubricants (unspecified), acid-free inorganic pigments (unspecified)

The literature researched does not indicate that the specified phthalates in this project are likely to be used as raw materials in the manufacture or processing of EVA or EVOH polymer.

1.25 Manufacturing Processes used Worldwide to Produce Ethylene Copolymers (EVA and EVOH)

1.25.1 EVA Copolymers

EVA copolymers are commercially manufactured worldwide by copolymerizing ethylene and vinyl acetate using solution polymerization, suspension polymerization, bulk polymerization, or emulsion polymerization (Salamone, 1996; Klingender, 2008; Robertson, 2013).

Klingender (2008) reported that EVA copolymers can be synthesized in every ratio of the comonomers. This leads to EVA polymers that exhibit the complete scale of properties from thermoplastic material to elastomers. According to Klingender (2008), the copolymerization reaction is a radical chain process that is initiated by, for example, azo compounds. In this reaction, vinyl acetate acts as a chain-transfer agent to give rise to a broad molecular weight distribution. Three different methods are used to produce EVA polymers: high-pressure process

(0–45 percent vinyl acetate); low-pressure emulsion process (55–100 percent vinyl acetate); and medium-pressure process in solution (30–100 percent vinyl acetate) (Klingender, 2008). The high-pressure polymerization is carried out in bulk and yields EVA copolymers with a vinyl acetate content of up to 45 percent, typically ranging between 5 percent and 30 percent. In contrast, the emulsion process yields a polymer with vinyl acetate content ranging between 45 percent and 100 percent.

A patented modified copolymerization process that prefers solution and bulk polymerization processes also is available (Nagao, 2003). In the modified solution polymerization process, ethylene and vinyl acetate are polymerized in a solvent (methanol preferred, although ethanol or propanol can be used) in the presence of a catalyst. The preferred catalysts are listed above (Section 6.1.1).

1.25.2 EVOH Copolymer

The worldwide production of EVOH follows a two-step process, comprising polymerization and saponification (hydrolysis) (IHS, 2003; Salamone, 1996). In the polymerization process, ethylene and vinyl acetate are polymerized to give the ethylene vinyl acetate (EVA) copolymer using an initiator/activator complex. In the saponification process, the EVA copolymer is saponified to the EVOH copolymer.

In this manufacturing process, vinyl acetate is transformed into vinyl alcohol in a controlled hydrolysis of EVA copolymer (Robertson, 2013). The first step involves copolymerizing ethylene and vinyl acetate in a solvent system to form EVOH resins (Salamone, 1996). Vinyl acetate, dissolved in a solvent (unspecified), and ethylene, are passed through a heat exchanger that is fitted with a cooling system (IHS, 2003). The mixture (the vinyl acetate with solubilized ethylene) is subsequently returned to the polymerization vessel where it is mixed with the polymerization solution (unspecified solvent and initiator). The EVA copolymer is then hydrolyzed with caustic soda (sodium hydroxide, as catalyst) in a methanol mixture (Salamone, 1996) to yield a high degree (99.5 percent) of saponification (PIS, 2015). Ellis and Smith (2008) have reported that methanolic potassium hydroxide in benzene has been used in the hydrolysis of EVA copolymer formed to yield the EVOH copolymer. The resulting EVOH copolymers undergo coagulation, and washing and drying processes to yield the purified EVOH copolymers (Salamone, 1996).

1.25.3 Processing

Conventional methods are used in processing EVA and EVOH copolymers (Klingender, 2008; Giles and Bain, 2000) and include: blow or cast film, sheet, extrusion blow and co-extrusion

blow-molding, extrusion coating, or injection and co-injection molding. Additives may be applied during processing of EVA and EVOH.

1.25.4 Additives – EVA copolymer

As an elastomer (a polymer that has both viscosity and elasticity) with a fully saturated backbone (Klingender, 2008), but lacking sulfur-curable sites in the site chain, EVA copolymers need to be free-radically cured (Klingender, 2008). The curing system comprises peroxides or high-energy radiation, and activators are used. The activators include triallyl cyanurate, triallyl isocyanurate, trimethylol propane trimethacrylate, or ethylene dimethylacrylate (Klingender, 2008). The peroxides, 1,4-bis(tertiary butyl peroxy isopropyl) benzene, 2,5-dimethyl-2,5-bis(tertiary butylperoxy) hexane or dicumyl peroxide can be used for curing at low temperatures (150 °C–160 °C). Zinc oxide, although not necessary with peroxide cures, can be used to slightly improve aging properties.

Antioxidants, fillers and flame retardants, and other additives are listed above (Section 6.1.1). These are used for heat resistance; stain resistance; fire retardancy; to protect from hydrolysis at elevated temperatures and higher humidity; or as release agents during the mixing process to reduce sticking of mixes and aid in the dispersion of fillers or as coloring agents (Klingender, 2008).

1.25.5 Additives – EVOH copolymer

The literature search approach applied for this project did not identify additives used in processing EVOH copolymer. However, it has been reported that EVOH copolymers are highly hygroscopic (tend to absorb moisture from the air). Water absorption by these copolymers results in the weakening of the inter- and intra-molecular hydrogen bonds, as well as an increase in the free volume of the chains, and loss of barrier capacity (Franco-Urquiza et al., 2010). To avoid this loss, these authors proposed to add organo-modified clays into the EVOH matrix via a melt-blending method, using internal mixers and twin-screw extrusion. Other investigators also suggested a melt-blending process for preparing thermoplastic/organo-modified clays that could be easily scaled to an industrial level. This process involves three steps of twin-screw extrusion: (a) preparation of a master batch with high clay content, (b) master batch homogenization, and (c) final dilution to the required clay contents (Franco-Urquiza et al., 2010). However, it is uncertain if this is now performed on an industrial scale.

Based on information available, the specified phthalates are unlikely to be used in manufacturing or processing of EVA or EVOH copolymers.

1.26 Applications for Ethylene Copolymers in Consumer Products

1.26.1 Toys and Child Care Articles

In the RAPEX database, a database of consumer product safety reports in Europe that spans 11 years and 4,320 products, there were only two toy items made with EVA. Of these two toys, one (a jewelry decoration set) was reported to contain DEHP at 33 percent by weight (no further information was available to indicate whether the DEHP was in the EVA component part) (RAPEX, 2016). Neither EVA nor EVOH were reported in the Washington State Department of Ecology Children's Safe Product Act Reported Database (ECY, 2016a, 2016b).

Over 25,000 items were identified in an online shopping search on Amazon.com (2016) for EVA or EVOH. Of these, 167 results were for toys and games and 44 results were for baby items. Toddler toys included baby teething rings, plush toys, and a puzzle mat; child care articles were lunch bags and bibs. Children's toys included plush toys, costumes, soft flying disc, sword and shield, gaming gloves, and foam discs. No information as to phthalate content was provided.

1.27 Potential Use of Recycled Materials Containing Phthalate in Production of Ethylene Copolymers

As described in Sections 6.1 and 6.2 above, no information was found regarding the use of recycled raw materials to make ethylene copolymers or any indication that phthalates are added to produce ethylene copolymers (EVA or EVOH).

EVOH industrial scrap and packages containing EVOH may be recovered and reused. Recycling of regrind containing up to 15 percent EVOH is used as a discreet layer in multilayer sheet structures for rigid thermoformed containers. A regrind less than 5 percent EVOH is used in discreet layers in thin film structures but the optical properties and mechanical properties may be less than optimal (Medlock, 2015). However, problems can occur with EVOH copolymer; imperfections as evidenced by elevations above the surface of the matrix material from injection molding processes may occur (Tall, 2000).

TERA's research found no evidence of post-consumer ethylene copolymer recycling. In a search of the World Wide Web for buyers and sellers of recycled polymers or resins, TERA found one company in Europe that offers EVA production scrap and off grade materials for sale; we found no recyclers of EVOH. Background information on plastic recycling is presented in Appendix E.

Based on review of the literature and World Wide Web searches, it appears that EVOH and EVA scrap may be recovered and reused in manufacturing, although apparently not for consumer

products such as toys or child care articles. No information was available as to phthalate content of the recycled materials.

Based on review of the literature and World Wide Web searches, TERA found no evidence that phthalates are routinely used in manufacturing or processing of EVA or EVOH. Therefore, while scrap may be used to make the copolymers, the resulting product is not likely to contain phthalates because phthalates are not used in the manufacture of EVA or EVOH. We found no evidence of routine recycling of EVA or EVOH.

1.28 Potential Phthalate Contamination/Migration

Although plasticizers are not generally used in EVA grades with low viscosity, other plasticizers such as paraffinic mineral oils, are used in high viscosity EVA grades (Klingender, 2008). Other types of plasticizers including adipates and sebacates can be used in the production or processing of high vinyl acetate. Available information does not indicate that phthalates are used as plasticizers in the production of EVA or EVOH copolymers. No migration studies were identified in the resources searched that indicated phthalates can leach out or migrate from plastic items made of EVA or EVOH copolymers, which would indicate indirectly the presence of phthalates.

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7. Ethylene-Propylene Monomer (EPM) and Ethylene-Propylene-Diene Monomer (EPDM) CASRNs: 61789-00-2; 9010-79-1; 25038-36-2

Ethylene-propylene elastomers (also called EPM and EPDM) are synthetic rubbers. They are made from the same monomers as polyethylene and polypropylene thermoplastics. Both EPM and EPDM have a completely saturated hydrocarbon backbone (the “M” in their name refers to the saturated backbone structure), but EPDM grades have a residual unsaturation in the side chains (Lanxess, 2007). Due to their stable, saturated polymer backbone structure, and depending on the grade and pigmentation, these polymers have excellent resistance to heat, oxidation, ozone and weathering (weather aging), good electrical resistivity, good resistance to polar solvents, such as water, acids, alkalis, phosphate esters and many ketones and alcohols, and good vulcanizate physical properties (Lanxess, 2007; IISRP, 2011).

Our research on EPM and EPDM focused on CASRN 9010-79-1, but all CASRNs listed above were included in the research per the search strategy.

EPM is a copolymer synthesized from ethylene and propylene monomers. However, EPDM is a terpolymer of ethylene, polypropylene, and a non-conjugated diene monomer, ethylidene norbornene, dicyclopentadiene), or trans-1,4- hexadiene (Mark, 2007; Lanxess, 2007; IISRP, 2011; Kirk-Othmer, 2002; IHS, 1981). The majority of EPDM compounds in the current market are based on either dicyclopentadiene or ethylidene norbornene (Skidmore, 2012; Kirk-Othmer, 2002). EPDM includes a small amount of diene to permit conventional vulcanization with sulfur (IHS, 1981).

1.30 Raw Materials Used in Production of EPM and EPDM

Several additives may be used to improve durability, flexibility, color stability, and wear resistance properties of EPM and EPDM (Ibeh, 2011). Plasticizers such as paraffinic mineral oils and naphthenic oils are used in the production or processing of EPM and EPDM elastomers (Lanxess, 2007). Based on the available information searched for this project, there is no evidence that the specified phthalates are added as a raw material during manufacturing or processing of EPM and EPDM. However, Ziegler-Natta catalysts are used in the production of EPM and EPDM. Available information indicates that these catalysts are prepared using magnesium- and titanium (IV) chloride, and an internal donor, which is very often a phthalate such as DBP, DIBP or DEHP (Borealis, 2014). The potential exists for these catalysts to survive the polymerization process, with the phthalates theoretically present in concentrations of about 1 mg/kg (or 0.0001 weight percent) in the final pellets (Borealis, 2014). This concentration does not exceed the limit of 0.1 percent for phthalates for children’s toys and child care articles.

1.30.1 Raw Materials Used in Making EPM and EPDM

The raw materials used in making EPM and EPDM (Mark, 2007; IISRP, 2011; Chemical Weekly, 2009; Lanxess, 2007; Kirk-Othmer, 2002; IHS, 1981; Alvarez-Grima, 2007) include:

- *Monomers*: EPM: ethylene and propylene; EPDM: ethylene; propylene; and ethylidene norbornene (most widely used diene monomer) or dicyclopentadiene, or trans-1,4-hexadiene
- *Solvents*: hexane; water
- *Catalysts*: EPM & EPDM: Ziegler-Natta catalyst (formed *in-situ* by reaction of vanadium salts and aluminum alkyl halides with phthalates (DBP, DEHP, DIBP as internal donors); metallocene (metallocene/alumoxane) catalysts
- *Peroxides*: 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane; dicumyl peroxide; di(tert-butylperoxyisopropyl)benzene; diamyl peroxide
- *Peroxide-curing accelerators/ultraaccelerators*: benzothiazole derivatives or sulfenamides with so-called ultraaccelerators like thiuram compounds (zinc-dithiocarbamate [Skidmore, 2012]); dithiocarbamates; dibenzyl dithiocarbamate or tetrabenzyl thiuramdisulfide
- *Sulfur-vulcanization accelerators/ultraaccelerators*: benzothiazole derivatives (*e.g.*, 2-mercapto-benzothiole and its zinc salts); sulfenamides (*e.g.*, N,N-diisopropyl 2-benzothiazolsulfenamide or N-cyclohexyl-2-benzothiazolsulfenamide); thiuram compounds (*e.g.*, dithiocarbamates (dibenzyl dithiocarbamate and tetrabenzyl thiuramdisulfide))
- *Activators/coagents*: sulfur; acrylates; allyl-cyanurates (triallylcyanurate); maleimides (*e.g.*, m-phenylene-bismaleimide); triallylphosphate; ethyleneglycol-dimethacrylate
- *Plasticizers*: paraffinic mineral oils; naphthenic oils
- *Fillers/partition aid*: carbon black; calcined clay; fine-particle-size calcium carbonates

Concluding from the literature reviewed for this project, the specified phthalates are not directly added as raw materials in the manufacture of EPM or EPDM. However, DBP, DIBP, or DEHP may be components of the Ziegler-Natta catalyst.

1.31 Manufacturing Processes used Worldwide to Produce EPM and EPDM

EPM and EPDM rubbers or elastomers are produced worldwide by three major commercial processes: the solution process, the suspension process (also known as the slurry process), and the gas-phase process (Mark, 2007; IISRP, 2011; Chemical Weekly, 2009; Lanxess, 2007; Nexant Chem Systems, 2005). The manufacturing systems vary but all are capable of producing a variety of EPM copolymer and EPDM terpolymer rubbers, which have different properties. The Ziegler-Natta vanadium-based catalysts and metallocene catalysts are typically used to

copolymerize ethylene-propylene elastomers. The monomers are combined in a random manner, which results in rubbery and stable polymers. Depending on polymer composition and how the monomers are combined, a wide family of ethylene-propylene elastomers that range from amorphous, non-crystalline to semi-crystalline structures can be made (IISRP, 2011). The copolymer products vary in form from solids to oil blends (Ibeh, 2011), and have a wide range of molecular weights. The specific details of the manufacturing processes of EPDM are proprietary and differ significantly between various suppliers (Mark, 2007; Kirk-Othmer, 2002); the general methods are described below.

1.31.1 Solution Process

The solution process is the most widely used process in which a catalyst is used to produce EPM or EPDM (Mark, 2007; Chemical Weekly, 2009; Lanxess, 2007). The polymer produced is in the dissolved state in an excess of a hydrocarbon solvent (*e.g.*, hexane). The manufacturing of EPM and EPDM rubber is based on Ziegler-Natta catalysis that uses vanadium compounds (of which vanadium oxytrichloride is the most widely used [Kirk-Othmer, 2002]) with an alkyl aluminum halogen as co-catalyst (Kirk-Othmer, 2002; Chemical Weekly, 2009). In addition to the Ziegler-Natta catalysis, the process also uses dry solvent, ethylene, diene (in the case of EPDM), a catalyst and cocatalyst solutions (not specified) that are continuously and proportionately fed to one or a series of polymerization vessels (Mark, 2007). EPDM can be manufactured using the solution process in which either ethylidene norbornene or 1,4-hexadiene is used as the nonconjugated diene in the terpolymer. In either case, either Ziegler-Natta or metallocene catalyst systems can be used for polymerization (IHS, 1998). In the solution process, the polymer molecules form on the catalyst, then dissociate from it and remain in solution that becomes more viscous with increasing polymer concentration. If stabilizers and oils are used, they are added directly after polymerization (Chemical Weekly, 2009). Unpolymerized ethylene, propylene, unpolymerized diene (in the case of EPDM), and about 5-10 percent EPDM, all in a homogenous solution, remain in the viscous rubber solution (Mark, 2007). Steam stripping is used to separate the rubber from its solvents. The polymer is freed from its carrier solvent, falls into the water in the form of crumb, and then dried and packaged for storage and shipment.

1.31.2 Slurry (or Suspension) Process

The slurry (or suspension) process is a modification of bulk polymerization (IISRP, 2011; Chemical Weekly, 2009). This process involves the use of a soluble (IHS, 1998) Ziegler-Natta catalyst in a nonsolvent diluent (*i.e.*, the monomer, propylene), and an operating temperature to enable the monomers, but not the polymer, to be soluble (Mark, 2007). Metallocene/alumoxane catalyst systems may also be used. The catalysts used in the slurry process leave residues that contribute significantly to the degradation of the rubber vulcanizates properties upon heat ageing. In the slurry process, soluble rubber particles are formed as a suspension in the reaction medium.

Following polymerization, water, antioxidants, and extender oils (for oil-extended EPDM grades) are added, and residual hydrocarbons are stripped from the suspension (Lanxess, 2007). The resulting rubber crumb is dewatered, dried and finished as in the solution process.

1.31.3 Gas-Phase Process

A recent development in the manufacture of high molecular weight ethylene-propylene rubbers, particularly EPDM, is the use of gas-phase polymerization technology (IISRP, 2011; Chemical Weekly, 2009; Kirk-Othmer, 2002). This process involves no solvents, thus eliminating the need for solvent stripping, washing and drying. Conventional Ziegler-Natta or metallocene catalysts may be used (Chemical Weekly, 2009; Nexant Chem Systems, 2005; Kirk-Othmer, 2002; IHS, 1998). The monomers and nitrogen in gas form along with a catalyst are fed into a vertical fluidized bed reactor and solid product is removed periodically. A substantial amount of carbon black is continuously injected as a partition aid to prevent the polymer granules from sticking to each other and to the reactor walls. The products are made in a granular form to enable rapid mixing (IISRP, 2011).

1.31.4 Processing

EPM and EPDM grades are compounded with reinforcing fillers if mechanical properties are required (Mark, 2007). Carbon blacks are usually used as fillers, but calcined clay or fine-particle-size calcium carbonates may be used to lower cost and improve the processability of light colored compounds, or to reduce the cost of black compounds. Plasticizers, such as paraffinic mineral oils (no mention of phthalates) are widely used and may sometimes be blended with naphthenic oils to prevent the exudation of paraffinic mineral oils at low temperatures from EPDM vulcanizates or from high ethylene EPDMs. Peroxide curing of EPM may be used (Lanxess, 2007). Some of the typically used peroxides for crosslinking rubber are listed in Section 7.1.1 (Alvarez Grima, 2007). For peroxide cures of EPM, and to a lesser degree of EPDM, activators (also called coagents) such as a small amount of those listed in Section 7.1.1 also are needed to increase the cross-link density (Alvarez Grima, 2007; Dierkes, 2007).

High levels of highly active accelerators are used for the sulfur vulcanization of EPDM (Kirk-Othmer, 2002). The typical accelerators used include combinations of benzothiazole derivatives) with so-called ultra-accelerators like thiuram compounds or dithiocarbamates as listed in Section 7.1.1 (Dierkes, 2007; Kirk-Othmer, 2002). Peroxide-cured EPM and EPDM are stabilized with antiozonants and antioxidants (Skidmore, 2012; Lanxess, 2007).

Several conventional methods are also used to process the EPM and EPDM rubbers (Kirk-Othmer, 2002; Lanxess, 2007; Mark, 2007). These include: extrusion, calendaring, and compression molding, transfer molding, steam cure, hot-air cure, and injection molding.

Based on the available information searched for this project, there is no evidence that the specified phthalates are added during the manufacturing processes and processing of EPM and EPDM. However, three of the specified phthalates (DBP, DIBP, and DEHP) may be added as part of the Ziegler-Natta catalyst. Although data are not available for phthalate concentration in EDM or EPDM, Ziegler-Natta catalysts are also used in manufacturing some other plastics [such as polypropylene (PP)]. For PP, test results indicated that the phthalate concentrations do not exceed 0.15 mg/kg polypropylene (or 0.00001 weight percent), and they are often below the threshold of the analytical method of 0.01 mg/kg PP (or 0.000001 weight percent) (Borealis, 2014). Based on the phthalate analyses for PP, it is reasonable to assume that the phthalate concentrations in EPD or EPDM from manufacturing, where phthalates would only be introduced with Ziegler-Natta catalysts, may theoretically be present in concentrations of approximately 1 mg/kg (1 ppm, or 0.0001 percent) in the final pellets (Borealis, 2014). are unlikely to be greater than 0.15 mg/kg EPD or EPDM (or 0.00001 weight percent). This concentration does not exceed the limit of 0.1 percent for phthalates for children's toys and child care articles.

