



TERA

# Exposure Assessment: Potential for the Presence of Phthalates and Other Specified Elements in Undyed Manufactured Fibers and their Colorants

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## Abbreviations

2, 6-NDC	2,6-Naphthalene dicarboxylic acid dimethyl ester
2,6-NDCA	2,6-Naphthalene dicarboxylic acid
A&HCI	Arts & Humanities Citation Index
AAFA	American Apparel & Footwear Association
AATCC	American Association of Textile Chemists and Colorists
Al	Aluminum
As	Arsenic
ASTM	ASTM International
Ba	Barium
BBP	Butyl benzyl phthalate
BDO	1,4-Butanediol
BHET	Bis-(2-hydroxyethyl)-terephthalate
BPO	1,4-Butanediol
Cd	Cadmium
Ca	Calcium
CASRN	Chemical Abstracts Service Registry Number
CDR-CDAT	Chemical Data Reporting-Chemical Data Access Tool
CEPA	Canadian Environmental Protection Act
CHAP	Chronic Hazard Advisory Panel
Co	Cobalt
Cr	Chromium
CPCI-S	Conference Proceedings Citation Index- Science
CPCI-SSH	Conference Proceedings Citation Index- Social Science & Humanities
CPSA	Consumer Product Safety Act
CPSC	U.S. Consumer Product Safety Commission
CPSIA	Consumer Product Safety Improvement Act of 2008
DBP	Dibutyl phthalate
DCHP	Dicyclohexyl phthalate
DEHP	Diethylhexyl phthalate
DHEXP	Di-n-hexyl phthalate
DIBP	Diisobutyl phthalate
DIDP	Diisodecyl phthalate
DINP	Diisononyl phthalate
DIOP	Diisooctyl phthalate
DMP	Dimethyl phthalate
DMT	Dimethyl terephthalate
DnOP	Di-n-octyl phthalate
DPENP	Di-n-pentyl phthalate
DTPA	Diethylenetriaminepentaacetic acid
EBSCO	EBSCO Information Services

EDTA	Ethylenediaminetetraacetic acid
EG	Ethylene glycol
EPA	Environmental Protection Agency
ESCI	Emerging Sources Citation Index
ETAD	Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers
EU	European Union
GAFTI	Global Apparel, Footwear, and Textile Initiative
HBET	Bis(4-hydroxybutyl) terephthalate
HDI	Hexamethylene diisocyanate
Hg	Mercury
HPA	High-pressure asher
HSDB	Hazardous Substances Data Bank
IARC	International Agency for Research on Cancer
ICP	Inductively coupled plasma- optical emission spectrometer
LOD	Limit of detection
LOQ	Limit of quantification
K	Potassium
MDI	Diphenylmethane-4, 4-diisocyanate
Mg	Magnesium
MRSL	Manufacturing restricted substances list
Mo	Molybdenum
Na	Sodium
ND	Not detectable
Ni	Nickel
NIOSH	National Institute for Occupational Safety and Health
NRL	Natural rubber latex
NSCEP	National Service Center for Environmental Publications
NPCS	NIIR Project Consultancy Services
NTA	Nitrilotriacetic acid
OECD	Organisation for Economic Co-operation and Development
OPPT	Office of Pollution Prevention and Toxics' (U.S. EPA OPPT's) InertFinder
owf	weight of the fiber
PAN	Polyacrylonitrile
PA	Polyamide
Pb	lead
PBT	Polybutylene terephthalate
PDO	1,3-Propanediol
PEN	Polyethylene naphthalate
ppm	parts per million
PES	Polyester
PET	Polyethylene terephthalate
PETE	Polyethylene terephthalate

PTT	Polytrimethylene terephthalate
RSL	Restricted-substances list
Sb	Antimony
Se	Selenium
SCI-EXPANDED	Science Citation Index Expanded
SDC	Society of Dyers and Colourists
SSCI	Social Sciences Citation Index
STWI	Sweden Textile Water Initiative
TERA	Toxicology Excellence For Risk Assessment
Ti	Titanium
TODI	3,3'-Dimethyl-4,4'-biphenyl diisocyanate
TPA	Terephthalic acid
TXRF	X-ray fluorescent spectrometry
TZ	LATZ latex
UC	University of Cincinnati
U.S.	United States
UV	Ultraviolet
ZDHC	Zero Discharge of Hazardous Chemicals Group
Zn	Zinc
$\omega$ -amino acid	Omega-amino acid
$\omega$ -aminoundecanoic	Omega-aminoundecanoic acid, 11-aminoundecanoic
$\omega$ -heptanoic acid	Omega-aminoanthic acid, 7-aminoheptanoic acid

## 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. The Consumer Product Safety Improvement Act of 2008 (CPSIA) restricts the presence of six phthalates in children's toys and child care articles and also restricts the solubility of specified heavy metals in toys intended for children under the age of six. This report summarizes the available information on the production of specified undyed manufactured fibers with regards to the possibility of these fibers, or the colorants typically used on these fibers, containing the specified phthalates or elements.

Section 108 of the CPSIA restricts the presence of six 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 three and younger, or to help children age three 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). These 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 three and younger, or to help children age three 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 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 CPSIA also requires toys intended for children under the age of six (or toys or toy parts that are likely to be "sucked, mouthed, or ingested") to comply with Section 4.3.5 of ASTM F963-11 (*Heavy Elements*), of the ASTM International (ASTM, 2011) Standard F963-11, *Standard Consumer Safety Specification for Toy Safety Products* (the Toy Standard). The Toy Standard sets solubility limits for eight chemical elements (antimony, arsenic, barium, cadmium, chromium, lead, mercury, and selenium) in paints, surface coatings, and accessible substrate materials.

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, or chemical elements in concentrations above the specified ASTM soluble limits, and thus, would not require third party testing to assure compliance to Section 108 of the CPSIA or the Toy Standard, respectively.

This report summarizes the available information on the production of specified undyed manufactured fibers (Table 1) with regards to the possibility of these fibers, or their typical colorants, containing certain phthalates at concentrations greater than 0.1 percent (1000 parts per million, or ppm) or specified elements at concentrations greater than their ASTM soluble limits (Table 2).

**Table 1. Manufactured fibers specified for this task order**

<b>Specified Manufactured Fibers</b>
Polyester (Polyethylene terephthalate or “PET”)
Nylon (aliphatic or semi-aromatic polyamides)
Natural latex rubber
Spandex
Rayon
Acrylic fiber (a synthetic fiber of polyacrylonitrile) and Modacrylic (long-chain synthetic polymers composed of less than 85 percent, but at least 35 percent weight acrylonitrile units)

**Table 2. Specified chemical substances and solubility limits**

Chemical	CASRN <sup>a</sup>	Limit
<b>Specified Phthalates</b>		
DEHP: di-(2-ethylhexyl) phthalate	117-81-7	0.1 percent (1000 ppm)
DBP: dibutyl phthalate	84-74-2	
BBP: benzyl butyl phthalate	85-68-7	
DINP: diisononyl phthalate	28553-12-0, 68515-49-1	
DIDP: diisodecyl phthalate	26761-40-0, 68515-49-1	
DnOP: di-n-octyl phthalate	117-84-0	
DIBP: diisobutyl phthalate	84-69-5	
DPENP: di-n-pentyl phthalate	131-18-0	
DHEXP: di-n-hexyl phthalate	84-75-3	
DCHP: dicyclohexyl phthalate	84-61-7	
<b>ASTM F963-11 Standard Consumer Safety Specifications for Toy Safety, Chemical Elements</b>		
Antimony (Sb)	7440-36-0	60 ppm
Arsenic (As)	7440-38-2	25 ppm
Barium (Ba)	7440-39-3	1000 ppm
Cadmium (Cd)	7440-43-9	75 ppm
Chromium (Cr)	7440-47-3	60 ppm
Mercury (Hg)	7439-97-6	60 ppm
Selenium (Se)	7782-49-2	500 ppm
Lead (Pb)	7439-92-1	100 ppm <sup>b</sup>

<sup>a</sup>CASRN stands for *Chemical Abstract Service Registry Number*. A CASRN or CAS number is a unique numerical identifier of a chemical substance.

<sup>b</sup>Lead is not a specified element under the scope of work for this project. With a few exceptions, CPSIA section 101 established a limit for lead content for accessible component parts for children's products. Separately, the Commission has addressed the lead content of certain textile materials. 16 C.F. R. § 1500.91.

The CPSC requested that Toxicology Excellence for Risk Assessment (TERA) investigate the following:

1. A description of the raw materials (including catalysts and additives) used worldwide in the production of the materials used to make the specified manufactured fibers and resultant undyed textiles;
2. A description of the raw materials used worldwide in the production of the colorants (including catalysts and additives) used to dye the specified manufactured fibers;
3. A description of the manufacturing processes used worldwide to create the specified manufactured fibers and the resultant undyed textiles, and their colorants, including the presence (and the concentration information, if available) of any of the specified phthalates or specified elements. If production processes have changed and the likelihood of the specific chemicals being present has significantly decreased over time, the description shall include this history.

4. The potential use of any recycled materials or other additives in the production of the specified manufactured fibers and the resultant undyed textiles, and their colorants which could contain the specified phthalates or the specified elements. Concentration limits or ranges of the specified phthalates or elements shall be included, if available.

TERA focused on fibers that are typically used in consumer applications (as opposed to industrial applications), why the specified phthalates and ASTM elements might be used in the specified fiber, and the range of concentrations used for each. Where appropriate, TERA sought out and reported information on why a specific phthalate or element is unlikely to be present in each of the fibers and explain the reasons why it would not likely be used for that fiber.

TERA's research approach is described in Section 2. Our research was not exhaustive of the worldwide primary literature. TERA first screened secondary sources such as books and government reports for information and supplemented this with information from the primary literature. TERA's focus was to identify relevant information on the most critical areas - raw materials and production of the manufactured fibers and raw materials in the most commonly used dyes. We investigated the potential for the fibers or dyes to contain the specified phthalates and elements in the seven manufactured fibers in order to address the question of whether their use in toys or child care articles may contain any of the specified phthalates or elements in concentrations above their respective limits.

## 1.1 References

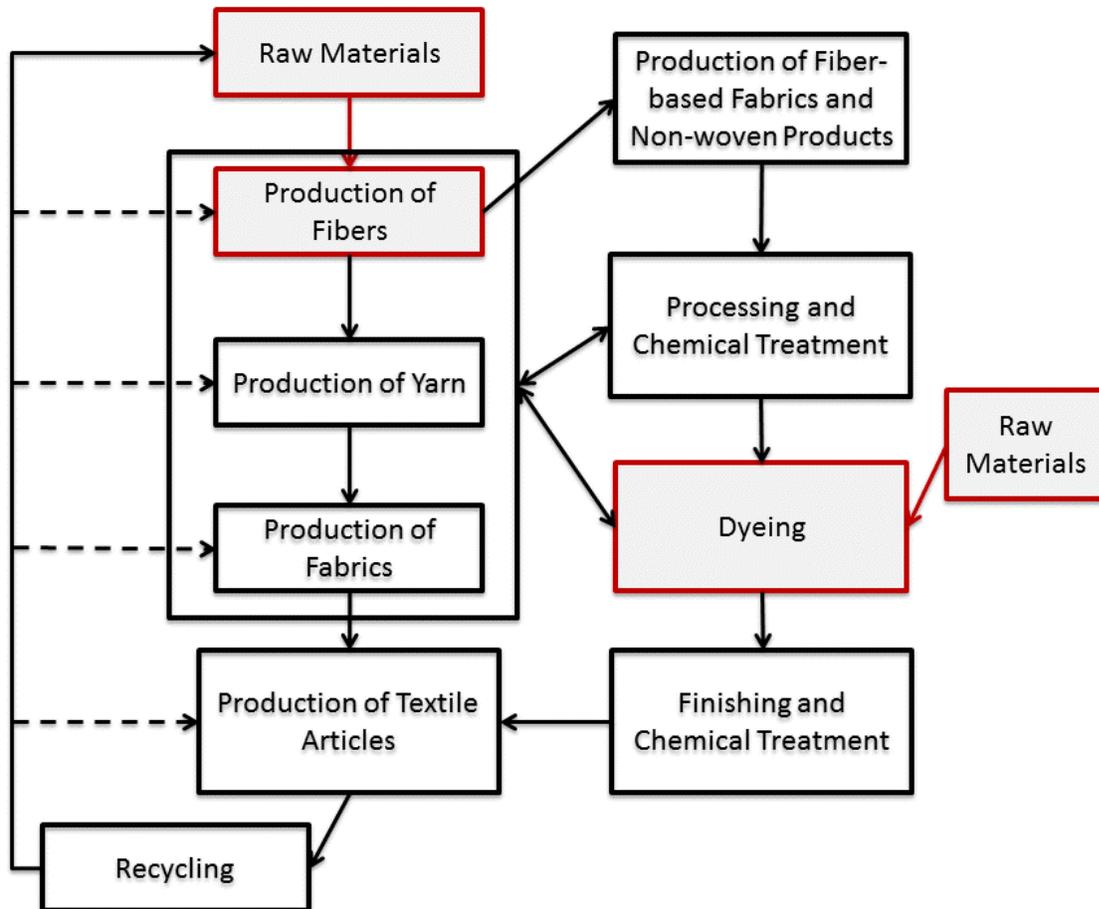
American Society for Testing and Materials (ASTM). 2011. F963-11, *Standard Consumer Safety Specification for Toy Safety Products* (the Toy Standard). ASTM Volume 15.11 Consumer Products; Light Sport Aircraft; Unmanned Aircraft Systems; Aircraft Systems; Unmanned Maritime Vehicle Systems (UMVS); Language Services and Products; General Aviation Aircraft

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 Technical Approach

### 2.1 Research Scope

Manufacturing of finished textile articles for consumer use involves a plethora of raw materials, colorants, additives, auxiliaries, finishing chemicals, and a complex series of production steps, processes, and treatments. The “world of textiles” is vast and intricate, with much of the information proprietary to the manufacturers. Similarly, the world of colorants is also complex, and is comprised of thousands of dyes and pigments, which differ in chemical structure and application processes. Figure 1 illustrates the major steps in the production of textiles.



**Figure 1. Overview of textile article production (modified from Assmuth et al., 2011)**

To focus efforts within the limits of available resources, TERA concentrated research on raw materials and production of fibers and dyes (see red shaded boxes in Figure 1). By focusing on these areas, TERA was able to address the central questions for this project on the presence of the specified phthalates or elements in manufactured fibers:

- What are the raw materials and production processes for the undyed specified fibers?
- What are the raw materials and production processes for the dyes that are most likely to be used on the specified fibers?
- Are any of the specified phthalates or elements used as raw materials or additives in the production of the specified fibers? Of the dyes?

In addition, TERA searched the literature for information for the presence (and concentrations) of the specified phthalates and elements in the specified fibers and their most common dyes. Because of the extremely large number and diversity of colorants used on fibers, research focused on the most commonly used dyes for the specified manufactured fibers in this task order. TERA did not specifically investigate the textiles made from the fibers, raw materials or processes for printing on textiles, or the potential use of recycled materials in manufacturing the fibers or dyes.

It is important to note that there are many other facets to the production of textile articles that were outside the scope of this project. Figure 1 illustrates numerous additional aspects of production that have not been addressed in this report, including processing of fibers to yarn, processing of yarn to fabrics, and processing of fabrics to textile articles. Use of recycled materials to make textiles was not addressed nor was processing or chemical treatment of the fiber, yarn, or fabric prior to dyeing. Finishing and chemical treatment of the textile product (e.g., flame retardancy, surface decoration) were outside the scope of this task. Whether the specified phthalates or elements could be raw materials or additives in processes other than those involved in manufacture of the undyed fiber or manufacture of the common dyes used to color the specified fibers was not investigated in this research.

## 2.2 Literature Review Strategy

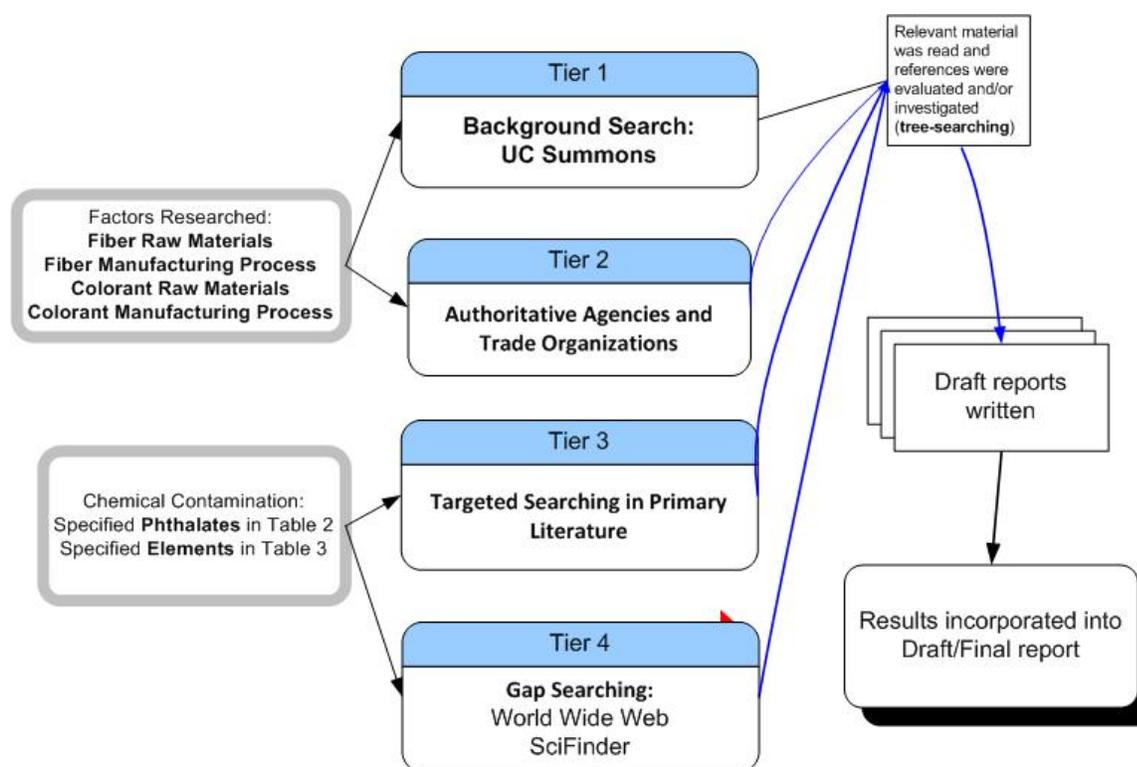
There are hundreds of thousands of factsheets, books, reports, and manuscripts on fibers, colorants, and textiles. TERA used a multi-tiered approach for collection, review, and compilation of relevant information on the six types of fibers and their common dyes for raw materials and manufacturing processes; along with the potential for the 10 specified phthalates and 7 specified elements to be present in the six fibers classes or their dyes. The research involved the following 4-tiered strategy.

Tier 1 determined the “universe” of information; TERA relied upon secondary sources to identify the fiber and dye categories and gather background information. These resources were screened for chemical name(s) and CASRN(s), when possible, to more specifically identify the subject material within each category. Tier 1 utilized the University of Cincinnati (UC) library catalog, a database called “Summon<sup>TM</sup>”, to evaluate all relevant findings for terms in Table 3 (see Section 2.2.1).

Tier 2 evaluated authoritative secondary sources, primarily federal, national, and international agency reports and databases. The databases searched included various United States Environmental Protection Agency (U.S. EPA) websites including the National Service Center for Environmental Publications (NSCEP), Chemical Data Access Tool (CDR-CDAT), the Office of Pollution Prevention and Toxics' (OPPT's) InertFinder , and CEPA Science Inventory . Other websites searched included NIOSH, HSDB, IARC, eChemPortal and Science.gov; the websites are listed in Table 6.

Tier 3 involved primary literature searching for literature related to the manufacturing, raw materials, or chemical concentrations of the specified phthalates and elements for the six subject fibers and the dyes most commonly used on those fibers. 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 using SciFinder and the World Wide Web, targeted for the specific topics with missing or little information. This tier focused primarily on seeking information on concentrations of phthalates and elements in the six fibers and common dyes. Tree searching was routinely performed on relevant sources. The overall research approach for this project is shown in Figure 2.



**Figure 2. Research approach for contamination of textiles and dyes**

### 2.2.1 Tier 1. Universe of Literature

The purpose of Tier 1 was to gain an overview of the available information about the specified undyed fibers and types of dyes. Later tiers would narrow the information from the universe of literature to focus specifically on the potential for the specified fibers or dyes to contain the specified elements or phthalates listed in Table 2 (in Section 1).

In Tier 1, compendia or reviews of literature on the fibers or dyes in reference books, encyclopedias, handbooks, and dissertations were searched with the University of Cincinnati (UC) “Summon<sup>TM</sup>” 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 raw materials used in manufacturing specified fibers, we used the chemical name and/or CASRN. Because this search is focused on books or encyclopedias for information, TERA conducted a test of results using CASRN to be sure it was an effective search term for identification of information for the specified fibers. Using polyethylene terephthalate CASRN “25038-59-9 OR 9003-68-3” as a key search term, only 4 results were found and none were relevant to the topics of this report. Therefore, for the Tier 1 searches, the CASRNs were not used.

As Summon<sup>TM</sup> search engine provides content based on relevance to search terms, the first 100 items in Summon<sup>TM</sup> were evaluated for content based on title, abstract, or Table of Contents. The Summon<sup>TM</sup> search was refined by: 1) limiting the search to articles from scholarly publications; 2) limiting the search to articles from peer-reviewed publications; 3) excluding newspaper articles; 4) limiting the search to content type specific for book chapter/book/eBook; 5) excluding from the search journal article/magazines; and 6) limiting the search to English language only. The Summon<sup>TM</sup> search for textile fibers was conducted in January 2016; and identified 445 sources (Table 3).

The number of books identified within the UC Book Catalog (via the Summon<sup>TM</sup> search engine) obtained with key chemical name relevant to the project is shown in Table 3. The identified information related to the specified fibers, textiles or dyes was reviewed for relevance to the research objective. Relevant books were either checked out of the library or obtained through online UC library resources. Approximately 14 books were used throughout this report and are shown in Appendix A.

**Table 3. Universe of literature for textile fibers from Summon™ (Tier 1)**

<b>Search Terms</b>	<b>No. Hits<sup>a</sup></b>
25038-59-9 OR 9003-68-3	4
Polyethylene terephthalate OR 25038-59-9 OR 9003-68-3	10
Polyethylene terephthalate AND fibers	13
Polyethylene terephthalate AND textile	4
Nylon AND fiber AND textiles	39
Natural latex rubber	78
Natural latex rubber AND fiber	24
Spandex OR Polyurethane OR 9009-54-5	7
Spandex AND fiber	27
Rayon and fiber	62
Acrylic fiber	173
Modacrylic	4
<b>Total Screened</b>	<b>445</b>

<sup>a</sup>Hits 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.

A slightly different approach was used for the Summon™ search on colorants and dyes conducted in May 2016. The results were refined extensively to ensure relevant books were identified. The refinements excluded: newspaper, magazine, market research, book review, and patents. Thousands of hits were returned by the searches. Using 10 different keyword dye searches, the first 40 results were closely screened and relevant items were added to an EndNote library and reviewed (shown in Table 4).

After review of titles and/or abstracts, 8 references were selected from Tier 1 to develop an introduction to the literature for the six fibers. For the dyes, 21 references (of the 400 screened) were utilized.

### **2.2.2 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 plastics, TERA obtained useful information for raw materials, manufacturing, applications, and potential contamination/migration from authoritative secondary sources based on a search of

**Table 4. Universe of literature for dyes and textile fibers from Summon™ (Tier 1)**

Search Terms	No. Hits	Relevant downloaded and reviewed
textile manufacturing AND dye	629,930	1
textile fiber AND dye	78,899	refined <sup>a</sup>
textile fiber AND dye: excluded: newspaper, magazine, market res, book review, patent	70,139	1
textile fiber AND colorant	12,046	refined
textile fiber AND colorant: excluded: newspaper, magazine, market res, book review, patent	8,797	4
textile fiber AND direct dye	60,931	refined
textile fiber AND direct dye: excluded: newspaper, magazine, market res, book review, patent	22,466	1
textile fiber AND reactive dye	29,136	refined
textile fiber AND reactive dye: excluded: newspaper, magazine, market res, book review, patent	17,001	4
textile fiber AND vat dye	19,525	refined
textile fiber AND vat dye: excluded: newspaper, magazine, market res, book review, patent	5,135	3
textile fiber AND disperse dye	23,237	refined
textile fiber AND disperse dye: excluded: newspaper, magazine, market res, book review, patent	10,615	1
textile fiber AND basic dye	61,017	refined
textile fiber AND basic dye: excluded: newspaper, magazine, market res, book review, patent	21,727	4
textile fiber AND acid dye	64,700	refined
textile fiber AND acid dye: excluded: newspaper, magazine, market res, book review, patent	27,699	1
azo dye AND nylon	7,603	1
<b>Total screened: 400</b>		<b>21</b>

<sup>a</sup>Refined – search was too large or off research target; screen was refined by adding additional key terms or limiting the results by publication type.

the World Wide Web. A total of 49 websites had been identified as potentially useful from previous projects (Appendix B). Of these, fewer than 10 contained relevant information on raw materials or manufacturing of various materials. The websites previously found to be most relevant were reviewed in this tier for potential data for phthalates and dyes in the fibers of interest. Many of the sources from government regulatory agencies contained information or reports of chemical agents and were familiar to TERA. While we searched only in English, we identified sources from all over the world.

TERA searched four U.S. EPA websites and five other authoritative web sites using the specified fiber class as the only search term (Table 5) so as to broadly identify any relevant sources. Potential for chemical concentrations was screened from the information obtained for each fiber from reviews, factsheets, regulatory documents, or risk assessments. Searches were conducted during July 2016 on the following websites: U.S. EPA websites including the National Service Center for Environmental Publications (NSCEP), Chemical Data Access Tool (CDR-CDAT), OPPT's InertFinder, and CEPA Science Inventory. Other websites searched included NIOSH, HSDB, IARC, RIVM, eChemPortal, and Science.gov. Table 6 lists the websites searched in Tier 2. Little useful information regarding concentration of the specified phthalates or elements in the specified fibers was found on these websites.

**Table 5. Tier 2 secondary literature (website) search terms**

Search Terms
Polyester
Nylon
Spandex
Polyurethane
Rayon
Viscose
Acrylic
Acrylic fiber
Modacrylic

**Table 6. Relevant websites searched in Tier 2**

Database	Website
U.S. EPA (CDR, NSCEP, OPPTS, Science Inventory)	<a href="http://www.epa.gov/nscep/">http://www.epa.gov/nscep/</a> <a href="http://java.epa.gov/oppt_chemical_search/">http://java.epa.gov/oppt_chemical_search/</a> <a href="http://cfpub.epa.gov/si/">http://cfpub.epa.gov/si/</a> <a href="http://iaspub.epa.gov/apex/pesticides/f?p=INERTFINDER:1:1395578990735::NO:1:">http://iaspub.epa.gov/apex/pesticides/f?p=INERTFINDER:1:1395578990735::NO:1:</a>
HSDB	<a href="http://toxnet.nlm.nih.gov/newtoxnet/hsdb.htm">http://toxnet.nlm.nih.gov/newtoxnet/hsdb.htm</a>
NIOSH	<a href="http://www.cdc.gov/niosh/">http://www.cdc.gov/niosh/</a>
IARC	<a href="http://monographs.iarc.fr/ENG/Monographs/PDFs/index.php">http://monographs.iarc.fr/ENG/Monographs/PDFs/index.php</a>
OECD	<a href="http://www.echemportal.org/echemportal/participant/page.action?pageID=9">http://www.echemportal.org/echemportal/participant/page.action?pageID=9</a>
U.S. Federal Science	<a href="http://www.science.gov/searchdbs.html">http://www.science.gov/searchdbs.html</a>

### 2.2.3 Tier 3. Literature Searching

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

- Evaluating the databases available through the UC library, to identify 3-4 databases that would provide wide coverage for textile fibers and dyes; and
- Searching the identified databases for fibers and dyes of interest in combination.

In the first approach, TERA searched three online databases: Web of Science Core Collection, EBSCO's (EBSCO Information Services) Academic Search complete, and ProQuest Research Library. Information regarding these databases is in Appendix C. A span of approximately ten years (2006-present) was used to narrow the results. The search string used for the various fibers, dyes, phthalates and elements is shown in Table 7. The number of hits within the three databases is shown in Table 8. Combinations of the search strings shown in Table 8 were the ultimate goal of this primary literature search. If the results were too numerous, then the search was narrowed with the addition of refinements as shown in Table 9. All hits for search strings were recorded, saved, and downloaded into an EndNote library. TERA thoroughly screened the literature search results for relevancy and likelihood for a study to contain needed information on phthalate and element concentrations in the specified textile fibers and/or their dyes.

Screening of the literature searches focused on English language articles in accessible and reputable journals; patents and literature in obscure journals or in foreign languages was not retrieved for this report.

**Table 7. Example of search term strings**

String search name	String searches for primary literature
Phthalates	DEHP OR di-2-ethylhexyl phthalate OR 117-81-7 OR DBP OR dibutyl phthalate OR 84-74-2 OR BBP OR benzyl butyl phthalate OR 85-68-7 OR DINP OR diisononyl phthalate OR 28553-12-0 OR 68515-48-0 OR DIDP OR diisodecyl phthalate OR 26761-40-0 OR 68515-49-1 OR DnOP OR di-n-octyl phthalate OR 117-84-0 OR DIOP OR diisooctyl phthalate OR 27554-26-3 OR DIBP OR diisobutyl phthalate OR 84-69-5 OR DPENP OR di-n-pentyl phthalate OR 131-18-0 OR DHEXP OR di-n-hexyl phthalate OR 84-75-3 OR DCHP OR dicyclohexyl phthalate OR 84-61-7
Elements	Antimony OR 7440-36-0 OR Arsenic OR 7440-38-2 OR Barium OR 7440-39-3 OR Cadmium OR 7440-43-9 OR Chromium OR 7440-47-3 OR Mercury OR 7439-97-6 OR Selenium OR 7782-49-2
Dyes	naphthol dye* OR azoic dye* OR vat dye* OR van dye* OR sulfur dye* OR Reactive Dye* OR acid dye* OR Basic dye* OR cationic Dye* OR

String search name	String searches for primary literature
	Disperse Dye* OR nonionic dye* OR Metal-complex dye* OR mordant dye* OR direct dye*
Textile Fibers	polyester OR spandex OR polyurethane OR acrylic OR modacrylic OR nylon OR polyamide OR Rayon OR viscose Polyethylene terephthalate OR Polytrimethylene terephthalate OR polyethylene naphthalate OR 30965-26-5 OR 24968-12-5 OR Polybutylene terephthalate OR Natural latex rubber OR natural rubber latex OR 25038-59 OR 9003-68-3 OR 9004-34-6 OR 25014-41-9 OR 26590-75-0 OR 25853-85-4 OR 30965-26-5 OR 24968-12-5 OR 32131-17-2 OR 25038-54-4 OR 9008-66-6 OR 50327-22-5 OR 24035-01-2 OR 25035-04-5 OR 24937-16-4 OR 9009-54-5 OR 61788-77-0

**Table 8. Primary literature search results using string searches<sup>a</sup>**

Database	String Combination	No. Hits
Web of Science	Phthalates	39,120
	Elements	1,364,704
	Dyes	126,535
	Textile Fibers	415,819
	<b>Total:</b>	<b>1,946,178</b>
EBSCO	Phthalates	30,327
	Elements	244,673
	Dyes	15,440
	Textile Fibers	145,967
	<b>Total:</b>	<b>436,407</b>
ProQuest Research Library	Phthalates	895
	Elements	10,370
	Dyes	2802
	Textile Fibers	6952
	<b>Total:</b>	<b>21,019</b>

<sup>a</sup>Literature search conducted July 2016

**Table 9. Primary literature search results using combination string searches<sup>a</sup>**

Database	String Combination	No. Hits
Web of Science	Phthalate+Materials	66
	Element+Materials	1040
	Element+Materials Refined by: TOPIC: (textiles OR fiber)	112
	Phthalate+Materials+Dyes	14
	Element+Materials+Dyes	176
	Element+Materials+Dyes: Refined to articles	35
	<b>Web of Science Total obtained:</b>	<b>227</b>
EBSCO	Phthalate+Materials	42
	Element+Materials	551
	Element+Materials Refined by: TOPIC: (textiles OR textile industry OR fiber*)	93
	Phthalate+Materials+Dyes	0
	Element+Materials+Dyes	4
	<b>EBSCO Total obtained:</b>	<b>139</b>
ProQuest	Phthalate+Materials	43
	Element+Materials	542
	Element+Materials Refined by: TOPIC: (fibers OR textiles)	266
	Element+Materials Refined by: TOPIC: (fibers OR textiles) Refined by: Peer Reviewed	35
	Phthalate+Materials+Dyes	8
	Element+Materials+Dyes	89
	<b>ProQuest Research Library Total obtained:</b>	<b>175</b>

<sup>a</sup>Literature string combination search conducted July 2016

In the second approach, literature search results were imported into EndNote libraries (excluding duplicates) resulting in a master library of approximately 1,454 references. The various search term strings were used to search through the high volume of references and to hone in on those fibers with specific types of dyes and concentrations of the specified phthalates and specified elements.

#### 2.2.4 Tier 4. Gap Searching

As a final step, TERA conducted searches on the World Wide Web to fill any remaining data gaps, primarily through Google ([www.google.com](http://www.google.com)), Google Scholar ([www.scholar.google.com](http://www.scholar.google.com)) and SciFinder. Based on the fiber, phthalate, element, dye, and type of information still needed,

these searches were performed using CASRN, chemical names, and keywords (keywords as listed in Table 10). Other terms used for this search include those shown in Table 4.

**Table 10. Example of search terms using combinations string searches for gap searching via Google, SciFinder, or Google Scholar**

<b>Contaminant</b>	<b>Contaminant, continued</b>
Phthalate AND Rayon	Phthalate AND Nylon
Antimony AND Rayon	Antimony AND Nylon
Barium AND Rayon	Barium AND Nylon
Cadmium AND Rayon	Cadmium AND Nylon
Chromium AND Rayon	Chromium AND Nylon
Mercury AND Rayon	Mercury AND Nylon
Selenium AND Rayon	Selenium AND Nylon
Phthalate AND Spandex	Phthalate AND Natural Latex Rubber
Antimony AND Spandex	Antimony AND Natural Latex Rubber
Barium AND Spandex	Barium AND Natural Latex Rubber
Cadmium AND Spandex	Cadmium AND Natural Latex Rubber
Chromium AND Spandex	Chromium AND Natural Latex Rubber
Mercury AND Spandex	Mercury AND Natural Latex Rubber
Selenium AND Spandex	Selenium AND Natural Latex Rubber
Phthalate AND Polyester	Phthalate AND Acrylic
Antimony AND Polyester	Antimony AND Acrylic
Barium AND Polyester	Barium AND Acrylic
Cadmium AND Polyester	Cadmium AND Acrylic
Chromium AND Polyester	Chromium AND Acrylic
Mercury AND Polyester	Mercury AND Acrylic
Selenium AND Polyester	Selenium AND Acrylic

## 2.3 References

Assmuth, T., P. Hakkinen, J. Heiskanen, et al. 2011. Case Study Textiles. The Finnish Environment Institute.

## 3 Undyed Fibers

### 3.1 Polyester Fibers

CASRN: 25038-59-9 and 9003-68-3 (Polyethylene terephthalate, PET); 26590-75-0 (Polytrimethylene terephthalate, PTT); 25853-85-4 (polyethylene naphthalate, PEN); and 30965-26-5 and 24968-12-5 (Polybutylene terephthalate, PBT)

#### 3.1.1 Introduction

Polyester is a family of polymers that contain the ester functional group in the polymer backbone (Edlund and Albertsson, 2003). The term “polyester” now seems to be synonymous with polyethylene terephthalate (PET; sometimes referred to as PETE). Polyester fiber is a manufactured fiber consisting of synthetic linear macromolecules having in the chain at least 85 percent (by mass) of an ester of a diol (Hauser, 2011; Chaterjee and Gupta, 2002; Afirm Group, 2016; Polymer Properties Database, 2015). Commercially, polyester fibers used in the textile industry are mainly semi-aromatic polyesters. Examples of the aromatic dicarboxylic acids used in the manufacture of these polyesters include terephthalic acid, phthalic acid, or anhydride and naphthalene dicarboxylic acid.

Polyester fibers include the following:

- PET, the most widely used polyester fiber, is produced from ethylene glycol (EG) and either dimethyl terephthalate (DMT) or terephthalic acid (TPA);
- Polytrimethylene terephthalate (PTT) is a polymer of 1,3-propanediol (PDO) and DMT or TPA;
- Polyethylene naphthalate (PEN), which is the polymer of EG and 2,6-naphthalene dicarboxylic acid dimethyl ester (2,6-NDC) or 2,6-naphthalene dicarboxylic acid (2,6-NDCA, also known as naphthalene-2,6-dicarboxylate);
- Polybutylene terephthalate (PBT) is produced by the polymerization of 1,4-butanediol (BDO) and TPA.

Polyester fibers exhibit a wide range of characteristics (Koh, 2011) including hydrophobicity, high resistance to bending deformations and to abrasion, resistance to chemical damage (by most common chemicals), and excellent resistance to oxidizing and reducing agents.

### 3.1.2 Raw Materials Used Worldwide to make Undyed Polyester fibers and Undyed Polyester Textile Fabrics

The raw materials used in making polyester fibers and undyed polyester textile fabrics (Afirm Group, 2016; Chan and Thomas, 2012; Banat and El-Rub, 2001; Kirk-Othmer, 2014; Wu, 2012; Broadbent, 2001; Koh, 2011; Nexant, Inc., 2010; Fink, 2014; Kurian et al., 2005; U.S. EPA 1995) include:

- *Monomers*: dimethyl terephthalate (DMT); terephthalic acid (TPA); ethylene glycol (EG); 1,3-propanediol (PDO); 2,6-naphthalene dicarboxylic acid dimethyl ester (2,6-NDC); 2,6-naphthalene dicarboxylic acid (2,6-NDCA); 1,4-butanediol (BDO)
- *Initiators/catalysts/reaction accelerators*: zinc acetate; zinc chloride; calcium acetate; manganese acetate; antimony trioxide; antimony acetate; antimony pentoxide; antimony triacetate; germanium dioxide; lead; stannous (tin) octanoate; tin oxalate; tetrabutyl titanate; dibutyltin oxide; sodium methoxide
- *Dispersing agents*: soap powder; Turkey Red Oil (sulphated castor oil); alkylsulfates; alkylarylsulfonates; fatty alcohol ethylene oxide condensates; naphthalene- $\beta$ -sulfonate; formaldehyde; ligninsulfonates; alkyl naphthalene formaldehyde condensates; sodium oleyl-*p*-anisidide sulphonate; polycondensates of arylsulfonic acids with formaldehyde; condensation products of naphthalene-beta-sulfonate and formaldehyde; the product obtained by condensing cresol with formaldehyde in the presence of sodium sulfite and further condensing with beta-naphthol-6-sulfonic acid
- *Crystallization of PEN prepolymer*: a low molar mass poly(ethylene); a low molar mass poly(amide); poly(1,4-butylene sebacate)
- *Stabilizers*: phosphates; phosphonates; phosphonic acid
- *Antioxidants*: sterically hindered phenols
- *Lubricants*: vegetable and mineral oils (unspecified); finishing oils (unspecified); 4-ethyl-4-hexadecyl morpholinium ethyl sulfate
- *Ultraviolet (UV) stabilizers or absorbers*: sterically hindered phenols; benzotriazole; hydroxybenzophenones
- *Fillers*: titanium dioxide; carbon black

### 3.1.3 Manufacturing Processes used Worldwide to Produce Undyed Polyester Fibers and Undyed Polyester Textile Fabrics

Polyester fibers are commercially prepared worldwide by transesterification and direct esterification processes followed by polycondensation (Afirm Group, 2016; Kirk-Othmer, 2014; Broadbent, 2001; Kent, 2012; U.S. EPA, 1995).

### **3.1.3.1 PET**

PET fiber is produced commercially from transesterification of DMT with EG or direct esterification of purified TPA with EG (U.S. EPA, 1995). The DMT process is the older of the two processes (U.S. EPA, 1995). Both batch and continuous operations are used to produce PET using DMT, while a continuous process is used to produce PET using TPA (U.S. EPA, 1995). The first stage of the manufacturing process using DMT is referred to as transesterification (ester interchange) and the process using TPA is known as direct esterification. Banat and El-Rub (2001) and Kirk-Othmer (2014) reported that a transesterification catalyst, particularly antimony-based, such as antimony trioxide, is required by the DMT process. A catalyst is omitted in the direct esterification process using TPA because the reaction is self-catalyzed by the carboxylic acid groups. Salts of divalent metals, such as zinc, calcium, and manganese, are the prevalent transesterification catalysts (Kirk-Othmer, 2014; Wu, 2012; Fakirov, 2002). Broadbent (2001) also reported that in the DMT process, DMT initially reacts with an excess of EG in the presence of sodium methoxide as catalyst. Both the DMT and TPA processes produce bis-(2-hydroxyethyl)-terephthalate (BHET) monomer as the intermediate in the first stage. In addition to BHET, the DMT process produces methanol while the TPA process produces water; these by-products are subsequently removed from the reaction vessel. The BHET formed is subjected to a polycondensation process that produces polyester PET fiber, and this process is driven by the removal of glycol (Kirk-Othmer, 2014). Wu (2012) reported that because the original fiber is transparent, fillers are added before polycondensation depending on the desired colors. The author indicated that titanium dioxide is commonly added during the transesterification process to dull the fiber and that carbon black is sometimes added for black coloration. After the polymer is formed, it is pumped directly to fiber spinning units or it is solidified and collected as pellets to be remelted later for spinning (Kirk-Othmer, 2014).

The Afirm Group (2016) and Kirk-Othmer (2014) reported that the polycondensation for both DMT and TPA processes occurs in the presence of catalysts such as antimony-, germanium-, and titanium-derivatives in the range of a few hundred ppm. In addition to the use of antimony trioxide as the most commercially popular catalyst for this stage, others (Banat and El-Rub, 2001) also reported that antimony acetate, antimony pentoxide, antimony triacetate, and germanium dioxide also have been used as catalysts. The Afirm Group (2016) and Kirk-Othmer (2014) further indicated that the resulting polycondensation polymer contains up to 4 percent by mass of oligomers (di- and trimers), mainly a cyclic trimer of ethylene terephthalate (Broadbent, 2001; Afirm Group, 2016). In addition, stabilizers, antioxidants, and UV-stabilizers (see Section 3.1.2) listed above are added as additives to avoid thermal, thermo-oxidative, or hydrolytic degradation (Afirm Group, 2016).

Fakirov (2002) reported that inorganic contaminants, including metal-containing colored species from catalyst residues and degradation products or originating from impurities in the TPA monomer feed, may be present in the fiber in ppm concentrations. Elements such as iron (Fe),

cobalt (Co), molybdenum (Mo), nickel (Ni), titanium (Ti), chromium (Cr), calcium (Ca), aluminum (Al), magnesium (Mg), sodium (Na), and potassium (K), in concentrations of 1 ppm or lower may be present in the TPA monomer. Banat and El-Rub (2001) also reported that PET is produced from very pure TPA and that the specifications for PET production include:

Ash content	≤ 15 ppm
Metals	≤ 10 ppm
Fe, Ca, Al, Na, K	≤ 2 ppm
Co, Mo, Cr, Ni, Ti, Mg	≤ 1 ppm
4- Carboxybenzaldehyde	≤ 25 ppm
Water content	≤ 0.5 percent

There was no mention of any of the phthalates of concern (specified for this project) contaminating the monomers or the PET product.

### **3.1.3.2 PTT**

As with all polyesters, PTT is produced by transesterification of DMT with 1,3-propanediol (PDO) or direct esterification of purified TPA with PDO, followed by a polycondensation reaction (Chan and Thomas, 2012; Kurian et al., 2005). The transesterification reaction between DMT and PDO is carried out in the presence of a hot catalyst such as titanium butoxide and dibutyl tin oxide. Kurian et al. (2005) also indicated that additives (unspecified) are also added at this stage in the ester exchanger. The important byproducts of this reaction include acrolein, methanol, and allyl alcohol (Kurian et al., 2005). The direct esterification involves the reaction between PDO and PTA, but this process is considered the less economic and commercially viable method compared to the transesterification method.(Chan and Thomas, 2012). According to Chan and Thomas (2012), titanium-based catalysts are used in PTT synthesis, but the PTT is discolored; antimony-based catalysts are only active in the polycondensation reaction, and tin-based compounds have lower catalytic activity. Studies conducted by other researchers (ShuYong et al., 2008) revealed stannous (tin) octanoate, tin oxalate, tetrabutyl titanate, and dibutyltin oxide as very promising catalysts for PTT synthesis, with tin oxalate as the most promising catalyst. However, it is not clear if these catalysts have found commercial use in the synthesis of PTT. The intermediate formed is prepolymerized PTT, which is then pelletized and may be shipped from production facilities in this form (Kurian et al., 2005). The pellets must be clean, dry, and free from other polymers or impurities before remelting. The pellets are remelted to molten polymer, which is cast, spun, or otherwise processed into intermediate and end-use products (Kurian et al., 2005).