1.31.5 Applications for EPM and EPDM in Consumer Products

1.31.5.1 Toys and Child Care Articles

In Amazon.com (Amazon.com, Inc.2016), a widely used online store, a search yields 77,479 products that contain the key word "EPDM". The types of products that included "EPM or EPDM are as follows:

- Patio, Lawn and Garden
- Water Garden, and Pond Liners, and Seals
- Industrial and Scientific
- O-Rings
- Industrial Coatings
- Tools and Home Improvement
- Masking Tape
- Wall Surface Repair Products
- Roofing Materials
- Office Products
- Literature Organizers
- Rubber Cement
- School Adhesives
- Film and Tape Dry Adhesives

- Arts, Crafts and Sewing

In Amazon.com's toys and games department, searching for "EPDM" revealed only 41 items, including 3 for hobbies, and 31 for sports and outdoor play. Only two items could be considered a toy or a component part of a toy. These were an O-ring for a toy action figure and a swing set rubber strap set. A search with the key word "EPM" yielded 61 items under toys and games, with only two that were relevant: swing set infant high back bucket seats and swing set rubber strap sets.

Neither EPM nor EPDM were found in consumer product databases (RAPEX, 2016; ECY, 2016a,b; HPD, 2015) with any toy applications. Contamination of rubber toys with phthalates is reported in the literature (Yacob et al., 2013); however, these authors called the items "soft rubber toys", yet identified them as made from PVC.

1.32 Potential Use of Recycled Materials Containing Phthalate in Production of EPM and EPDM

As described in Section 7.2.1, unpolymerized monomers are collected and reused in the manufacturing process for EPM and EPDM. Information on recycled EPM routinely being used to make new EPM was not found in the sources searched. One paper investigated making a polymer composite with recycled EPDM (from waste rubber gaskets of old washing machines) and LDPE using supercritical carbon dioxide foaming technology (Jeong et al., 2014). Scrap from manufacturing of EPDM is cleaned and reused to make rubber flooring (Infinity Performance, 2016). EPDM roofing membrane is regularly removed and recycled around the United States in systematic efforts initiated by manufacturers of roofing products (Evanko, 2010). The material is collected from the job site and shipped to a regrinding facility where it is used to make walkway pads for new roofs and other products (Evanko, 2010). Rubber recycling companies take EPDM scrap and regrind into granulated rubber for sport, playground, and landscaping surfaces (Evanko, 2010). We did not find evidence that the recycled EPDM is used for toys or child care products. Background information on plastic recycling is presented in Appendix E.

In summary, our research did not find evidence that phthalates are used in the manufacture of EPM or EPDM (except for use in Ziegler-Natta catalysts; the resulting concentrations are not expected to exceed the limit of 0.1 percent). We also determined that EPDM scrap is used in manufacturing and made into rubber flooring, and that roofing products are recycled to make new materials such as walkway pads for roofs. EPDM materials are also ground to be used as sports surfaces or in landscaping. TERA did not find information on recycled EPM nor EPDM being made into children's toys or child care articles. Because EPM and EPDM do not contain

the specified phthalates at concentrations greater than 1000 ppm, any recycled EPM or EPDM is not likely to contain phthalates above 1000 ppm.

1.33 Potential Phthalate Contamination/Migration

Paraffin mineral oils and naphthenic oils are reportedly used in the manufacture or processing of EPM and EPDM materials (Lanxess, 2007), but none of the specified phthalates are directly added during manufacture or processing, based on the literature searched. However, use of Ziegler-Natta catalysts in the production of EPM and EPDM implies that DBP, DIBP and DEHP that are components of this catalyst could end up in the processed plastics (Borealis, 2014).

No migration studies were identified that evaluated the potential of EPM and EPDM plastics to leach out phthalates during use of products made of EPM or EPDM, that would indicate indirectly the presence of phthalates.

Based on the phthalate analyses for PP, it is reasonable to assume that the phthalate concentrations in EPD or EPDM from manufacturing, where phthalates would only be introduced with Ziegler-Natta catalysts, may theoretically be present in concentrations of approximately 1 mg/kg (1 ppm, or 0.0001 percent) in the final pellets (Borealis, 2014). By analogy, it is unlikely that DBP, DIBP and DEHP can leach out of toys or child care articles made of EPM or EPDM plastics, as these are made from the same monomer building blocks, and would not be expected to exceed the CPSC limit of 0.1 percent.

1.34 References

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8. Ionomers (Surlyn®) CASRN: 9078-96-0

Ionomers (ionic or ion-containing polymers) are thermoplastic polymers whose bulk properties are governed by ionic interactions in discrete regions of the material, specifically in materials where the maximum ion content is 15 to 20 mol percent (Tant et al., 1997; Zhang and Zhao, 2013); others report the maximum ion content as up to 10 to 15 mol percent (Salamone, 1998). Ionomers are derived from precursor copolymers containing both ionic and non-ionic repeat groups. The ionic component has been neutralized, forming an ionic pair with a metallic cation. A number of different polymers have been modified to create ionomers (Tant et al., 1997). The ionic groups include anionic, cationic, zwitterionic, and ligand-metal complexes (Pineri and Eisenberg, 1986), placed along the backbone of the polymer and may be distributed evenly, randomly, or only at the ends (Tant et al., 1997).

Many types of ionomers are available, for example, carboxylate, sulfonate, phosphonate, triglyconate, ammonium, and pyridinium ionomers (Tant et al., 1997; Schlick, 1996). The focus of this document is the carboxylate ionomers, an example of which is Surlyn®.

Surlyn® is a group of thermoplastic polymers produced by a large U.S. corporation (DuPont, 2003; 2016a). Surlyn® is based on copolymers of ethylene and methacrylic acid, with metallic salts (such as zinc, sodium, lithium or magnesium salts) to form ionic crosslinks between the acid groups within a chain, or between neighboring chains (DuPont, 2003; 2014; 2016a). Varying grades of Surlyn® ionomers are produced depending on the cation used during neutralization. Surlyn® can be molded, compressed, extruded and foamed into different shapes (Berteaux et al., 1988). The Surlyn® ionomers exhibit enhanced mechanical strength, clarity, oil and grease resistance, and excellent scratch, abrasion and chemical resistance (DuPont, 2016a).

1.35 Raw Materials Used in Production of Surlyn®

1.35.1 Raw Materials Used in Making Surlyn®

The raw materials used in making Surlyn® (DuPont, 2016b; Reynolds, 2011; Tant et al., 1997; Rees, 1966; Pineri and Eisenberg, 1986) include:

- *Monomers*: ethylene; methacrylic acid
- *Solvents*: tetrahydrofuran
- *Neutralizers*: sodium methoxide; magnesium acetate; sodium hydroxide; zinc hydroxide
- *Additives*:
 - *UV absorbers*: a transparent blue or violet pigment (unspecified), carbon black, or antioxidant (unspecified)
 - *Colorants*: transparent or opaque pigments (unspecified)

- *Flame retardants*: brominated organic compounds; antimony oxide
- *Reinforcers*: glass fiber
- *Plasticizers*: zinc stearate; aliphatic di- and tri-carboxylic acids
- *Anti-fogging agents*: ethylene-methacrylic acid carrier resins

1.36 Manufacturing Processes used Worldwide to Produce Surlyn®

The process for manufacturing Surlyn® ionomer involves copolymerization of ethylene with a small amount of an unsaturated carboxylic acid such as methacrylic acid via a high-pressure, free-radical reaction (Reynolds, 2011; Tant et al., 1997; Rees, 1966). The polymerization results in the formation of poly(ethylene-co-methacrylic acid) (Reynolds, 2011), which is generally available as a free acid (Pineri and Eisenberg, 1986). The free acid is neutralized to processing specifications using the derivatives listed in Section 8.1.1 (Reynolds, 2011; Tant et al., 1997; Pineri and Eisenberg, 1986). Once the solvent is removed, the final product is a polymer with low levels of covalently attached metal ions that forms ionic cross-links (Reynolds, 2011).

1.36.1 Processing

Processing options for Surlyn® include extrusion coating, blown film, cast film, sheet extrusion, co-extrusion, and injection molding (DuPont, 2014; 2016a). Additives may be added to provide, for example, UV resistance (sunlight or weathering resistance), colors, foamed products, flame retardant products, glass reinforcement, or combinations of these characteristics (DuPont, 2003). Anti-fogging agents and plasticizers can be blended with Surlyn® (DuPont, 2016b; Zhang and Zhao, 2013). The additives are listed above in Section 8.1.1.

While plasticizers may be used as a raw material in the manufacture of Surlyn®, our findings did not indicate that the specified phthalates for this project were among the plasticizers used.

1.37 Applications for Ionomers (Surlyn®) in Consumer Products

1.37.1 Toys and Child Care Articles

No toys or child care articles made of Surlyn® were identified based on Tier 1, 2 or 3 research. Tier 4 gap searching from the World Wide Web identified use of Surlyn® in shrinkable beverage containers such as juice pouches and snack packaging (DuPont, 2015). Surlyn® is not a common material used in consumer products; only 24 items were identified as containing Surlyn® in an online search of Amazon.com (Amazon.com, Inc., 2016). The items reported were golf balls, football helmets, soccer shin shields and a body surf board.

Consumer database searches for ionomer or Surlyn[®] yielded no results (HPD, 2015; SPIN, 2015; RAPEX, 2016; ECY, 2016a,b). All of these databases list many products made from plastics, but when the specified phthalates are identified as in plastic, the specific type of plastic is not stated.

Surlyn[®] is used in a wide variety of other consumer products as discussed in Appendix D.

1.38 Potential Use of Recycled Materials Containing Phthalate in Production of Surlyn[®]

We found no mention of use of recycled raw materials to make ionomers or Surlyn[®]. In a search of the World Wide Web for Surlyn[®] recycling, we found very few recyclers. One large recycling company in the U.S. offers to buy and sell scrap, film and purgings or die bleeds from manufacturers that are clean and have no print or contamination (<http://www.poly-americanrecycling.com/polyethylenewanted.html>). Another large recycler in Europe buys Surlyn[®] and offers Surlyn[®] ionomer grind and film, as well as Surlyn[®] from cosmetic cap production for sale (<http://www.sonepa.com/available.html>). We were not able to determine what the recycled Surlyn[®] is being used to make; however if it is being used to make Surlyn[®] for consumer products, because no phthalates are used in producing Surlyn[®], the use of the recycled Surlyn[®] material, particularly if it is clean manufacturing waste, would indicate that phthalates would not be introduced into Surlyn[®] from recycling. Background information on plastic recycling is presented in Appendix E.

1.39 Potential Phthalate Contamination/Migration

There were no migration or contamination studies regarding the specified phthalates in the literature consulted for this report.

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9.

10. Polycarbonate (PC) CASRNs: 25037-45-0; 24936-68-3; 25971-63-5; 111211-39-3; 103598-77-2

Polycarbonate (PC) is a thermoplastic, synthetic resin that becomes plastic on heating and hardens on cooling. It is composed of many ("poly") identical units of bisphenol A (BPA) connected by carbonate-linkages in its backbone chain (Plastics Europe, 2015). A carbonate group is a di-ester of carbonic acid, and with BPA, forms a polymeric chain. PC has excellent high impact strength, high transparency, high strength, high temperature or heat resistance, scratch resistance, good electrical insulation properties, is biologically inert, has a hard coating, is readily recyclable, and is easy to process (Campo, 2008; Plastics Europe, 2015).

1.41 Raw Materials Used in Production of PC

Several additives may be blended with PC polymer, but commercial PC does not usually include plasticizers. Plasticizers, if used, include dibutyl succinate, DBP (greater than 20 weight percent), DnOP (0.8 weight percent), 1,3- and 1,4-dichlorobenzene (0 to 5 weight percent), and dinitrophenyl (0 to 25 weight percent) (Ellis and Smith, 2008). The phthalates, DBP and DnOP, are, therefore, likely to constitute a concentration of more than 0.1 percent if used as plasticizers in PC.

1.41.1 Raw Materials Used in Making PC

The raw materials used in making PC include (The Danish Environmental Protection Agency [Danish EPA], 2015; Kirk-Othmer, 2014; Crafttech Industries, 2015; Carraher, 2010; Ellis and Smith, 2008; Campo, 2008; Elias, 2003; Serini, 2000):

- *Monomers*: bisphenol A (BPA) (or other bisphenols such as bisphenol F; bisphenol E; bisphenol C); trisphenols or tetrakisphenols; carbonyl chlorides (*e.g.*, phosgene); diphenyl carbonate
- *Chlorinated solvents*: methylene chloride (most commonly used); chloroform; cis-1,2-dichloroethylene; *sym*-tetrachloroethane
- *Catalysts*: tertiary amine (mostly pyridine); a quaternary ammonium salt, sodium lithium, potassium, tetraalkylammonium; tetraalkylphosphonium hydroxides or carbonates
- *Phase transfer catalysts*: tetrabutyl ammonium hydroxide; methyltributyl ammonium hydroxide
- *Chain stoppers or terminators*: phenol; tertiary butylphenol; cumylphenol
- *Strong base*: sodium hydroxide
- *Additives*: PC may contain impact modifiers such as:
 - *UV stabilizers or absorbers*: benzotriazoles (hydroxyphenyl benzotriazoles; hydroxyphenyltriazines), hydroxybenzophenones; cyanoacrylates

- *Heat stabilizers*: less than 0.5 percent phosphites; phosphonites or phosphines in combination with epoxide compounds, or also organosilicon compounds
- *Flame retardants*: such as brominated oligomers or polymer from tetrabromo-BPA; small amounts of salt-like compounds (*e.g.*, potassium perfluorobutylsulfonate or sodium 2,4,5-trichlorobenzenesulfonate, potassium diphenylsulfonesulfonate); chlorinated sulfones; polytetrafluoroethylene; tetraphenyl resorcinol diphosphonate; tetraphenyl bisphenyl-A diphosphonate)
- *Plasticizers*: dibutyl succinate; dibutyl phthalate (DBP); dioctyl phthalate (DnOP); 1,3- and 1,4-dichlorobenzene; dinitrophenyl
- *Fillers*: such as glass fibers or metal
- *Mold release agents*: less than 1 percent esters of long-chain carboxylic acids
- *Dyes*: phthalocyanine, cyanine or metal-stabilized azo
- *Fire resistance agent*: tetrabromobisphenol A

1.42 Manufacturing Processes used Worldwide to Produce PC

The manufacturing process of PC involves a phosgene and a non-phosgene process. The phosgene process is a Schotten–Baumann reaction of phosgene and an aromatic diol in an amine-catalyzed interfacial condensation reaction. The non-phosgene process occurs by a base-catalyzed transesterification of a bisphenol with a monomeric carbonate (such as diphenyl carbonate) (Kirk-Othmer, 2014; Ellis and Smith, 2008; Serini, 2000).

1.42.1 Phosgene Process (Schotten–Baumann Reaction)

The Schotten-Baumann Reaction is currently the most common manufacturing process. The process involves reaction of BPA with phosgene in the interfacial polymerization process (Kirk-Othmer, 2014; Ellis and Smith, 2008; Serini, 2000). Interfacial polymerization involves stirring slurry or solution of BPA and 1 to 5 percent of a chain stopper in a mixture of a chlorinated solvent and water, while adding phosgene in the presence of a small amount (0.1 to 3 percent) of a tertiary amine as a catalyst. Other chlorinated solvents (listed above) may also be used. Concurrent addition of sodium hydroxide maintains the appropriate basic reaction pH. The process involves continuous addition of phosgene until free phenolic groups can no longer be detected, signifying complete reaction. The excess phosgene becomes hydrolyzed and the solvent is washed to remove residual base and amine.

Kirk-Othmer (2014) reported that many variations of the basic interfacial process have been patented. These variations include continuous or semi-continuous processes, various workup procedures, many types of catalysts (*e.g.*, phase-transfer catalysts and bifunctional catalysts), methods that rely on the intermediacy of bischloroformate oligomers, and various schemes to control the formation of low molecular weight oligomeric species or cyclics.

1.42.2 Non-phosgene (Transesterification or Melt) Process

Some manufacturers have developed non-phosgene processes in the manufacture of PC. These processes are thought to be greener alternatives than the phosgene method (Serini, 2000). As in the phosgene process, the non-phosgene process also involves the transesterification of diphenyl carbonate (DPC) with BPA (ICIS, 2007; Kirk-Othmer, 2014; Serini, 2000). The reaction takes place between 180 and 220 °C, resulting in a phenol molecule and PC. This is more commonly termed “the melt process” because it is a two-stage polymerization process that takes place in the absence of solvents, and produces the neat polymer directly, without the use of chlorinated solvents. The phenol produced as a byproduct during the reaction is removed and the PC forms directly (Kirk-Othmer, 2014).

The methods employed by manufacturers using the non-phosgene process differ depending on the method used to make the dialkyl carbonates (ICIS, 2007):

- (1) One company produces DPC from dimethyl carbonate (DMC), the latter being produced from carbon monoxide, methanol, and oxygen using a proprietary DMC/DPC technology;
- (2) A second company reacts nitric oxide and methanol oxidatively to give methyl nitrite, which undergoes carbonylation to produce DMC;
- (3) A third company has technology for making DPC from di-n-butyl carbonate, which is produced from urea and n-butyl alcohol; and
- (4) A fourth company produces DPC from DMC, which is produced via methanolysis of ethylene carbonate.

1.42.3 Other Polymerization Techniques

Other techniques have been reported in the literature for preparing PC but these have not yet been commercialized (Kirk-Othmer, 2014). One such technique is an analog of the transesterification process that utilizes the diacetate of BPA. In this process, BPA diacetate is transesterified with DMC using a titanate catalyst, resulting in the production of PC with methyl acetate as the byproduct. Another technique is the ring-opening polymerization of cyclic oligomers that can lead to many novel applications, but the preparation and purification are difficult, the yield is low and the melt polymerization is difficult. Another process utilizes a trimethylamine-catalyzed hydrolysis and condensation of BPA bischloroformate in a pseudo-dilution reaction that results in production of a mixture of cyclic oligomers.

Information available also indicates that many other diols [*e.g.*, 1,1-bis(4-hydroxyphenyl)cyclohexane and dihydroxybenzoate] have been tested in place of BPA (Serini, 2000). Tetramethylcyclobutanediol has reportedly been developed as a replacement for BPA.

Elias (2003) also reported that special linear PC types use other bisphenols (such as bisphenol F, bisphenol E, bisphenol C) while crosslinked PC types employ trisphenols and tetrakisphenols.

1.42.4 Processing

Several (proprietary) techniques are used to isolate the product PC. The isolation methods include antisolvent precipitation, removal of solvent in boiling water, spray drying, and melt devolatilization using a wiped film evaporator or similar equipment (Kirk-Othmer, 2014). The isolated product, either pellet or powder, is dried prior to processing to prevent hydrolysis of the polymer by dissolved water (Kirk-Othmer, 2014; Ellis and Smith, 2008). Processing then occurs by:

- Injection molding;
- Extrusion;
- Compression molding;
- Cold forming; or
- Casting.

Processing temperatures range from 230 to 300 °C. The two dominant processes involved in making products from PC are injection molding and extrusion (Plastics Europe, 2015). The injection molding results in single-end products, such as housings, plates, bottles and many other applications. Extrusion makes it possible to create long pipes, profiles, films, or sheets. During processing, stabilizers, additives, and colors may be added (Kirk-Othmer, 2014).

To extend the lifetime of commercial grade PC, different kinds of stabilizers are added (Danish EPA, 2015). For example, low levels (usually less than 5000 ppm) of heat stabilizers are usually added during processing (Kirk-Othmer, 2014). Several PC grades include additives (as listed in Section 9.1.1) to increase the flame-retardant properties and to decrease smoke (Danish EPA, 2015; Kirk-Othmer, 2014). Commercial grades may contain UV stabilizers or absorbers. Mold release agents (less than 1 percent esters of long-chain carboxylic acids) may also be added to PC to make processing easier. Plasticizers such as dibutyl succinate, DBP (less than 20 weight percent), DnOP (approximately 0.8 weight percent), 1,3- and 1,4-dichlorobenzene (0 to 5 weight percent), and dinitrophenyl (0 to 25 weight percent) may be additives. Some of these plasticizers show both plasticizing and antiplasticizing properties, depending on the concentration and temperature of the additives. For example, DBP is an antiplasticizer at concentrations of 5 to 20 weight percent and a plasticizer at concentrations greater than 20 weight percent (Ellis and Smith, 2008). Plasticizers also accelerate the rate of crystallization of PC. Polycarbonate can be filled with glass fibers to increase strength, especially for metal

replacement applications (Carragher, 2010).

Paint and inks (unspecified), an adhesive system (*e.g.*, epoxy, polyurethane, silicone, tape; sealant) or a cleaning agent (methyl alcohol, ethyl alcohol, butyl alcohol, isopropyl alcohol, white spirit, heptane, hexane, or petroleum ether) can be applied to PC (Kirk-Othmer, 2014). Kirk-Othmer (2014) indicated that, for sheet applications, PC is commonly coated with a silicone–silicate or acrylate hardcoat that provides abrasion resistance as well as increased solvent resistance. High performance dyes (*e.g.*, phthalocyanine, cyanine and metal-stabilized azo) may be added to products such as CD-R and DVD-R discs.

In summary, our findings indicate that phthalates such as DBP and DnOP, may be used in manufacturing of PC. These phthalates may be found at concentrations greater than 0.1 percent, the limit for phthalate concentration for toys and child care articles.

1.43 Applications for PC in Consumer Products

1.43.1 Toys and Child Care Articles

PC is permitted as an inert ingredient for non-food use (U.S. FDA, 2015). Thus, a common application for PC is in baby bottles, sippy cups, and other feeding utensils. Amazon.com was searched using the chemical name and the results were inspected to evaluate if they had PC specified in the title of the product or listed as a component. Toys located on Amazon.com for online shopping that specify they are made from PC include: bead necklace, badge, toy cars and trucks, children’s sunglasses, swim goggles, spin top, pegs, and baby mirrors (Amazon.com, Inc., 2016). Basketball backboards, kid chairs, masks, and shields are also made from PC. PC used in combination with ABS was identified in a kid’s backpack; PC with polystyrene and polypropylene were used in a bike helmet.

No toys or child care articles specifically made from PC had information as to the content of the specified phthalates.

The numerous other applications for PC are discussed in Appendix D.

1.44 Potential Use of Recycled Materials Containing Phthalate in Production of PC

To determine if phthalates could be introduced into PC through the use of recycled materials to make PC, we considered whether phthalates are present in the virgin plastic that may be recycled, and if so, whether and how PC is being recycled.

While we found no data on measurements of phthalates in PC from recycled PC, or in PC recycle, as discussed in Sections 9.1 and 9.2 phthalates may sometimes be used in manufacturing PC. Dibutyl phthalate (DBP) (greater than 20 weight percent) and dioctyl phthalate (DnOP) (0.8 weight percent) are sometimes used as plasticizers or anti-plasticizers in the manufacture of PC. Because phthalates are sometimes used to make PC (Ellis and Smith, 2008) if the PC containing the phthalates were recycled to make new PC, then the phthalates would also be present in the new PC. Therefore, we explored whether PC is recycled to make new PC.

In the U.S., products made with PC are labeled with resin identification code (also called plastic recycling code) #7 (“Other”). Background information on plastic recycling is presented in Appendix E. There are no standard reuse and recycling protocols for this category (Eartheasy, 2012). However, PC is recyclable and is being recycled in the United States (Recycledplastics, 2014.). PC is recovered from plastic automotive parts for reuse (Merrington, 2011) and from recycling compact discs (CDs) and PC bottles (Azo Materials, 2016b; Plasticsmarkets, 2016), although the manufacture of PC water and baby bottles is declining due to the presence of bisphenol A (Azo Materials, 2016b).

In addition, the Association of Post-consumer Plastic Recyclers (APR) lists a number of recycling companies in the U.S. in their 2016 Market Directory that offer to sell or purchase recycled PC bottles and moldings and recycled PC pellets (APR, 2015). World Wide Web searching reveals multiple buyers and sellers of recycled PC (post -consumer, -commercial, and - industrial); including CDs, electronic scrap plastic, manufacturing scrap, construction and demolition scrap (Plasticsmarkets, 2016). Some buyers were seeking reprocessed PC for various uses, including sheet extrusion, injection molding, and thermoforming applications, indicating a wide variety of products potentially made from the recycled materials (Plastemart, 2014).

The usual process for recycling PC is to mechanically shred the PC into a granulate for reuse (Plastics Expert, 2016). Chemical recycling or depolymerization of PC is also reported with the resultant BPA and DPC monomers, which can be used as virgin material to produce more polymer (Azo Materials, 2016b). If phthalates were present in the PC being recycled, the depolymerization process presumably would separate the BPA and DPC monomers from the phthalates and any new recycled PC would not contain the phthalates from the original material. Therefore, recycling of PC using a depolymerization method would likely not contribute phthalates to the resulting new PC resin made from the recycled monomers.

Mechanical recycling does not convert the PC back into its component chemicals and therefore, if phthalates are present in the mechanically-recycled PC, they could remain present in any new material made from the recycled PC. A post-consumer example of PC recycling is of compact discs (CDs) and DVDs. These discs are made of PC, with a thin reflective layer of metal (usually

aluminum) and a layer of acrylic lacquer (CD Recycling Center, 2016). Recycled CDs are ground or shredded and then melted; metals are separated from the plastic and the result is a lower grade of raw plastic that is used for the automotive and building materials industries (CD Recycling Center, 2016). There was no information located in the sources searched for this project about whether the recycled CDs could be used for toys or child care products.

PC is also used as a component in electrical and electronic equipment, which is a fast growing waste stream due to large numbers of products and relatively short life of the products (Antonakou et al., 2014). Recycling of waste electrical and electronic equipment (WEEE) will likely increase due to political pressure (*e.g.*, EU directive with recycling targets for WEEE) (Kantarelis et al., 2011, as cited in Antonakou et al., 2014). However, recycling WEEEs is difficult due to many types of diverse materials within a product and separation of individual component plastics is challenging (De Marco et al. 2008, as cited in Antonakou et al., 2014).

Our research did not definitively conclude whether or not recycled PC is used to make new PC. Use of recycled plastics may result in lesser quality plastics or be used in blends. For example, Takatori (2014) notes that there are differences in properties of plastics made from recycled plastic as opposed to those made from virgin plastic; and specifically notes that with the recycling of PC there is a difference in Izod impact strength. Others (Azo Materials, 2016b) report lesser resilience and impact resistance qualities in recycled PC compared to newly manufactured PC, but also state that “chemicals can be used to improve impact resistance in recycled PC and they could be used for most of the applications that virgin PC is used” (Azo Materials, 2016b). The recycled plastics are reported to “have good stiffness, impact resistance, toughness and are transparent. These profiles have a high colorability with a lovely gloss finish that can imitate metal and glass” (Azo Materials, 2016b).

In summary, research conducted for this project found that phthalates may be used in manufacturing of PC, specifically DBP and DnOP, and are likely to constitute greater than 0.1 percent if used as plasticizers in manufacturing. PC is recycled using mechanical methods; new PC material may be made from the recyclate, and if so, then phthalates present in the original PC could be present in the plastic made with the recyclate. If depolymerization methods were used to recycle PC, then the phthalates would not be expected to be present in the resulting new PC. However, data indicating how much, or how often, recycled PC is used to make new PC, or if the resulting PC is used to make toys or child care articles was not found. It could not be definitively determined from the research whether recycled PC materials are routinely used to make new PC.

1.45 Potential Phthalate Contamination/Migration

The monomer, BPA, is known to migrate from containers (Guart et al., 2011). However, no studies have been identified that indicate that any of the specified phthalates have migrated or

leached out of PC, which would indicate indirectly the presence of phthalates. Migration studies were identified for PC water bottles, but not for toys or child care articles. Autoclaved (121 °C for 2 hours) PC water bottles leached approximately 1 to 4 ppb of BPA and other organic compounds. The author also analyzed for DEHP but this phthalate was not detected.

Guart et al. (2011) tested PC plastics using three kinds of migration tests: (1) standard method UNE-EN ISO 177; (2) ultrasonic forced extraction; and (3) standard method UNE-EN 13130-1. Specified phthalates for this project such as DBP, BBP, and DEHP were not present in the PC bottles analyzed. Amiridou and Voutsas (2011) tested water in commercially available PC bottles purchased from local markets for selected phthalates including DBP, BBP, DEHP, and DNOP. The authors reported that the examined compounds were detected at low levels (unstated) in bottled water purchased from a local market.

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11. Polystyrene [Crystal and General-Purpose (GPS)], Medium-Impact Polystyrene (MIPS), Super-High-Impact Polystyrene (SHIPS) Grades] and Styrene-Butadiene Copolymers CASRNs: 9003-53-6; 9003-55-8

General-purpose Polystyrene (GPS; the abbreviation, GPPS, is also used in the literature; also known as crystal polystyrene or atactic polystyrene (PS) (Lobo and Bonilla, 2003) is a high-molecular weight, transparent, amorphous thermoplastic, which exhibits high stiffness, good dimensional stability, and electrical insulation properties. GPS is polystyrene that is not impact-modified.

The Medium-Impact Polystyrene (MIPS), just like the High-Impact Polystyrene (HIPS), is a butadiene-modified polystyrene (Lobo and Bonilla, 2003). The styrene-butadiene copolymers that are the focus of this report are MIPS and SHIPS. HIPS is not addressed in this report but was the subject of an earlier report (TERA, 2015). Compared to HIPS, MIPS is modified usually by copolymerization to a lesser degree than HIPS (Soroka, 2008).

The Super High Impact Polystyrene (SHIPS) is also a rubber-modified polystyrene, which is made from blends of polystyrene (GPS) with butadiene-styrene block copolymers (*e.g.*, HIPS) (Durst et al., 1976; Sperling, 1981) with superior gloss characteristics, and superior corner and surface impact strength in finished component parts (Canadian Plastics, 2015). The polymer is reported to have stable impact strength over a wide range of conditions (not specified). In this report, GPS and polystyrene (PS) are used interchangeably. MIPS and HIPS and, to a lesser extent, SHIPS are treated as being similar to each other although the extent of the butadiene modifications differs.

1.47 Raw Materials Used in Production of GPS, MIPS, and SHIPS

Several additives may be blended with GPS, MIPS, or SHIPS. Kirk-Othmer (2014) reported that plasticizers are used in the manufacture and/or processing of these types of styrene polymers. Among these plasticizers, are phthalate esters; however, the specific phthalate esters are not mentioned and it is not possible to determine if any of the specified phthalates for this project are the same phthalate esters used in GPS, MIPS, or SHIPS.

Additionally, Ziegler-Natta catalysts are used in the polymerization of polybutadiene, a potential starting material for the production of the rubber-modified, high-impact polystyrenes. These catalysts “are prepared starting from a pre-catalyst (proCAT) mixture, containing, besides magnesium- and titanium (IV) chloride, an internal donor, which is very often a phthalate such as dibutyl phthalate (DBP), diisobutyl phthalate (DIBP), or bis(2-ethylhexyl) phthalate (DEHP)” (Borealis, 2014). Based on this information, there is the potential of the high-impact polystyrene

plastics to contain one or more of the specified phthalates. No analyses were identified in the available resources that measured the phthalate levels in GPS, MIPS, or SHIPS. When used as a catalyst, it is unlikely that these phthalates will constitute more than 0.1 percent of the high-impact grades; it is unknown whether the specified phthalates are used as plasticizers, or if so, at what concentrations.

Most of the raw materials listed below are for the production of GPS (Kirk-Othmer, 2014; Nexant Chem Systems, 2006; Wunsch, 2000; Mishra and Yagci, 2008; Ibeh, 2011; Elias, 2003; EPA, 1991). For MIPS, it is assumed that the raw materials will be similar to those for GPS and are not listed separately. There is a paucity of information regarding the raw materials for SHIPS or its manufacturing process.

1.47.1 Raw Materials Used in Making GPS, MIPS, and SHIPS

The raw materials for the production of GPS and MIPS, (and likely) SHIPS are:

- *Monomers*: styrene; butadiene
- *Solvents*: water; ethylbenzene
- *Initiators/catalysts/reaction accelerators*: benzoyl peroxide; diacetyl peroxide; lauroyl peroxide; caproyl peroxide; t-butylhydroperoxide
- *Suspension agents*: methylcellulose; ethyl cellulose; polyacrylic acids
- *Chain transfer agents/molecular weight modifier/chain terminator*: α -methylstyrene dimer; terpinolene; dodecane-1-thiol; 1,1-dimethyldecane-1-thiol; benzene; toluene; ethylbenzene; isopropylbenzene; 1-hexanethiol
- *Polymerization regulator/inhibitors*: dimer of alpha-methylstyrene
- *Dispersing agent*: partially hydrolyzed polyvinyl acetate; inorganic phosphates; magnesium silicates
- *Plasticizers/lubricant*: mineral oil; butyl stearate; mineral oil; phthalate esters (unspecified); adipate esters
- *Polymerization inhibitors*: phenolic/quinone family (for example, 4-tert-butylcatechol); nitrophenol compounds; hydroxylamine derivatives; nitrogen oxides (for example, nitric oxide); carbon black ;and unspecified sulfur and certain sulfur compounds; picrylhydrazyl derivatives; soluble transition-metal salts
- *Stabilizers*:
 - *UV absorbers*: benzotriazoles (for example, Tinuvin P); benzophenones
 - *Antioxidants*: phenolic antioxidants (unspecified); alkylated phenols; phosphite esters thioesters (such as ionol tris-(nonylphenyl)phosphite); Irganox 1076
 - *Others*: calcium carbonate; calcium phosphates; bentonite clay
- *Costabilizer*: tridecyl phosphite

- *Flame retardants*: inorganic (hydrated aluminum oxide, antimony oxide); organic (alkyl and aryl phosphates)
- *Antistatic agents*: alkyl and/or aryl amines; amides; quaternary ammonium compounds; anionics
- *Mold-release agents*: stearic acid metal stearates; stearate esters; silicones;amide waxes
- *Ignition suppression agents*: halogenated compounds (unspecified); antimony oxide; aluminum oxide; phosphate esters

From the literature researched for this project, some of the specified phthalates such as DBP, DIBP and DEHP are used as components of Zeigler-Natta catalysts. However, their concentrations are not expected to exceed the limit of 0.1 percent in the polymers.

1.47.2 GPS

Styrene can be polymerized by all macromolecular chain-building mechanisms such as free-radical, ionic (anionic and cationic) and coordination (Ziegler) polymerization (Kirk-Othmer, 2014; Nexant Chem Systems, 2006; Wünsch, 2000).

GPS is commercially manufactured worldwide by the addition polymerization of styrene monomer units and can be produced by bulk (or mass), solution (a modified bulk), suspension, or emulsion polymerization processes (Kirk-Othmer, 2014; Ibeh, 2011; Elias, 2003; U.S. EPA, 1991). The suspension process is only used for specialty grades (Nexant Chemical Systems, 2006; U.S. EPA, 1991), while the use of the emulsion process in the production of styrene homopolymer has decreased significantly over the last several decades (U.S. EPA, 1991).

1.47.2.1 Mass (bulk) Polymerization step

The bulk process, also known as the mass process, is the most commonly used process for the production of GPS (Ibeh, 2011; Wünsch, 2000; U.S. EPA, 1991). The polymerization can be carried out using a batch or continuous process, but the production of GPS operates continuously and under (unspecified) thermal conditions (Wünsch, 2000). The batch bulk polymerization process involves pumping pure styrene monomer from storage into a tank regarded as prepolymerization reactor, where the monomer is mixed with small amounts of mineral oil (as a lubricant and plasticizer) and butyl stearate, the dimer of alpha-methylstyrene (as a polymerization regulator), and an antioxidant (not specified) (U.S. EPA, 1991; Kirk-Othmer, 2014). Once the polymerization is complete, the polymer melt (molten product) containing some unreacted styrene monomer, ethylbenzene (an impurity from the styrene feed), and low molecular weight polymers (dimers, trimers, and other oligomers), is pumped to a vacuum devolatilizer (U.S. EPA, 1991). The molten polystyrene is extruded, cooled, and stored (U.S. EPA, 1991).

For the continuous process, the styrene monomer, mineral oil, and small amounts of recycled polystyrene, antioxidants, and other additives are added from storage into a feed dissolver mixer. The blended feed is pumped continuously to a reactor system where it is thermally polymerized to polystyrene (U.S. EPA, 1991). Some polymerization occurs in the initial reactor (the prepolymerizer), but successively higher levels of polymerization occur in subsequent reactors in the series. The molten polystyrene is cooled and the solidified strands are pelletized and stored (U.S. EPA, 1991).

1.47.2.2 Solution (or Modified Bulk) Polymerization

In the solution (or modified bulk) polymerization, the reaction takes place as the styrene monomer is dissolved in a small amount of solvent, such as ethylbenzene (U.S. EPA, 1991). All other steps are similar to that of the mass (bulk) polymerization.

1.47.2.3 Suspension Polymerization

This type of polymerization is reported to be declining in importance (Kirk-Othmer, 2014). Most manufacturers use the batch process for the suspension polymerization of GPS. The suspension polymerization is carried out in large reactors. The process involves suspending a number of small styrene drops in water by use of a dispersing agent and in the presence of a suspending agent as well as a stabilizing agent. The suspended droplets are polymerized with the use of initiator/catalyst (see Section 10.1.1). After polymerization, the water, styrene, and the other impurities are discharged, the polystyrene dried, and then converted into pellets.

1.47.2.4 Emulsion Polymerization

This polymerization is not a generally commercially accepted method of manufacturing GPS, but it is generally used for the polymerization of styrene with other monomers or polymers or specialty grades. Emulsion polymerization is carried out similarly to suspension polymerization except that the monomer droplets are microscopic in size.

1.47.3 Medium-Impact Polystyrene (MIPS)

Impact-modified polystyrenes such as MIPS are produced by grafting styrene monomers free-radically on rubber (that is, polybutadiene) and this involves the use of Ziegler-Natta catalyst (Kirk-Othmer, 2014). The manufacturing process for MIPS is not expected to be different from that described for HIPS (see Chapter 5 of TERA, 2015). What distinguishes MIPS from HIPS was not clearly explained in the reviewed literature.

1.47.4 Super High Impact Polystyrene (SHIPS)

Very little information was available in the literature reviewed for this project regarding the manufacturing process of SHIPS.

1.47.5 Processing

The following processes are used to formulate the final styrene homopolymer and rubber-modified styrene plastics (Kirk-Othmer, 2014):

- Injection molding;
- Extrusion (one of the most convenient and least expensive fabrication methods);
- Blow molding; or
- Thermoforming.

Several additives (or processing aids) are reportedly used for polystyrene homopolymer and rubber-modified polystyrene (*e.g.*, MIPS, HIPS, or SHIPS) (Kirk-Othmer, 2014). However, it is sometimes unclear at what point these additives are added during the manufacturing processes or processing of these polymers. The additives include chain transfer agents, stabilization agents, flame retardants, antistatic agents (antistats), polymerization inhibitors, mold-release agents, and ignition suppression agents. A list of these additives is provided under Section 10.1.1. The following plasticizers are reportedly used as additives during processing of these polymers:

- mineral oil;
- phthalate esters (unspecified); or
- adipate esters.

Although phthalate esters may be used as additives, how and when particular phthalates are used (and at what concentration) is not reported in the literature consulted, precluding determination of the phthalate concentrations in the final products. Regarding use of phthalates in catalysts used in the manufacturing process for, for GPS, MIPS, or SHIP polymers, it is unlikely that the concentration of the phthalate would exceed the 0.1 percent limit for the specified phthalates due to low concentrations generally used with catalysts.

1.48 Applications for GPS, MIPS, and SHIPS in Consumer Products

1.48.1 Toys and Child Care Articles

Polystyrene toys (GPS, MIPS or PS copolymer) make up to 3 to 5 percent of all toys; however, the specific types of PS used are not generally stated (Netherlands Food and Drug Administration, 2005; Rosato, 2011). Snedeker (2014) specifies that PS is used in “hard” toys. A search of

styrene in Amazon.com's online store under the toys and game category returns a list of thousands of toys. In the screening of this list for "hard" plastic toys, building blocks made from HIPS are identified. Other hard plastics found with polystyrene include action figures, lunch boxes, and riding pony toy. HIPS (and by extension, MIPS) resins are used in toys (Sastri, 2014), in applications such as disposable cups for vending and soda fountain cups, and kitchenware including plastic cutlery, imitation crystal "glassware," lids, plates, and bowls (Siddique, 2008).

Other consumer products are discussed in Appendix D.

1.49 Potential Use of Recycled Materials Containing Phthalate in Production of GPS, MIPS, and SHIPS

To determine if phthalates could be introduced into GPS, MIPS, and SHIPS through the use of recycled materials to make new GPS, MIPS, and SHIPS, TERA considered whether phthalates are present in virgin plastic that may be recycled, and if so, if and how these plastics were being recycled.

While TERA did not find any information on concentrations of phthalates in these plastics or in plastics made from recycled polymers, as discussed above in Section 10.3, we found that plasticizers such as phthalate esters are reportedly used in the manufacture and/or processing of GPS, MIPS, and SHIPS, but specific phthalates were not identified. In addition, Ziegler-Natta catalysts are used in manufacturing of these polymers, which implies that DBP, DIBP, and DEHP could be present in the processed plastics (Borealis, 2014), but are likely to be at very low concentrations (less than 0.1 percent). We did not find any evidence that there would be phthalates in any of the raw materials (except for the use of phthalates as additives for their plasticizer properties). Because phthalates may be an additive in manufacture of GPS, there is a possibility that if the PS containing the phthalates were recycled to make new GPS, then the phthalates could also be introduced into the new GPS. Therefore, we explored whether GPS is recycled to make new GPS; however, we were not able to find data to indicate how much or how often recycled GPS is used to make new GPS, MIPS, or SHIPS. The reader is referred to TERA (2015) regarding recycling of HIPS. It is assumed that, because these materials are closely related, they would be similarly recycled, although we do not have that information.

GPS is recyclable and is being recycled in the United States. Recycled GPS products include: clothes pegs, coat hangers, office accessories, spools, rulers, and video/CD boxes (Siddique, 2008).

EPA reported that 1.5 percent of GPS (*i.e.*, PS) in the United States was recycled in 2007 (U.S. EPA, 2008); and the Association of Post-consumer Plastic Recyclers (APR) provides design

recommendations for plastic packaging in order to maximize post-consumer recyclability of products (APR, 2015).

GPS can be mechanically recycled by regrinding into PS materials and making new PS (Azo Materials, 2013). World Wide Web searching revealed suppliers offering recycled or reprocessed PS for sale and also some postings looking for reprocessed or regrind PS for various uses, including sheet extrusion, injection molding, and thermoforming applications (Plastemart, 2014) and finished products by small local end users (RecPlas Ltd., 2016). Buyers and sellers were noted for MIPS and GPPS (GPS) injection regrind or scrap or pellets of reprocessed PS (*e.g.*, Phoenix Recycling, 2016; RecPlas Limited, 2016; Plastics Markets, 2016). Toys are mentioned as a common use for GPPS (GPS) and HIPS by one plastic processor and exporter (RecPlas Ltd., 2016).