### **3.1.3.3 PEN**

Two processes are similarly used in the commercial production of PEN. The first step is either transesterification or a direct esterification (Cho et al., 1999). In the ester-interchange reaction, 2,6-naphthalene dicarboxylic acid dimethyl ester (2,6-NDC) and EG are reacted in the presence of catalysts such as zinc acetate or manganese acetate. For the direct esterification, 2,6-naphthalene dicarboxylic acid (2,6-NDCA) is reacted with EG. For the dimethyl ester process, Fink (2014) lists zinc acetate, zinc chloride, calcium acetate, and manganese acetate as catalysts; no catalyst is used when the acid is used in the direct esterification process. Similar to PET production, bis(beta-hydroxyethyl)naphthalate, initially formed from either the ester-exchange reaction or direct esterification, undergoes polycondensation in the presence of antimony trioxide as the polymerization catalyst (Cho et al., 1999; Fink, 2014). Methanol is the by-product of the dimethyl ester process. Cho et al. (1999) and Fink (2014) reported that metal compounds such as antimony (especially the trioxide), titanium, germanium (e.g., germanium oxide), tin, zinc (e.g., zinc acetate), manganese (e.g., manganese acetate), lead, as well as or a combination of antimony trioxide and trimethyl phosphate are also used to accelerate and advance the reaction in producing PEN (Cho et al., 1999; Fink, 2014).

### **3.1.3.4 PBT**

PBT also is produced by a batch or continuous production process via transesterification of 1,4-butanediol (BDO) with DMT, followed by polycondensation of the resulting bis( $\delta$ -hydroxy butyl)terephthalate (HBET). The other process, a continuous production process, involves the direct esterification of purified TPA with BDO, followed by a pre-polymerization and polycondensation steps with HBET (Nexant, Inc., 2010; Fink, 2014).

Unspecified fillers, reinforcing materials, and additives can be incorporated during compounding to produce materials suitable for many different applications. The materials are then processed mainly by injection molding, but PBT is also used in special extrusion and fiber spinning processes.

## **3.1.4 Processing of Polyester Fibers**

Polyester fibers are made from the various polyester polymers by direct melt spinning or by melting and spinning the polymer chip (Kirk-Othmer, 2014; U.S. EPA 1995). Melt spinning uses heat to melt the polymer. The heated polymer is forced through a spinneret to form filaments that are passed into relatively cooler air that solidifies the filament (U.S. EPA, 1995; Broadbent, 2001). Alternatively, the molten polymer can be processed in an inert gas atmosphere (usually nitrogen). The cooled filaments can either be cut into staple or wound onto spools. The molten polymer fiber also can be pumped out to form blocks as it cools and solidifies. At many facilities, the chips or pellets are stored prior to being shipped. Chips or pellets may be melted to

molten polymer, which is cast, spun, or otherwise processed into intermediate and for end-product fabrication (U.S. EPA, 1995; Kurian et al., 2005).

In summary, none of the specified phthalates were reportedly used in the manufacture or processing of the undyed polyester fiber. Among the specified elements, antimony compounds may be used as a catalyst in polycondensation for both DMT and TPA processes at a concentration that may exceed the 60 ppm limit (100 ppm). Thiele (2004) corroborated that greater than 90 percent of worldwide polyester is manufactured by adding antimony-based catalysts at concentrations of 150-300 ppm antimony during polycondensation. In addition, chromium was identified as a potential impurity at  $\leq 1$  ppm, lower than its soluble limit of 60 ppm (Banat and El-Rub, 2001).

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## 3.2 Nylon Fibers

Aliphatic polyamides:

Nylon 6/6, CASRN 32131-17-2; Nylon 6, CASRN 25038-54-4; Nylon 6/10, CASRN 9008-66-6; Nylon 6/12, CASRN 24936-74-1; Nylon 4/6, CASRN 50327-22-5; Nylon 7, CASRN 24035-01-2; Nylon 11, CASRN 25035-04-5; Nylon 12, CASRN 24937-16-4

### 3.2.1 Introduction

Nylon is the generic name for all long-chain polyamides containing recurring amide groups (-NH-CO-) as an integral part of the main polymer (Gooch, 2011). Nylon is also defined by the U.S. Federal Trade Commission as “any polyamide having less than 85 percent of the amide groups directly connected to two aromatic groups.” This definition is specifically for a fiber (Kirk-Othmer, 2014). The fibers are made of both aliphatic and aromatic polyamides. Polyamides containing 85 percent or greater of the amide bonds attached to aromatic rings are classified as aramids (Kirk-Othmer, 2014). However, aramids are not a subject of this research.

The aliphatic nylons are manufactured from intermediates including dicarboxylic acids, diamines, amino acids, and lactams. Nylons are crystalline polymers. They are identified by dual numbers that denote the number of carbon atoms in the polymer chain derived from specific constituents (Gooch, 2011). The number of the carbon atoms in the diamine is given first in denoting the polymer. If a second number is used, it denotes the number of carbons derived from a diacid. For example, in the case of nylon 6,6, the first “6” indicates the number of carbon atoms in the diamine (hexamethylenediamine) and the second “6” indicates the number of carbon atoms in the acid (adipic acid). It is noted here that in the literature, these numbers may be written as 6,6, 6/6, 6.6, 6-6, and sometimes the numbers precede, rather than follow, the word “nylon” or “polyamide”. A single numeral can also be used to denote the polymer, as in nylon-6. In this case, the number signifies that the monomer was an omega-amino acid ( $\omega$ -amino acid) or a lactam (Gooch, 2011; Brydson, 1999). Nylon-6,10 (6.10, 610, or 6/10) is formed from reacting hexamethylenediamine with sebacic acid (10-carbon atoms (Brydson, 1999). The common practice in Europe is to use the designation “polyamide,” often abbreviated PA, instead of “nylon” in the name [Polyamide (or PA) 6/6].

The bulk of polyamide materials are used in the form of fibers (Brydson, 1999). There are many types of nylon fibers. Among the nylons, nylon-6,6 and nylon-6 are the principal commercial nylons and they account for nearly all of the polyamides produced for fiber applications (Brydson, 1999; Kirk-Othmer, 2014). Nylon-6,12 and its copolymers are also used as engineering resins for specialty applications and in the manufacture of toothbrush bristles and fishing line (Kirk-Othmer, 2014). As nylon-6,12 does not have applications relevant to textiles, it is not further addressed in this report.

### **3.2.1.1 Raw Materials Used Worldwide to make Undyed Polyamide fibers and Undyed Polyamide Textiles**

The focus of this research is on specific undyed fibers and textiles. The raw materials used in making undyed polyamide fibers and undyed polyamide textile fabrics include (Kirk-Othmer, 2014; Brydson, 1999):

- *Monomers*: hexamethylenediamine; adipic acid; sebacic acid; decane-1, 10-dicarboxylic acid (dodecanedioic acid); azelaic acid; 1,4-diaminobutane; hexamethylenediammonium adipate; caprolactam; laurolactam; dodecanolactam; acetic caprolactum; 11-aminoundecanoic acid
- *Initiators/catalysts/reaction accelerators*: water; unspecified acid, base, or amino acid; nylon-6,6 salt; phosphoric acid; hypophosphoric acid
- *Solvents*: water; methanol
- *Molecular weight modifier or chain termination agents*: acetic acid; bislactams; bisoxazolines

### **3.2.1.2 Manufacturing Processes used Worldwide to Produce Undyed Polyamide Fibers and Undyed Polyamide Textile Fabrics**

Many processes are used commercially for the production of the fiber-forming aliphatic polyamides. However, three major processes are in use and include (Brydson, 1999; Kirk-Othmer, 2014):

1. Polycondensation that involves reaction of diamines with dicarboxylic (diacids), via a 'nylon salt';
2. Ring-opening polymerization or opening of a lactam ring; and
3. Self-condensation of an  $\omega$ -amino acid.

#### **3.2.1.2.1 The reaction of diamines with dicarboxylic acids, via a “nylon salt”**

This process is used in the production of aliphatic polyamides including nylon-6,6 and other aliphatic nylons such as nylon-4,6, 6,9, and 6,10 (Brydson, 1999; Kirk-Othmer, 2014).

In the case of nylon-6,6, the polymer is produced by the reaction of hexamethylenediamine with adipic acid in boiling methanol (Brydson, 1999). The resulting insoluble salt, hexamethylenediammonium adipate, precipitates out. The salt is then diluted to a 60 percent aqueous solution and then run in an autoclave in the presence of a trace of acetic acid, which acts as a molecular weight modifier. The vessel is sealed and purged with oxygen-free nitrogen. The reaction proceeds at specified temperatures and pressures, and the polymer is extruded onto a

water-cooled casting wheel, resulting in the formation of a ribbon that is subsequently disintegrated (Brydson, 1999). A similar technique is used to prepare nylon-6,10 from the appropriate salt (the acid being sebacic acid).

Kirk-Othmer (2014) indicated that nylon-6,6 can be prepared starting from the nylon-6,6 salt, hexamethylenediammonium adipate, using either the batch or autoclave process and the continuous polymerization process that produces a dry salt. According to Kirk-Othmer (2014), this dry salt is quite stable and used to transport ingredients for nylon-6,6 over long distances.

In the case of the autoclave process, the salt is concentrated and polymerized, resulting in the formation of oligomers. Additives, such as stabilizers, can be injected at this point in the process (Kirk-Othmer, 2014). Adjusting the temperature and pressure, and allowing sufficient time, enables the reaction to reach an equilibrium. When the polymerization is complete, a series of continuous polymer strands have been formed, which can be cut into small cylindrical pellets. The pellets are dried and stored for further processing or sale.

In the continuous process, the salt solution is concentrated is followed by an initial polymerization that leads to the production of a higher molecular weight polymer (Kirk-Othmer, 2014) that is pelletized. Additives (not specified) can be added at various points along the continuous process (Kirk-Othmer, 2014).

Kirk-Othmer (2014) also described a batch and continuous solid-phase polymerization process as an alternative method for making high molecular weight nylon-6,6. The pellets produced via the batch or continuous process are dried, spun, compounded, and cooled, and then packaged or stored.

### **3.2.1.2.2 Ring-opening polymerization or opening of a lactam ring – Nylon 6 and Nylon 12**

Ring-opening polymerization is the method used to convert lactams to polyamides. The predominantly used commercial process for the production of nylon-6 involves hydrolytic polymerization (Brydson, 1999; Kirk-Othmer, 2014). This involves heating lactams in the presence of water above the melting point of the polyamide (Brydson, 1999). The hydrolytic process can be batch or continuous (Kirk-Othmer, 2014).

Brydson (1999) described a manufacturing process for nylon-6 where caprolactam, water (acting as a catalyst), and a molecular weight regulator, for example, acetic acid, are charged into a reaction vessel. The opening of the caprolactam ring involves an equilibrium reaction that is catalyzed by water. The ring-opening reaction can also be catalyzed by an acid or base, an amino acid, or an amine carboxylate (e.g., nylon-6,6 salt) (Kirk-Othmer, 2014). The reaction is allowed to proceed under a nitrogen blanket at a specified temperature for a specified time, resulting in

the formation of a growing polymer chain. The products formed include high molecular weight polymer (about 90 percent) and low molecular weight material (10 percent), such as the monomer. The monomer is then removed. Nylon-12 is produced from the self-condensation of laurolactam (Kirk-Othmer, 2014).

Kirk-Othmer (2014) described a hydrolytic process that involves the following steps:

1. Caprolactam and additives addition;
2. Hydrolysis;
3. Addition;
4. Condensation;
5. Pelletizing (for remelt processing);
6. Leaching/extraction of monomers;
7. Drying; and
8. Packaging (for pellet sales).

According to Kirk-Othmer (2014), the batch processing of nylon-6 is generally used to produce specialty polymers such as very high molecular weight polymer or master batch polymers for special additives. A typical modern batch processing involves a two-stage polymerization process. In the first stage, caprolactam is mixed with desired additives (unspecified), autoclaved, and hydrolyzed, followed by a condensation reaction step. Ribbons of polymer are formed. The ribbons are cooled and cut into pellets. Monomers and oligomers are then extracted and the pellets are dried.

The continuous polymerization for nylon-6 involves a three-step process (Kirk-Othmer, 2014). Similar to the batch process, the continuous process is designed to provide water-rich reaction media to accelerate hydrolysis and the initial coupling of the monomers, and to provide a low water environment for the polycondensation reaction to approach equilibrium. Similar to the batch process, the polymer can be cast and cut into pellets in a continuous pelletizing and drying operation. The polymer is spun directly into fiber or cast into resin.

Both anionic and cationic polymerization processes are also reportedly employed in processing of nylon- 6 (Kirk-Othmer, 2014). The anionic polymerization is used in commercial processing of nylon-6, but it is not used for fiber production. On the other hand, the cationic polymerization process is not used successfully in a commercial process (Kirk-Othmer, 2014).

As a more recent development, a polymerization casting technique is used to produce nylon-6 (Brydson, 1999). This involves casting the nylon-6 *in situ* in a mold. Anionic polymerization is employed that uses acetic caprolactum as a catalyst and sodium salt of caprolactum (Brydson,

1999). A variation of the polymerization casting technique is reaction injection molding techniques (Brydson, 1999).

For the production of nylon-12, the monomer is dodecanelactam and the opening of its ring structure involves higher temperatures (Brydson, 1999). This is not an equilibrium reaction as in the case of nylon-6, but this condensation process yields almost 100 percent of high nylon-12 polymer (Brydson, 1999).

### **3.2.1.2.3 Self-condensation of $\omega$ -amino acids – Nylon 11 and Nylon 7**

An example of polymer produced from a self-condensation of  $\omega$ -amino acids is nylon-11. The polymer is prepared in a continuous process using molten  $\omega$ -aminoundecanoic (11-aminoundecanoic) acid in the presence of a catalyst such as phosphoric or hypophosphoric acid under inert atmosphere at ambient pressure (Kirk-Othmer, 2014; Brydson, 1999). In the case of nylon-7,  $\omega$ -aminoanthanic acid (7-aminoheptanoic acid) is polymerized in an aqueous solution. The reaction takes place under nitrogen for several hours (Brydson, 1999).

### **3.2.2. Processing of Undyed Polyamide Fibers and Fabrics**

For all the nylons, a variety of additives are incorporated into commercial polyamide products (Kirk-Othmer, 2014). These additives are designed to impart desired properties to the base polymer. Among these are amide-forming compounds that copolymerize with the main product. There are three classes of additives that are used for polyamide products:

1. *Endcappers or stabilizers*: Acetic acid is the most common stabilizer for aliphatic polyamides. The acid is used to reduce the molecular weight achievable under whatever conditions the polymerization is carried out.
2. *Branching agents*: No specific agents were mentioned in the available literature, but branch points are defined as atoms or rings from which three or more polymer chains emanate. Kirk-Othmer (2014) indicated that because the polyamides are generally intended to be linear polymers, and branching points are not desired, measures are taken to avoid creating branch points.
3. *Chain-couplers or chain extenders*: These chemicals react with the ends of two polymeric molecules and unite them into a single, larger molecule. For polyamides, two main families of extenders, the bislactams and bisoxazolines, are used to react with one or the other of carboxylic acid or amine ends.

The polyamide fibers are melt extruded in a process in which polyamide polymer granules are fed into a screw extruder containing a series of heated chambers in an atmosphere of dry nitrogen (Mather and Wardman, 2015). Following extrusion, the molten filaments are allowed to flow

through a spinneret and are passed through a cooling chamber. The filaments are moistened before being wound or fed directly to a drawing unit.

In summary, none of the specified phthalates or elements were reportedly used in the manufacture of any of the undyed polyamide fiber or fabric.

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### 3.3 Acrylic fiber and Modacrylic fiber

Acrylic fiber CASRN 63231-45-8 and 25014-41-9; modacrylic fiber CASRN 9010-76-8 and 124322-63-0

#### 3.3.1 Introduction

The largest portion of an acrylic fiber is made up of polyacrylonitrile (PAN) (Aspland, 1993); the fibers are produced by the polymerization of acrylonitrile (Mather and Wardman, 2015). In the United States, acrylic fibers are defined as those containing at least 85 percent by weight of acrylonitrile monomer (Mather and Wardman, 2015; Aspland, 1993a). Modacrylic fibers are manufactured fiber made of:

- vinyl chloride-acrylonitrile copolymers containing between 35 and 85 percent by weight of acrylonitrile monomers in the United States (Mather and Wardman, 2015; Kirk-Othmer, 2014);
- more than 15 percent but less than 65 percent of alternative comonomers (normally vinyl chloride or vinylidene chloride) to achieve particular properties, such as improved flame retardancy (Aspland, 1993);
- at least 50 percent but less than 85 percent by weight of acrylonitrile in Europe (Mather and Wardman, 2015); and
- 35 to 85 percent of the acrylonitrile monomer, as defined by the International Standards Organisation (Mather and Wardman, 2015).

The remaining composition of the fiber typically includes at least one of the following: methyl methacrylate, methyl acrylate, vinyl acetate, vinyl chloride, or vinylidene chloride (U.S. EPA, 1990), but for textile-end-use acrylics (probably modacrylic fibers although not specifically stated), the most common comonomer is vinyl acetate, followed by methyl acrylate (Kirk-Othmer, 2014). Acrylonitrile fibers are considered inert, hygroscopic, resistant to degradation by light, resistant to insect larvae and microbiological attack, can soften above their glass transition temperature, and can be dyed to an extraordinarily wide range of shades of very good fastness with basic (cationic) dyes, but only in light to medium shades of moderate fastness with disperse dyes (Aspland, 1993) (see Section 3.3.3). Modacrylics have flame retardant properties (Aspland, 1993).

#### 3.3.2 Raw Materials Used Worldwide in Making Polyacrylonitrile Fibers and Undyed Polyacrylonitrile Textile Fabrics

The raw materials used in making undyed acrylic and modacrylic fibers (Mather and Wardman, 2015; Kirk-Othmer, 2014) include:

- *Monomers*: acrylonitrile
- *Comonomers*: methyl methacrylate; methyl acrylate; vinyl acetate; vinyl chloride; vinylidene chloride
- *Solvents*: sodium thiocyanate; dimethyl sulfoxide; N,N-dimethylformamide; N,N-dimethylacetamide
- *Emulsifier*: sodium lauryl sulfate
- *Initiators/catalysts/reaction accelerators*: sodium bisulfite; ammonium persulfate; sodium persulfate; potassium persulfate; sulfur dioxide; sodium bisulfite; sodium metabisulfite; azobisisobutyronitrile; benzoyl peroxide; ammonium persulfate–sodium bisulfite–copper system; sodium chlorate; hydrogen; ferric or ferrous ion
- *Buffering agent*: sodium bicarbonate
- *Molecular weight modifier or chain termination agents*: dimethyl sulfoxide; dimethylformamide; methyl acrylate; vinyl acetate; sodium bisulfite; ethylene diamine tetraacetic acid, tetrasodium salt (EDTA); sodium oxalate; sodium bicarbonate
- *Dispersing agents*: surfactant or soap
- *Stabilizers*: unspecified

### **3.3.3 Manufacturing Processes used Worldwide to Produce Acrylic and Modacrylic Fibers and Undyed Acrylic and Modacrylic Textiles Fabrics**

Several polymerization methods that utilize any free-radical method are employed commercially in the manufacture of acrylic and modacrylic fibers (U.S. EPA, 1990; Johnson, 2006; Kirk-Othmer, 2014). Solution polymerization and aqueous suspension (also called dispersion) polymerization methods are most used to polymerize the monomer, acrylonitrile (for acrylic fibers), and the monomer and comonomers (for modacrylic fibers) (U.S. EPA, 1990). The suspension method is the most common commercial method (Kirk-Othmer, 2014). Bulk polymerization process can be used for the acrylics (both acrylic and modacrylic fibers), but it has not been commercialized because the autocatalytic nature of the reaction makes control difficult (Kirk-Othmer, 2014). Modacrylic acid also is commercially manufactured using emulsion polymerization (Mather and Wardman, 2015; Kirk-Othmer, 2014; Johnson, 2006). In the manufacture of acrylic fibers, a copolymer with some dye sites (i.e., charged areas on a fiber to which oppositely charged dyes are attracted), specific molecular weight and controlled composition is required (Johnson, 2006).

#### **3.3.3.1 Aqueous suspension polymerization**

Either batch or continuous aqueous suspension polymerization methods may be employed (Kirk-Othmer, 2014). In aqueous suspension polymerization, radical initiation is normally used to polymerize the monomer, acrylonitrile (for acrylic fibers), or the monomer and comonomers (for modacrylic fibers). A redox system that generates free radicals in the aqueous medium consists

of inorganic compounds such as ammonium, sodium, or potassium persulfate (oxidizer, sometimes called the “catalyst”), sulfur dioxide, sodium bisulfite or metabisulfite (reducing agent, sometimes called the “activator”), and ferric or ferrous ion (the actual catalyst) (Kirk-Othmer, 2014; Masson, 1995). This redox system also adds the benefit of supplying dye sites for the fiber (Masson, 1995). Sodium chlorate (as oxidizing agent) and sodium bisulfite (as reducing agent) or hydrogen peroxides can also be used as initiators (Kirk-Othmer, 2014; Masson, 1995). Sodium bisulfite acts both as a reducing agent and chain-transfer agent (to control molecular weight and impart acid dye sites) (Kirk-Othmer, 2014; Masson, 1995). The ratio of bisulfite to persulfate in the reaction mixture is also reported to have a strong effect on the dye-site content of the polymer (Kirk-Othmer, 2014). In a typical continuous aqueous dispersion process (Kirk-Othmer, 2014), a monomer mixture composed of acrylonitrile and a neutral comonomer, such as methyl acrylate or vinyl acetate is fed continuously into the reactor. Polymerization is initiated by the addition of aqueous solutions of potassium persulfate (oxidizer), sulfur dioxide (reducing agent), ferrous iron (promoter), and sodium bicarbonate (buffering agent). A sodium bisulfite-sulfur dioxide or a sodium bisulfite-sulfuric acid buffer may also be used as the initiation system (Kirk-Othmer, 2014). The polymerization is stopped by chelating the iron using agents such as EDTA or sodium oxalate, or by increasing the pH of the slurry using sodium bicarbonate or other bases (Masson, 1995). After polymerization, the unreacted monomer is removed and the slurry that is formed is removed. The polymer is then separated using a continuous vacuum filter, washed, pelletized, dried, ground, and then stored for later spinning (Kirk-Othmer, 2014).