Research on chemical recycling was also found in the primary literature. Achilias et al. (2007) tested catalytic and non-catalytic pyrolysis of PS waste in a fixed bed reactor using either model polymer or commercial waste products as the feedstock and found that the virgin PS could be re-polymerized from the pyrolysis oil fraction to make virgin PS. However, whether the repolymerized PS can be used commercially was not clear.

In summary, our research found that phthalates may be used in manufacturing or processing of PS, but the specific phthalates and concentrations were not reported. We also determined that PS is recycled by various means, including mechanical processes. If new PS material is made from the recycle, then phthalates present in the original PS could (likely) be present in the plastic made with the recycle. Efforts are being made to use PS previously used for food contact appliances (refrigerators) to make plastic toys (Lauzon, 2013) in an effort to minimize unwanted toxic materials. Efforts to reduce recycled PS products containing phthalates have resulted in new regulations on standards for recycling and recovery, for example, ISO 15270 ('Plastics – Guideline for the Recovery and Recycling of Plastics Waste') or EN 15342 series characterizing specific types of plastic recyclates (polystyrene) (Sartorius and Krähling, 2012).

1.50 Potential Phthalate Contamination/Migration

Although plasticizers such as phthalates are reportedly used in the manufacture and/or processing of GPS, MIPS, SHIPS, the specific phthalates were not identified. In the manufacturing of these polymers, Ziegler-Natta catalysts are used, implying that DBP, DIBP, and DEHP as components of this catalyst could end up in the processed plastics (Borealis, 2014). However, the concentrations are not likely to exceed the 0.1 percent limit (Borealis, 2014). No migration studies were identified in the literature reviewed for this project that evaluated the potential of GPS, MIPS, SHIPS plastics to leach out the specified phthalates from consumer products (such

as plastic toys and/or child care articles), that would indicate indirectly the presence of phthalates.

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12. Silicone Rubber (SR) CASRN: 63394-02-5

Silicon-based polymers, also known as polysiloxanes, polyorganosiloxanes or simply, silicones, are synthetic polymers made by the polymerization of monomers called silanes (Strong, 2006). Silicone rubber (SR) is an elastomer (rubber-like material) that has a three-dimensional (3D) network structure consisting of cross-linked polydiorganosiloxane chains (Kirk-Othmer, 2014). The silicone rubbers have excellent thermal and electrical properties, are physiologically inert and have low compressibility (Brydson, 1999).

1.52 Raw Materials Used in Production of Silicone Rubber

Several additives may be blended with silicone rubber (Kirk-Othmer, 2014). Silicone rubber is reported to require few additives, but “particularly notable is the fact that silicone rubber is free of curing accelerators or retarders, organic plasticizers and organic antioxidants” (Wacker Chemie AG, 2015).

1.52.1 Raw Materials Used in Making Silicone Rubber

The raw materials used in making silicone rubber (Wacker Chemie AG, 2015; Kirk-Othmer, 2014; Ellis and Smith, 2008) include:

- *Monomers*: silanes: dichlorodimethylsilane; hexamethylcyclotrisiloxane (D3); octamethylcyclotetrasiloxane (D4)
- *Solvents*: water
- *Emulsifiers*: dodecylbenzene sulfonic acid; unspecified anionic, cationic, or nonionic surfactants
- *Initiators/catalysts/crosslinkers*: hydrochloric acid; hydrobromic acid; sulfuric acid; perchloric acid; trifluoromethanesulfonic (or triflic) acid; HSnCl_5 (product of reaction between titanium tetrachloride and water); phosphonitrilic chlorides; oxygen-containing chlorophosphazenes; potassium hydroxide; sodium hydroxide; tetramethylammonium hydroxide; amines; amine salts of carboxylic acids; ion exchange resins; clays activated with mineral acids; potassium silanolate, tetraalkylammonium and tetraalkylphosphonium hydroxides; silanolates; phosphagene bases acid-treated graphite; acid-treated clays; titanium tetrachloride; dibenzoyl; bis-*p*-chlorobenzoyl; bis-2,4-dichlorobenzoyl peroxides; dicumyl peroxide; di-*tert*-butyl peroxide, 2,5-dimethyl-2,5-di-*tert*-butylperoxyhexane; diaroyl peroxides; platinum complexes; platinum-divinyltetramethyldisiloxane complex; rhodium (I) complexes; tin (II) and tin (IV) complexes (*e.g.*, organotin silanoate); chelated salts of titanium and tetraalkoxytitanates; dibutyltin dilaurate; ethylboron sesquitriflate; antimony chloride – acid chloride pairs; trimethylsilyl triflate; lithium silanolate; tetrahydrofuran;

hexamethylphosphoric triamide; dimethyl sulfoxide; cryptates; dodecylbenzene sulfonic acid; benzyldimethyldodecylammonium

- *Inhibitor complexes or complexing ligands*: phosphines; amines; acetylenic alcohols; acetylene dicarboxylates; dimethyl maleate; dimethylfumarate; cyclodextrin; thermoplastines (not specified); silicones (not specified)
- *Molecular weight modifier or chain termination agents or chain stoppers*: water; triorganosilyl chain-terminating groups
- *Fillers*: pyrogenic silica; precipitated silica; carbon black; magnesium oxide; quartz; calcium carbonate; clays; silicates; aluminates; fumed titanium; titanium oxides; alumina; zircona

1.53 Manufacturing Processes used Worldwide to Produce Silicone Rubber

Multiple processes are used worldwide to commercially produce silicone rubbers (Strong, 2006; Kirk-Othmer, 2014). This process includes: hydrolysis and/or methanolysis; polycondensation; ring-opening polymerization; anionic polymerization of cyclic siloxanes; cationic polymerization of cyclic siloxanes; emulsion polymerization; radiation-induced polymerization; and plasma polymerization. Silicone rubbers may be produced using the monomers, dichloromethylsilane, D3 or D4. The production of the rubber starts with the hydrolysis or methanolysis of the chlorosilane monomers into oligomers (linear and/or cyclic). The oligomers are then directly used in the manufacture of the silicone polymers via various processes as described below (Kirk-Othmer, 2014).

The hydrolysis of the chlorosilanes can be carried out in a batch or continuous process. A typical industrial production involves mixing dichloromethylsilane with aqueous hydrochloric acid in a continuous reactor (Kirk-Othmer, 2014). An alternative to the hydrolysis process is the methanolysis process. This process involves a one-step synthesis of organosiloxane oligomers and methyl chloride without formation of hydrochloric acid. Linear silanol-stopped oligomers are formed using the continuous methanolysis.

Polycondensation results in the further conversion of the linear fraction of hydrolysate to silicone fluids and high molecular weight gums. The catalysts employed in the polycondensation reaction are strong acids, strong bases, amines, amine salts of carboxylic acids, ion exchange resins, and clays activated with mineral acids (Kirk-Othmer, 2014).

An alternative to the polycondensation method of production of siloxane polymers is the ring-opening polymerization of cyclic oligoorganosiloxanes (Kirk-Othmer, 2014). A chainstopper (unspecified) is added to control the molecular weight of the polymer; the amount of chainstopper added can vary the molecular weight from very low to very high.

The cyclic siloxanes can also undergo anionic or cationic polymerization or be formed by polycondensation or ring-opening polymerization in aqueous emulsions (Kirk-Othmer, 2014).

1.53.1 Silicone Cross-linking or Network Formation

In the uncured state, silicone rubber contains polymers of different chain lengths (Wacker Chemie AG, 2015). Organic groups such as methyl, vinyl, phenyl or other groups may be bound to silicone in the siloxane backbone (the siliconoxygen chain). The silicone rubber may be solid or liquid (Wacker Chemie AG, 2015). The solid silicone rubber contains polymers with a high molecular weight and relatively long polymer chains. In contrast, the liquid silicone rubber contains polymers of lower molecular weight and shorter chains (Wacker Chemie AG, 2015). To convert the raw rubber (the long polydiorganosiloxane chains) into a mechanically stable cured product, a cross-linker such as peroxides or platinum or other catalysts is required (Wacker Chemie AG, 2015; Kirk-Othmer, 2014). Generally, three reaction types are used in forming silicone networks:

- Peroxide-induced free-radical processes,
- Hydrosilylation addition reactions, or
- Condensation reactions.

Peroxide-induced free-radical process (or peroxide curing) is one of the most common methods for the preparation of silicone networks (Kirk-Othmer, 2014). Peroxide catalysts/cross-linkers are commonly used (see list above in Section 11.1.1).

Hydrosilylation is another common process for the formation of silicone networks (Kirk-Othmer, 2014). This is a reaction between a silicone hydride group and an olefin (alkene) to form an alkynelic linkage. This typically involves the vinyl groups attached to silicon in the polymer chain. Catalysts, inhibitor complexes or complexing ligands, thermoplastines (not specified), or silicones (not specified) are often added (see Section 11.1.1).

Condensation reaction/cure involves condensation of silanol groups to form siloxanes. This is also reported to be a common industrial reaction (Kirk-Othmer, 2014). The catalysts used in this reaction include acids and bases and organic complexes of metals. The condensation reactions can be carried out in emulsions, where the cross-linker and polydimethylsiloxane are emulsified using anionic, cationic, or nonionic surfactants and catalyst (Kirk-Othmer, 2014).

Other types of curing systems have been reported, including high energy radiation cure and photoinitiated radiation cure. The high energy radiation cure involves vulcanizing silicones by high energy radiation such as gamma-irradiation, X-rays, and electron beams.

1.53.2 Processing

Several conventional methods are used to process silicone rubbers (Wacker Chemie AG, 2015; Kirk-Othmer, 2014). These include:

- Extrusion: used for tubing, profiles, cables, flat tape, and round cord;
- Coextrusion;
- Compression molding;
- Transfer molding;
- Injection molding;
- Knife coating;
- Calendering; or
- Low pressure filling.

1.53.2.1 Additives

In addition to crosslinkers and catalysts, fillers, additives, stabilizers, and colorants may be employed during processing of the silicone rubber (Wacker Chemie AG, 2015; Kirk-Othmer, 2014) (see Section 11.1.1).

Silicone rubber requires few additives and is free of curing accelerators or retarders, organic plasticizers and organic antioxidants (Wacker Chemie AG, 2015). However, additives such as stabilizers, (special oxides of transition metals [*e.g.*, iron, such as ferric oxides]), carbon black, and unspecified masticating aids, release agents, flame retardants, pigments and colorants may be added (Wacker Chemie AG, 2015).

Manufacture and processing of silicone rubber requires few additives (Wacker Chemie AG, 2015). No information was identified in the literature researched that indicates that the phthalates specified for this project are added during the manufacture or processing.

1.54 Applications for Silicone Rubber in Consumer Products

There are numerous uses for silicone rubber. The items identified in this report are not meant to be exhaustive but to give an indication for the many uses of this rubber. Applications in toys and child care articles are described below; other applications are discussed in Appendix D.

1.54.1 Toys and Child Care Articles

SR is used in numerous (over 350) child care articles such as baby bottle nipples, pacifiers, bottle valves, breast pumps, tether toys and drinking straws. SR was reported in more than 4,500 toys

including action figures, dolls, jewelry, and silly putty when a search on Amazon.com (Amazon.com, Inc., 2016) website included “silicone rubber” as a search term. A detailed list is shown below in Table 11.

Johnson et al. (2010), measured DEHP in baby teethers made from non-toxic food grade silicone rubber that was intended to be placed in mouth and that was manufactured in Taiwan. The concentration of DEHP found was 0.3 percent. DBP was also found in a soft and hard biter at a concentration of 0.2 percent.

Table 11. Types and Numbers of Toys and Child Care Articles containing Silicone Rubber in Material Description (Amazon.com, Inc., 2016)

Child Care Articles (number)	Toys (number)
Baby Bottle Nipples (9)	Shaped Rubber Wristbands (632)
Baby Teether Toys (25)	Jewelry (175)
Baby Grooming & Health Kits (2)	Bracelets (240)
Baby Pacifiers (5)	Baby Teether Toys (332)
Utensils (12)	Stickers (3)
Health & Baby Care (35)	Race Tracks (3)
Baby Bottles (46)	Building Sets (3)
Humidifier Absorption Sleeves (6)	Miniatures (24)
Bathing & Skin Care (6)	Buildings & Scenery (8)
Feeding (101)	Arts & Crafts (265)
Baby & Toddler Toys (65)	Hobbies (119)
Car Seats & Accessories (17)	Action Figures & Statues (131)
Gifts (4)	Dolls & Accessories (165)
Nursery (11)	Sports & Outdoor Play (119)
Potty Training (1)	Novelty & Gag Toys (812)
Safety (7)	Baby & Toddler Toys (513)
Strollers & Accessories (2)	Building Toys (7)
	Dress Up & Pretend Play (291)
	Kids' Electronics (46)
	Games (62)
	Grown-Up Toys (68)
	Kids' Furniture, Décor & Storage (33)
	Learning & Education (58)
	Party Supplies (336)
	Puppets (7)
	Puzzles (11)
	Stuffed Animals & Plush Toys (11)
	Toy Remote Control & Play Vehicles (34)
	Tricycles, Scooters & Wagons (73)

1.55 Potential Use of Recycled Materials Containing Phthalate in Production of Silicone Rubber

As described in Section 11.2.2.1 above no evidence was identified that phthalates are used to produce silicone rubber, although reports of phthalates in silicone rubber products were found Johnson et al. (2010).

Recycling of silicone rubber is not part of local consumer recycling programs. A World Wide Web search found some companies offering to recycle silicone rubber. Depolymerization is used to recover silicone monomers such as D3 and D4 and produce recycled silicone rubber oil or grease, which is used as a lubricant for industrial machinery (Harmony Industries, Inc., 2011; ECO USA, 2014). ; There was no evidence found in the literature researched that silicone rubber is recycled into new silicone rubber that is made into toys or child care products.

1.56 Potential Phthalate Contamination/Migration

Simoneau et al. (2012) reported that phthalates were found in silicone rubber at concentration levels from first migration test of 50-150 µg/kg (ppm) (0.000005 – 0.000015 percent) for DIBP and DBP and DEHP at levels of 25-50 µg/kg (ppm) (0.0000025 – 0.000005 percent). Aside from this report, no other studies were identified that evaluated potential migration of phthalates out of materials made of silicone rubber.

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13. Styrene-Acrylonitrile Copolymers (SAN) CASRN: 9003-54-7

Styrene-acrylonitrile (SAN) resin is a random linear amorphous copolymer plastic. The resin consists of the monomers, styrene and acrylonitrile. The chains of the polymer have alternating repeat units of styrene and acrylonitrile. The resin is rigid, hard, transparent, and dimensionally stable with load-bearing capabilities, has high heat distortion temperatures, possesses excellent gloss and chemical resistance, and adapts easily to conventional thermoplastic fabrication techniques (Kirk-Othmer, 2014; Ellis and Smith, 2008). A typical composition of SAN resin is 76 percent styrene and 24 percent acrylonitrile (Azo Materials, 2016c; Olabisi, 1979; Ku, 1988). Generally, SAN resin contains 70 to 80 percent styrene and 20 to 30 percent acrylonitrile (UL LLC, 2015), although patents exist for manufacturing SAN resin with a level of acrylonitrile of generally 40 to 50 percent by weight (Azimipour et al., 2001).

1.58 Raw Materials Used in Production of SAN

Several additives may be blended with SAN polymer. Normally, no plasticizers are used in the production or processing of SAN copolymer [NIIR Board of Consultants & Engineers (NIIR Board, 2005)]. The extensive literature research conducted for this project also did not identify any plasticizers, including phthalates, as additives in SAN manufacture or processing.

The raw materials used in making SAN include [Green Polymer Additives (GP), 2015; Kirk-Othmer, 2014; Ellis and Smith, 2008; Dow Corning, 2005; Olabisi, 1997; Indirect Food Additives, 2016):

- *Monomers*: styrene; acrylonitrile
- *Emulsifier*: sodium alkanesulfonate; dodecyl benzene sulfate; or polyorganosilizanes and polyethylene oxide grafted with maleic anhydride and vinyl acetate
- *Initiators/catalysts/reaction accelerators*: potassium persulfate; *tert*-butyl peroxyvalerate; potassium persulfate/*tert*-butyl peroxybenzoate (mixed initiator system); zinc chloride; di-*tert*-butyl peroxide; *t*-butyl cumyl peroxide; 2, 5-dimethyl-2, 5- di (*tert*-butylperoxy) hexane
- *Molecular weight modifier or chain termination agents*: 4-(benzyloxymethylene)cyclohexene; *tert*- decylmercaptan (TTDM); 4-isopropenyl-1-methylcyclohexane (dipentene)
- *Suspending agents/aids*: tricalcium phosphates; poly(vinyl alcohol)s and acrylic acid/alkyl acrylate copolymers; or a copolymer of acrylic acid and of 2-ethylhexyl acrylate
- *Other additives*:
 - *Lubricants*: fatty acid ester; wax ester; high-mono glycerol monostearate; glycerol ester, ethylene-bis-stearamide; fatty alcohol (GP, 2015);

- *Release agents*: fatty acid ester; wax ester; mixture based on polyglycol ester (GP, 2015)
- *Antistatic agent/aids*: mixture of anionic and non-ionic compounds; polyol partial ester; sodium alkyl sulfonates
- *Reinforcing agents*: such as fillers (unspecified) and fibers
- *UV stabilizers or absorber*: such as sterically hindered amines
- *Elastomers*: e.g., butadiene/styrene elastomer
- *Residual monomer scavengers*: monoamines (methylamine, ethylamine, isopropyl amine, butylamine, ethanolamine, diethylamine, dimethylamine, ethylenediamine, or diethanolamine); and dialkylamines (dimethyl amines and diethyl amines); ammonium-alkali metal sulfates; unsaturated fatty acids (linoleic acid, hypogeic acid, ricinoleic acid, teracrylic acid, linolenic acid, linseed oil, safflower oil. or a mixture of oleic acid, linoleic acid and linolenic acid) or their glycerides; their aldehydes (including retinaldehyde and citral); esters of olefinic alcohols and fatty acid (specifically vinyl stearate, citral or triallyl cyanurate); myrcene
- *Colorants/Dyes*: unspecified

1.59 Manufacturing Processes used Worldwide to Produce SAN

SAN copolymer is commercially manufactured worldwide by three processes: emulsion, suspension, and continuous mass (bulk) polymerization (Kirk-Othmer, 2014; Mark, 2007; Ellis and Smith, 2008). All three processes involve free-radical-initiated copolymerization. Of these processes, continuous mass polymerization is preferred or has become more popular for applications requiring high optical quality, better color, and/or low haze (Ellis and Smith, 2008; Olabisi, 1997), while the majority of production is by batch emulsion (U.S. EPA, 1993; 2012). U.S. EPA (1993) indicated that the majority of SAN for captive use (*i.e.*, to produce other resins, such as acrylonitrile-butadiene-styrene [ABS] resins) is produced using emulsion polymerization, while SAN for sale in the marketplace is most often produced by mass polymerization.

1.59.1 Continuous Mass (Bulk) Polymerization

There are two types of bulk polymerization: continuous and batch (Kirk-Othmer, 2014; U.S. EPA, 2012). This polymerization process is a self-contained system that does not require emulsifiers, suspending agents, salts, or water, but solvents (unspecified) are used to control the viscosity. In this polymerization process, the monomer mixture (acrylonitrile and styrene) is prepared and heated together with modifier-solvent (unspecified) and fed continuously into a pre-polymerizer reactor at a specified rate. U.S. EPA (1993) indicated that a catalyst (unspecified) is added. Ku (1988) and Ellis and Smith (2008) stated that initiators/catalysts are normally not used in thermal polymerization due to runaway heating, but a moderate

accelerator/catalyst such as zinc chloride may be used to improve the rate of copolymerization. The pure polymer melt is pumped through an extruder, cooled and pelletized, while the modifier-solvent and unreacted monomers are recycled to the feed tanks.

1.59.2 Emulsion Polymerization Process

Both batch (and semibatch) and continuous emulsion processes are used, with the batch process being more common (Mark, 2007; U.S. EPA, 1993). In both processes, water is utilized as a continuous phase and the reactants are suspended as microscopic particles. This is a low viscosity system that allows easy mixing and heat transfer for control purposes. Emulsion polymerization proceeds as follows:

- a. the monomers (acrylonitrile and styrene) are injected into a monomer makeup tank along with recovered acrylonitrile and chemical additives;
- b. the monomer mix is pumped into the polymerization reactor with initiator, emulsifier, deionized water, and chain-transfer agent or molecular weight modifier; and
- c. SAN copolymer melt (latex) is pumped to a steam stripper to recover unreacted monomers.

A second initiator or a mixed initiator system is used to effectively increase final conversion and to decrease residual monomer levels (Kirk-Othmer, 2014). Other agents (residual monomer scavengers as listed above) also may be used to reduce or scavenge residual acrylonitrile postreaction, after polymerization reaction has occurred (Kirk-Othmer, 2014).

The emulsion process for the continuous production of copolymer can also be modified (Kirk-Othmer, 2014) by using multiple tank reactors, surfactants, and temperature to increase the conversion of the monomer to the polymer. The polymer latex can be subjected to filtration, washing and drying to produce the solid SAN polymer.

1.59.3 Suspension Polymerization

Suspension polymerization may also be conducted in either batch or continuous mode (Kirk-Othmer, 2014; U.S. EPA, 1993).

In the batch process, the monomers, styrene and acrylonitrile, are fed into a pressure reactor and are mechanically dispersed in water containing catalysts/initiators, molecular weight control agents, suspending agents, and chain transfer agents (Azimipour et al., 2001). The pressure reactor is flushed repeatedly with nitrogen and water is added to remove heat and control particle size. Kirk-Othmer (2014) mentions use of a small amount of the copolymer, acrylic acid-2-

ethylhexyl acrylate, in addition to styrene and acrylonitrile monomers. The monomer droplets copolymerize to form insoluble beads of polymer. The polymer slurry is washed and dewatered, and “stripped” for recovery of unreacted monomers. Solid and liquid phases of the slurry are separated, and the solid phase is dried and ready for processing.

In another suspension process, styrene monomer is continuously added until monomer conversion reaches 75 to 85 percent, after which the excess acrylonitrile monomer is removed by stripping with an inert gas (Kirk-Othmer, 2014).

1.59.4 Processing

Several conventional methods are used to process the SAN resin (Kirk-Othmer, 2014; Mark, 2007). These include:

- Injection molding,
- Extrusion,
- Blow molding,
- Thermoforming, or
- Casting.

SAN is reported to be mainly processed by injection molding (Plastics Europe, 2015). During processing, small amounts of additives or fillers may be used to achieve a specific set of properties or to enhance desirable performance characteristics (Kirk-Othmer, 2014; CCOHS, 2004; Olabisi, 1997). The additives (as listed above) may include release agents, UV stabilizers antistatic aids (Olabisi, 1997), elastomers (Indirect Food Additives, 2016), reinforcing agents (such as fillers and fibers), flow and processing aids [such as lubricants (GP, 2015; Dow Corning, 2005)], colorants/dyes, and antioxidants (unspecified).

None of the ten specified phthalates are used as additives in manufacturing or processing of SAN according to the literature consulted in this research.

1.60 Applications for SAN in Consumer Products

SAN has numerous uses due to its chemical and heat resistance. Applications for toys and child care articles are presented below. Applications for other consumer products are discussed in Appendix D.

1.60.1 Toys and Child Care Articles

SAN is reported to be used in custom molding for toys, however specific information for the types of toys were not reported (Kirk-Othmer, 2014). No other references were identified that support use of SAN in toys. For example, only three toy items were identified from an online shopping site that reports the use of SAN. These included an action figure, a drink tumbler, and a few high tech costume masks (Amazon.com, Inc. 2016). For babies, only two items were identified with SAN, both of these items were sippy cups. SAN was not identified in any toy or children's products from searching other consumer use databases (RAPEX, 2016; ECY, 2016a,b; HPD, 2015; SPIN, 2015) by chemical name or by CASRN.

SAN is used in numerous household products, including kitchenware and bathroom items (Biron, 2007; Kirk-Othmer, 2014). Kitchenware such as food mixers, mixing bowls and basins; drinking tumblers, tableware, cutlery; storage containers for foods and liquids (*e.g.*, jars and outer casings of thermally insulated jugs); coffee filters and small appliances. Bathroom items include electric toothbrushes and toothbrush handles; soap dispensers; sanitary ware.

No searches identified the presence of phthalates in toys or children's products made specifically with SAN.

1.61 Potential Use of Recycled Materials Containing Phthalate in Production of SAN

As described in Sections 12.1 and 12.2 above, no evidence was found in the research investigated for this project that recycled SAN is used in the SAN manufacturing process. Nor was there any evidence that phthalates are used to produce SAN. SAN is labeled with resin identification code (plastic recycling code) #7 ("Other") and considered difficult to recycle; although froth floatation can be used to separate it in a mixed waste stream of plastics (Azo Materials, 2016c). We did not locate companies that buy or sell SAN for recycling in a search of the World Wide Web. We found a few references to research into the feasibility of recycling SAN with other resins (*e.g.*, ABS, PLA, PVC, EPDM) (Garcia et al. 2007; Vugrinec et al., 2004) to make blends, but no evidence of SAN being used to make new SAN. Therefore, it is not likely that phthalates could be introduced into SAN through use of recycled material. Background information on plastic recycling is presented in Appendix E.

1.62 Potential Phthalate Contamination/Migration

Plasticizers are not typically used in the commercial manufacture or processing of SAN polymer (NIIR Board, 2005). No information was located in the literature searched for this project

regarding migration or leaching of the specified phthalates from materials or products made from SAN, which would indicate indirectly the presence of phthalates.

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14. Styrene-Butadiene-Styrene Rubber (SBS) and Styrene-Butadiene Rubber (SBR) CASRN: 308076-28-0; 61789-96-6

Styrene-butadiene-styrene rubber (SBS) is a type of styrene block copolymer (IHS, 2015), composed of at least three blocks (a triblock), namely two hard polystyrene end blocks and one soft, elastomeric (polybutadiene) midblock or center (IISRP, 2009; IHS, 2015; Shanks and Kong, 2012). Structurally, SBS is made of a short chain of polystyrene, followed by a long chain of polybutadiene, followed by another short chain of polystyrene (Patankar, 2010). It is a thermoplastic elastomer with rubberlike properties and is soft and flexible with excellent tack and adhesive properties. SBS has excellent surface coefficient of friction, little permanent deformation, great tensile strength, excellent low-temperature behavior, great workability, and good electric properties (Rubber World Magazine, 2016).

Styrene-butadiene rubber (SBR) [also known as Buna-S or Government rubber-styrene (GR-S)] is a nonpolar, unsaturated hydrocarbon polymer that is produced by randomly copolymerizing styrene and butadiene (Oswald, 2010; Brydson, 1999). SBR is a mixture usually containing approximately 75 percent butadiene and 25 percent styrene (Encyclopedia Britannica, 2016). SBR is available both as a synthetic liquid or solid rubber (Burdock, 1996). Chemically, SBS triblocks are reportedly similar to SBR (Brydson, 1999).

1.64 Raw Materials Used in Production of SBS and SBR

SBS and SBR, as styrenic block copolymers, are not used as pure substances. Instead, they are mixed with additives, fillers, oils, and other polymers until the desired characteristics for the use are achieved.

Several additives may be blended with SBS or SBR. Drobny (2007) reported that many types of plasticizers are used in the manufacture and/or processing of SBS block copolymer and SBR polymer. Among these plasticizers, phthalate esters are reportedly used in thermoplastic elastomers such as SBS and SBR. However, which phthalate esters are not stated in the literature and it is not possible to determine if they could be amongst those specified for this project.

1.64.1 Raw Materials Used in Making SBS and SBR

The raw materials used in making SBS and/or SBR (Shanks and Kong, 2012; IISRP, 2009; Drobny, 2007; Burdock, 1996) include:

- *Monomers:* styrene, butadiene
- *Solvents:* water; cyclohexane; toluene; n-hexane; divinylbenzene

- *Emulsifiers*: rosin acid; fatty acid; mixed rosin acid/fatty acid emulsifier system or soaps of these acids
- *Initiators/catalysts/reaction accelerators*: chelated iron and cumene hydroperoxide using sodium formaldehyde sulfoxide as reducing agent; free radicals from potassium persulfate (peroxydisulfate) and dodecyl mercaptan; organolithium compounds (*n*- or *sec*-butyl lithium)
- *Molecular weight modifier/chain termination/shortstop agents*: dodecyl mercaptan; sodium dimethyldithiocarbamate; diethyl hydroxylamine; alcohol
- *Coagulating aids/agents*: sulfuric acid; sulfuric acid/sodium; chloride; glue/sulfuric acid; aluminum sulfate or amine
- *Coupling agents*: silicon tetrachloride; dibromoethane
- *Curing agents*: sulfur (accelerators); peroxides (unspecified) and phenolic resins (unspecified); zinc oxide; zinc stearate; N-t-butylbenzothiazole-2-sulphenamide
- *Stabilizer*: UV absorbers: 2-hydroxybenzophenones; 2-hydroxyphenylbenzotriazoles; organic nickel compounds; sterically-hindered amines (hindered amine light stabilizers); carbon blacks and certain pigments (*e.g.*, titanium dioxide, zinc oxide); quenchers; organic nickel complexes; 2,2'-thiobis(4-octylphenolato)-n-butylamine nickel (II); nickel salts of thiocarbamate; nickel complexes with alkylated phenol phosphonates
- *Plasticizers*: oils (unspecified); phthalate esters; phosphoric esters; adipic, azealic, sebacic esters; citric esters; trimellitic ester; halogenated hydrocarbons; hydrocarbons (aliphatic, naphthenic, and aromatic); benzoic esters; fatty acid esters (oleates, stearates, ricinoleates); pentaerithrol; fatty esters (epoxidized); polyesters (polymeric plasticizers); polymers; polycondensates
- *Nucleating agents*: talc; silica; clay; sodium benzoate; ethylene/acrylic ester copolymers
- *Colorants (dyes and pigments)*: oxides, sulfides, hydroxides, chromates, and other complexes based on metals such as cadmium, zinc, titanium, lead, and molybdenum); white pigments [such as titanium oxide (rutile)], zinc oxide, zinc sulfide, and lead carbonate (lead white); black pigments (pure carbon, iron oxide); yellow pigments (chrome yellow, nickel-chrome-titanium yellow, iron oxides, lead chromates); orange pigments (molybdate orange and cadmium orange); brown pigments (iron oxide or combination of chrom/iron oxides); red pigments (iron oxide, cadmium sulfide/selenide); blue pigments (ultramarine, aluminosilicate with sodium ion and ionic sulfur groups); mixed metal oxides (based primarily on cobalt aluminate); green pigment (chrome oxide, cobalt-based mixed oxides); organic pigments (azo pigments such as monoazo and polyazo pigments); nonazo pigments (phtalocyanine blues and greens complexed with copper); quinacridones (red, violet, orange); dioxazines (violet); isoindolines (yellow, orange, red); perylenes; flavanthrones; anthroquinone
- *Antioxidants*: phenolics (*e.g.*, butylated hydroxytoluene or 2,6-di-t-butyl-4-methylphenol); phosphites and thioesters
- *Flame retardants*: alumina trihydrate; magnesium hydroxide; antimony trioxide; phosphorus; zinc borate; halogens (chlorine or bromine)

- *Antistatic agents (antistats)*: quaternary ammonium; phosphonium; sulfonium salts; sodium salts of sulfonates, phosphates and carboxylic acids; glycerol esters of fatty acids; ethoxylated tertiary amines
- *Slip agents*: erucamide; oleamide
- *Antiblocking agents*: natural and manufacturing waxes; metallic salts of fatty acids; silica compounds; polymers (such as polyvinyl alcohol, polyamides, polyethylene, polysiloxanes, and fluoroplastics)
- *Processing aids*: lubricants (metal soaps, hydrocarbon waxes, polyethylenes, amide waxes, fatty acids, fatty alcohols, and esters); copolymers of vinylidene fluoride and hexafluoropropylene
- *Fillers and Reinforcements*: natural calcium carbonate; precipitated calcium carbonate; barium sulfate (barite); glass and ceramic beads; synthetic silica; carbon black
- *Platy fillers*: talc (magnesium silicate hydrate); mica (muscovite and phlogopite); kaolin; clay
- *Fibrous fillers*: glass fibers (chopped strand); carbon fibers and aramid fibers
- *Nanofillers*: nanoclays (montmorillonite, smectite)

1.65 Manufacturing Processes used Worldwide to Produce SBS and SBR

1.65.1 SBS

SBS can be synthesized either in one, two, or three reaction steps (Shanks and Kong, 2012; Drobny, 2007). SBS triblock copolymer is commercially prepared worldwide using anionic polymerization (Shanks and Kong, 2012; Polimeri Europa, 2015; IISRP, 2015; Drobny, 2007) with inert hydrocarbon solvents such as cyclohexane or toluene. In this process, oxygen, water, or any other impurity must be completely eliminated to prevent undesirable reaction of the highly reactive propagating species (Drobny, 2007). The most preferred and also most frequently used initiators are organolithium compounds. Drobny (2007) listed essentially three synthetic methods for manufacturing SBS:

1. Sequential;
2. Coupling; and
3. Multifunctional initiation.

The sequential method involves a polymerization that starts at one end and continues to add to the molecule; the three blocks (styrene, butadiene, and styrene) are formed sequentially.

In the coupling method, reactive polymerization chains are joined together by a coupling or linking agent; diblock precursors are linked by a coupling agent to form the final triblock copolymer. *Sec*-butyllithium is the preferred initiator (although *n*-butyllithium is also used) for

the sequential and coupling polymerization methods (Drobny, 2007). In the initiation reaction, the initiator first reacts with one molecule of styrene, and then attaches to it; further polymerization occurs until the reaction is terminated by addition of a protonating species. A higher functionality coupling agent such as silicon tetrachloride (or dibromoethane) is used to produce branched or star-shaped molecules. The addition of divinylbenzene at the end of the reaction results in products that are highly branched (Drobny, 2007).

In the multifunctional initiation, polymerization starts at the center of the molecule and continues to the ends, using initiators, which have more than one active group. A multifunctional initiator is first reacted with butadiene; the next steps are similar to the corresponding steps in the sequential polymerization (Drobny, 2007) described above. Drobny (2007) indicated that the multifunctional initiation is used less frequently than the sequential and coupling polymerization processes.

1.65.2 SBR

SBR is commercially manufactured worldwide by the copolymerization of butadiene with styrene in the approximate proportion of 3:1 by weight (25 percent styrene to 75 percent butadiene (Ellis and Smith, 2008), using two polymerizations processes: solution (S-SBR) or emulsion (E-SBR). Production of emulsion and solution SBR can be carried out by either batch or continuous process configuration (IISRP, 2012). E-SBR is the more widely used manufacturing process.

1.65.2.1 Emulsion Polymerization

E-SBR is produced by emulsion polymerization and is initiated by free radicals. The materials required for E-SBR polymerization include monomers (styrene and butadiene), water, emulsifying agents, initiator system (depends on whether cold or hot polymerization is used) chain transfer agent/modifier or molecular weight controllers, shortstop (addition of an agent to the mixture to stop the reaction), and a stabilizer system (if required) (IISRP, 2009; Burdock, 1996). Extender oils and carbon black master batch may be added as dispersions to the stripped latex. The oils act as plasticizers during processing. The latex is coagulated, washed, dewatered, dried, baled, and packaged (IISRP, 2009).

1.65.2.2 Solution Polymerization

Solution-SBR (S-SBR) is produced by both continuous and batch polymerization processes depending on desired product and application (Polimeri Europa, 2015). S-SBR is a termination-free, anionic “living” polymerization process, initiated by alkyl lithium compounds (IISRP, 2015). Water is excluded and all components are dissolved in hydrocarbon solvents such as

hexane or cyclohexane in the process. The styrene content of the commercial products varies typically from 10 to 40 percent (IISRP, 2015).

1.65.3 Processing

SBS is seldom used in the pure form to fabricate finished products, but is compounded in most cases (Drobny, 2007). The SBS rubber is commonly used with a series of additives and other polymers to formulate the final product to meet required characteristics. As thermoplastic elastomers, SBS can be processed using the following standard techniques (Shanks and Kong, 2012; Ellis and Smith, 2009; Drobny, 2007):

- Extrusion,
- Injection molding,
- Compression molding,
- Transfer molding,
- Blow molding,
- Rational molding and rotolining,
- Thermoforming, or
- Calendaring.

Injection molding is the most commonly used processing technique for producing parts from thermoplastic elastomers (Shanks and Kong, 2012).

SBR can be cured with a variety of cure systems including sulfur, peroxides and phenolic resins (IISRP, 2009). The polymer can be cured in a variety of ways by compression, injection molding, hot air or steam autoclaves, hot air ovens, microwave ovens and combinations of these techniques. However, SBS block copolymer does not require vulcanization.

Additives are added during or after polymerization to prevent polymer degradation, during monomer recovery, drying and compounding, and also storage (Shanks and Kong, 2012). For example, in the formulation of adhesives and sealants, SBS block copolymer can be compounded with halogenated rosin esters, naphthenic oils, or aromatic esters (Drobny, 2007).

Several additives are reportedly used in thermoplastic elastomers (Shanks and Kong, 2012; Drobny, 2007). These include antioxidants, light stabilizers (UV absorbers and quenchers), nucleating agents, colorants (dyes and pigments), flame retardants, antistatic agents (antistats), slip agents, antiblocking agents, processing aids, fillers and reinforcements, platy fillers, fibrous fillers, and nanofillers. These additives are listed in Section 13.1.1. Specific information is not readily available on which of these additives are used; however, it is conservatively assumed that

the additives are also used in the manufacture and processing of SBS block copolymer and SBR polymer. The following plasticizers are also used as additives during processing of SBS and SBR copolymers:

- Phthalate esters (unspecified)
- Phosphoric esters
- Adipic, azelaic, and sebacic esters
- Citric esters
- Trimellitic ester
- Halogenated hydrocarbons
- Hydrocarbons (aliphatic, naphthenic, and aromatic)
- Benzoic esters
- Fatty acid esters (oleates, stearates, ricinolieates), pentaerithrol
- Fatty esters, epoxidized
- Polyesters (polymeric plasticizers)
- Polymers, polycondensates

While phthalate esters may be used as plasticizers during the processing of these polymers, there is no information regarding which phthalates are used and at what concentration they are added during processing. Thus, we are unable to determine that the specified phthalates are not used in the manufacture of SBS and SBR.

1.66 Applications for SBS and SBR in Consumer Products

1.66.1 Toys and Child Care Articles

SBR is reported to be used in toys; however no additional information on the type of toy is provided by these authors (Kirk-Othmer, 2014). The Netherland Food and Drug Administration (2005) identified toys containing SBR including a pink doll, a rattle, a teething ring with noise and a teething key with noise; one of the toys (unspecified toy) contained DBP (unspecified concentration) when analyzed by GC-MS (gas chromatography-mass spectrometry). One of the main problems with identification of toys made out of SBR or SBS is the lack of speciation by analytical techniques for chemical components.

Other household consumer databases searches for SBS or SBR yielded no results (SPIN, 2015; RAPEX, 2016; ECY, 2016a,b). All of these databases list most of the products made from plastics; however, when the chemicals of interest are identified in plastic, the specific type of plastic is not stated.

A discussion of other consumer applications and uses of SBS and SBR is included in Appendix D.

1.67 Potential Use of Recycled Materials Containing Phthalate in Production of SBS and SBR

As described in Section 13.1 above, Drobny (2007) reported that many types of plasticizers are used in the manufacture and/or processing of SBS block copolymer and SBR polymer including phthalate esters, but the specific phthalate esters are not identified.

TERA's research did not find information on recycled SBR or SBS routinely being used to make new SBR or SBS. Appendix E presents an overview of plastics recycling.

Reports of waste rubber powder incorporated into (SBS) block copolymer show improved tear strength and tension set as compared to no waste rubber powder SBS block copolymer (Drobny, 2007).

Recycled SBR tires are recycled into granulated tire crumb which is used as mulch in landscaping, in athletic field surfaces, and playground applications, and used to make flooring (Busch, 2010; Infinity Performance, 2016).

1.68 Potential Phthalate Contamination/Migration

Although phthalate esters are reportedly used in the manufacture or processing of SBS rubber or SBR rubber (Drobny, 2007), the specific phthalates were not mentioned. The Netherland Food and Drug Administration (2005) reported migration of DBP from SBR, but neither the amount of migration nor the migration rate was reported. No additional migration studies were located in the literature resources researched, that would indicate indirectly the presence of phthalates.

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15. Summary

The tiered approach used to research the 5 factors for 11 plastics for the presence of the 10 specified phthalates is an effective and efficient way to identify relevant information (or data) sources.

In Tiers 1 and 2, secondary sources were used to narrow the field of possible information for further investigation of the primary literature in Tier 3. The tiered approach also assisted us in identifying what information was *not* available and what gaps existed to better focus further efforts on specific phthalate(s), specific plastic(s), or specific factor(s) in Tier 4. The “universe” of over 179,000 sources in Tier 1 for the 11 specified plastics formed the “universe” of information from which we pared relevant library sources (from over 150 to 15). Secondary sources from authoritative websites were pared (from 48 to 11) in Tier 2. Tier 3 involved a unique strategy using two approaches; 1) search of the primary literature in four online databases and 2) search of EndNote libraries from previous CPSC projects with information on phthalates. This dual approach yielded more than 7500 articles, which were then screened by scientists for relevance to the phthalates, factors, and plastics for this task (Appendix C). Gap searching (Tier 4) was conducted with closer scrutiny of the EndNote libraries for the specified materials and specified phthalates, as well as searches of Google, Google Scholar, and Amazon.com. We searched by a variety of search terms/strategies, numerous sources and yielded what we considered to be a nonbiased and representative sample of the “universe” of information on the specified phthalates in the 11 specified plastics for the five factors. The more than 179,000 sources found in Tier 1, the 48 websites and 106 library sources in Tiers 2 and 3, and the 2,100 articles in Tier 4 located using several different search approaches, terms, and strategies to identify the “universe” of information on the specified plastics, phthalates and factors relevant to this project support our contention that the research approach was nonbiased and representative of the world wide literature on this subject matter.

Our search techniques for this task and previous tasks have identified significant information on the phthalates, their uses, as well as a lot of information on the plastics, and information on manufacturing and additives used in the specified plastics. However, very little information on the phthalate content of the specified plastics has been found using our tiered search techniques (as described in Section 2 of this report). As TERA learned on a previous project (Task 11), the 10 specified phthalates are produced in large quantities, making them High Production Volume (HPV) chemicals. The phthalates, both as a class and individually, are widely researched. In addition, the 11 specified plastics are used for toys and child care articles as well as for household and medical products. Given the search strategy and its success at getting the other information, we can be confident that if there had been information on the phthalate content of the 11 plastics we would have found it. In fact, the consistent lack of information amongst the

many places we searched, both secondary authoritative web and library sources and primary literature sources made us highly confident that there was very little information on the specified phthalates in the 11 plastics.