### ***3.3.3.2 Solution polymerization***

Solution polymerization is reportedly used by a few producers in the industry (Kirk-Othmer, 2014). The polymerization reaction is carried out in a homogeneous medium in a solvent such as sodium thiocyanate or dimethyl sulfoxide, using initiators (e.g., azobisisobutyronitrile, ammonium persulfate, or benzoyl peroxide). However, these initiators are used mainly in batch processes (Kirk-Othmer, 2014). The most common redox system for this polymerization process is ammonium or potassium persulfates (as oxidizers) and sodium bisulfite (as a reducing agent). When sodium thiocyanate is used as a solvent, one manufacturer uses ammonium persulfate-sodium bisulfite-copper system as the redox initiators (Kirk-Othmer, 2014). Dimethyl sulfoxide and dimethylformamide used as the organic solvents for the polymerization also act as chain transfer agents. Other chain-transfer reactions may introduce dye-sites, branching, and structural defects, which reduce thermal stability (Kirk-Othmer, 2014). These authors also listed methyl acrylate and vinyl acetate as the two common comonomers that can be incorporated into the manufacture of textile-grade acrylics. One advantage of solution polymerization is that the polymer can be converted directly to spin dope (a polymer melt), when the unreacted monomer is removed (Kirk-Othmer, 2014; Johnson, 2006). Additionally, additives such as pigments or stabilizers (unspecified) may be incorporated before the dope is transferred to the spinning area (Kirk-Othmer, 2014).

### **3.3.3.3 Emulsion polymerization**

Emulsion polymerization is limited to the manufacture of modacrylic compositions (Kirk-Othmer, 2014; Johnson, 2006). In this process, a small amount of monomer is added to the reaction vessel and the emulsifier (surfactant such as sodium lauryl sulfate or soap) disperses the monomer into aggregates of molecules. The polymerization reaction is initiated using water-soluble initiators including ammonium persulfate, potassium persulfate, or sodium bisulfite.

### **3.3.4 Processing**

The most frequently used techniques in the processing of acrylic/modacrylic fibers are wet and dry spinning (Johnson, 2006). The polymers from the manufacturing process are dissolved in a suitable solvent depending on the processing method.

Acrylic and modacrylic fibers are produced by wet spinning when solutions of the polymers are extruded, followed by removal of the solvent (Aspland, 1993a; U.S. EPA, 1990). For the dry spinning method, dimethylformamide or aqueous sodium thiocyanate is used as the solvent (U.S. EPA, 1990; Aspland, 1993a; Johnson, 2006).

For wet spinning, the polymers are dissolved in dimethylformamide or dimethylacetamide (U.S. EPA, 1990). Additives and delustrants (unspecified) may be added to the extruded polymer (Johnson, 2006; U.S. EPA, 1990). Johnson (2006) mentioned the addition of dye site modifiers that include methyl methacrylate as the dye modifier if dimethylformamide is used as the solvent (for dry spinning); and for wet spinning, the dye site modifier is vinyl acetate (with dimethyl acetamide as the solvent) or methyl methacrylate if aqueous sodium thiocyanate is the solvent. After the addition of these additives, the solution is filtered in plate and frame presses, followed by pumping the solution through a manifold to spinnerets (U.S. EPA, 1990), and then subjecting the solution to wet or dry spinning to form the acrylic fibers. For wet spinning, the spinnerets are in a spinning bath; whereas for dry spinning, the spinnerets are at the top of an enclosed column (U.S. EPA, 1990). The solvents are removed by evaporation (dry spinning) or by washing out the solvent (wet spinning) (Aspland, 1993a). After washing, the wet spun filaments are pulled from the bath and taken up on wheels to remove more solvent (U.S. EPA, 1990). Both wet and dry filaments are gathered into a tow band, stretched, dried, crimped, heat set, and then cut into staple (U.S. EPA, 1990; Aspland, 1993a; Johnson, 2006).

In summary, none of the specified phthalates or elements were reportedly used in the manufacture or processing of undyed acrylic or modacrylic fiber or fabric.

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## 3.4 Spandex – Polyurethane

Spandex – Polyurethane, CASRN 9009-54-5

### 3.4.1 Introduction

Spandex fiber is defined by the U.S. Federal Trade Commission as “a manufactured fiber in which the fiber forming substance is a long-chain synthetic polymer comprised of at least 85 percent by mass of a segmented polyurethane” (Textile Exchange, 2016; Kirk-Othmer, 2009; Drobny, 2014; Brydson, 1999). The fibers consist of hard and soft segments (Brydson, 1999). The spandex fiber is made up of a long chain polyurethane polymer that is produced by reacting a macroglycol (e.g., poly(tetramethylene ether) glycol) with a diisocyanate (Spandex Forum, 2016). These fibers can be stretched repeatedly, and will return almost exactly back to their original size and shape. They are lightweight, soft, smooth, easily dyed, resistant to abrasion, and the deleterious effects of body oils, perspiration, and detergents. Spandex fiber is compatible with other materials, and can be spun with other types of fibers to produce unique fabrics (Spandex Forum, 2016).

### 3.4.1 Raw Materials Used Worldwide to make Undyed Polyurethane Fibers and Undyed Polyurethane Textile Fabrics

The raw materials used in making undyed polyurethane fibers and undyed polyurethane textile fabrics (Spandex Forum, 2016; Drobny, 2014; Kirk-Othmer, 2009) include:

- *Monomers*: poly(tetramethylene ether) glycol; bis(4-isocyanatophenyl) methane (or diphenylmethane-4, 4'-diisocyanate); hexamethylene diisocyanate (HDI); 3,3'-dimethyl-4,4'-biphenyl diisocyanate (TODI); adipates; polycaprolactones; polycarbonates; polyethers such as poly(oxypropylene diols) and poly(oxytetramethylene diols)
- *Solvents*: N,N-dimethylformamide; N,N-dimethylacetamide
- *Initiators/catalysts/reaction accelerators*: diazobicyclo[2.2.2]octane
- *Molecular weight controls*: low molecular weight amines (unspecified)
- *Chain extenders*: ethylene glycol; 1,4-butadiene diol; 1,6-hexanediol; hydroquinone
- *Cross-linkers*: glycerol; 2-ethyl-2- (hydroxymethyl)-1,3-propanediol
- *Stabilizers*: unspecified
- *Pigments*: unspecified

### 3.4.2 Manufacturing Processes used Worldwide to Produce Undyed Polyurethane Fibers and Undyed Polyurethane Textile Fabrics

Spandex fibers are currently commercially manufactured worldwide using four different processes (Spandex Forum, 2016; Kirk-Othmer, 2009). These processes include melt extrusion,

reaction spinning, solution dry spinning, and solution wet spinning. The initial step in each of the manufacturing processes involves production of an isocyanate terminated prepolymer (Kirk-Othmer, 2009). The prepolymer is formed by reacting a macroglycol with a diisocyanate monomer. The macroglycol forms the soft segment of spandex fibers and can be either a polyether, a polyester, a polycarbonate, hydroxyl-terminated polycaprolactone, or a combination of these (Kirk-Othmer, 2009). The prepolymer is reacted further with either a glycol or diamine under controlled conditions, in the presence of a catalyst [e.g., diazobicyclo(2.2.2)octane] to initiate the reaction (Spandex Forum, 2016). A small amount of a secondary monoamine (not specified) may be included to control final polymer molecular weight (Kirk-Othmer, 2009). According to Kirk-Othmer (2009), the diol or diamine(s) reaction with the prepolymer can be carried out in a solvent and the resulting block copolymer may be wet or dry spun into fiber. A fiber also can be formed by reaction-spinning the prepolymer in a bath containing the diamine. Alternatively, the prepolymer can be allowed to react in bulk with a diol; the resulting polymer is melt extruded in fiber form.

### ***3.4.2.1 Solution Dry Spinning***

Solution dry spinning is used to produce over 90 percent of the world's spandex fiber (Spandex Forum, 2016; Kirk-Othmer, 2009). The initial step in preparing the polymers for wet or dry spinning involves reacting the macroglycol with a diisocyanate. Different characteristics of the fibers are produced, depending on the ratio of the glycol to diisocyanate. Poly(tetramethylene ether) glycol and bis(4-isocyanatophenyl) methane [also known as diphenylmethane-4, 4'-diisocyanate (MDI)] are the most commonly used macroglycol and diisocyanate for the prepolymer reaction (Kirk-Othmer, 2009). Other raw materials for the soft segments include polyester and polyethers (Drobny, 2014). Drobny (2014) also reported that the hard segment of the polyurethanes is formed by the addition of the chain extenders (such as those listed above in Section 3.4.1) to the isocyanate (in most cases, MDI, although other isocyanates such as HDI and TODI may be used).

The prepolymer is further reacted with an equal amount of diamine in a reaction known as a chain extension reaction (Spandex Forum, 2016). The prepolymer is dissolved in a solvent and reacts with diamine(s) to form a urethane-urea polymer in solution. Kirk-Othmer (2009) reported that one or two diamines are normally used as chain extenders. Diluting the solution with a solvent produces the spinning solution. Branching reactions are minimized in order to obtain a stable polymer solution for spinning (Kirk-Othmer, 2009). Kirk-Othmer (2009) also stated that stabilizers, pigments, and other additives (none of them specified) are milled in the spinning solvent after chain termination, along with small amounts of urethane polymer to improve stability. According to these authors, most producers combine prepolymerization, chain extension, additive addition, and blending into a single integrated continuous production line.

The spinning solution is pumped into a cylindrical spinning cell to be cured and converted to fibers (Spandex Forum, 2016). From this cell, the polymer solution is forced through a spinneret, forming strands of liquid polymer. The solution dry-spun fibers also are called continuous multifilaments or coalesced multifilaments (Kirk-Othmer, 2009). A finish (description of which is beyond the scope of this project) is then applied to the multifilament bundle before it is wound onto a tube and then transferred onto spools to be packaged and shipped to textile manufacturers and other customers (Spandex Forum, 2016).

#### ***3.4.2.2 Wet spinning***

In a typical wet spinning process, the spinning solution (similarly produced as in the solution dry spinning process) is pumped through spinnerets into a solvent-water coagulation bath, followed by concurrently washing the multifilament bundles in successive extraction baths (Kirk-Othmer, 2009). The bundles are then dried and heat-relaxed. A finish is applied and the multifilaments wound on individual tubes. Productivity constraints of wet spun processes have limited the utility of wet spinning (Kirk-Othmer, 2009).

#### ***3.4.2.3 Melt Spinning***

Melt extrusion is employed only with polymers that contain all urethane hard segments, in which the prepolymer was extended using a glycol (Kirk-Othmer, 2009). The melt-spun fibers normally have higher diisocyanate–glycol ratios. In a more recent development, melt-spun biconstituent sheath-core elastic fibers that consist of a hard fiber sheath (polyamide or polyester) along with a segmented polyurethane core polymer have been commercialized (Kirk-Othmer, 2009).

#### ***3.4.2.4 Reaction Spinning***

The manufacture of spandex fiber using reaction spinning involves reacting polyester or polyether glycol with a diisocyanate (Kirk-Othmer, 2009). A small amount of inert solvent (not specified) may be added to adjust the viscosity of this isocyanate-terminated prepolymer. The prepolymer is then extruded into a coagulating bath that contains a diamine to simultaneously form the filament and polymer. Filament curing and solvent evaporation completes the reactions. A finish is then applied, and the fibers are wound on tubes or bobbins. Covalent cross-links may be formed in the reaction-spun spandex fiber by adding glycerol or 2-ethyl-2-(hydroxymethyl)-1,3-propanediol with the macroglycol. It is also reported that stabilizers and pigments are normally slurried with macroglycol and added to the polymeric glycol, prior to diisocyanate addition (Kirk-Othmer, 2009).

### 3.4.3 Processing of Polyurethane Fibers

Prior to processing, the polyurethanes must be dried, as they tend to absorb moisture rapidly upon exposure to atmospheric air (Drobny, 2014). The fibers can be subjected to injection molding (to shape the polymeric materials into desired articles), extrusion, calendaring, blowmolding, and thermoforming (Drobny, 2014).

In summary, none of the specified phthalates or elements were reportedly used in the manufacture or processing of undyed spandex fiber or fabric.

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## 3.5 Viscose Rayon (Cellulose)

Viscose Rayon (Cellulose), CASRN 61788-77-0

### 3.5.1 Introduction

Rayon is the generic name for a semisynthetic fiber composed of regenerated cellulose. Rayon fibers are defined by the U.S. Federal Trade Commission as “a manufactured fiber composed of regenerated cellulose, as well as manufactured fibers composed of regenerated cellulose in which substituents have replaced not more than 15 percent of the hydrogens of the hydroxyl groups” (U.S. EPA, 1982). Rayon fibers can be broadly categorized into regular (conventional) rayon, modified high tenacity rayon, high-wet-modulus rayon, and polymosic rayon (U.S. EPA, 1982). These fibers are made from chemical cellulose, also known as dissolved wood pulp (that is derived from naturally occurring material), sodium hydroxide, carbon disulfide, and sulfuric acid (U.S. EPA, 1982). Some of the common rayon’s are viscose rayon, acetate rayon, local, cuprammonium rayon, and pyroxilin rayon. Among these types of rayon, viscose rayon is the most commonly commercially manufactured rayon and is the focus of this research.

### 3.5.1 Raw Materials used Worldwide in Making Undyed Viscose Rayon Fibers and Undyed Viscose Rayon Textile Fabrics

The main raw material used in the production of viscose rayon fibers is cellulose, which is a natural polymer of D-glucose, the repeating monomer unit of which is a pair of anhydroglucose units (Kirk-Othmer, 2014). Raw materials for manufacturing of rayon are limited to solvents and catalysts; the literature does not report other additives:

- *Solvents*: sodium hydroxide solution (caustic soda); carbon disulfide; sulfuric acid; water
- *Catalysts*: manganese; cobalt

### 3.5.2 Manufacturing Processes used Worldwide to Produce Undyed Viscose Rayon Fibers and Undyed Viscose Rayon Textile Fabrics

The manufacturing process of viscose rayon (also known as the viscose process) involves a series of chemical reactions (Kent, 2012; U.S. EPA, 1982) that consists of the following stages:

1. Wood cellulose and concentrated caustic soda react to form soda cellulose;
2. The soda cellulose reacts with carbon disulfide to form sodium cellulose xanthate;
3. The sodium cellulose xanthate is dissolved in dilute caustic soda to give viscose solution;
4. The solution is ripened; and
5. It is extruded into sulfuric acid that regenerates the cellulose, now in the form of long filaments (viscose rayon).

Rayon manufacturing starts when manufacturers receive the dissolving pulp (or dissolving wood) in sheet or roll form. The pulp is a bleached wood pulp that has a high cellulose content. The dissolving wood pulp is prepared only from the wood of certain trees. The pulp also can be made from cotton fibers (linters), but this type of pulp is no longer used in viscose rayon production (Kirk-Othmer, 2014). The production of dissolving pulp involves drastic chemical action at elevated temperatures that separate the cellulose fibers from the unusable lignin and other wood components. The cellulose fibers undergo a process of washing, bleaching, and drying, and are then made into sheet or roll form or bales (Kent, 2012). The most desirable form of dissolving pulp is characterized by a high level of alpha cellulose.

The dissolving pulp in sheet or roll form is steeped in a combination steeping bath and press, which is slowly filled with caustic soda. The cellulose reacts with the soda to form alkali or “soda” cellulose (Kent, 2012; Kirk-Othmer, 2014; U.S. EPA, 1982). The sheets of soda cellulose are discharged into a shredder that tears the sheets into white crumbs. The white crumbs are aged for up to two or three days. The aging process can be accelerated by using higher temperatures and traces of metal ions (e.g., manganese or cobalt) as catalysts. The viscosity of the viscose depends on the aging process (Kirk-Othmer, 2014; Kent, 2012; U.S. EPA, 1982). The aged soda is mixed with carbon disulfide to form cellulose xanthate (sodium cellulose dithiocarbonate) (Kent, 2012). After xanthation, the xanthate is dissolved in a cold, dilute solution of sodium hydroxide to form viscose. This is referred to as the dissolving stage of the viscose manufacturing process. The mixing conditions are reportedly crucial (Kirk-Othmer, 2014). The dissolution step is followed by an aging/ripening process where the viscose solution is allowed to stand (age) for a period of time to “ripen”; longer times at low temperatures allow reactions that favor more spinnable viscose (Kirk-Othmer, 2014). However, the correct viscose age or ripeness for spinning depends on the type of fiber being made (Kirk-Othmer, 2014). At the ripening stage, actual chemical decomposition of cellulose takes place and results in gelation of the viscose solution (Kent, 2012). The viscose solution is then filtered and degassed and subjected to processing.

### 3.5.3 Processing

Viscose rayon is processed using a wet spinning technique (Kent, 2012; Kirk-Othmer, 2014). In the wet spinning method, the polymer is dissolved in an appropriate solvent and this solution is pumped through a spinneret that is submerged in a coagulating/precipitating bath. The high molecular weight linear polymer is first converted to a gel structure and then to a fiber (Kent, 2012). The spinning bath usually contains a mixture of an acid bath that contains (Kent, 2012; Kirk-Othmer, 2014):

- zinc sulfate (to add strength by cross-linking the cellulose molecules);
- sulfuric acid (to convert the xanthate into cellulose);
- sodium sulfate (to precipitate sodium cellulose xanthate into filament form);

- water; and
- surface-active agent (unspecified; to prevent minute deposits from forming around the holes in the spinneret).

The partially regenerated filaments from the spinning machine are contaminated with sulfuric acid, zinc sulfate, sodium sulfate, carbon disulfide, and the numerous incompletely decomposed by-products of the xanthation reactions. These contaminants are removed by washing, desulfurizing, bleaching, conditioning/oiling, and drying. For example, washing with a solution of sodium sulfide removes minute traces of suspended sulfur resulting from the chemical decomposition of cellulose xanthate, and bleaching with hypochlorite improves whiteness of the fibers (Kent, 2012). The final step involves adding a small amount of lubricant on the filaments to reduce friction and improve processing in subsequent operations (Kent, 2012). The large number or group of rayon filaments (termed “tow”) formed in the precipitation bath is stretched to the desired degree and immediately cut into staple fiber, followed by washing and drying, and packaging for shipment.

In summary, none of the specified phthalates or elements were reportedly used in the manufacture or processing of undyed viscose rayon fiber or fabric.

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## 3.6 Natural Rubber Latex Fiber

Natural Rubber Latex Fiber, CASRN 9006-04-6

### 3.6.1 Introduction

Natural rubber latex (NRL) is obtained from *Hevea brasiliensis* [the Brazilian rubber tree; one important commercial source (Kohjiya and Ikeda, 2014)] and is primarily the polymer of cis-1,4-polyisoprene (the monomer is isoprene, also known as 2-methylbuta-1,3-diene) (Kent, 2012; Kohjiya and Ikeda, 2014). Another source of NRL is Guayule (*Parthenium argentatum*). The rubber latex produced from this tree is mainly used for advanced medical and consumer products (e.g., rubber gloves) (Kohjiya and Ikeda, 2014) and is not a focus of this research because it is not made into a textile fiber. As a polymeric material, NRL shows high elasticity and ability to stretch, has high mechanical strength, and resistance to aging, temperature changes, dilution, and exposure to electrolytes (Laurentowska et al., 2012).

### 3.6.2. Raw Materials used Worldwide in Making Natural Rubber Latex Fibers and Undyed Natural Rubber Latex Textile Fabrics

The raw materials used in the manufacture of natural rubber latex fiber include:

- field latex (raw rubber latex);
- field coagulum latex (coagulated rubber latex);
- acetic acid;
- formic acid;
- diammonium phosphate;
- water;
- *Preservatives*: ammonia; LATZ latex; boric acid; sodium pentachlorophenate;
- *Accelerators*: dithiocarbamates (zinc diethyldithiocarbamate, zinc dibutyl dithiocarbamate); thiazole (zinc mercaptobenzothiazole); thiuram (tetramethyl thiuram disulfide);
- sulfur.

### 3.6.3. Manufacturing Processes used Worldwide to Produce Undyed Natural Rubber Latex Fiber and Natural Rubber Latex Textile Fabrics

The naturally occurring liquid latex is first tapped from the rubber tree and a field preservative (e.g., ammonia or a mixture of tetramethyl thiuram and zinc oxide) is added (Kirk-Othmer, 2014). Formaldehyde also has been mentioned as added to the field latex (Azo Materials, 2016). The field latex goes to a processing factory to be creamed using batch processing and creaming agents (e.g., ammonium alginate), and then evaporated. Other authors reported coagulating the

field latex by the addition of acetic acid or dilute formic acid to precipitate a high molecular weight polymer (or field coagulum) (Azo Materials, 2016; Kohjiya and Ikeda, 2014; Kent, 2012). The precipitate (coagulum) may be rolled into sheets [known as crepe (Kirk-Othmer, 2014)] and dried (Latex Forum, 2016). The rubber sheets are shipped to factories for further processing.

### 3.6.4 Processing

At the processing factory, the field latex is further ammoniated, using ammonia gas to raise the pH of the latex to promote hydrolysis of some natural lipids (Kirk-Othmer, 2014). Naturally occurring magnesium ions in the latex can be precipitated at this stage by the addition of diammonium phosphate. The field latex is concentrated by centrifugation (Latex Forum, 2016), the rubber content of the concentrate is adjusted, and final preservation is carried out using ammonia or TZ (LATZ latex), boric acid, or sodium pentachlorophenate, although the use of these preservatives has declined due to concerns about toxicity of these products (Kirk-Othmer, 2014).

The latex or the rubber sheets are compounded with sulfur (i.e., vulcanized) or other additives (Kirk-Othmer, 2014; Kent, 2012). Chemicals (unspecified) required for vulcanization, stiffness, coloring, antioxidant protection, or other processes are added as solutions, emulsions, or fine dispersions to the latex before forming the latex product (Kirk-Othmer, 2014). These chemicals are mixed in the presence of ultrafast accelerators, such as dithiocarbamates. When dithiocarbamates are used, secondary accelerators (e.g., thiazoles, such as zinc mercaptobenzothiazole) are added. Tetramethyl thiuram disulfide, may be used instead of dithiocarbamates (Kirk-Othmer, 2014).

Prior to vulcanizing the rubber sheets, sheets are usually masticated to reduce the molecular weight and improve processability. The masticated product is then compounded with sulfur or other additives (not specified), calendered, and vulcanized under water (Kent, 2012). The vulcanizing product, referred to as skin, is spirally cut into strips. The strips are desulfurized, washed, dried, and packaged (Kent, 2012). The resulting product is known as a thread (Kent, 2012). The field latex can also be manufactured into a monofilament known as a latex thread (Kent, 2012). The solution (field latex) is compounded with sulfur and other chemicals (unspecified) that are needed for curing. A “precurving” step follows where the latex is converted into a form to be coagulated when it is extruded through spinnerets into a coagulation bath containing dilute acetic acid. The filament passing out of the bath is washed, dried, vulcanized, and packaged. This thread is used primarily in the garment industry (Kirk-Othmer, 2014).

In summary, none of the specified phthalates or elements are reportedly used in the manufacture or processing of undyed natural rubber latex.

### 3.6.7 References

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## 4 Fiber Colorants

### 4.1 Introduction

Fibers may be colored using various colorants such as dyes and pigments. This research focuses on dyes, as dyes are the colorants most frequently used for the specified fibers. An overview of textile dye chemistry provides the background for research on dyes of various chemical structures as well as dye application types for the specified fibers.

TERA's research indicates that natural rubber latex is colored with pigments. In this section, NRL coloring is briefly described.

As part of TERA's research efforts, regulations and/or standards related to the allowable concentration of certain contaminants in textiles and dyes as well as trade and professional organizations were investigated. This research is summarized in Appendix D.

### 4.2 Colorants for Natural Rubber Latex

Rubber fibers, or "elastic," were historically used in textiles, covered by, or woven into yarns of other fibers due to its low dye acceptance.

NRL begins as a milky fluid consisting of small particles of rubber dispersed in an aqueous medium (West Pharmaceutical Services, 2014). Anti-coagulants (e.g., sodium sulfite, ammonia, sodium carbonate, and formaldehyde) may be added (Whelan, 1994). Clay fillers may also be added during the compounding phase to increase the firmness and decrease build-up time in a plaster mold (McLaughlin, 2013).

Dyes do not appear to be used for natural latex rubber. However, pigments, such as organic pigment powders, titanium dioxide, carbon black, fluorescent pigments, molybdenum, cadmium, zinc oxide, and bifunctional organic silicon compounds (Kolorjet, 2016; Alliance Organics, 2016; Noble, 1953), water-soluble acrylic paints (NPCS Board of Consultants and Engineers, 2000; McLaughlin, 2013), water-based color dispersions (McLaughlin, 2013; Noble, 1953) and bacterial prodigiosin (Krishna et al., 2013) may be added or applied to the liquid rubber, although the basis for these statements does not appear sufficiently robust or replicated in the literature. Ultramarine, indanthrene, and anthraquinones also may be used (Noble, 1953), although this statement could not be corroborated by more recent literature. Antimony sulfide is reportedly not used in latex because of the availability of better red organic colors and chrome green is used only in exceptional cases (Noble, 1953). Rubber-soluble pigments may also be applied directly to latex using a benzol solution (Noble, 1953). Paints may also be applied to natural rubber latex products after they are formed, but this is less ideal due to flaking or rotting the latex (e.g., oil-based paints) (McLaughlin, 2013).

## 4.4 Textile Dye Chemistry Overview

Textiles, specifically the specified manufactured fibers and fabrics, can be dyed through various processes and by thousands of dyes. It has been assumed that dyed textiles contain roughly 2 percent (w/w) of dye (KEMI, 2014), although this would be expected to vary based on dye and fiber type. There are a number of chemicals involved in producing the specified textile fibers, from fiber manufacture, fiber processing, fiber dyeing, and through fiber finishing (see Figure 1 in Section 2.1). This section aims to cover the fiber-dyeing step only. Fibers may be colored using various colorants such as dyes and pigments. This research focuses on dyes.

Typically, dyes contain an excitable (light absorbing) aromatic ring system (such as benzene or anthraquinone) and a chromophore (Broadbent, 2001). A chromophore, the color-producing group in the dye molecule, can contain nitrogen-nitrogen (azo) or carbon-carbon (alkene) double bonds, carbonyl groups, or other arrangements of the carbon, nitrogen, and oxygen atoms that involve double bonds and valence electrons that are excitable by visible light to create the color (EC, 2003; IARC, 2010). Additional groups that make up the dye molecule (auxochromes) may contain lone electron pairs such as hydroxyl groups or nitrogen-containing groups that enhance the color intensity (IARC, 2010). Other molecular modifications to the basic chemical dye structure are common, including those that alter dye solubility, modify dye interaction with the fiber of interest, or that can enhance other dye characteristics.

During the dyeing process, the dye molecules are incorporated into the fiber. Dyes are mainly applied from solution to fibers, and bond to the fiber molecules of the textile (Broadbent, 2001; EC, 2003). This is in contrast to pigments which are mainly insoluble compounds applied to fibers (but also used in paints, inks, and plastics) on the surface (Broadbent, 2001). Pigments are not covered under the scope of the current task, even though they are used in natural latex rubber fibers (Section 4.2). When dyeing a fiber, the aqueous (dissolved) dye actually moves from the dye liquor (solution containing the dye and any additional auxiliaries added) to the fiber surface, penetrates (diffuses) into the fiber, and reacts with and bonds (fixes) to the fiber; the dye solution is typically depleted (EC, 2003). This dye fixation to the fiber varies depending on the dye applied and the fiber type, and includes chemical reactions forming covalent bonds (reactive dye) or intermolecular bonding such as Van der Waals forces and hydrogen bonding (direct dyes) (EC, 2003). Other fiber-dye interactions include ionic bonds.

## 4.5 Dye Chemical Structures and Manufacturing

There are at least 25 structural (molecularly based) classifications for dyes; the most important classes include azo dyes (~66 percent), anthraquinone dyes (~15 percent), triarylmethanes (~3 percent), and phthalocyanines (~2 percent) (Holme, 2002; Fleischmann et al., 2015). Azo dyes are the largest class of dyes, representing roughly 50 to 66 percent of all commercial dyes, containing azo groups in combination with auxochromes (such as hydroxyl groups, amines, or

substituted amine groups) that modify the color and intensity of the resulting dye (Holme, 2002; Chakraborty et al., 2010; Kirk-Othmer, 2009). Azo dye structures are found in acid/metal-complex dyes, disperse dyes, direct dyes, reactive dyes, and basic dyes (IARC, 2010). Anthraquinone dyes comprise roughly 15 percent of commercial colorants and are based on quinone structures or anthracene backbones (Holme, 2002). As with azo dyes, the addition of auxochromes alters the color and intensity of these dyes. Phthalocyanines are complex chemical compounds that make up two percent of synthetic dyes, and are composed of four isoindoles linked through the nitrogen group (Holme, 2002). The phthalocyanine dyes interact with metal atoms, typically copper; sulfonic acid groups may be added to modify water solubility. Nitrodiphenylamine, triarylmethane, perylene, heterocyclic, and methine (styryl) dyes are a much smaller proportion of dye chemistries making up less than 1 to 5 percent (Holme, 2002; Choudhury, 2011; Fleischmann et al., 2015), and so are not discussed in detail in this report. Additionally, it has been suggested that the azo dye chemistry is in decline and being replaced by the anthraquinone dye chemistry, in part due to the potential to generate certain toxic arylamine derivatives (e.g., benzidines) from some of the azo dye structures (Holme, 2002). Conversely, others suggest that anthraquinone dyes were in decline due to their high cost as compared to azo dyes (Kirk-Othmer, 2009; Kirk-Othmer, 2000).

Overall, there are at least 25 chemical classes for dye structure, and at least nine fiber application methods that are used for industrial classification (see Table 11) (Holme, 2002). This means that the number of dyes is extensive and the chemical class and application methods heavily overlap, making the assessment of individual dyes very difficult (Table 11) (Holme, 2002). Because of this difficulty, only the manufacturing methods for the major chemical classes of dyes [azo, anthraquinone, (copper) phthalocyanine] are discussed below, and are anticipated to cover over 83 percent of the available dyes, but likely a much higher percentage of the dyes as applicable to the specified fibers (for example, excluding cotton and wool fibers). Specific dyes are only compatible with specific fibers (as discussed in Section 4.6 below) due to the fiber type and dye chemistry, wherein certain incompatible dyes could damage the fibers (Chakraborty, 2014). Additionally, the total scope of dyes for this research was narrowed based on the applicability to the specified fibers, or those dyes that are used on the fiber types investigated here. For example, phthalocyanine dyes are discussed in more detail than triarylmethanes as they were encountered more frequently as used for the specified fibers, although both make up just a small proportion of dyes applied to the specified fibers.

**Table 11. Distribution of dye chemical class per dye application type<sup>a</sup>**

Chemical Class	Acid	Basic	Direct	Disperse	Mordant	Reactive	Vat
Unmetallized Azo	X	X	X	X	X	X	
Metal-complex azo	X		X			X	
Thiazole		X	X				
Stilbene			X				
Anthraquinone	X	X		X	X	X	X
Indigoid	X						X
Quinophthalone	X	X		X			
Aminoketone	X			X	X	X	X
Phthalocyanine	X	X	X		X	X	X
Formazan	X					X	
Methine		X		X			
Nitro, nitroso	X	X		X	X		
Triarylmethane	X	X	X	X	X		
Xanthene	X	X			X	X	
Acridine		X		X			
Azine	X	X					
Oxazine		X	X	X	X	X	
Thiazine		X			X		X

<sup>a</sup>Table modified from Holme, 2002. The azoic/naphthol dyes are not included.

It would be difficult to report manufacturing processes for all individual dyes, or even for all chemical classes of dyes. Even the reporting on the manufacturing for the most common dye types is not anticipated to be comprehensive of the worldwide methods, due to proprietary processes, unpublished structures, and mixtures of dye types. This discussion is not anticipated to cover every manufacturing method, starting material, or intermediate, but gives the general processes of manufacture for the major dye types.

In general, synthesis of dyes involves modifications to dye intermediates derived from petroleum and coal tar products, which are mostly derivatives of benzene, naphthalene, and anthraquinone (Kent, 2012; Kirk-Othmer, 2009). There are well over 3,000 different dye intermediates (Kirk-Othmer, 2009), which would be outside the scope of this report to cover fully. The organic chemistry of dyes includes electrophilic substitutions via nitration, sulfonation, and halogenation (mainly chlorination or fluorination), or nucleophilic substitutions via hydroxylation and amination (Kent, 2012; Kirk-Othmer, 2009). For more information on these intermediates and their organic chemistry, see Gregory (2009).

### 4.5.1 Azo Dye Manufacturing

Azo dyes contain at least one azo group attached to an aromatic or substituted aromatic carbon-based molecule, such as benzene, naphthalene, thiazole, or thiophene, with available molecular orbitals for electron excitation via visible light,(Koh, 2011). One of the most important subgroups of azo disperse dyes are the aminoazobenzene derivatives (Choudhury, 2011; Koh, 2011). The synthesis of azo dyes involves diazotizing primary ( $1^\circ$ ) aromatic amines and coupling with suitable components, such as an electron-rich nucleophile (IARC, 2010; Chakraborty et al., 2010; Kirk-Othmer, 2009). Diazotization is mainly conducted through the reaction of an aromatic primary amine (such as aniline) with sodium nitrite in the presence of acid, which produces a diazo ( $-N_2^+$ ) compound. This diazotization product, combined with various coupling components (e.g., phenolic substrates), leads to thousands of possible azo dye structures (Broadbent, 2001; Chakraborty et al., 2010).

The general steps involved in the production of azo dyes include:

1. *Diazotization*: involves reacting the primary amine with a nitrosating species, for example, nitrous acid, which is generated *in situ* by reacting sodium nitrite with an aqueous solution of a mineral acid such as hydrochloric acid or sulfuric acid. (SDC, no year). Azoic diazo agents such as substituted anilines (phenylamine) and naphthalene sulfonates can be used (SDC, no year). A diazonium salt is formed and it behaves as an electrophilic species. Excess nitrous acid used in the reaction can undergo an unwanted reaction with couplers in the next step. Therefore, it is destroyed by the addition of urea or sulfamic acid. Stabilized forms of diazonium compounds can be produced by forming a complex double salt of the diazonium chloride with inorganic salts, such as zinc chloride, tin chloride, cadmium chloride, manganese chloride, or sodium fluoroborate. The resultant “Fast Color Salts” have been used in azoic dye synthesis (von Glahn and Bergstrom, 1952).
2. *Coupling*: the diazo solution is then reacted with a coupling agent and the azo compound results. Couplers contain an aromatic ring; phenols, naphthols, and (aromatic) amines (phenylamine, aniline) are commonly used (IARC, 2010). Others can use derivatives of naphthalene (naphthalene-2-ol, beta-naphthol), or naphthols (beta-oxynaphthoic acid derivatives or arylamides of acetoacetic acid) and sometimes require the use of additional compounds, such as sodium hydroxide (SDC, no year).

Dispersion is a final step for disperse azo dyes, when the actual dye formed is sparingly water-soluble and has to be dispersed in the dyebath. This is accomplished by adding large amounts of suitable dispersing agents. Some of the recommended dispersing agents for azo disperse dyes are discussed below in Section 4.6.5.

Azo dyes include copper, chromium, and cobalt complexed acid, direct, and reactive dyes (Kirk-Othmer, 2009). They also include carbocyclic azo dyes based on either benzene or naphthalene derivatives (Kirk-Othmer, 2009). Heterocyclic azo dyes involve coupling with ring systems such as indoles, pyrazolones, or pyridines (Kirk-Othmer, 2009).

#### 4.5.2 Anthraquinone Dye Manufacture

Anthraquinones are the second most important class of dyes next to azo, and are all based on 9,10-anthraquinone and derivatives (Kirk-Othmer, 2009).

The basic synthesis involves two steps:

1. synthesis of the anthraquinone (from benzene or naphthalene), and
2. substitution of the anthraquinone molecule, mainly through nitration and sulfonation (Kirk-Othmer, 2000 ).

Simple anthraquinone dyes contain an alkylamino or hydroxyl group, or can be derivatized with more polar substituents to modify fiber affinity and/or coloration (Koh, 2011; Kirk-Othmer, 2009). Anthraquinone dye synthesis can involve a number of process steps, in some cases up to 11 steps (Kirk-Othmer, 2000 ). Anthraquinone dyes are commercially prepared by first synthesizing anthraquinone or anthraquinone intermediates [such as 1,4-disubstituted anthraquinones (e.g., 1,4-hydroanthraquinone or quinizarin)]. The anthraquinone manufacturing process can involve:

- Oxidation of naphthalene in the presence of potassium permanganate to phthalic anhydride.
- Friedel-Crafts acylation of benzene with phthalic anhydride using aluminum chloride as a catalyst to give a keto acid.
- Cyclodehydration using sulfuric acid, resulting in the formation of anthraquinone (Kent, 2012).

Oxidation of naphthalene to the naphthoquinone, followed by condensation with butadiene and ring oxidation can yield anthraquinones (HSDB, 2006). Another method of anthraquinone synthesis was reported via oxidation of anthracene using a chromium oxidant (chromic acid, sodium dichromate), vanadium pentoxide, sodium chlorate, glacial acetic, and/or sulfuric acids, or naturally from the mineral hoelite (HSDB, 2006; Fleischmann et al., 2015; Kirk-Othmer, 2000). Additionally, it was reported that four different anthraquinone dyes were synthesized from 1-amino-2-sulfo-4-bromo-9,10-anthraquinone (bromanine acid) reacted with primary and secondary amines in the presence of copper sulfate (Grabchev and Philipova, 1998). The dyes were dissolved in acetic acid, acylated, and isolated by precipitation using ethyl acetate (Grabchev and Philipova, 1998). An additional method to produce dyes from anthraquinone

intermediates, in the presence of sodium hydrosulfide, reduces quinizarin to leuco quinizarin. The latter undergoes condensation with alkyl- or arylamines and reoxidation to produce anthraquinone dyes (Kent, 2012; Choudhury, 2011). Leuco quinizarin is used to prepare several anthraquinone disperse dyes (Kent, 2012).

Other methods of preparation report the use of derivatives of anthraquinone- $\alpha$ -sulfonic Hattori acid that used a mercury catalyst, but it was suggested that alternative methods are being or have been established (Choudhury, 2011). Use of a mercury catalyst in synthesis was reiterated in Kirk-Othmer (2000) referring to the year 1901, but with a mercury-free method being introduced in the year 1980, the relevance of mercury to current practice is likely small. No information was provided on the possible concentration of mercury catalyst used.

Anthraquinone-based dye structures can vary with the different dye application methods used for the specified fibers. For example, anthraquinone vat dyes can have very complex structures, such as thiazole ring systems, benzanthrones, benzoylaminoanthraquinones, anthrimides, and anthrimidocarbazoles; their general methods of synthesis are described in Kent (2012) and; Kirk-Othmer (2000 ). Additionally, more specific details on the production of anthraquinone disperse dyes, acid dyes, basic dyes, and reactive dyes (from precursors such as bromamine acid) can be found elsewhere (Kent, 2012; Kirk-Othmer, 2000 ).

### **4.5.3 Phthalocyanine Dye Manufacture**

Phthalocyanine dyes can be synthesized by sulfonation and chlorosulfonation of copper phthalocyanine (Kent, 2012). The phthalocyanine molecule is a large heterocyclic system typically containing nitrogen-substituted rings, or derivatives can be substituted to include halogens, hydroxy, amino, alkyl, aryl, thiol, alkoxy, or nitro groups. Phthalocyanine is synthesized from nitrogen containing phthalic acid derivatives, such as phthalonitrile/phthalodinitrile or diiminoisoindole, or additional precursors such as o-cyanobenzamide and phthalimide (HSDB, 2010). For example, copper phthalocyanine is synthesized by condensing phthalonitrile with copper chloride (HSDB, 2010). Additional methods for copper phthalocyanine synthesis involve reacting phthalic anhydride with urea in trichlorobenzene or dichlorobenzene, with the addition of copper in the form of copper chloride, copper bromide, or copper cyanide (HSDB, 2010). Other methods employ reactants and solvents, such as anhydrous sodium sulfate, ethylene glycol, and quinoline (HSDB, 2010).

### **4.5.4 Dye Chemical Structures and Manufacturing Summary**

In general, it is outside the scope of this report to cover the synthesis of all dyes and dye types used for the specified fibers. However, synthesis of the most common dyes was generally reviewed and mostly involves reactions with benzene, aniline, naphthalene, anthraquinone, and phthalic anhydride (and derivatives), with a number of intermediates such as phenols, naphthols,

and quinizarin. The basic chemistry involves electrophilic and nucleophilic substitution reactions on aromatic compounds. Key substances used are typical laboratory reagents such as hydrochloric acid, sulfuric acid, chlorobenzenes, and acetic acid, and salts such as sodium nitrate, aluminum chloride, and copper chloride. While this list of compounds is not comprehensive of those used in the potential worldwide manufacturing processes, it suggests that the specified phthalates would not be used as starting materials or reactants in the dye manufacture processes. Phthalic anhydride was identified as a starting material in anthraquinone ring formation, but is a chemical compound that is distinct from the specified phthalates. For the specified elements, mercury and chromium were listed as a catalyst or metallizing agent used in synthesis reactions, however limited references to mercury were found and the authors noted the limited use (particularly in the last few decades); there were little data indicating if chromium is commonly used, although dyes such as Acid Orange 60 and Acid Black 52 (chromium complexes) are well known. Concentrations of either element in dye products were not located.

#### **4.6 Dye Classification by Application Method**

In textile dyeing, the method of dye application is important, and was the most common classification method encountered. The application method was used to categorize the specified fibers by type of dye typically used (Table 12). The most common dye categories for the fibers of interest include acid, basic, direct, disperse, reactive, sulfur, vat, metal-complex/mordant, and azoic/naphthol. However, these categories are not clearly delineated, and there exists significant dye chemistry overlap between them. For example, mordant dyes are actually a type of acid dye, and mainly based on the azo chemical structure (Holme, 2002). Additionally, acid dyes can be comprised of azo, anthraquinone, or phthalocyanine dye structures (Broadbent, 2001). This inter-related chemical structure and application method classification system makes it difficult to assess dye classes and dye structures in a systematic way.

Acid dyes are mainly used on nylon/polyamide fibers, with some limited evidence for use on spandex (polyurethane). Fibers of acrylic/modacrylic and polyester are typically incompatible with acid dyes, but there is evidence these fibers can be modified to accept these dyes. Basic dyes are almost exclusively applied to acrylic/modacrylic fibers. There is some evidence that both nylon/polyamide and polyester fibers can be modified to accept this dye type, but they are typically incompatible. Direct dyes are used almost exclusively for rayon/viscose fibers. There is little evidence that direct dyes can also be used for nylon/polyamide fibers. Disperse dyes are probably the most widely applicable, as they can be used to dye acrylic/modacrylic, nylon/polyamide, and polyester, with some limited evidence for their use on spandex as well. Reactive dyes can be used on nylon/polyamide or rayon/viscose. For both sulfur and vat dyes, the only identified use was for rayon/viscose fibers (however, expert guidance suggested that this would be very limited, if actually in practice at all). For these fibers, there is also limited evidence that naphthol/azoic dyes can be used. Finally, for metal-complex/mordant dyes,

evidence was mainly found for their use on nylon/polyamide, and very limited evidence for use in spandex/polyurethane. These data are summarized with references in Table 12.

**Table 12. Evidence for each type of dye as applied to the specified fibers<sup>a</sup>**

Dyes <sup>b</sup>	Acrylic/ modacrylic	Nylon (polyamide)	Polyester	Spandex (polyurethane)	Rayon (viscose)
Acid	<i>m</i>	+++++++	<i>m</i>	+	
Basic (cationic)	+++++++	<i>m</i>	<i>m</i>		
Direct		+			+++++++
Disperse (nonionic)	+++++++	+++++++	+++++++ +	++	
Reactive		++++			++++
Sulfur					+++
Vat					++++
Metal- complex/mordant		++++		+	
Naphthol (azoic)		<i>m</i>	<i>m</i>		++

<sup>a</sup>Sources include: Broadbent, 2001; Holme, 2002; IARC, 2010; Aspland, 1993a; Choudhury, 2011; Koh 2011; Kent, 2012; Greenpeace, 2005; EC, 2003.

<sup>b</sup>all dyes listed are anionic in nature except for those as indicated (Chakraborty, 2014)

(*m*) fiber can be modified to accept the dye type, but it is not typically compatible

(+) number of plus symbols shows the number of references identified for each fiber and dye

The Colour Index is a joint publication from the Society of Dyers and Colourists (SDC) and the American Association of Textile Chemists and Colorists (AATCC) that lists the chemical structures and additional information for over 9,000 dyes (Kent, 2012). In the 1992 version, the publishers reported 2,169 acid dyes, 1,493 direct dyes, 1,309 disperse dyes, 978 reactive dyes, 545 basic dyes, 405 vat dyes, 213 sulfur dyes, and 573 mordant (metal-complex) dyes (Kent, 2012). It is expected that this listing has grown since 1992 to include even more dyes.