While the volume of information available for the 11 plastics varied, as did the volume of information on the five factors for each plastic, and the volume of literature for the 10 phthalates, there was relatively little information as to the concentration for any of the phthalates in the 11 plastics. The largest information gaps were for the potential use of recycled materials containing the specified phthalates in the production of the 11 plastics as well as for the potential for phthalate contamination during packaging, storage, use or other factors.

1.70 PMMA/PAN

The raw materials for production of the acrylic resins, PMMA/PAN include phthalates. DBP (up to 5 percent) is a plasticizer in PMMA production and DnOP is reportedly used in the manufacture of PAN (concentration not specified). These phthalates could theoretically be present in the finished material at concentrations of greater than 0.1 percent, although no test data are reported in the literature searched for this project. PMMA/PAN is used in children's toys and child care articles as well as a wide variety of other products. The presence of phthalates in these products was not reported, with the exception of two products (both nail polish) with DBP at 4.7 and 8.9 percent. Rarely is the presence or concentration of phthalates reported. Acrylic plastics can be recycled. Theoretically, phthalates could be present in mechanically recycled and new acrylic resins made from recycle. There were no reports for phthalate contamination or migration from acrylic resins in the research consulted for this report.

1.71 EBR

Little information is available on the manufacturing methods and processing of EBR. Although heterogenous Ziegler-Natta catalysts used in the manufacturing of EBR have phthalates such as DEHP and DIBP as internal donors, their concentrations in the final resins are not likely to be greater than 0.1 percent. No toys or child care articles made of EBR could be located in the literature searched for this project, although EBR is reportedly used in household, medical, and other products. No applications of uses specific for EBR or recycled EBR were identified. Similarly, there were no migration or leaching studies performed with EBR.

1.72 EBC

There is a paucity of information on EBC. Specific information regarding raw materials, manufacturing, processing, recycling, and migration is lacking. By analogy to polyethylene (HDPE and LLDPE) because both ethylene and 1-butene are used for manufacture of PE plastic,

Ziegler-Natta catalysts may be used. In preparing these catalysts, DIBP or DEHP serve as internal donors and could theoretically survive the polymerization process. Also by analogy, DIBP, DBP, and DOP (isomer not specified) could be additives in the manufacturing of EBC. In both these cases, it is unlikely the concentration of the phthalates would be greater than 0.1 percent. The only use for EBC that could be located in the literature searched was for four-gallon size plastic bags.

1.73 EVA/EVOH

Based on the literature reviewed for this report, the phthalates specified for this project are unlikely to be used in the manufacturing or processing EVA or EVOH. Our research identified over 200 toys and child care articles (out of 25,000) on Amazon.com with EVA/EVOH as search terms; no information on phthalate content was provided. However, in the RAPEX database (spans 11 years and 4,320 products), two toy items made of EVA were reported; one contained DEHP. No additional information is available on that item, which was a jewelry decoration set. We concluded that recyclates of EVA/EVOH were unlikely to contain phthalates as phthalates are not used in their manufacture.

1.74 EPM/EPDM

The ethylene-propylene monomers, EPM and EPDM, are manufactured with Zeigler-Natta catalysts. Three of the specified phthalates (DEHP, DBP, DIBP) may be added as part of the catalyst in very low concentration. The concentration in EPM/EDPM would be unlikely to exceed the limit of 0.1 percent for phthalates. Only two of over 77,000 products located on Amazon.com for EPM or EPDM yielded less than 100 items that were toys or games. No other databases contained toys made of the plastic or data regarding phthalate content in the plastics. No information was located regarding recycled EPM/EPDM being made into children's toys or child care articles. No migration studies were identified that evaluated the potential of EPM or EPDM to leach out phthalates during use of products made of these plastics.

1.75 Surlyn®

While plasticizers may be used as a raw material in the manufacture of the ionomer, Surlyn®, the findings did not indicate that the specified phthalates for this project were among the plasticizers use. No toys or child care articles made of Surlyn® were identified nor were migration or contamination studies located. Surlyn® appears to be recycled but because there are no phthalates in processing Surlyn® there would be no phthalates in the recycled plastic.

1.76 Polycarbonate

Polycarbonate manufacture may use plasticizers. If used, the plasticizers could be DBP (greater than 20 weight percent) and DnOP (0.8 weight percent), concentrations greater than the limit of 0.1 percent. PC is widely used in consumer products including toys and child care articles; however, no data as to the content of the specified phthalates were identified. PC is recycled both mechanically and chemically (via depolymerization). If the former recycling method is used, phthalates could be present if present in the original PC. If the latter method is used, phthalates would not be expected to be present. Data indicating how much or how often recycled PC is used to make new PC, or what products the recycled material is used to make was not found. While studies of migration were limited, it is reasonable to suggest that the potential exists for phthalates to leach out of PC plastic.

1.77 GPS/MIPS/SHIPS

The raw materials for production of GPS and MIPS include additives, such as plasticizers that may be blended for the manufacture of these styrene polymers. Very little information is available in the literature reviewed for this project regarding SHIPS. By analogy to GPS and MIPS (and HIPS in TERA, 2015), it is assumed that the processes would be essentially the same. Among plasticizers used in manufacture of these polymers are phthalate esters (specific phthalate esters not mentioned). Additionally, Zeigler-Natta catalysts (use DEHP, DBP, DIBP) are used in the polymerization of polybutadiene. These phthalates could theoretically be present at concentrations of 0.0001 percent, although no test data are reported in the literature. How and when particular phthalates are used (and at what concentration) is not reported in the information consulted. It is unlikely that even when the specified phthalates are used during manufacture as catalysts for processing of GPS, MIPS, or SHIPS polymers, the concentration of the phthalate would exceed the 0.1 percent CPSIA limit.

Polystyrene copolymers may be used for hard plastic toys, although the literature searched for this report did not present data specific for GPS, MIPS, or SHIPS in toys or child care articles, nor was information available on the presence of phthalates in these products. These polymers are also used in a variety of household products and building materials. GPS is recycled; however, data indicating how much or how often recycled GPS is used to make new GPS, MIPS, or SHIPS could not be located. No data regarding migration of phthalates from GPS, MIPS, or SHIPS or contamination of these polymers by phthalate-containing materials were found in the sources searched for this report.

1.78 SR

Manufacture and processing of SR requires relatively few additives. No information was identified that indicated the specified phthalates were added during manufacture or processing. Amongst the numerous applications for silicone rubber are child care articles, such as bottle nipples and pacifiers, as well as toys. In one study, DEHP concentration in teethers was reported at 0.3 percent and DBP in biters was reportedly 0.2 percent. Recycling of SR is not part of local consumer recycling programs. No evidence was found in the literature searched for this project that SR is recycled into new silicone rubber that is made into toys or child care articles. One migration study reported that less than 0.0001 percent DEHP was found in SR from a migration test.

1.79 SAN

The raw materials for SAN production or processing do not include phthalates. Few toys or child care articles (sippy cups) were identified that were made of SAN; however, SAN applications include numerous household products (such as kitchenware and bathware items). Not surprisingly, no phthalates were identified in toys or child care articles made of SAN. SAN is considered difficult to recycle. No evidence was found in the research investigated for this project that recycled SAN is used to manufacture new SAN. No migration studies were found for SAN products.

1.80 SBR/SBS

Phthalate esters are plasticizer additives for processing of SBS and SBR. Information regarding which phthalates are used and at what concentration they may be added during processing was not reported in the literature. SBR may be used for toys and child care articles, including teethers. Lack of speciation of chemical analytical techniques challenges identification of specific phthalates in consumer products. One study reported DBP (at an unspecified concentration) in an unspecified toy. SBR may be recycled and used as landscaping mulch. This research did not find recycled SRS or SBR being used to make new SBS or SBR. One report noted migration of DBP from SBR but neither the amount of migration nor the migration rate was reported.

1.81 Summary of Findings

An overview of the plastics that may contain one of the 10 specified phthalates is presented in Table 12. The phthalates noted are used in the production of EBR, EBC, EPM/EPDM, and GPS/MIPS/SHIPS as Ziegler-Natta catalyst.

Despite the research limitations, some generalizations can be derived from the research conducted for this report on the 11 plastics and the potential for the presence of phthalates in the selected plastics. All of the plastics (except EBR and EBC where information is scanty) are used in toys; seven of those plastics are also used in child care articles. Most of the plastics are also used as household products.

Table 12. Overview of Plastics found in certain Products

Plastic	Toys	Child Care Articles	Household	Medical Care Products & Devices	Building Materials	Other Products
Acrylic resins:						
Polymethylmethacrylate (PMMA) and Polyacrylonitrile (PAN)	√	√	√	√	√	√
Butadiene-ethylene resins (EBR)			√	√		√
Ethylene-butene copolymers (EBC)			√			√
Ethylene copolymers:						
Ethylene vinyl acetate (EVA) and Ethylene vinyl alcohol (EVOH)	√		√	√	√	√
Ethylene-propylene monomer (EPM) and Ethylene-propylene-diene monomer (EPDM)	√			√	√	√
Ionomers (Surlyn [®])	√	√	√			√
Polycarbonate (PC)	√	√	√	√	√	√
Polystyrene (crystal and general-purpose [GPS]), medium-impact (MIPS), and super-high-impact (SHIPS) grades; Styrene-butadiene copolymers (SBC)	√	√	√	√		

Silicone rubber (SR)	√	√	√	√		√
Styrene-acrylonitrile copolymers (SAN)	√	√	√	√		√
Styrene-butadiene-styrene rubber (SBS), and styrene-butadiene rubber (SBR)	√	√			√	√

The paucity of information and data on the presence or concentration of the 11 specified plastics does not reflect the lack of searching for data. There simply is limited information available. As shown in Table 13, of the 10 specified phthalates, six phthalates were not reported in any of the plastics: BBP, DINP, DIDP, PENP, DHEXP, DCHP. However, eight of the plastics (PMMA/PAN, EBR, EBC, EVA/EVOH, EPM/EPDM, PC, GPS/MIPS/SHIPS, SR) were reported to have two to four phthalates (DEHP, DBP, DIBP, and occasionally DnOP).

The concentration of phthalates when reported and which exceed the limit of 0.1 percent were: PMMA/PAN - 4.7 to 8.9 percent DBP; PC - 20 percent DBP and 0.8 percent DnOP; SR - 0.3 percent DEHP and 0.2 percent DBP. For the other plastics, the concentration of phthalates is anticipated to be less than the 0.1 percent limit specified in section 108 of the CPSIA.

Table 13. Overview of Phthalates found in Plastics

Phthalate	Plastic										
	PMMA / PAN	EBR ^a	EBC ^a	EVA/ EVOH	EPM/ EPDM ^a	Surlyn [®]	PC _d	GPS/ MIPS/ SHIPS / SBC _{a,d}	SR	SAN	SB S/ SB R
DEHP		√	√	? ^c	√			√	√		
DBP	√		? ^b		√		√	√	√		?
BBP											
DINP											
DIDP											
DnOP	√						√				
DIBP		√	√ ^b		√			√			
DPENP											
DHEXP											
DCHP											
Phthalate esters								√			√

^a used as Ziegler-Natta catalysts, concentrations likely less than 0.0001 percent

^b could be additive (by analogy to PE)

^c one noted (no further explanation)

^d may be a plasticizer

^e reported in two teether/bites



TERA

**Exposure Assessment:
Potential for the
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in Specified
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Appendix A: Book List

Task Order 16

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1. Appendix A. Authoritative Secondary Sources (Library)

Appendix A lists the 15 books identified from the broader Tier 3 search of the UC Book Catalog. These books were used to research various factors throughout the project.

- Biron, M. 2007. Thermoplastics and Thermoplastics Composites. Oxford: Butterworth-Heinemann.
- Brydson, J.A. 1999. Plastics Materials. Oxford Publishing. Seventh edition. Available at: <http://www.sciencedirect.com/science/book/9780750641326>.
- Drobny, J.G. 2007. Handbook of Thermoplastic Elastomers. Second Edition. Plastics Design Library (PDL) Handbook Series. Elsevier, William Andrew.
- Elias, H-G. 2003. An Introduction to Plastics. 2nd Completely Revised Edition. Wiley-VCH.
- Ellis, B., Smith, R. 2009. Polymers: A Property Database. Second Edition. CRC Press.
- Fink, J.K. 2013. Reactive Polymers, Fundamentals and Applications: A Concise Guide to Industrial Polymers. Second Edition. ISBN: 978-1-4557-3149-7.
- Ibeh, C. 2011. Thermoplastic Materials: Properties, Manufacturing Methods, and Applications. CRC Press. Boca Raton, FL.
- Kirk-Othmer. 2014. Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley and Sons, Inc. Available at: <http://onlinelibrary.wiley.com/book/10.1002/0471238961>.
- Mark, H.F. 2007. Encyclopedia of Polymer Science and Technology. Concise Third Edition. John Wiley & Sons. ISBN-13: 978-0470046104.
- Mark, J.E., Erman, B., Roland, M. 2013. The Science and Technology of Rubber. Amsterdam: Elsevier Academic Press.
- McKeen, L.W. 2012. Markets and Applications for Films, Containers, and Membranes. Permeability Properties of Plastics and Elastomers. Third Edition. Oxford, William Andrew Publishing. p 219-224.
- Olabisi, O. 1997. Polyacrylonitrile. Handbook of Thermoplastics. Marcel Dekker, Inc.
- Park, S-J, Heo, G-Y. 2014. Carbon Fibers. Chapter 2. In: Precursors and Manufacturing of Carbon Fibers. Available at: http://link.springer.com/chapter/10.1007%2F978-94-017-9478-7_2.
- Salamone, J.C. 1996. Polymeric Materials Encyclopedia. Volume 3 (D-E). CRC Press. ISBN 0-8493-2470-X.
- Sastri, V.R. 2014. Properties, Requirements, and Applications. Science Direct, Elsevier/William Andrew, Amsterdam.



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Appendix B:
Authoritative Secondary
Sources (Websites)

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1. Appendix B. Authoritative Secondary Sources (Websites)

Appendix B lists the 48 websites identified as authoritative secondary sources searched in Tier 2. Shaded sites indicate the sites pared down from the 48 for further research.

Secondary Authoritative References--Background Check of 48 websites searched^a		
Country	Office	Website (n = 48)
Australia	Dept. of Health	http://www.nicnas.gov.au/home
	NICNAS	http://www.nicnas.gov.au/industry/aics/search.asp
Canada	Canadian Centre for Occupational Health & Safety - RTECS	http://www.ccohs.ca/search.html
	Draft Assessments	http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&xml=6892C255-5597-C162-95FC-4B905320F8C9
	Environment Canada	http://www.ec.gc.ca/default.asp?lang=En&n=ECD35C36
	Health Canada	http://www.hc-sc.gc.ca/index-eng.php
	Health Canada First Priority List Assessments	http://www.hc-sc.gc.ca/ewh-semt/pubs/contaminants/psl1-lsp1/index-eng.php
	Health Canada Second Priority List Assessments	http://www.hc-sc.gc.ca/ewh-semt/pubs/contaminants/psl2-lsp2/index-eng.php
	Risk Management reports - Final Assessments	http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&xml=09F567A7-B1EE-1FEE-73DB-8AE6C1EB7658
	Toxic Substances Managed under CEPA	http://www.ec.gc.ca/toxiques-toxics/Default.asp?lang=En&n=98E80CC6-1
Europe	ECHA	http://echa.europa.eu/
	ECHA	http://echa.europa.eu/en/search?p_p_id=echasearch_WAR_echahaportlet&p_p_lifecycle=0&p_p_state=normal&p_p_mode=view&p_p_col_id=column-
	European Commission	http://ec.europa.eu/consumers/consumers_safety/safety_products/rapex/index_en.htm

Secondary Authoritative References--Background Check of 48 websites searched^a		
Country	Office	Website (n = 48)
International	ITER TERA Database	https://iter.ctc.com/publicURL/pub_search_list.cfm
	OECD eChemPortal	http://www.echemportal.org/echemportal/substancesearch/page.action?pageID=9
Norway, Sweden, Denmark and Finland	SPIN	http://195.215.202.233/DotNetNuke/
USA	ACGIH	http://www.acgih.org/home.htm
	CPSC	http://www.cpsc.gov/
	Federal Docket	http://www.regulations.gov/#!/home
	OSHA	https://www.osha.gov/dts/chemicalsampling/toc/toc_chemsamp.html
USA - NIH	ChemIDPlus	http://chem.sis.nlm.nih.gov/chemidplus/rn/117-81-7
	HPD	http://householdproducts.nlm.nih.gov/cgi-bin/household/searchall
	HSDB	http://toxnet.nlm.nih.gov/newtoxnet/hsdb.htm
	NTP	http://ntp.niehs.nih.gov/index.cfm
	PubChem	https://pubchem.ncbi.nlm.nih.gov/search/
	Haz-Map	http://hazmap.nlm.nih.gov/index.php

Secondary Authoritative References--Background Check of 48 websites searched^a

USA - CA	Biomonitoring - Priority Chemicals California	http://www.oehha.ca.gov/multimedia/biomon/pdf/PriorityChemCurrent.pdf
	Biomonitoring California- Designated Chemicals	http://www.oehha.ca.gov/multimedia/biomon/pdf/DesignatedChemCurrent.pdf
	Cal/Ecotox database	http://www.oehha.ca.gov/scripts/cal_ecotox/CHEMLIST.ASP
	Non-cancer health effects Table (RELs) and Cancer Potency Factors (Appendix A & B)	http://www.oehha.ca.gov/air/hot_spots/index.html
	OEHHA	http://www.oehha.ca.gov/
	OEHHA Toxicity Criteria Database	http://www.oehha.ca.gov/tcdb/index.asp
	Office of Environmental Health Hazard Assessment	http://www.oehha.ca.gov/risk.html
USA - CDC	ATSDR	http://www.atsdr.cdc.gov/substances/index.asp
	NIOSH	http://www.cdc.gov/niosh/topics/
	AEGLs	http://www.epa.gov/oppt/aegl/pubs/chemlist.htm
USA - EPA	CDR-CDAT	http://java.epa.gov/oppt_chemical_search/
	EPA Science Inventory	http://cfpub.epa.gov/si/
	IRIS Track/New Assessments & Reviews / NSCEP	http://www.epa.gov/ncepihom/

	National Service Center for Environmental Publications (NSCEP)	http://www.epa.gov/nscep/
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Secondary Authoritative References--Background Check of 48 websites searched^a		
	OPPT	http://iaspub.epa.gov/apex/pesticides/f?p=INERTFINDER:1:1395578990735::NO:1::
	RfD/RfC & CRAVE meeting notes	http://cfpub.epa.gov/si/
	TRI	http://www.epa.gov/enviro/facts/tri/search.html
USA - WA	ECY	http://www.ecy.wa.gov/programs/swfa/cspa/
WHO	IARC	http://monographs.iarc.fr/ENG/Monographs/PDFs/index.php
	IFCS	http://www.who.int/ifcs/en/
	IPCS - INCHEM	http://www.inchem.org/

^aNICNAS - National Industrial Chemicals Notification and Assessment Scheme; RTECS - Registry of Toxic Effects of Chemical Substances; ECHA - European Chemicals Agency; SPIN - Substances in Products in Nordic Countries; ACGIH - American Conference of Governmental Industrial Hygienists; CPSC - Consumer Product Safety Commission; ITER - International Toxicity Estimates for Risk; TERA - Toxicology Excellence for Risk Assessment; OECD - Organisation for Economic Cooperation and Development; NSCEP - National Service Center for Environmental Publications; OSHA - Occupational Safety and Health Administration; HPD - Household Products Database; HSDB - Hazardous Substances Data Bank; NIH - National Institutes of Health; NTP - National Toxicology Program; OEHHA - Office of Environmental Health Hazard Assessment; REL - Reference Exposure Levels; CEPA - Canadian Environmental Protection Act; U.S. CDC - U.S. Center for Disease Control; ATSDR - Agency for Toxic Substances and Disease Registry; NIOSH - National Institute for Occupational Safety and Health; U.S. EPA - U.S. Environmental Protection Agency; AEGL - Acute Exposure Guideline Levels; CDR-CDAT - Chemical Data Reporting-Chemical Data Access Tool; IRIS - Integrated Risk Information System; OPPT - Office of Pollution Prevention and Toxics; RfD/RfC - reference dose/reference concentration; CRAVE - Carcinogen Risk Assessment Verification Endeavor; TRI - Toxics Release Inventory Program; WSDE - Washington State Department of Ecology; WHO - World Health Organization; IARC - International Agency for Research on Cancer; IFCS - Intergovernmental Forum on Chemical Safety; IPCS - International Programme on Chemical Safety.