Additionally, many of the most recent dye structures are not published, many of the sulfur dye structures are unknown, and some of the dyes are mixtures, which precludes the ability to identify all known and available dyes (Holme, 2002). More information on the most commonly used dyes for each of the specified fibers is reported below, including the most commonly used auxiliaries in the fiber dyeing process.

Holme (2002) suggests that azoic dyes are in decline, while reactive and disperse dyes are growing in importance. This author suggests that azoic, chrome (mordant), sulfur, and vat dyes,

all of which have potential environmental or toxicity issues, also will likely have reduced importance over time (Holme, 2002).

#### **4.6.1 Acid Dyes**

Acid dyes are mostly used to dye polyamide (nylon) fibers, with 90 percent of polyamide in European markets dyed with acid dyes (KEMI, 2014). There is very limited evidence for their use on spandex (polyurethane), and some evidence that they can be used on modified acrylic/modacrylic fibers and modified polyester fibers. Acid dyes are soluble in water, and can be comprised of azo (represents the majority), anthraquinone, (copper) phthalocyanine, or triphenylmethane/ triarylmethane chemistries (Broadbent, 2001; EC, 2003; Kent, 2012; Greenpeace, 2005; Lacasse and Baumann, 2004; Kirk-Othmer, 2009). Acid dyes are named as such due to the use of an acid dyebath in application, and are typically anionic in aqueous solution (Broadbent, 2001; Kent, 2012; Greenpeace, 2005). The pH of acid dyes can be adjusted upward or downward through the addition of strong or weak acids (Broadbent, 2001; EC, 2003; Lacasse and Baumann, 2004). Of the dye types listed, metal-complex/mordant dyes are also considered a subset of acid dyes, but those are discussed in detail in Section 4.6.2 (Broadbent, 2001).

Chemical structures of the major types of acid dyes include, but are not limited to (Broadbent, 2001):

- mono-azo and bis-azo;
- anthraquinone;
- triphenylmethane and xanthene chromophores; and
- sulfonated copper phthalocyanine.

A typical dyeing procedure for acid dyes (in the example for polyamide fibers) involves the use of one or more auxiliaries added into the dye liquor that includes the dye structure itself, retarding agent (which acts to block action of dye temporarily), surfactants (leveling agents), and acids (Lacasse and Baumann, 2004; Broadbent, 2001; Greenpeace, 2005). The most common auxiliaries and ingredients in acid dye liquors include: sodium sulfate, sodium acetate, and ammonium sulfate, acetic acid, formic acid, sulfuric acid, ammonia salts, phosphoric acid salts, and higher (hydroxy)carboxylates (EC, 2003). After-treatments (post dyeing) are also applied, but are mostly outside the scope of this report (EC, 2003).

#### **4.6.2 Metal-Complex/Mordant Dyes**

Technically, metal-complex/mordant dyes are a sub class of acid, direct, and reactive dyes, and are not their own application class (EC, 2003). Metal-complex/mordant dyes are mainly applied to nylon/polamide, with limited evidence for use on spandex/polyurethane. The metal-

complex/mordant dyes are soluble in water and can be comprised of azo (typically monoazo) or formazan compounds and also contain a metal atom within the dye structure (Broadbent, 2001; Lacasse and Baumann, 2004). The azo base structure contains additional groups such as hydroxyl, carboxyl, or amino groups, which are the groups that form bonds with the metals (Lacasse and Baumann, 2004; EC, 2003). Typically, the metal used for these dyes is a form of chromium salt, such as potassium dichromate, sodium dichromate, sodium chromate, with other metals less commonly used including cobalt, nickel, and copper (refer to Table 13) (Broadbent, 2001; Greenpeace, 2005; Lacasse and Baumann, 2004; EC, 2003).

The mordant dyes are acid dyes applied in their metal-free form and then complexed in the fiber through the addition of mordants (typically metals) by the dyer, while metal-complex dyes are metallized by the dye manufacturer then applied by the dyer. Mordant dyes are essentially acid dyes with a metal added as a 'mordant' (a substance used to set dyes in the fibers), and those that use chromium are also called 'chrome dyes', but the European Commission stated that these are no longer in use for polyamide fibers (EC, 2003; Broadbent, 2001; Lacasse and Baumann, 2004). Other metals can be used as the mordant, but Lacasse and Baumann (2004) suggest that chromium is almost exclusively used. Broadbent (2001) suggests that the mordant application method is the current method for metal-complex formation. In metal-complex dyes, metal ions can be added in 1:1 or 1:2 ratios with the dye molecule, with the 1:2 metal:dye complexes more applicable to polyamide/nylon fibers (Greenpeace, 2005; Lacasse and Baumann, 2004; EC, 2004).

Mordant dyeing can take place in a strongly acidic to essentially neutral acid dyebath, hence the overlap with the acid dye category (Broadbent, 2001; EC, 2003; Lacasse and Baumann, 2004). Common pH regulators include sulfuric, formic, and acetic acids, or other organic acids such as tartaric to aid in chromium speciation (EC, 2003). Auxiliaries include the use of electrolytes (sodium sulfate, ammonium acetate, ammonium sulfate) and leveling agents (mixtures of anionic and non-ionic surfactants) (Greenpeace, 2005; EC, 2003; Lacasse and Baumann, 2004; Broadbent, 2001). Fixation of the dye in the fiber can be increased with the addition of a complexing agent or other after-treatment (post-dyeing) (Greenpeace, 2005).

Because of residual chromium in millhouse effluent, additives such as metal sequestering agents (such as ethylenediaminetetraacetic acid, EDTA), or additional commercial products can be added to reduce the amount of remaining chromium or other metal in wastewater or effluents (Broadbent, 2001). Broadbent (2001) also suggests that metal-complex/mordant dye use may be in decline due to the need to meet water quality standards (particularly for chromium and cobalt), and the need for more sustainable and environmentally friendly dyeing practices (Broadbent, 2001).

### 4.6.3 Direct Dyes

Direct dyes (also called substantive dyes) are soluble in water, are comprised mostly of azo compounds, and are applied in an aqueous solution containing an electrolyte auxiliary (Broadbent, 2001; Aspland, 1991; Greenpeace, 2005; Holme, 2002; EC, 2003; Lacasse and Baumann, 2004). Direct dyes are nearly exclusively used for rayon/viscose fibers, with limited evidence for their application to nylon/polyamide. Dyeing with direct dyes takes place under neutral conditions adjusting for temperature and salt concentration (Broadbent, 2001). Sometimes polyvalent metal salts can be used but the expense is prohibitive (Broadbent, 2001). The salts help to ease the repulsive force when the negatively charged fiber, due to the zeta potential, interacts with an anionic dye. Salts (electrolytes) also reduce dye solubility in water, promoting dyebath exhaustion. Direct dyes typically contain a solubilizing group, such as sulfonic acid, carboxylic, or hydroxyl groups, and are typically long planar molecules that help them to non-covalently bind to fibers (mainly cellulosic) (Lacasse and Baumann, 2004; EC, 2003). Broadbent (2001) suggests that sometimes there is no clear molecular distinction between direct and acid dyes other than differences in molecular weight. In the 1980s, there were more than 200 types of direct dyes, representing more than 800 commercial products (Aspland, 1991). KEMI (2014) reports 1,568 different direct dyes found in the Colour Index.

Important direct dye structures include azo (disazo, trisazo and polyazo dyes) (roughly 82 percent), stilbene (roughly 5 percent), oxazine, and phthalocyanine, with some thiazole and copper complex azo dyes (Kent, 2012; Holme, 2002; Lacasse and Baumann, 2004; EC, 2003; Kirk-Othmer, 2009). Other phthalocyanine direct dyes also contain copper (Broadbent, 2001). Some stilbene direct dyes derived from 4-nitrotoluene-2-sulfonic acid have an imprecise composition, but contain stilbene and azo groups (Broadbent, 2001). Others are derived from triphenodioxazine (Broadbent, 2001). Previously manufactured direct dyes derived from benzidine and 2-naphthylamine are no longer in use as these compounds are known carcinogens, and there have been some reports investigating replacement compounds for these toxic components (Broadbent, 2001; Holme, 2002).

The dyeing process can be modified through the addition of substituents that alter water solubility, length of time needed for dyeing, temperature, electrolyte (salt) concentration, pH, and the addition of other auxiliaries (Aspland, 1991). Metals, such as copper or iron that might be present in the water supply, could adversely affect the dye hue and so soft water or a sequestering agent may be recommended (Broadbent, 2001).

Common auxiliaries include electrolytes (as noted above), such as sodium chloride or sodium sulfate (EC, 2003). Wetting agents to help evenly disperse the dye (such as nonionic/anionic surfactants) are common for this dye class, as well as after-treatments such as fixative agents (EC, 2003; Greenpeace, 2005; Lacasse and Baumann, 2004). Retardants for direct dyes can be

used (Greenpeace, 2005; Lacasse and Baumann, 2004). Additionally, when dyeing rayon/viscose, a buffer can be added (Aspland, 1991).

After-treatments for direct dyes can be costly and can impact the shade or hue (Broadbent, 2001). After-treatments include diazotization followed by developer application, treatment with formaldehyde and derivatives, metal-complex formation (potassium dichromate or coppering), cationic fixing, quaternary ammonium compounds, polynuclear aromatic phenols, cyanamide, or dicyandiamide and use of resins and cross-linking agents (Broadbent, 2001; EC, 2003; Kirk-Othmer, 2009). Reducing agents can be used during washing (Lacasse and Baumann, 2004). However, many of these approaches, including coppering and use of chromium, are rarely used due to either environmental problems or hue changes (Holme, 2002; EC, 2003). As noted under the metal-complex dyes, due to environmental concerns these post-metallization techniques are less desirable (Broadbent, 2001). Instead, the metallization step is conducted by the dye manufacturer to minimize the presence of unbound metal in dyehouse wastewater.

#### **4.6.4 Basic Dyes**

Basic dyes are slightly soluble in water (EC, 2003), and are the only cationic dye class investigated here. Due to their cationic nature, basic dyes are only applicable for use on acrylic/modacrylic fibers, with limited evidence to suggest their use on modified nylon/polyamide and modified polyester fibers. There are nearly 85 basic dyes represented by over 400 commercial products, which can be comprised of azo and anthraquinone compounds, although some use arylcarbonium ions, tri- or diphenylmethane, triarylmethane, ketone imines, acridine, oxazine, thiazine, azine, xanthene, polymethines, and other groups (Aspland, 1993a; Choudhury, 2011; Kirk-Othmer, 2009). Basic dyes are applied from weakly acidic dyebaths, and are soluble in acetic acid, ethanol, and certain other organic solvents (Aspland, 1993a; Kent, 2012; Lacasse and Baumann, 2004; EC, 2003). These cationic dyes mostly contain a quaternary amino group, and less commonly a positively charged oxygen or nitrogen heterocycle (EC, 2003). The chromophore is a cation leading to an ion-ion interaction, and an electrolyte is typically added to the dyebath during application (Broadbent, 2001).

The weakly acidic dyebaths for basic dyes include the dye itself and a number of additives, such as sequestrants to complex with metal ions that would interfere with the dyes, wetting agents, pH adjusters, salts, and retardants/levelers to help in dye leveling (Broadbent, 2001; Aspland, 1993a; Lacasse and Baumann, 2004; Kent, 2012). Levelers and retarders are the most common auxiliaries, with the most common of these being quaternary ammonium compounds, with additional electrolytes or condensation products and their salts also used (EC, 2003). Other additives are cationic or less frequently anionic, and include organic ammonium salts that contain hydrophobic chains and cationic polymers (Broadbent, 2001). For the dyeing of modified nylons, dye carriers and emulsifying agents can be used (Broadbent, 2001). After-treatments

(such as tannins) can be added to increase dye fastness, but after-treatments can also lead to shifts in hue (Broadbent, 2001; Aspland 1993a).

#### 4.6.5 Disperse Dyes

Disperse dyes are non-ionic, and relatively insoluble at room temperature (with limited solubility at higher temperatures), although a small amount of dye is in true aqueous solution (Broadbent, 2001; Aspland, 1992a). Their slight solubility is due to polar substituents (e.g., hydroxyethylamino groups) that create dipole forces and hydrogen bonds with water, which allow for some migration of the dye back out of the fiber (Broadbent, 2001; Greenpeace, 2005). Disperse dyes were the broadest class of dye investigated, and are applicable to acrylic/modacrylic, nylon/polyamide, and polyester fibers, with some limited use on spandex (polyurethane). These dyes are applied in water as fine aqueous suspensions utilizing a dispersing agent or leveling agent (Broadbent, 2001; Greenpeace, 2005). Metal ions (e.g., iron or copper) may react with the dye and cause shade changes, so sequestering agents may also be added, resulting in dyes that are considered unmetallized (Aspland, 1993b). There are more than 200 types of disperse dyes, representing more than 700 commercial products (Aspland, 1992a).

Disperse dyes are comprised of mainly (~50 to 59 percent) non-ionic azo (mono and bisazo) and to a lesser extent (~25 to 32 percent) anthraquinone compounds, with the remaining dyes comprised of diphenylamine, methine, nitro, benzodifuranone, or naphthoquinone (Freeman and Mock, 2012; Koh, 2011; Broadbent, 2001; Aspland 1993b, 1992a; Greenpeace, 2005; Lacasse and Baumann, 2004; Chakraborty et al., 2010; EC, 2003). They are characterized by the lack of a water-solubilizing group (EC, 2003). Newer disperse dyes have substituted aromatic heterocyclic structures containing sulfur, nitrogen, or oxygen (Aspland, 1993b). Azo-based disperse dyes are more commonly used than anthraquinone-based disperse dyes due to the higher cost of materials, complex processes, and use of mercuric ion catalysts in the latter class of dyes (Table 13) (Broadbent, 2001). The monoazo class of disperse dyes are based mainly on a substituted aminoazobenzene parent compound, with the potential to generate almost 30,000 different structures (Aspland, 1993b). Other monoazo dyes can be based on the parent compound hydroxyazobenzene (Aspland, 1993b). Heterocyclic azo disperse dyes can be based on azothiophenes, azobenzothiazoles, or azopyridones, among others (Aspland, 1993b). The anthraquinonoid disperse dyes are based on substitutions to the anthraquinone molecule (Aspland, 1993b).

Other important classes of disperse dyes (Koh, 2011; Aspland, 1993b; Chakraborty et al., 2010) include:

- Nitroaryl amino or nitrodiphenylamine disperse dyes;
- Coumarin disperse dyes;
- Methine (styryl or arylidene) disperse dyes;

- Naphthostyryl or naphthalimide disperse dyes;
- Quinophthalone disperse dyes;
- Formazan disperse dyes; and
- Benzodifuranone disperse dyes.

Because of their hydrophobic, sparingly water soluble properties, disperse dyes have an affinity for hydrophobic fibers (e.g., nylon and polyester), but can also be used for other synthetic and cellulose acetate fibers (Broadbent, 2001). Disperse dyes (mainly azo and anthraquinone) are particularly utilized for polyester fibers (EC, 2003). Acrylic fibers can also be dyed with disperse dyes, but dye adsorption is limited and color build-up is poor (Broadbent, 2001). The method of application is consistent across fiber types, with the exception of the dyebath temperature (Broadbent, 2001) or the addition of carriers/dispersing agents (i.e., for polyester fibers).

Polyester fibers are crystalline and very hydrophobic. Large dye molecules cannot easily penetrate the fiber. Polyesters have no ionic groups, meaning they are almost exclusively dyed with disperse dyes (Broadbent, 2001). Because the dyes diffuse extremely slowly into the polyester fibers at water temperatures below 100°C, a carrier/dispersant, an organic compound that increases the rate of dyeing, may be added to the dyebath (Broadbent, 2001; Aspland 1992a). Commonly used dispersants include formaldehyde condensation products and ligninsulfonates (EC, 2003). High temperature pressure dyeing (i.e., raising the temperature from 100 to 130°C) is an alternate dyeing process that increases the rate of dye diffusion without the need for a carrier. A reducing agent can be added in the final washing step, with the most common being sodium hydrosulfite (EC, 2003). Additional use of proprietary auxiliaries is common, as described in more detail in Section 4.7.

Post-dyeing, fibers can have a number of after-treatments applied, to either remove surface particles or for stripping purposes (Hauser, 2011). In this process, a strong reducing or oxidizing bath is utilized to help extract residual dye and auxiliaries (Hauser, 2011). Colorless fading inhibitors can be added to reduce gas fume or ozone fading and are added to the dyebath at the end of the dyeing process or post-treatment (Broadbent, 2001). Developing agents have included derivatives of aniline, toluidine, ortho- and meta-anisidine, and diphenylamine (Lacasse and Baumann, 2004). *ortho*-Toluidine and *ortho*-anisidine are now on the list of restricted aromatic amines (TFL, 2004). Commercial formulations can include non-ionic surfactants such as sulfated castor oil or formaldehyde (Broadbent, 2001).

For some polyester fiber blends, such as wool/polyester, there is some evidence for the use of phthalates [dimethyl phthalate (DMP), DBP, and DEHP] as carriers/accelerants (Table 13) (Greenpeace, 2005). The evidence for the use of phthalates is limited and no concentrations were given, other than the suggestion that the carrier content in the finished fibers is expected to be low (<0.2 percent) using the best available practices, but could be as high as 2.7 percent (Greenpeace, 2005). However, for non-specified phthalates that are used as carriers, Kirk-

Othmer (2013) suggests carriers are optimized from 1 to 12 percent calculated on the weight of the fiber (owf), depending on the dyeing methods. The manufacturing process and the raw materials used in synthesizing the disperse dyes differs for each class as well as for each color (Aspland, 1993b).

**Table 13. Summary of the CPSC specified phthalates or elements in dyes**

Chemical	Dye Type	Application/Use in Dyes
Chromium	Metal-Complex/Mordant	Mordant
Chromium	Direct	After-treatment/ metal-complex formation
Mercury	Disperse	Catalyst
DBP	Disperse	Carrier/ accelerant
DEHP	Disperse	Carrier/ accelerant
Mercury	Vat	Catalysts/ reagent
Arsenic	Vat	Catalysts/ reagent
Barium	Vat	Catalysts/ reagent
Chromium	Vat	Catalysts/ reagent
Chromium	Sulfur	After-treatment/ oxidation

#### 4.6.6 Reactive Dyes

There are more than 200 different reactive dyes, representing more than 400 different commercial products (Aspland, 1993b). Reactive dyes are applicable for use on nylon/polyamide and rayon/viscose fibers. They are characterized by the presence of at least one reactive group (sometimes containing more than one) linked to the chromogen, or chromophore, a group whose presence is responsible for the color of the compound (EC, 2003; Afirm Group, 2016). Some reactive dyes may be bifunctional, meaning they have two different reactive groups. Reactive dyes are water-soluble and react with the hydroxyl groups of cellulosic fibers to form covalent bonds in a two-step process (exhaustion, fixation) (Broadbent, 2001; Aspland, 1993b). Examples of chromophores are azo (mono), anthraquinone, triphenodioxazine, formazan, or metal-complex molecules, some of which contain copper or nickel complexes of phthalocyanines (EC, 2003; Broadbent, 2001; Afirm Group, 2016; Kirk-Othmer, 2009). Most reactive dyes are comprised of azo compounds (95 percent). The remaining 5 percent are comprised of anthraquinone, dioxazine, and phthalocyanine compounds. The most commonly used molecules for the reactive component of the dyes include vinylsulfone (the most common), chlorinated triazines, fluoropyrimidine, or chlorofluoropyrimidine (Afirm Group, 2016; Aspland, 1993b). Dyeing typically takes place in an alkali bath (sodium carbonate, bicarbonate, caustic soda) and with the addition of a salt (sodium chloride and sodium sulfate) (Aspland, 1993b; Greenpeace, 2005; EC, 2003). Urea has been used as a solubilizing agent for reactive dyes, but its use has been in

decline since the 1990s (Greenpeace, 2005; EC, 2003). Specialty leveling agents can also be used (EC, 2003).

Reactive dyes are prone to hydrolysis, which prevents the dye from fully reacting with the fiber. Dye solutions cannot be stored for later use without risk of hydrolysis (Broadbent, 2001). Reactive dyes, as with direct dyes, are susceptible to precipitation by calcium, magnesium, or heavy metal ions in the dyebath water. The dyes may also react with the metals to form insoluble metallic hydroxides during the alkaline fixation phase (Broadbent, 2001). Polyphosphate sequestering agents may be used to avoid these reactions (Broadbent, 2001).

#### 4.6.7 Vat Dyes

Vat dyes are chemically complex and insoluble in water (Baptista, 2009; Broadbent, 2001; Greenpeace, 2005). There is very limited information for the use of vat dyes as applied to the specified fibers. Only limited evidence was found for their use on rayon/viscose. However, the identified references suggest that vat dyes have some applications, and so they are included here, although the issue might be related to the authors not distinguishing general cellulosic fibers from rayon/viscose.

Vat dyes are comprised mostly of anthraquinone-based compounds (80 to 82 percent of vat dyes) or polycyclic quinones/indigoid (~9 percent) (Kent, 2012; Broadbent, 2001; Greenpeace, 2005; Kirk-Othmer, 2009). All vat dyes contain a quinonoid system based on a pair of conjugated carbonyl groups (Broadbent, 2001). Indigo was one of the earliest vat dyes, with many modern vat dyes being derivatives of indigo (i.e., indigoid dyes); these dyes are typically applied to denim (IARC, 2010; Lacasse and Baumann, 2004). The starting materials for creation of vat dyes include naphthalene, benzene, toluene, formaldehyde condensation products, ligninsulfonates and/or sulfuric acid to form anthraquinone (Baptista, 2009). Further reaction of anthraquinone, for example, through sulfonation, reaction with ammonia, or the addition of an aromatic ring can modify the end properties of each vat dye (Baptista, 2009). The chemical synthesis of the different vat dyes involves modification of these starting materials and the addition of various others through multiple synthetic steps leading to a plethora of available vat dye formulations (Baptista, 2009).

Vat dyes are reduced to a water-soluble (leuco) form in an alkaline solution before application to fibers, a process called “vatting” (Broadbent, 2001; Baptista, 2009; Greenpeace, 2005; Lacasse and Baumann, 2004). Once adsorbed by the fiber, the insoluble parent dye is regenerated in the fiber through oxidation (Broadbent, 2001; Baptista, 2009; Greenpeace, 2005). Strong reducing agents are necessary for the reduction of quinones—hydrosulfite, or “hydro” (the dehydrate of sodium dithionite) is used almost exclusively (EC, 2003; Broadbent, 2001). Thiourea dioxide, hydroxyacetone, sulfoxylic acid derivatives, and glucose are also used as “environmentally friendly” alternatives to hydro (EC, 2003; Broadbent, 2001). Common oxidative agents include

hydrogen peroxide, perborate, or 3-nitrobenzenesulfonic acid (EC, 2003). Finally, after-treatments are employed to improve fastness, such as boiling in a weak base with soap (EC, 2003). Solubilized vat dyes are also commercially available. These dyes avoid the complicated and time-consuming process of preparing the leuco solution. Solubilized vat dyes are prepared with sulfate esters of the leuco vat acid.

Common solvents in the manufacture of common vat dyes are nitrobenzene, naphthalene, and chlorinated solvents, including chlorobenzene, 1, 2-dichlorobenzene, and 1,2,4-trichlorobenzene (Baptista, 2009). Some of the key intermediate steps involve the use of heavy metal catalysts and reagents, such as mercury, arsenic, barium, copper, iron, manganese, lead, and chromium (concentrations not reported, but was noted that they can sometimes persist above the ETAD chemical limits in the vat dye waste stream (see Appendix D for details on ETAD) (Table 13) (Baptista, 2009; Lacasse and Baumann, 2004; Greenpeace, 2005).

Dispersing agents are often used in vat dye mixtures (mainly formaldehyde condensation products and ligninsulfonates) (EC, 2003; Greenpeace, 2005; Lacasse and Baumann, 2004). Leveling agents/surfactants can also be used, including ethoxylated fatty amines, betaines, polyalkylenamines, and polyvinylpyrrolidone (EC, 2003). Additional auxiliary agents include reducing agents, oxidizing agents, alkali agents, dispersing agents, anti-migration agents (polyacrylates and alginates), and leveling agents/surfactants (EC, 2003; Lacasse and Baumann, 2004).

#### **4.6.8 Sulfur Dyes**

Sulfur dyes are related to vat dyes in that they are also initially water insoluble, but are applied as a soluble anion (reduced using an alkali agent to a leuco form), and are then oxidized back (using hydrogen peroxide or halogen-containing compounds such as bromate, iodate, or chlorite) to the parent form once adsorbed to the fiber (EC, 2003; Broadbent, 2001; Greenpeace, 2005). Again, as with vat dyes, there was very limited information about the use of sulfur dyes as applied to the specified fibers. Only limited evidence was found for their use on rayon/viscose.

Sulfur dyes are simple to make through reacting organic compounds with sulfur, but their molecular structures are variable and in many cases unknown (IARC, 2010; Broadbent, 2001; EC, 2003). They are comprised of the reaction products of sulfur compounds with amines, phenols, or nitro compounds (EC, 2003; Lacasse and Baumann, 2004; Kirk-Othmer, 2009). Sulfur dye manufacturing involves modifying organic materials (such as amines, nitro compounds, phenols, and phenol derivatives) using either sodium polysulfide in solution, sodium sulfide, or sulfur (Broadbent, 2001; Greenpeace, 2005). Some starting chemicals include: amino derivatives, nitrobenzenes, nitro and aminobiphenyls, substituted phenols, substituted naphthalenes, condensed aromatic compounds, indophenols, azines, oxazine, thiazol, azine, or thiazine rings (Lacasse and Baumann, 2004; EC, 2003).

An example is given for the synthesis of benzothiazole sulfur dyes, involving *para*-toluidine and sulfur to produce 2-(*para*-aminophenyl) benzothiazole (Kent, 2012). Additional sulfur dyes can be manufactured using organic solvents (*n*-butanol) and indophenol intermediates (Kent, 2012). One of the most common sulfur dyes is synthesized by heating 2,4-dinitrophenol with sodium polysulfide (Kirk-Othmer, 2009).

The most common types of sulfur dyes are sulfur, leuco sulfur, and solubilized vat dyes (Broadbent, 2001). The solubilized sulfur dyes are prepared with sodium sulfite and are applied with a base and reducing agent (Broadbent, 2001; Lacasse and Baumann, 2004). The vating process involves the sulfur dye, sodium sulfide, sodium carbonate, and caustic soda (Broadbent, 2001). In some cases, glucose can be used to replace sodium sulfide as the reducing agent as it is more environmentally friendly (Broadbent, 2001). Other reducing techniques include electrolytic reduction, typically using sodium sulfide or sodium hydrogensulfide (EC, 2003; Broadbent, 2001). Due to environmental concerns, the use of sulfide-based reducing agents is in decline, and alternatives include glucose, sodium dithionite, or hydroxyacetone (Greenpeace, 2005; EC, 2003; Lacasse and Baumann, 2004). During dyeing, wetting/penetrating agents, sequestrants, and salts are used (EC, 2003; Broadbent, 2001). As with vat dyes, dispersing agents can be used (Greenpeace, 2005). Additional auxiliaries include alkali agents (caustic soda), salts (sodium chloride, sodium sulfate), dispersing agents (naphthalenesulfonic acid-formaldehyde condensates, ligninsulfonates and sulfonated oils), and complexing agents (EDTA and polyphosphates) (EC, 2003; Lacasse and Baumann, 2004). In the continuous dyeing process with sulfur dyes, the dyed fabric can be rinsed using sodium bromate and a catalyst (metavanadate) (Broadbent, 2001). Chromium salts can be used for oxidation and post-dyeing treatments but the use is in decline due to environmental concerns (Table 13) (Broadbent, 2001; Greenpeace, 2005).

#### 4.6.9 Azoic/Naphthol Dyes

More than half of all textile dyes contain azo groups and can be classified as azo dyes (Greenpeace, 2005). Azoic/naphthol dyes are similar to other azo dyes, but structurally lack the sulfonic acid solubilizing group (EC, 2003; Lacasse and Baumann, 2004). Naphthol dyes are distinguished from other classes of azo dyes by the method of dye fixation (Greenpeace, 2005). These dyes are water insoluble, but are technically considered dye ‘combinations’ in that the colorant is actually formed inside the pores of the textile fiber, sometimes referred to as an ingrain dye (Kent, 2012; Broadbent, 2001). Diazotization and coupling reaction steps similar to other azo dyes are conducted, but the dye formation takes place in two steps in the fiber as opposed to prior to dyeing (EC, 2003). These dyes also are limited in their application to the specified fibers, with just a few sources suggesting their use on rayon/viscose, and some evidence of their use on modified nylon/polyamide and modified polyester.

Ingrain dyes have limited uses in the specified fibers, and are more useful for printing than dyeing, with some limited application to viscose and polyester (EC, 2003; Broadbent, 2001).

Azoic/naphthol dyes all contain a naphthol component (derivatives of the anilides of 2-hydroxy-3-naphthoic acid, also called naphthol AS), and so are also known as naphthol dyes, which are formed using caustic soda, and in some cases alcohol or formaldehyde (Kent; Broadbent, 2001; EC, 2003; Lacasse and Baumann, 2004). Because of the precise chemistry needed to apply this complex dye, many companies opt instead to use other dyes with simpler application/formulation processes (Greenpeace, 2005; EC, 2003).

#### **4.7 Pre-treatment, Auxiliaries, and Post-Dyeing Treatments**

There are a number of factors involved in modification of the dye transfer from the solution to the fiber. The main modifiable features include solution pH, addition of an electrolyte, temperature, and the addition of dispersing agents that aid in the formation of stable aqueous solutions for low solubility dyes (Chakraborty, 2014; Aspland, 1991; Broadbent, 2001). Additional auxiliary chemicals are added to the dye solution in addition to the acids, bases, and salts, either prior to, during, or after the dyeing process (see Figure 1 in Section 2.1). These include surfactants, wetting/dispersing/leveling agents, carriers, emulsifiers, and after-treatments (dye fixers). Many of these products can be purchased commercially which limits the ability to identify the chemicals in the proprietary formulations (Broadbent, 2001). Additionally, many of the same chemical auxiliaries can be used for multiple purposes throughout the dyeing process, which further complicates their evaluation (Broadbent, 2001).

For proper dyeing, fibers should not contain any impurities, and it is recommended that the fibers be appropriately prepared prior to dyeing to remove fiber processing aids and impurities on the fabric (Chakraborty, 2014; Aspland, 1991). The presence of impurities in fibers would hinder the dyeing process and lead to irreproducible results. Man-made fibers typically do not have naturally occurring impurities, such as soil, and impurities would most likely be acquired through the manufacturing processes, such as machining oils (Chakraborty, 2014). For example, fibers can be oiled, waxed, or can contain sizing materials and other synthetic chemicals that need to be removed or scoured from the fabric prior to dyeing (Aspland, 1992a; Broadbent, 2001; Aspland, 1991). The presence of impurities can impact the dye deposition/adsorption onto and diffusion into the fiber, and ultimately impacts the resulting shade of the color and the dye fastness (Broadbent, 2001; Chakraborty, 2014; Aspland, 1991). For example, the presence of metal ions in processing water, such as calcium, magnesium, copper, and iron can impact the hue of direct dyes and their removal is recommended using sequestering agents (such as EDTA, nitrilotriacetic acid (NTA), or sodium hexametaphosphate) (Aspland, 1991, 1992a). Calcium and magnesium can interfere with dispersing agents, leveling agents, and wetting agents (Aspland, 1992a). Even chlorine compounds found in water can affect some direct dyes, and antichlors can be recommended (such as sodium bisulfite or sodium thiosulfate) (Aspland, 1991). Pre-treatment, such as washing and scouring of fibers, helps to remove impurities prior to dyeing (Broadbent, 2001; Chakraborty, 2014). Other pre-treatments, such as bleaching and stripping, are needed in order to start with a white ‘background’ fiber to ensure even absorption for the correct

shade of color (although such pre-treatments are not always needed for synthetic fibers) (Broadbent, 2001; Chakraborty, 2014). Bleaching is typically performed with hydrogen peroxide, and stripping is performed with reducing agents, such as sodium hydrosulfite (Broadbent, 2001).

Due to initial scoping of this work (Figure 1 in Section 2.1), much of the fiber pre-treatment and fiber/dye after-treatments were outside the scope of this research. However, auxiliaries that are added to the dyebath during dyeing are covered below.

#### 4.7.1 Auxiliaries

A number of auxiliary chemicals may be added during the dyeing process to aid in dye affinity to a fiber (Lacasse and Baumann, 2004). Leveling agents (retarders) are added to promote dye leveling and act by retarding dye absorption at a certain pH or temperature (Broadbent, 2001; Aspland, 1992a). Wetting agents, penetrating agents, and de-aerating agents all perform the same function, and are typically nonionic surfactants (Aspland, 1992a). Additional auxiliaries are involved in the dyeing process, such as dispersing agents (EC, 2003). Many of these auxiliary agents, however, do not remain on the fiber post-dyeing (EC, 2003; Lacasse and Baumann, 2004; KEMI, 2013). For example, volatile substances are expected to evaporate from the finished textile; others can be removed as they function to aid the dyeing process but are not taken into the fiber themselves and do not provide any additional properties to the finished textile (KEMI, 2013). The typical auxiliaries, such as surfactants, detergents, emulsifiers, salts, acids, and bases, are typically washed off of the fiber when best available practices are used (KEMI, 2013, 2014). This is in contrast to potential unintended contaminants that may remain in the textile, such as formaldehyde, polyaromatic hydrocarbons, arylamines, heavy metal impurities, or unreacted raw materials (KEMI, 2014).

Specific auxiliaries that can be added to each of the dye classes are listed in Table 14. General information on what the auxiliaries are and the kinds of chemicals used are described in brief below. Because the terminology is often repetitive, there can be multiple names for auxiliaries that perform similar functions, and there can be alternative uses for auxiliaries that might be added for one reason yet used *in situ* for another. For example, surfactants can be used as washing agents, dispersing agents, or leveling agents. For this reason, there is overlap of the auxiliary categories and chemicals in the below lists and Table 14.

The following bullet list explains what each auxiliary is and the most common types, while Table 14 covers all auxiliaries TERA identified in association with the fiber dyes.

- *Complexing agents/sequestering agents* are used to remove the presence of ions in process/dye water that might disrupt the dyeing process. The most common include:

EDTA, NTA, Diethylenetriaminepentaacetic acid (DTPA), phosphonic acid, and gluconic acid derivatives (EC, 2003).

- *Dispersing agents or solubilizing agents* are used to aid in dissolution of dye in water and to promote of the formation and stability of dye dispersions and are typically used with vat, disperse, and sulfur dyes (Lacasse and Baumann, 2004; EC, 2003). These agents can include alcohols, polyols, fatty alcohol ethoxylates, esters, naphthalene sulfonic acid-formaldehyde condensates, naphthalene sulfonates, lignosulfonates, fatty alcohol ethoxylates, alkylsulfonates, alkylaryl sulfonates, ethylene oxide/propylene oxide copolymers, acrylic acid-maleic acid copolymers, and polyacrylates (KEMI, 2013; Choudhury, 2011; EC, 2003).
- *Wetting agents* are a type of dispersing agent and are used to increase wetting capacity of the dye liquor and to improve dye penetration and absorption. These agents can include alkylsulfates, alkanesulfonates, alkylarylsulfonates, salts of sulfosuccinic acid esters, fatty alcohol ethoxylates, alcohols of higher valence, phosphoric acid esters, and hydrocarbons (KEMI, 2013; EC, 2003).
- *Leveling agents* (also termed *retarding agent, migration or anti-migration agent*), are another type of auxiliary that overlaps with the dispersing agent category. These agents aid in obtaining an even distribution of dye across the textile fibers, and can include alkyl-, alkylaryl-, alkylamine-, and alkylarylamine ethoxylates, fatty acid esters and amides, fatty acid condensates, alkylphenol ethoxylates, polyvinyl pyrrolidone, quaternary ammonium salts, alkyl sulfates, and alkyl aryl sulfonates (KEMI, 2013; EC, 2003).
- *Carriers* (also termed *accelerants*) are similar to dispersants in that they accelerate dye absorption and diffusion (particularly for polyester fibers) (EC, 2003). These agents include aromatic hydrocarbons, chlorinated aromatic compounds, benzoic acid esters (benzylbenzoate), phthalic acid esters (i.e., phthalates), alkyl phthalimides, halogenated benzenes (1,2 dichlorobenzene, 1,2,4-trichlorobenzene, dichlorotoluene), phenols (including *o*-phenylphenol and benzylphenol), and alkylphenoethoxylates (KEMI, 2013; EC, 2003; Guzman et al., 2013). Some of the specified phthalates have been noted as carriers for polyester fiber, including DBP and DEHP (Greenpeace, 2005; Lacasse and Baumann, 2004; EC, 2003). Other phthalates (dimethyl phthalate, diethyl phthalate, diallyl phthalate, and dimethyl terephthalate) were noted for use as carriers, but are not the phthalates specified for this project (Guzman et al., 2013). Concentrations of these phthalates were not reported. However, Kirk-Othmer (2013) suggest carriers are optimized from 1 to 12 percent calculated on the weight of the fiber, depending on the dyeing equipment.
- *Surfactants/emulsifiers* that are commonly used include fatty alcohol ethoxylates, fatty amine ethoxylates, fatty acid ethoxylates, triglyceride ethoxylates, alkylphenol ethoxylates, ethylene oxide/propylene oxide adducts (EC, 2003). Anionic surfactants are more common than cationic or amphoteric surfactants, and include sulfates (e.g., alcohol ethoxysulfates, alkanolamides sulfates, sulfated vegetable oils), sulfonates (e.g.,

alkylbenzene sulfonates, sulfonated vegetable oils, naphthalene sulfonates, ligninsulfonates), alkyl ether phosphates, and carboxylates (fatty acid condensation products, alkali salts of fatty acids) (EC, 2003). Cationic surfactants include quaternary ammonium compounds (salts) (EC, 2003). Amphoteric surfactants include betaine derivatives, imidazolines, and modified fatty amino ethylates (EC, 2003).

- *Buffers* and/or *oxidizing substances* may be used for protection of sensitive fibers include nitrobenzene sulfonate, urea, or alkylarylsulfonates (KEMI, 2013).
- *Lubricants* and *anti-static agents* include mineral oils, ester oils, or synthetic lubricants (EC, 2003).
- *After-treatments* and some *fixative agents* include the use of metal salts, such as potassium dichromate (Lacasse and Baumann, 2004). Butyl benzyl phthalate (BBP) may be used as a dye fixative agent, along with chromium, cobalt, and copper compounds (concentrations were not reported) (Lacasse and Baumann, 2004).

Additional finishing processes that are outside the scope of this current report may include the specified metals and phthalates (barium sulfate, antimony trioxide, mercuric compounds, cadmium, DEHP, and DBP) (Lacasse and Baumann, 2004). Concentrations were not reported, and additional research into textile finishes was not conducted. However, Lacasse and Baumann (2004) reported “expected” concentrations in textiles for some of these compounds, which would vary depending on the fiber material and type of dye used (e.g., mercury-0.01 ppm; chromium-a few ppm).

**Table 14: Listing of identified chemical auxiliaries for use in dye manufacture, the dyeing process, or limited finishing<sup>a</sup>**

Dye	Auxiliaries
Reactive	<ul style="list-style-type: none"> <li>• <u>Alkali/acid/base/pH</u> – sodium carbonate, bicarbonate, caustic soda, sodium hydroxide, formic acid, acetic acid, sodium dihydrogenphosphate</li> <li>• <u>Salt/electrolyte</u> – sodium chloride, sodium sulfate</li> <li>• <u>Sequestering agents</u> – EDTA, polyphosphates</li> <li>• <u>Leveling agents</u></li> <li>• <u>Others</u> – urea, cyanoguanidine, sodium silicate</li> <li>• <u>After-treatment</u> – ammonia</li> </ul>
Direct	<ul style="list-style-type: none"> <li>• <u>Salt/electrolyte/reducing agent</u> – sodium chloride, sodium sulfate (anhydrous or decahydrate), Glauber’s salt</li> <li>• <u>Wetting/dispersing agents</u> – non-ionic surfactants, fatty amines, fatty acids, alkylphenols, propylene oxide polymers, ethoxylated fatty alcohols) and anionic surfactants (fatty alcohol sulfates, alkyl aryl sulfates, sulfonated castor oil)</li> <li>• <u>Leveling agent</u> – surfactants derived from polyethylene oxides</li> <li>• <u>Retardants</u> – quaternary ammonium compounds</li> <li>• <u>Buffers</u> – ammonium sulfate, <i>m</i>-nitrobenzene sulfonic acid salts</li> <li>• <u>Sequestering agents</u> – EDTA, sodium hexametaphosphate</li> <li>• <u>Fixative cationic agents</u> – quaternary ammonium compounds, formaldehyde condensation products, polynuclear aromatic phenols, cyanamide, dicyanamide, polyamines, polyethyleneimine derivatives, metal salts (copper sulfate, potassium</li> </ul>

Dye	Auxiliaries
	<p>dichromate)</p> <ul style="list-style-type: none"> <li>• <u>After-treatment</u> – formaldehyde, coppering</li> </ul>
Vat	<ul style="list-style-type: none"> <li>• <u>Alkali/base/reducing agents/salts</u> – sodium dithionite, sulfoxylic acid derivatives, thiourea dioxide, glucose, hydroxyacetone, sodium hydrosulfite, sodium chloride, sodium dithionite, thiourea dioxide, sulfoxylic acid, hydroxyacetone, caustic soda</li> <li>• <u>Leveling agents</u> – surfactants (fatty amine ethoxylates, fatty alcohol ethoxylates), betaines, polyalkylenamines, polyvinylpyrrolidone, polyamide amines</li> <li>• <u>Dispersing agents</u> – formaldehyde condensation products, naphthalenesulfonic acid, ligninsulfonates</li> <li>• <u>Oxidizing agents</u> – hydrogen peroxide, halogen containing agents, perborate, 3-nitrobenzensulfonic acid, air</li> <li>• <u>Anti-migration agents</u> – polyacrylates, alginates</li> <li>• <u>Others</u> – caustic soda, sodium sulfate</li> <li>• <u>After-treatment</u> – soap, weak alkaline detergent liquor</li> </ul>
Sulfur	<ul style="list-style-type: none"> <li>• <u>Reducing agents</u> – sodium sulfide or disulfide, sodium hydrosulfide, glucose-based agents (glucose/sodium dithionite, glucose/thiourea dioxide), hydroxyacetone, formamidine sulfinic acid, or proprietary agents, iron-amine complexes</li> <li>• <u>Wetting/penetrating agents</u> – phosphated 2-ethylhexanol, sodium polysulfide</li> <li>• <u>Alkali/base</u> – caustic soda, sodium carbonate</li> <li>• <u>Salt</u> – sodium chlorite or chloride, sodium sulfate</li> <li>• <u>Dispersants</u> – naphthalenesulfonic acid-formaldehyde condensates, ligninsulfates, sulfonated oils</li> <li>• <u>Sequestrants/complexing agents</u> – EDTA, polyphosphates</li> <li>• <u>Oxidizing agents</u> – hydrogen peroxide, halogenated compounds (bromate, iodate, chlorite), chromium salts</li> <li>• <u>Rinsing agent/after-treatment</u> - sodium bromate, metavanadate</li> </ul>
Naphthol/ azoic	<ul style="list-style-type: none"> <li>• <u>Preparation of naphtholate</u> – caustic soda, formaldehyde, sodium chloride</li> <li>• <u>Preparation of diazotized base</u> – sodium nitrite, hydrochloric acid, sodium acetate, disodium phosphate, acetic acid</li> </ul>
Disperse	<ul style="list-style-type: none"> <li>• <u>Acid/base/pH</u> – acetic acid, ammonium sulfate, formic acid, sodium dihydrogen phosphate</li> <li>• <u>Leveling agents</u> – aliphatic carboxylic esters, ethoxylated products, mixtures of alcohols, esters or ketones of emulsifying agents, ethoxylated castor oil, stearic acid, sulfuric or phosphoric esters of ethoxylated fatty alcohols or alkylphenols, cyclodextrins, carboxylic esters</li> <li>• <u>Complexing agents</u> – EDTA</li> <li>• <u>Carriers</u> – <ul style="list-style-type: none"> <li>○ Aromatic hydrocarbons – diphenyl, naphthalene, toluene</li> <li>○ Phenols – phenol, <i>o</i>- and <i>p</i>-chloro-phenols, <i>o</i>- and <i>p</i>-phenylphenol, <i>m</i>-cresol</li> <li>○ Chlorinated aromatics – mono, di, and trichlorobenzene, chlorinated naphthalene</li> <li>○ Aromatic acids – benzoic, chlorobenzoic, <i>o</i>-phthalic.</li> <li>○ Aromatic esters – methyl benzoate, butyl benzoate, dimethyl and diethyl phthalate, dimethyl terephthalate, phenyl salicylate</li> <li>○ Aromatic ethers – <i>p</i>-naphthyl methyl ether</li> <li>○ Miscellaneous – acetophenone, phenyl cellosolve, phenylmethyl carbinol, methyl salicylate, benzanilide, halogenated toluene, aliphatic carboxylic esters, tetralin, phthalic acid <i>N</i>-butylimide, chlorophenoxyethanol</li> </ul> </li> <li>• <u>Dispersing agent</u> – sodium salt of sulfated ricinoleic acid, lignosulfonates, sulfonates of alkylnaphthalene-formaldehyde condensates, or sodium oleyl-<i>p</i>-anisilidide sulfonate, condensation products of naphthalene-<i>beta</i>-sulfonate and formaldehyde, alkylsulfates, alkylarylsulfonates, soap powder, Turkey Red Oil, fatty alcohol-ethylene oxide condensates, polycondensates of arylsulfonic acids with formaldehyde, sodium oleyl-<i>p</i>-</li> </ul>