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**Appendix C: Literature
Search Results**

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Pub Med

Name of database	PubMed	
Date conducted	December 16, 2015	
Limits placed on search	none	
Material	Second approach for Primary Literature (search string used)	Number of Hits
Acrylic Resins	(9011-14-7 OR 9008-29-1 OR Plexiglass OR 25014-41-9)	
	(acrylic resins AND phthalate)	97
Butadiene-ethylene resin	(butadiene-ethylene resin OR 25068-01-3)	
EPDM	(ethylene-propylene-diene monomer OR EPDM OR 25038-36-2 OR 27155-45-9)	35
EPM	(ethylene propylene monomer OR EPM OR 61789-00-2 OR 9010-79-1)	98
Ethylene copolymers	(ethylene vinyl acetate OR 24937-78-8)	10
	(ethylene vinyl alcohol OR 25067-34-9)	9
Ethylene-Butene copolymers	(ethylene-butene copolymers OR 25087-34-7)	1
Ionomer	(Surlyn [®] OR 9078-96-0)	12
	(ionomers)	-
Polycarbonate	(polycarbonate OR 25037-45-0 OR 24936- 68-3 OR 25971-63-5 OR 111211-39-3 OR 103598-77-2)	14
Polystyrene	(polystyrene OR 9003-53-6)	45
	MPS or SHIPS	25
Silicone rubber	(Silicone rubber OR 63394-02-5)	6
Styrene-acrylonitrile copolymers (SAN)	(Styrene-acrylonitrile copolymers OR 9003- 54-7)	8
Styrene-butadiene copolymers	(styrene-butadiene copolymers OR 9003-55- 8)	23
Styrene-butadiene-styrene rubber (SBS), and styrene- butadiene rubber (SBR)	(styrene-butadiene-styrene rubber OR SBS OR 9003-55-8)	5
	(styrene-butadiene rubber OR SBR OR 308076-28-0 OR 61789-96-6)	3
Total		391
Duplicates		150
Total minus duplicates		313

Scopus

Name of database	Scopus	
Date conducted	December 16, 2015	
Limits placed on search	none	
Material	Second approach for Primary Literature (search string used)	Number of Hits
Acrylic Resins	(9011-14-7 OR 9008-29-1 OR Plexiglass OR 25014-41-9)	54
	(acrylic resins AND phthalate)	1184
Butadiene-ethylene resin	(butadiene-ethylene resin OR 25068-01-3)	39
EPDM	(ethylene-propylene-diene monomer OR EPDM OR 25038-36-2 OR 27155-45-9)	22
EPM	(ethylene propylene monomer OR EPM OR 61789-00-2 OR 9010-79-1)	200
Ethylene copolymers	(ethylene vinyl acetate OR 24937-78-8)	1200
	(ethylene vinyl alcohol OR 25067-34-9)	1153
Ethylene-Butene copolymers	(ethylene-butene copolymers OR 25087-34-7)	5
Ionomers	(Surlyn [®] OR 9078-96-0)	512
	(ionomers)	146
Polycarbonate	(polycarbonate OR 25037-45-0 OR 24936-68-3 OR 25971-63-5 OR 111211-39-3 OR 103598-77-2)	1200
Polystyrene	(polystyrene OR 9003-53-6)	1200
Silicone rubber	(Silicone rubber OR 63394-02-5)	200
Styrene-acrylonitrile copolymers (SAN)	(Styrene-acrylonitrile copolymers OR 9003-54-7)	58
Styrene-butadiene copolymers (SB)	(styrene-butadiene copolymers OR 9003-55-8)	129
Styrene-butadiene-styrene rubber (SBS), and styrene-butadiene rubber (SBR)	(styrene-butadiene-styrene rubber OR SBS OR 9003-55-8)	12
	(styrene-butadiene rubber OR SBR OR 308076-28-0 OR 61789-96-6)	101
Total		7416
Duplicates		6240

Total minus duplicates		3107
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Web of Science

Name of database	Web of Science	
Date conducted	December 16, 2015	
Limits placed on search	none	
Material	Second approach for Primary Literature (search string used)	Number of Hits
Acrylic Resins	(9011-14-7 OR 9008-29-1 OR Plexiglass OR 25014-41-9)	9
	(acrylic resins AND phthalate)	501
Butadiene-ethylene resin	(butadiene-ethylene resin OR 25068-01-3)	64
EPDM	(ethylene-propylene-diene monomer OR EPDM OR 25038-36-2 OR 27155-45-9)	79
EPM	(ethylene propylene monomer OR EPM OR 61789-00-2 OR 9010-79-1)	233
Ethylene copolymers	(ethylene vinyl acetate OR 24937-78-8)	500
	(ethylene vinyl alcohol OR 25067-34-9)	236
Ethylene-Butene copolymers	(ethylene-butene copolymers OR 25087-34-7)	16
Ionomers	(Surlyn [®] OR 9078-96-0)	357
	(ionomers)	11
Polycarbonate	(polycarbonate OR 25037-45-0 OR 24936-68-3 OR 25971-63-5 OR 111211-39-3 OR 103598-77-2)	500
Polystyrene	(polystyrene OR 9003-53-6)	500
Silicone rubber	(Silicone rubber OR 63394-02-5)	246
Styrene-acrylonitrile copolymers (SAN)	(Styrene-acrylonitrile copolymers OR 9003-54-7)	61
Styrene-butadiene copolymers	(styrene-butadiene copolymers OR 9003-55-8)	237
Styrene-butadiene-styrene rubber (SBS), and styrene-butadiene rubber (SBR)	(styrene-butadiene-styrene rubber OR SBS OR 9003-55-8)	39
	(styrene-butadiene rubber OR SBR OR 308076-28-0 OR 61789-96-6)	366
Total		3957
Duplicates		1328
Total minus duplicates		3188

Toxline

Name of database	Toxline	
Date conducted	December 16, 2015	
Limits placed on search	none	
Material	Second approach for Primary Literature (search string used)	Number of Hits
Acrylic Resins	(acrylic resins AND phthalate)	8
Butadiene-ethylene resin	(butadiene-ethylene resin OR 25068-01-3)	6
Ethylene-Butene copolymers	(ethylene-butene copolymers OR 25087-34-7)	7
EPDM	(ethylene-propylene-diene monomer OR EPDM OR 25038-36-2 OR 27155-45-9)	2
EPM	(ethylene propylene monomer OR EPM OR 61789-00-2 OR 9010-79-1)	37
Ethylene copolymers	(ethylene vinyl acetate OR 24937-78-8)	145
	(ethylene vinyl alcohol OR 25067-34-9)	2
Ionomers	(Surlyn [®] OR 9078-96-0)	81
	(ionomers)	1
Polycarbonate	(polycarbonate OR 25037-45-0 OR 24936-68-3 OR 25971-63-5 OR 111211-39-3 OR 103598-77-2)	16
Polystyrene	(polystyrene OR 9003-53-6)	21
Silicone rubber	(Silicone rubber OR 63394-02-5)	296
Styrene-acrylonitrile copolymers (SAN)	(Styrene-acrylonitrile copolymers OR 9003-54-7)	68
Styrene-butadiene copolymers	(styrene-butadiene copolymers OR 9003-55-8)	102
Styrene-butadiene-styrene rubber (SBS), and styrene-butadiene rubber (SBR)	(styrene-butadiene-styrene rubber OR SBS OR 9003-55-8)	205
	(styrene-butadiene rubber OR SBR OR 308076-28-0 OR 61789-96-6)	95
Total		1479
Duplicates		941
Total minus duplicates		850



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Appendix D: Other
Uses in Consumer
Products

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5	Ethylene Copolymers [Ethylene Vinyl Acetate (EVA) CASRN 24937-78-8] and Ethylene Vinyl Alcohol (EVOH) CASRN 25067-34-9]*	7
6	Ethylene-Propylene Monomer (EPM) and Ethylene-Propylene-Diene Monomer (EPDM) CASRNs: 61789-00-2; 9010-79-1; 25038-36-2.....	9
7	Ionomers (Surlyn®) CASRN: 9078-96-0.....	11
8	Polycarbonate CASRNs: 25037-45-0; 24936-68-3; 25971-63-5; 111211-39-3; 103598-77-2	12
9	Polystyrene [Crystal and General-Purpose (GPS)], Medium-Impact Polystyrene (MIPS), Super-High-Impact Polystyrene (SHIPS) Grades] and Styrene- Butadiene Copolymers CASRNs: 9003-53-6; 9003-55-8	13
10	Silicone Rubber (SR) CASRN: 63394-02-5	14
11	Styrene-Acrylonitrile Copolymers (SAN) CASRN: 9003-54-7.....	15
12	Styrene-Butadiene-Styrene Rubber (SBS) and Styrene-Butadiene Rubber (SBR) CASRNs: 308076-28-0; 61789-96-6	16
13	References.....	17

1 Introduction

This appendix presents additional information, if available, on the uses other than for toys and child care articles, for the specified plastics.

2 Acrylic Resin (Polymethylmethacrylate (PMMA) and Polyacrylonitrile (PAN)) CASRNs: 9011-14-7; 9008-29-1; 25014-41-9

Textile uses with acrylic include knitwear, rugs, and fiber used for indoor and outdoor furniture, tents, and awnings (HazMap, 2015; HSDB, 2015).

Acrylic sheet (PMMA) is a common alternative for glass, allowing light/UV to pass through, and thus is used as enclosures for skylights, swimming pools, greenhouses, and fluorescent lighting covers, lamp covers and components. PMMA is used in many optical components, for example: camera lenses, sunglasses, watch glasses, and magnifying glasses. Acrylic is used for personal care products, and plumbing fixtures and accessories. Acrylic resins are used in artificial marble used for kitchen counters, lavatory dressing tables, and waterproof pans (Fink, 2013). There are 22 products that contain acrylic (CASRN 9011-14-7) in the HPD (2015), within 6 different categories. Acrylic is mainly used as a component in superglues, printer ink toner, and personal care items or cosmetics.

In Nordic countries, the SPIN database shows numerous National Use categories (35 records; 7 categories listed for CASRN 25014-41-9 and 208 records; 45 categories for CASRN 9011-14-7). No records were found for CASRN 9008-29-1. In addition to the SPIN (2015) database, the HPD (2015), the European RAPEX (2016), and the Washington State consumer product (ECY, 2016a,b) databases were searched using the chemical names and/or CASRNs, and no records were found for the PMMA or PAN CASRNs. A RAPEX search of the years 2005-2016 for acrylic with a chemical risk reported 21 items. Nail polish containing high levels of DBP was found for three of the 21 items ranging by weight from 4.17-8.89 percent (RAPEX, 2016).

Acrylic plastic also has major applications for use in gaskets, hoses, and printing roll (not specified) surfaces (HazMap, 2015; McKeen, 2012). Acrylic plastic is used for all kinds of illuminated display signs both indoors and outdoors, name plates and medallions, lamp fittings, light diffusers, light-control lenses, and juke boxes (Biron, 2007; Sale, 1993; Brydson, 1999).

Acrylic plastics have uses in the automobile/ transportation industry for automobile

lights, marine, and motorcycle windscreens, dashboards, and display lighting (IARC, 1979). Shatter resistant window glazing systems can be made out of acrylic PMMA (McGowan, no year). Acrylic also is reported to be used for anode bags in electroplating, and for glazing household items including doors, windows, fanlights, skylights, and other lighting fixtures (HazMap, 2015; Biron, 2007).

The medical uses of acrylic plastics (PMMA/PAN) are many, including use of acrylic resin in hip socket replacement, drug delivery components and adapters, catheter accessories, blood plasma separators, tubing, cuvettes and other specimen containers, instrument housings, and in various parts for medical and scientific devices (Sastri, 2014). In medical research PMMA is used in fibers for electrophoresis apparatus (Chen and Lee, 1999) and in synthetic textile prostheses in cardiovascular medicine (HSDB, 2015).

3 Butadiene – Ethylene Resins (EBR) CASRN: 25068-01-3

Butadiene ethylene resin is considered an olefin, which is commonly used for films, household goods, packaging, plastic bags, and pipes (type not specified) (Nsiri et al., 2016). No uses in consumer products were identified for EBR by the tiered process used for this research. The tire industry is reported to have developed this olefin and it is used to make styrene-ethylene-butadiene-styrene block terpolymer, a thermoplastic polystyrene elastomer; also called a thermoplastic polyamide elastomer (Sastri, 2014). Thermoplastic elastomers are often used by blending different percentages of ethylene and butadiene for various uses (Fink, 2013). Medical uses for thermoplastic elastomers are numerous and include tubing and medical films (Sastri, 2014).

4 Ethylene-butene (EB) Copolymers CASRN: 25087-34-7, 9019-29-8

Potential uses for EB copolymers were identified based on the patents using EB as an ingredient. A patent submitted by Chen et al. (2014) uses EB and diethyl phthalate as a component in the polyurethane layer of communication cables. Another patent by Oyama et al. (2004) uses EB as a component of a thermoplastic resin used in the exterior portion of automobiles. Finally, Szulc et al. (2011) have developed a patent for thermoplastic polyolefin that consists of a variety of additives including EB and DBP.

5 Ethylene Copolymers [Ethylene Vinyl Acetate (EVA) CASRN 24937-78-8] and Ethylene Vinyl Alcohol (EVOH) CASRN 25067-34-9]*

The major application of EVA is in products for household maintenance. HPD reported six products, caulks, and sealants that include EVA as an ingredient (HPD, 2015). EVA is permitted by EPA for food and nonfood pesticide uses, such as packaging, household maintenance, and artificial flowers. Packaging using EVA includes liquids, meats, produce bags, bag in box food, and low temperature-seal shrink wrap (Biron, 2007; U.S. EPA, 2015).

The SPIN database reports chemicals used in the Nordic Countries. It lists 364 records for EVA under 19 different use categories (SPIN, 2015). These uses include agents for adhesives, cleaning, coloring, fillers, foam, and reprographics. EVA is used as an additive in fuel, lubricants, and surface treatments of sheetrock and concrete. EVOH is used for rigid packaging of food entrees, edible oils, juice, cosmetics, pharmaceuticals, heating pipe, as a barrier layer in automotive plastic fuel tanks, and packaging for condiments and toothpaste (Biron, 2007; McKeen, 2012). EVOH also is used in films, pouches or lids for flexible packaging of processed meats, bag-in-box, red meat, coffee, tea, soup, cereal, pesticides and agrichemicals (Biron, 2007; McKeen, 2012). EVOH is used in combination with HIPS and PE to produce co-extrusion structures for juice and sausage packaging (Norbert et al., 2013). It also is used for apron waterproofing, and for personal protective clothing such as boot covers, sleeve protectors, and gloves (Amazon.com, 2016). While information is available as to what products may contain EVA or EVOH, no information on phthalate(s) content or concentration was located in the information cited.

Films for technical packaging use EVA to improve clarity and puncture resistance. EVA has applications in film extrusion, wire and cable insulation, adhesives, coatings, compounding, laminating, and molding (HazMap, 2015; Mark, 2009). EVA also is used in cap liners, plastic film pallet stretch wrapping, surfboards, skimboards, swimming pool hoses, and traction pads (Biron, 2007; HazMap, 2015; Mark, 2009; McKeen, 2012). It is used to enhance the grip in plastic wraps, improve cold flow of diesel fuel, and in HEPA filters (HazMap, 2015). EVA also is permitted for use as an inert ingredient in non-food pesticide products such as thermoplastic mouth guards, kneepads, orthotics, and vaginal contraceptives (HazMap, 2015). It also is used in medical bags for intravenous administration for which detection of DEHP has been reported (Veiga et al., 2012). Information about EVOH was not available in HazMap (2015).

EVA or EVOH is used in other consumer products because they are effective air barriers; data regarding phthalate content could not be located for EVA or EVOH products in the sources researched for this project (*e.g.*, HPD, 2015; HazMap, 2015).

6 Ethylene-Propylene Monomer (EPM) and Ethylene-Propylene-Diene Monomer (EPDM) CASRN: 61789-00-2; 9010-79-1; 25038-36-2

EPM and EPDM are used in numerous consumer products based on a broad global search for consumer products on Amazon.com (Amazon.com, 2016). In addition, EPM (CASRN 9001-21-1) is permitted for use by EPA as an inert ingredient in non-food pesticide products (HazMap, 2015).

The main uses of EPM or EPDM are in:

- 1) automotive applications such as profiles, hoses, and seals (41 percent of worldwide consumption);
- 2) building and construction as profiles, roofing membranes, seals, and sealing washers (21 percent);
- 3) cable insulation and jacketing (6 percent); and
- 4) molded appliance parts.

An important application for EPDM is in blends with general-purpose rubbers (HC, 2015; Rodgers, 2004; James et al., 2013). EPDM is used as a component of barrier linings in geomembranes for waste containment systems (U.S. EPA, 2015). EPDM is used for the tubes of automotive coolant hoses (Rodgers, 2004).

Ethylene-propylene copolymer (CASRN 9010-79-1) was found as an ingredient in three consumer products in the HPD (2015); no information was found for other CASRN. HazMap (2015) reports EPM usage in coatings with a risk of exposure from painting that use pigments, binders, and biocides with EPM. The SPIN database listed uses for 172 records with 28 different categories. The categories, as presented in the SPIN database, for ethylene-propylene copolymer, include accelerators, construction materials, lubricants and filling agents (SPIN, 2015).

EPDM was not found in the HPD as an ingredient for any product, but was found listed under the Health Effects Field for 87 consumer products, all used for home maintenance, primarily caulk or paint (HPD, 2015). Ethylene/propylene/diene terpolymer (CASRN 25038-36-2) was found as an ingredient in eight automotive products (HPD, 2015).

In addition to the SPIN, HPD, and the European RAPEX (2015) databases, the Washington State consumer product (ECY, 2016a,b) databases were searched using the chemical names and/or CASRN. No records were found for EPM or EPDM.

Only two medical uses were identified from the search strategy employed for this project, both were found using Tier 2 search strategy. Medical uses for EPM include its use in O-rings for heart machines, and EPDM as a gasket material (HC, 2015; CDC, 2003). Overall, there are numerous uses and applications for EPM and EPDM. No information was found for phthalates in EPM or EPDM in the literature researched for this project.

7 Ionomers (Surlyn®) CASRN: 9078-96-0

Ionomers may provide grease-barrier coatings for packaging (Echt et al., 2014). Surlyn® is used for surface coating of perfume bottles (self-standing squeezable bottle), cosmetic jars, sea food, meat, cheese, and dry food (Du Pont, 2015). In sports equipment, Surlyn® is used as the cover for golf balls, and is found in waterproof snow boots (Amazon.com, Inc., 2016; Statz, 1990).

Surlyn® is used as a sheath of electrical wires and cables, thermoplastic sealant film and packaging sealant, polymer matrix for nanocomposites, and a joint adhesive for nickel-polyethylene terephthalate (Costa et al., 2015; Ansari et. al., 2015; Haijun et al., 2014; Visioli and Chen, 2011).

8 Polycarbonate CASRNs: 25037-45-0; 24936-68-3; 25971-63-5; 111211-39-3; 103598-77-2

Numerous applications for PC were found in food containers, which include the following: re-useable water bottles (sports bottles), pitchers, water carboys, milk containers, tableware, food storage containers, and beverage containers (CDC, 2010; U.S. EPA, 1997; Biron, 2007; HazMap, 2015). PC also may be used in household appliances such as food processor bowls, food mixer housing, coffeemaker water reservoirs, power tool housings, hair dryer and electric razor housings, vacuum cleaner housings, phone cases and microwave cookware (Brydson, 1999). It is used in spray paints, storage boxes, luggage, safety protective glasses, and sunglasses (Amazon.com, Inc., 2016).

The largest application of PC is in electronic and electrical engineering for coil formers, battery covers, relays, and switches (Brydsin, 1999). PC is also used in desktop computer displays, LCD plastic frames, light plate and rear plate assembly for the backlight assembly, and LED light plates (U.S. EPA, 2001). A major market for PC is in compact discs (CDs) and digital video discs (DVDs). It also has a broad range of uses in copy cartridges, calculating machines, enclosures for fluorescent lamps, luminaire and safety lenses, goggles, and face and body shields (Brunelle and Korn, 2005; U.S. EPA, 1998).

Polycarbonate is widely used in medical devices that include baffles, blood bags or reservoirs, bottles, cylinders, centrifuge, tubes, cages, exposure chambers, cell culture chamber filters, water filters, and DNA purification filters (HazMap, 2015). It is used in corrective lenses, contact lenses holders (also called cases), dental lamps, membranes for hemodialysis, intravenous (IV) stopcocks, accessories for tubing, surgical instrument handles, and housings for oxygenators used during open-heart surgery (Biron, 2007).

PC is used for architectural glazing applications and protective glazing for windows (McGowan, no year). It also is used for lighting (*e.g.*, light globes, light diffusers, outdoor light fixtures (U.S. EPA, 1985; Biron, 2007)). PC is used in films for fireman's masks, space and sports helmets, automobile headlight lenses, interior instrument panels, and bullet-resistant windows (HazMap, 2015; HC, 2015). Sweden reports using PC for only two uses: raw materials for production of plastics and intermediates (plastics manufacture) (SPIN, 2015). RAPEX identifies PC use in safety goggles, and in a basketball backboard (RAPEX, 2015).

Many products are made of polycarbonate, and DBP and DnOP may be used as plasticizers in the manufacture of PC (Section 9.1 of report). However, there is no information regarding the content or concentration in consumer products of the specified phthalates in sources researched for this project (*e.g.*, U.S. EPA, 1985; 1998; HazMap, 2015).

9 Polystyrene [Crystal and General-Purpose (GPS)], Medium-Impact Polystyrene (MIPS), Super-High-Impact Polystyrene (SHIPS) Grades] and Styrene-Butadiene Copolymers CASRNs: 9003-53-6; 9003-55-8

GPS and the modified polystyrene copolymers, such as MIPS and HIPS, are used in numerous household consumer products, automotive and construction materials, packaging, and in medical research.

There is a paucity of information on household products containing MIPS; however, there is information on the closely related HIPS, which is likely relevant to MIPS. HIPS (and by extension, MIPS) resins are used in household appliances, consumer electronics, premium office accessories, and consumer products (Sastri, 2010). One example is a DVD/CD holder that looks like a book; it allows one to flip the pages for the different CD/DVDs (Rosato, 2011). HIPS resins also are used in applications such as food packaging, foamed food trays and egg cartons, dairy containers (yogurt containers), disposable cups for vending and soda fountain cups, kitchenware including plastic cutlery, imitation crystal “glassware”, lids, plates, and bowls (Siddique, 2008). Jewel boxes are another application for GPS (Rosato, 2011; Snedeker et al., 2014). No specific products were identified for household products with SHIPS or MIPS (Ebnesajjad and Landrock, 2015).

GPS is used in combination with other polymers such as acrylonitrile and acrylates (termed styrenics) or with styrene butadiene rubbers like styrene or styrene-ethylene-butylstyrene (termed thermoplastic elastomers). It is used in many medical and research products (Sastri, 2013; Snedeker, 2014), including labware such as petri dishes and tissue culture trays, and medical tubing (Snedeker, 2014). Both GPS and HIPS find uses in respiratory care equipment, syringe hubs, and suction canisters (Sastri, 2010).

High impact grades of polystyrene that are modified with polybutadiene elastomers (ranging from 6 to 12 percent) are used in home test kits, diagnostic equipment housings, and thermoformed products including catheter trays, heart pump trays, and epidural trays (Sastri, 20110).

The presence of phthalates in GPS used for the above consumer product applications was not noted nor were concentration data reported.

10 Silicone Rubber (SR) CASRN: 63394-02-5

Kitchenware using SR include: bakeware, spatulas and handles, baking pans and trays, and pastry scrapers. Other products such as soft touch pens and handles, jewelry molding, wristbands, bathing caps, scuba masks, swimming goggles, snorkel mouthpieces, grommets, and diaphragms have also been reported (Sarkar et al., 2009).

Silicone rubber (depending on the type of processing) is used for potting compounds, caulk, fabric, and coatings (by either being roll-coated or sprayed-on), O-rings, seals, boots, high voltage insulators, wires and cables by moldings, and extrusion or calendaring (Sarkar et al., 2009).

SR is used for seals and tubing in vending machines and release coatings for food transportation belts and sweet molds (Forest, 2006). SR elastomers are used for electrical insulation, medical devices, seals, surface-treated fillers, elastic textile coatings, and foams. Liquid injection molding is used for electrical connectors, O-ring seals, valves, electrical components, health care products, and sporting equipment such as goggles and scuba diving masks (Datta, 2004). Silicone rubber uses in the automotive, aerospace, and electronics industry include gaskets, insulation, silicone rubber coating, and textile coatings (Dow Corning, 2015).

Medical products using SR include catheters, insulated wires, breast prostheses, O-rings, seals, diaphragms, valves, seals, stoppers, bag caps, drug delivery tubes, joint replacements, and blood culture devices (Sarkar et al., 2009). SR is also reported to be used in hand prosthesis (Sastri et al., 2014).

11 Styrene-Acrylonitrile Copolymers (SAN) CASRN: 9003-54-7

Household items identified to be made from SAN are dishwasher parts, shelves, refrigerator parts, shower cubicle and other bathroom fittings, washing machine trims, radio dials, TV set screens, humidifiers, vacuum cleaner parts, hi-fi covers, furniture parts, camera parts, sports goods, telephone parts, pens, and pencil barrels (Biron, 2007; HC, 2015; Kirk-Othmer, 2014).

Household consumer databases searched for SAN yielded no results (HPD, 2015; SPIN, 2015; RAPEX, 2015; ECY, 2016a,b). All of these databases list products made from plastics; however, when the specified phthalates are identified as in plastic, the specific type of plastic is not stated.

SAN is used in a variety of telecommunication equipment, consumer electronics, and tools for writing and drawing. In addition, it is found in typewriter keys, transparent covers for PCs and copiers, outer covers of printers, calculators, battery and tape cassette cases, computer reels, electrophotographic toners, and camera parts such as meter lenses (Biron, 2007).

SAN is used in safety glazing, water filter housing, and faucet knobs (HC, 2015). It has a wide variety of industrial uses including coatings, dispersing agents, and safety glasses (Kirk-Othmer, 2014). Other uses include automotive parts such as batteries, interior trim, instrument lenses, and dashboards (Kirk-Othmer, 2014).

Medical devices that require optical clarity, heat or chemical resistance, and possibly sterilization contain SAN. Some examples are hemodialyzer housings, disposable fluid collection containers, and labware (Sastri, 2013). SAN is also used in medical equipment (e.g., syringes, intravenous connectors, and valves), packaging, custom molding, and in the production of acrylonitrile-butadiene-styrene (ABS) resins (HC, 2015).

12 Styrene-Butadiene-Styrene Rubber (SBS) and Styrene-Butadiene Rubber (SBR) CASRNs: 308076-28-0; 61789-96-6

Block SBR is used for rubber bands, filler putty for arts and crafts, and rubber floor tiles (Brydson, 1999). Solubilized SBR is used in unspecified shoe soling (HPD, 2015; Kirk-Othmer, 2014).

SBR is frequently used to manufacture tires and tire products (IARC, 1979; 1986). Other automotive applications include mechanical goods such as brake cups (HC, 2015), gaskets, hose, automobile body and chassis parts (seals, mountings, bushings, and belting), bumpers, weather strips, door and window seals, and mats (IARC, 1979; 2002).

SBS is used in sound deadening materials, grips, wire, cable insulations, and flexible automotive parts (Drobny, 2007). SBS is used as a polymer-bitumen mixture in roofing (Chanda and Roy, 2008). A modified bitumen system is a low-slope (commercial or industrial) roofing system that uses a polymer, usually atactic polypropylene or styrene-butadiene-styrene (SBS) (NIOSH, 2003). SBS is used in adhesives, particularly pressure-sensitive adhesives and hot melt sealants that are solvent based (Drobny, 2007).

Six record(s) were found in the HPD (2015) for products in the Health Effects fields that contained styrene-butadiene-styrene. These were filler putty and wood filler for home maintenance, and tire dyes for auto products (HPD, 2015). SBS is listed for the following use categories in the HPD: adhesives, solvent-based adhesives, and adhesives.

SBR is used for appliance parts, latex applications (carpet backing), wire and cables, conveyors, footwear specifically the soles and heels (IARC, 1979, 2002; McKeen, 2011).

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TERA

**Exposure Assessment:
Potential for the
Presence of Phthalates
in Specified
Materials at
Concentrations
Above 0.1 Percent**

Appendix E:
Overview of
Recycling

Task Order 16
Contract Number
CPSC-D-12-0001

INDEPENDENT
NON-PROFIT
SCIENCE
FOR PUBLIC HEALTH
PROTECTION

1 Recycling of Plastics

Recycling is increasing as companies, the public, and governments address issues of sustainability, including the use of finite resources and waste disposal. Plastic recycling is the process of recovering scrap or waste plastics and reprocessing the material into useful products, sometimes completely different in form from their original state (Merrington, 2011). There is growing interest in, and research being conducted on, reusing and recycling plastics. Scrap plastic and recovered monomers are routinely used in plastic manufacturing within house or purchased for feedstock by others. Post consumer plastic is routinely collected and recycled to produce more of the same plastic type or downcycled to a lesser quality product.

Resource Recycling Systems (RRS, an engineering and consulting firm in solid waste management, recycling and solid waste planning) studied Material Recovery Facilities (MRFs) material flow and concluded that post consumer recycling is a complicated process that is impacted by consumer behavior, collection programs, sorting at the MRFs, and the needs and preferences of the buyer markets (RRS, 2015).

Plastic recycling presents difficulties that explain, in part, the low percentage of some types of plastics recycled. There are many kinds of plastics with different physical and chemical properties, and plastic waste can contain other materials, such as metals, glass materials, rubbers, or other plastics. Mixtures of recycled plastics may result in a heterogeneous plastic with mechanical properties that are inferior to the virgin plastic. The inferior performance creates a need to separate or sort waste plastics. Furthermore, during usage and the recycling process, the plastic may be degraded or contaminated. Thus, products made from recycled plastics can have reduced or inferior properties (Fisher, 2005). In some cases, additives are included to meet application needs or rejuvenate the properties diminished by use or the recycling process (Merrington, 2011). Phthalates are of particular concern with polyvinyl chloride (PVC) where they are used to soften the plastic. Contamination of other plastics with PVC could introduce phthalates into the resulting recycled plastic. The presence of PVC complicates recycling of plastics, thus, plastic recyclers go to great measures to remove PVC from the recycling stream. PVC's thermal stability is poor and it contaminates other plastics, creating problems such as discoloration, odors, and corrosion of process equipment. MRFs use industry-established specifications for plastic recycling bales and the reclaimers use a variety of technologies to sort out PVC by density (*e.g.*, using float/sink separation methods), and near infrared optical sorting or X-ray technologies (RRS, 2015).

The U.S. Food and Drug Administration (U.S. FDA) has suggested that the potential for acute contamination of food containers made of plastic using secondary or tertiary recycling is likely “extremely low” although they note it is possible trace amounts of

toxic substances could be carried through the secondary or tertiary recycling processes (U.S. FDA, 2006).

In addition to problems of degraded chemical properties, the recycled plastics can be contaminated or have high levels of potentially toxic chemicals. Typical WEEE-wastes are reported to contain about 10 to 30 weight percent plastic (Martinho et al., 2012). Analysis of WEEE recycled plastics showed 200 ppm of lead and 70 ppm of cadmium (Stenvall et al., 2013). Major constituents of WEEE plastics were styrene-based (84 wt percent) and consisted mainly of ABS (including ABS + acrylate, ABS + ester, and styrene-acrylonitrile copolymer) and HIPS (including PS + acrylate and poly (vinyl cyclohexane) (Stenvall et al., 2013).

The main obstruction of material recovery of HIPS and ABS from WEEE is the wide variety of polymers that are being used, in addition to the other materials including glass and metals, which results in elaborate sorting and recycling processes (Stenvall et al., 2013). Magnetic separation is a new method being employed to provide high volume throughput (Drobny, 2012).

In general, recycling efforts can be divided into four major types or processes:

- 1) mechanical recycling;
- 2) thermal reprocessing;
- 3) chemical recycling; and
- 4) energy recovery.

Other processes include dissolution based recycling that uses acetone as a solvent (Arostegui et al., 2006), and reuse, for example, where beverage plastic bottles are returned, cleaned, and reused (Hamad et al., 2013).

Note that this report is focused on specific plastics and the potential for these plastics to contain phthalates. Therefore, what is of most relevance is the potential for recycling of single resins, such that these recycled plastics are then used in whole or in part to produce a new single resin plastic, as opposed to a blend of plastics or composite plastic product. Recycling processes that involve mechanical or thermal reprocessing are the most likely to retain any phthalates from the original plastic

Primary recycling is when the recyclate retains the mechanical properties of the original plastic. If a recyclate cannot meet the original plastic's specifications, then it is described as secondary recycling or downcycling, and the material is used for lower quality applications, for example floor tiles made from mixed polyolefins (Merrington, 2011).

1.1 Mechanical Recycling

Mechanical recycling is a process of recovering solid waste by mechanical means for reuse in manufacturing (Al-Salem et al., 2009). Mechanical recycling destroys the structural organization of the plastic through grinding, but the molecular structure remains unchanged (Yoshioka and Grause, 2015). Mechanical recycling processes can be categorized as “primary,” wherein the mechanical properties of the recyclate are similar to the virgin material and can be used for similar end products, or “secondary,” wherein the recyclate does not meet the original specifications and is used for lesser quality application (Yoshioka and Grause, 2015). Mechanical (or physical) recycling starts by sorting; shortwave infrared (SWIR) hyperspectral imaging has been successfully used to sort PP, PE, PVC, PET, and PS (Karaca et al., 2013). The recovered plastic is melted and molded into a new product. This recycling process is limited to thermoplastics (plastics that can melt); the recycled plastic should be exclusively of one kind of plastic in order to yield a reusable pure product (Dreher et al., 2004). In mechanical recycling, the molecular structure remains unchanged although the structural organization is lost due to grinding (Merrington, 2011; Yoshioka and Grause, 2015).

An example of mechanical recycling is recycling damaged crates made from PP or HDPE for packaging of fruits and vegetables, or meat products. The damaged crates are separated based on type of plastic and then ground into flakes. The regrind is washed and dried to remove potential adhering contamination. This provides recycled PP or HDPE material for the production of new crates by injection molding with or without blending with virgin material (EFSA, 2013).

Figure 1 provides an illustration of the various steps in the mechanical recycling process. The first step is to cut the large plastics into small pieces or flakes, removing paper and dust, and then floating the plastic flakes is done to remove any different type of plastic (plastics are separated by density). The recycling starts by milling or grinding the plastic followed by washing. The product is gathered together (agglutination), melted, and then forced through a die (extrusion) into strands or pellets. The product is cooled and then granulated into the final product.

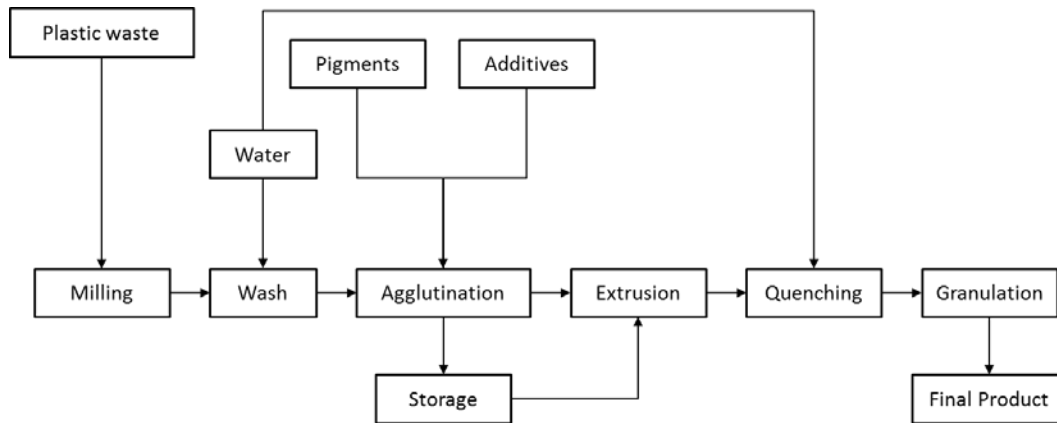


Figure 1. Mechanical recycling steps as described in Al-Salem et al. (2009).

Recycled plastics (LDPE, PET, and PVC) are frequently mixed with the specific virgin plastic in the manufacture of a new product. The amount of the recycled material in relation to the new or virgin plastic is variable and has an effect on the impact strength, hardness and tensile strength of the final product. In general, the mechanical properties of the recycle/virgin blend depends on the characteristics of the recycled plastic (Marulanda et al., 2014).

1.2 Thermal Reprocessing

Thermal reprocessing (also called thermal pyrolysis) consists of heating a thermoplastic to high temperatures converting the solid plastic to a liquid (Siddique, 2008). The plastic can be converted or remolded into a new product. This method does not involve the modification of the chemical composition of the plastic. For example, CDs made of HIPS can be heated and the styrene monomer can be recovered (Antonakou et al., 2014). Another example is recycling acrylic wastes by thermal decomposition into methyl methacrylate (MMA) that can be used in aircraft windows and neon signs (Siddique, 2008). Unmixed PMMA wastes are recommended for recycling since PMMA depolymerizes nearly qualitatively (*ca.* 96 percent) on pyrolysis into MMA (Fink, 2013). An initial mechanical sorting is most likely required because the separation of liquids with similar densities can be difficult.

1.3 Chemical Recycling (Depolymerization)

Chemical recycling, or tertiary, or “feed stock” (Dreher et al., 2004) recycling is an advanced technology process resulting in depolymerization of the plastic converting the plastic materials into smaller molecules suitable for use as a feedstock or starting material for the production of new petrochemicals and plastics (Al-Salem et al., 2009). Tertiary recycling results in purified monomers or oligomers that may or may not be blended with

virgin materials. The regeneration process may include washing and purification steps such as distillation, crystallization, or additional chemical reactions (FDA 2006). An example of tertiary recycling is using a polymer blend of polylactic acid/polyethylene (PLA/PE) (Hamad et al., 2013). Two methods for PLA/PE chemical recycling are direct separation and by the selective degradation of PLA in the PLA/PE blend. The end product PE remains unchanged and can be recovered by a reprecipitation method for material recycling (Hamad et al., 2013).

Chemical recycling provides a high yield of product with minimum waste, and can be profitable (Al-Salem et al., 2009). Chemical recycling can be used for a heterogeneous mixture of plastics.

1.4 Energy Recovery

Energy Recovery is the burning of plastic waste to produce energy. All types and mixture of thermogenic plastic or plastics that can be melted can be used as a substitute for traditional fuel (Dreher et al., 2004). Plastic materials have a very high calorific value comparable to oil (see Table 11 in Al-Salem et al., 2009). Plastics solid waste is derived from petroleum and thus has recoverable energy comparable to other energy sources.

2 Recycling of Rubbers

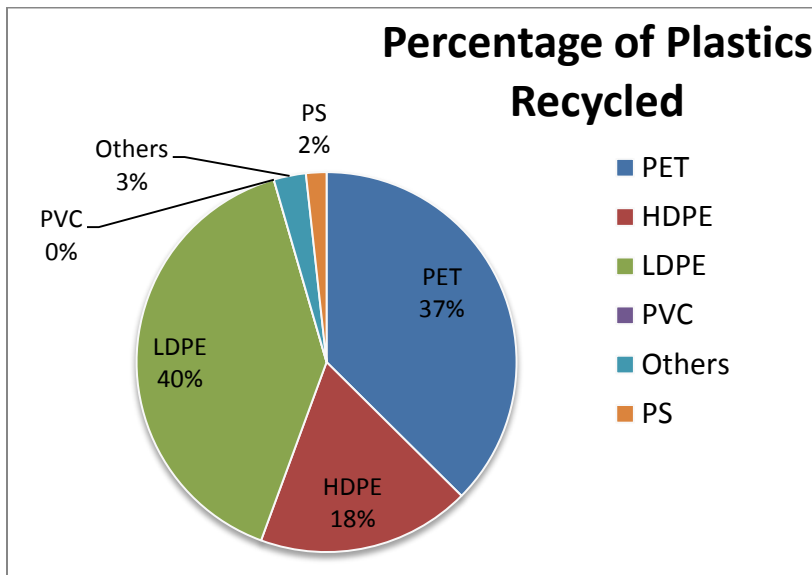
The major method of recycling rubber products is first to grind the material into small pieces using three methods: ambient, cryogenic, and wet grinding (Klingensmith and Rodgers, 2004). Each of these grinding processes results in different sizes and characteristics of the recycled material. Recycled rubber can be used in asphaltic concrete mixes or as a filler material in road construction (Siddique, 2008). Recycled rubber is also being used with polymers such as EVA or SBS copolymers to produce thermoplastic elastomers (TPEs) (Drobny, 2012). The advantages of adding recycled rubber to the asphalt mix are increased skid resistance under icy conditions, improved flexibility and crack resistance, and reduced traffic noise (Siddique, 2008).

In addition, rubbers can be recovered to the original elastomers by several devulcanization processes (Klingensmith and Rogers, 2004). Devulcanization of thermoset rubber materials can result in the loss of physical properties. Ground rubber waste from tires, waste ethylene propylene diene monomer (EPDM) rubber, acrylonitrile rubber, recycled rubber latex waste, silicone rubber and waste plastics also can be recycled into TPEs (Drobny, 2007, a class of copolymers of plastic or rubbers having thermoplastic (melt) and elastomeric properties (McKeen, 2012).

Each class of rubber waste listed above requires specific process and blending components to produce TPEs. For example, latex waste blended with polypropylene to yield a TPE. Vulcanized blends of EPDM, from ground tire scrap and high density polyethylene (HDPE) modified by acrylic acid yield true TPE. SBS (styrene-butadiene – styrene) can be incorporated with rubber powder waste and converted to TPE. Silicone rubber can be converted to a TPE (Basuli et al., 2008). Once the recycled rubber is converted to TPEs, the physical properties remain unchanged with repeated recycling (Drobny, 2012).

3 Volumes of Recycled Plastics

The most widely recycled thermoplastic for the year 2007 was PE (as reported in Merrington, 2011).



Other thermoplastics recycled include polyamides (nylon 6, nylon 6,6, etc.), polycarbonates (PC), acrylics (polymethyl methacrylate (PMMA), styrenics (acrylonitrile butadiene styrene ABS), and blends (thermoplastic polyolefin TPO, PC/ABS, etc.).

4 Problems Associated with the use of Recycled Plastics

The recycling process yields a recovered plastic that can be useful but it can also cause a degradation of the recovered product (Zitting, 1998). Degradation is a complex process related to the forces of mechanical processing, melting temperature (thermo-oxidation) or mechanical-thermo degradation (an increase in temperature created by the mechanical force) (Najafi, 2013). This can result in the following changes in the recovered plastic (Takatori, 2014):

- 1) irreversible changes in the molecular structure or higher order structure during the recycling process;
- 2) deformation caused by heat used in the process;
- 3) chemical reactions occurring during the process that can result in changes in the chemical structure; or
- 4) accumulation of metal catalysis residues.

Recently, Marulanda et al. (2014) examined the effects of how variation in the ratios of recycled to virgin plastic with LDPE, PET and PVC impact the properties of these plastics. Variation in the content of recycled plastics altered the impact strength, hardness, and tensile strength; pointing to the critical importance of a careful characterization of the recycled material before reuse.

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