Dye	Auxiliaries
	<p>aniside sulfonate, sulfoaromatic condensation products or nonionic surfactants</p> <ul style="list-style-type: none"> <li>• <u>Anti-migration/thickeners</u> – polyacrylates, alginates, commercial formulations (polymeric electrolytes)</li> <li>• <u>After-treatment</u> – sodium hydrosulfite (sodium dithionite), caustic soda/sodium hydroxide, benzophenone, triazole compounds, acetone, zinc sulfoxylate-formaldehyde, sodium chlorite, nitrosated amines, phenol anti-oxidants</li> </ul>
Acid	<ul style="list-style-type: none"> <li>• <u>pH/acid/retarding agent</u> – ammonium sulfate, ammonium acetate, ammonium tartrate, sodium pyrophosphate, sodium sulfate (decahydrate), sodium acetate, esters of organic acids, acetic acid, formic acid, sulfuric acid, sodium salts of sulfonic acids, acetic acid/ethanoic acid, ammonium ethanoate, sodium pyrophosphate, esters of organic acids, Glauber's salt</li> <li>• <u>Surfactants/leveling agents</u> – anionic, cationic, non-ionic surfactants, salts, quaternary ammonium compounds <ul style="list-style-type: none"> <li>○ anionic leveling agents – mono- and polysulfonates of aliphatic and aromatics,</li> <li>○ cationic leveling agents – fatty amines, ethoxylated fatty amines</li> <li>○ nonionic surfactants – ethylene oxide adducts, ethoxylated fatty alcohols, fatty acids, alkylphenols, fatty mercaptans</li> </ul> </li> <li>• <u>Anti-foaming agent</u></li> <li>• <u>After-treatment</u> – tannic acid (polygalloyl glucose), synthetic tannins, potassium antimony oxide tartrate, synthanes (condensation products of aromatic sulfonic acids with formaldehyde), condensation products of phenol, cresol, catechol, naphthol</li> </ul>
Chrome/ mordant	<ul style="list-style-type: none"> <li>• <u>pH/acid/liquor formation</u> – ammonium sulfate, acetic acid, formic acid, calcined sodium sulfate, ammonia, tartaric acid, lactic acid, sulfuric acid, sulfamic acid</li> <li>• <u>Reducing/complexing agent</u> – sodium phosphate, ammonium phosphate, sodium thiosulfate</li> <li>• <u>Chroming/mordant</u> – potassium dichromate, sodium chromate or dichromate, chromate salt</li> <li>• <u>Leveling agents</u> – typically amphoteric or non-ionic, ethoxylated fatty alcohols, alkyl phenols, fatty amines</li> <li>• <u>Salts</u> – sodium sulfate, ammonium acetate, sulfates, sodium phosphate, or ammonium phosphate</li> <li>• <u>After-treatment</u> – syntans, thiosulfate</li> <li>• <u>Metal sequestering agent</u> – lactic acid, tartaric acid, additional commercial products</li> </ul>
Metal- complex (pre- metalized) (1:1, 1:2)	<ul style="list-style-type: none"> <li>• <u>pH/acid</u> – sulfuric acid, formic acid, acetic acid, calcined sodium sulfate, ammonia, sodium acetate, ammonium sulfate, ammonium acetate</li> <li>• <u>Metals</u> – chromium salts, cobalt salts, nickel salts, copper, aluminum, tin, iron</li> <li>• <u>Leveling agent</u> – alkanethoxylates, polyethyleneoxide, ethoxylated fatty amines, Glauber's salt, anionic, cationic, non-ionic surfactants, salts, quaternary ammonium compounds, sulfate salts <ul style="list-style-type: none"> <li>○ anionic leveling agents – mono- and polysulfonates of aliphatic and aromatics</li> <li>○ cationic leveling agents – fatty amines</li> <li>○ nonionic surfactants – ethylene oxide adducts, ethoxylated fatty alcohols, fatty acids, alkylphenols, fatty mercaptans</li> </ul> </li> </ul>
Basic	<ul style="list-style-type: none"> <li>• <u>pH/acid/liquor formation</u> – acetic acid, ethanol, ether, sodium acetate, water</li> <li>• <u>Salt/electrolyte</u> – sodium chloride, sodium sulfate, sodium acetate, sulfate anions</li> <li>• <u>Retardants/leveling</u> – anhydrous sodium sulfate, cationic agents (quaternary ammonium salts, quaternary amines, polymeric compounds, polyethoxylated amines), anionic (naphthalenesulfonic acid-formaldehyde condensation products), Glauber's salt</li> <li>• <u>Sequesterants</u> – EDTA</li> <li>• <u>Wetting agents</u> – nonionic surfactants</li> <li>• <u>Dispersing agents/migration aids</u> – non-ionics, quaternary ammonium salts (trimethylbenzylammonium chloride), electrolytes (sodium chloride, sodium sulfate, organic salts)</li> </ul>

Dye	Auxiliaries
	<ul style="list-style-type: none"> <li>• <u>Accelerants</u> – ethylene and propylene carbonate, benzyloxypropionitrile</li> <li>• <u>Modacrylic carriers</u> – triisobutyl phosphates</li> <li>• <u>After-treatments</u> – tannins</li> </ul>

<sup>a</sup>Sources include: Aspland, 1993a, 1992a, 1991; Kent, 2012; Lacasse and Baumann, 2004; Choudhury, 2011; EC, 2003; Broadbent, 2001; Greenpeace, 2005; Holme, 2002; Baptista, 2009; Koh, 2011; Science Tech Entrepreneur, 2006.

## 4.8 Summary of the Specified Elements and Phthalates in Dyes and Auxiliaries

Heavy metals may be present either as impurities in certain fibers themselves or through their use in the manufacture of dyes (Greenpeace, 2005). They may be found as impurities in the fibers due to their use as catalysts in fiber manufacturing, such as antimony trioxide (EC, 2003). They are found in the dyes mainly due to their use as mordants/complexing agents (EC, 2003). As noted above, most manufacturers are aiming to reduce the use and concentration of metals as impurities (EC, 2003). Voluntary limits, such as the ETAD limits that restrict the emission of heavy metals in manufacturing wastewater, encourage decreasing metal usage (see Appendix D) (ETAD, 2016; EC, 2003).

The most common metals include chromium, copper, nickel, and cobalt (Greenpeace, 2005). These metals, however, are expected to be bound in the dye matrix: copper and nickel in phthalocyanine dyes, copper in reactive dyes, and chromium in metal-complex acid dyes (EC, 2003). Bound metals are anticipated to be of lesser concern for human and environmental exposures as manufacturers minimize losses of metal throughout the dyeing process and because the bound metals are minimally bioavailable once incorporated into the dye (EC, 2003). The main concern would be from metal impurities that are not intentionally added or that persist after washing (EC, 2003).

The potential for some of the elements and phthalates to be present in the dyes for the specified fibers is summarized below. Little to no information was found on the potential concentrations, and some of these uses were in finishes that would be introduced after dyeing and are outside the scope of this research. For example, DEPA (2003) reports the use of flame-retardants containing antimony, cadmium use in added biocides, and barium in pigment manufacturing, all of which are outside the scope of this research. It has been suggested that the use of best available practices and fiber washing will remove much of these residuals from the fiber, but that cannot be guaranteed (KEMI, 2014; Lacasse and Baumann, 2004). Table 15 summarizes the potential uses of the specified elements and phthalates, including some information for applications that are outside the scope of this research.

**Table 15. Potential for elements and phthalates to be used in dyes for the specified textile fibers (Lacasse and Baumann, 2004)**

Compound	Use
Antimony trioxide/oxide	Flame retardant auxiliary
Antimony pentoxide	Flame retardant additive
Antimony trichloride	Flame retardant additive
Arsenic	Catalyst/reagent
Barium chloride	Dyeing auxiliary; mordant; catalyst
Barium hydroxide	Dyeing auxiliary; mordant; catalyst
Barium sulfate	Coloring 'pigment' auxiliary
Butyl benzyl phthalate	Fixative agent
Cadmium	Metal impurity from fiber production
Cadmium selenide	Biocide
Chromic acid	Oxidizing agent
Chromium (III) oxide	Catalyst; mordant
Chromium compounds (salts)	Fixative agent; mordant
Chromium (III)	Acid dye
Chromium VI	Fixative agent
Dibutyl phthalate	Softener (finishing); plasticizer (finishing); carrier/accelerant
Di-2-ethylhexyl phthalate	Softener (finishing); plasticizer (finishing); carrier/accelerant
Diisodecyl phthalate	Plasticizer (finishing)
Dioctylphthalate	Coloring 'pigment' auxiliary
Mercury	Metal impurity from fiber production; biocide

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## **5 Summary of the Potential for the Specified Elements and/or Specified Phthalates to be Present in the Specified Fibers and Resultant Textiles and their Dyes**

Using our research approach, TERA found relatively little information on the concentrations of the specified phthalates or elements in the fibers or the common dyes used in these fibers, although, we did find evidence of their use. The tiered approach (described in Section 2) employed for this project to research the raw materials and manufacturing for undyed fibers and their commonly used dyes for presence of the 10 specified phthalates and 7 specified elements was an effective way to identify relevant information (or data) sources. An area for additional searching that was identified in research for this report, but was outside of the project scope is the presence of the phthalates or elements in finished textiles (and is briefly summarized in Appendix E).

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 element(s), specific fibers(s), and/or dye type(s) in Tiers 3 and 4. The more than 5,100 sources identified in Tier 1 searches for fibers and dyes formed the “universe” of information from which we pared relevant library book sources (from 445 to 21). Secondary sources from authoritative websites were pared (from 49 to 9) in Tier 2.

Tier 3 involved:

- 1) a search of the primary literature in three online databases for specified textile fibers and the commonly used dyes on those fibers, and
- 2) more targeted search of the three online databases using search string combinations of the fibers, dyes, phthalates, and elements of interest to this project.

The first approach yielded over 2,403,000 “hits” or citations, whereas the more targeted approach yielded 1,454 references from which 541 were screened as potentially relevant to the phthalates, elements, fibers, and dye classes for this task (Table 9). Gap searching (Tier 4) was conducted with searches of Google, Google Scholar, and SciFinder for concentration data for the specified phthalates and elements. This search resulted in a number of hits related to whole textiles of unknown finishing. TERA searched by a variety of search terms/strategies and numerous sources, and yielded what we considered to be a nonbiased and representative sample of the “universe” of information on the specified phthalates and elements in the six specified undyed fibers and the dyes commonly used on those fibers. This assertion is supported by the more than 5,100 sources found in Tier 1, the 49 websites, and 541 library sources in Tiers 2 and 3, respectively. Limited additional relevant articles were found in Tier 4.

Our search techniques for this task and previous tasks have identified large amounts information on the phthalates and the specified elements, as well as information on raw materials, manufacturing, and additives used in the various polymers and materials. The 10 specified phthalates are produced in large quantities, making them High Production Volume (HPV) chemicals and they have been widely studied, as have the specified elements. Given the similar search strategies and the limited success at getting this information for previous tasks, we can be confident that if there had been information on the phthalate or element content of the six fibers and dyes we most likely would have found it. In fact, the consistent lack of information amongst the many sources we searched, both secondary authoritative web, library sources, and primary literature sources, made us highly confident that there was very little information to be found on the specified phthalates and elements in the six fibers and commonly used dyes on those fibers.

## 5.1 Summary of Findings of the Presence of Specified Phthalates and Elements in Undyed Fibers

Little data on the presence and/or concentration of the specified phthalates and elements were found for each of the undyed fibers. Nearly all of the information on concentration came from studies of whole textiles with unknown applied finishes; these are compiled in Appendix E.

- *Polyester*: Literature sources for concentrations of the specified phthalates and elements in polyester were very limited. While trace inorganic contaminants such as arsenic and chromium may be found as residuals in polyester fibers, they are considered impurities and reported at concentrations less than or equal to 1 ppm, below its soluble limit (Banat and El-Rub, 2001). Antimony compounds may be used as a catalyst in polycondensation processes at a concentration that may exceed the 60 ppm limit. Thiele (2004) corroborated that greater than 90 percent of worldwide polyester is manufactured by adding antimony-based catalysts at concentrations of 150-300 ppm antimony during polycondensation. Research with finished textiles indicates antimony may be a concern (see Section 6 and Appendix E).
- *Polyamide/Nylon*: Literature sources for concentrations of the specified phthalates and elements in nylon were very limited.. The information for the raw materials and manufacturing do not indicate chromium is used in the undyed fiber. However, concentration in one sample of textile was above its soluble limit of 60 ppm (Appendix E).
- *Acrylic/modacrylic*: No specified phthalates or elements are reportedly used in the manufacture or processing of undyed acrylic or modacrylic fiber or fabric. No studies of concentrations of the specified elements in acrylic or modacrylic were found in the literature searched.
- *Spandex/polyurethane*: No specified phthalates or elements are reportedly used in the manufacture or processing of undyed spandex fiber or fabric. No studies were located in

the resources searched regarding the concentrations of the specified phthalates or elements in spandex fiber.

- *Natural latex rubber*: No studies were identified reporting the concentrations of the specified elements in natural latex rubber. Only one migration study, with several limitations, measured phthalates in natural latex rubber was found. Jayawardena et al. (2016) reported DBP, DIBP, or BBP migration concentrations of 1.33 to 3.07 percent in 3 of 8 samples, indirectly indicating that these phthalates were present.
- *Viscose/rayon*: There were no studies on the specified phthalates in unfinished viscose rayon fiber. An overview of the undyed fibers that may contain one of the 10 specified phthalates or one of the 7 specified elements is presented in Tables 16 and 17, respectively. The conclusion regarding concentrations is based on very limited data despite extensive research. The potential for either the phthalates to be present above the limit or the elements to be present above their ASTM soluble limits is indicated in the table with shading. Two reports (Dogan et al., 2001; Rezic and Steffan, 2007) reported levels of chromium, arsenic and cadmium less than their respective soluble limit.

**Table 16. Overview of Specified Phthalates found in Undyed Fibers and Textiles**

Phthalate	Polyester <sup>a</sup>	Nylon <sup>a</sup>	Acrylic/ Modacrylic <sup>a</sup>	Spandex	Rayon	Natural Latex Rubber
	DEHP	√	√	√		√ <sup>b</sup>
DBP	√	√	√			√
BBP						√
DINP						
DIDP						
DnOP						
DIBP	√	√	√			√
DPENP						
DHEXP						
DCHP						

<sup>a</sup> Concentrations less than 1000 ppm limit

<sup>b</sup> May have resulted from printing

Shaded: potential for phthalate to be present above 1000 ppm limit

Blank cells indicate no data

Antimony was reported only in polyester and at concentrations above its soluble limit; antimony is used as a catalyst in the manufacture of polyester. While arsenic may be found in polyester, nylon and rayon, it is considered an impurity and reported at concentrations less than or equal to

1 ppm, below its soluble limit. Similarly, chromium may be found in polyester, nylon and rayon with concentrations below its soluble limit. Cadmium may also be found in polyester, nylon, rayon and natural rubber latex, although there are no studies of concentrations in the latter fiber. While cadmium concentration is usually below its soluble limit, one sample was found with greater levels (although it appears this was a finished textile and not the undyed fiber). No information on barium, mercury or selenium was located in the research.

**Table 17. Overview of Specified Elements found in Undyed Fibers and Textiles**

Element	Polyester	Nylon	Acrylic/ Modacrylic	Spandex <sup>a</sup>	Rayon	Natural Latex Rubber
Antimony	√					
Arsenic	√	√			√	
Barium	√ <sup>a</sup>					
Cadmium	√	√			√	?
Chromium	√	√			√	
Mercury		√				
Selenium						

Shaded: potential for element to be present above the solubility limit

<sup>a</sup> may be due to printing

Blank cells indicate no data

## 5.2 Summary of Findings of Presence or Use of Specified Elements and Phthalates in Dyes and Auxiliaries

Addressing the synthesis of all dyes and dye types used for the specified fibers was beyond the scope of this project. Therefore, we focused on the most common dyes and dye types. Most of these involved reactions with derivatives of benzene, aniline, naphthalene, anthraquinone, and phthalic anhydride (and derivatives), with a number of intermediates such as phenols, naphthols, and quinizarin. The basic chemistry involves electrophilic and nucleophilic substitution reactions on aromatic compounds. Key substances used are typical laboratory reagents such as hydrochloric acid, sulfuric acid, chlorobenzenes, and acetic acid, and salts such as sodium nitrate, aluminum chloride, and copper chloride. While this list of compounds is not comprehensive of those used in the potential worldwide manufacturing processes, it suggests that the specified phthalates would not be used as starting materials or reactants in the dye manufacture processes. Phthalic anhydride was identified as a starting material in anthraquinone ring formation, but it is a distinct chemical from the specified phthalates for this project.

For the specified elements, mercury and chromium were listed as catalysts or metallizing agents used in synthesis reactions; however, limited references to mercury were found and the authors noted the limited use (particularly in the last few decades). The most common metals used in fabric dyeing include chromium, copper, nickel, and cobalt (Greenpeace, 2005). It is anticipated that chromium in metal-complex acid dyes would be bound in the dye matrix (EC, 2003). There were little data on how common chromium use is, although dyes such as Acid Orange 60 and Acid Black 52 (chromium complexes) are well known. No concentrations for either element were found. Heavy metals may be present either as impurities in certain fibers themselves or through their use in the manufacture of dyes (Greenpeace, 2005). The metals are found in the dyes mainly due to their use as mordants/complexing agents (EC, 2003). However, Lacasse and Baumann (2004) reported ‘expected’ concentrations in textiles for some of these compounds, which would vary depending on the fiber material and type of dye used (e.g., mercury–0.01 ppm; chromium–a few ppm).

Note that the dyes researched for this report do not appear to be used for natural latex rubber; instead pigments are reportedly used as colorants for this material. We did not investigate pigments in this project.

Little to no information was found on the potential concentrations for the specified phthalates and elements in dyes or undyed specified fibers. For some polyester fiber blends, such as wool/polyester, there was some evidence for the use of phthalates (DMP, DBP, and DEHP) as carriers/accelerants (Greenpeace, 2005; Lacasse and Baumann, 2004; EC, 2003). The evidence for the use of phthalates was limited and no concentrations were given, other than the suggestion that the carrier content in the finished fibers is expected to be low (<0.2 percent) using the best available practices, but could be as high as 2.7 percent (Greenpeace, 2005). However, for non-specified phthalates that are used as carriers, Kirk-Othmer (2013) suggests carriers are optimized at 1 to 12 percent, calculated on the weight of the fiber, depending on the dyeing methods.

Some of the specified phthalates and elements used as auxiliaries (additives) may be present and could be introduced after dye manufacture. For example, DEPA (2003) reports the use of flame-retardants containing antimony or cadmium use in added biocides, both of which are considered finishing processes and are outside the scope of this research. Barium use was found in pigment manufacturing, which was also outside the scope of this research (DEPA, 2003). It has been suggested that the use of best available practices and fiber washing will remove many of these residuals from the fiber, however that cannot be guaranteed (KEMI, 2014; Lacasse and Baumann, 2004). Lacasse and Baumann (2004) provide a comprehensive overview of the compounds used in dye manufacture and finishing, and the specified elements and phthalates that were reported by them and that were found from additional sources are summarized in Table 185. In order to be comprehensive, this table includes some of the specified elements and phthalates that are used for finishing or other uses that were outside the scope of this research.

**Table 18. Potential for elements and phthalates to be used in dyes for the specified textile fibers (Lacasse and Baumann, 2004)**

Compound	Use
BBP	Fixative agent
DBP	Softener (finishing); plasticizer (finishing); carrier/accelerant
DEHP	Softener (finishing); plasticizer (finishing); carrier/accelerant
DIDP	Plasticizer (finishing)
DOP (isomer not specified)	Coloring 'pigment' auxiliary
Antimony trioxide/oxide	Flame retardant auxiliary
Antimony pentoxide	Flame retardant additive
Antimony trichloride	Flame retardant additive
Arsenic	Catalyst/reagent
Barium chloride	Dyeing auxiliary; mordant; catalyst
Barium hydroxide	Dyeing auxiliary; mordant; catalyst
Barium sulfate	Coloring 'pigment' auxiliary
Cadmium	Metal impurity from fiber production
Cadmium selenide	Biocide
Chromic acid	Oxidizing agent
Chromium (III) oxide	Catalyst; mordant
Chromium compounds (salts)	Fixative agent; mordant
Chromium (III)	Acid dye
Chromium VI	Fixative agent
Mercury	Metal impurity from fiber production; biocide

The concentrations of phthalates, when reported in undyed fibers, were less than the 0.1 percent limit (1000 ppm) specified in section 108 of the CPSIA. Data for concentrations of the specified phthalates in the dyes commonly used on the specified fibers were not available. This was not unexpected as several of the specified phthalates, BBP, DBP, DEHP, DIDP, and DOP are more likely to be found in fabric finishing processes than in fiber or dye manufacturing. Additionally, it is expected that much of the information on concentrations and dye formulations is proprietary.

### 5.3 References

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## 6 Specified Elements and Phthalates in Finished Textiles

### 6.1 Summary

Finished textiles were outside the scope of this research. In the process of searching for the specified elements and phthalates in fibers and unfinished textiles, TERA identified some studies and information about phthalates and/or elements in textiles. These reports did not always specify whether the textile was finished or provide information on what finishing processes may have gone into the textile. Because there was such limited information on fibers, dyes, and unfinished textiles, TERA has included summary information where concentrations of the specified phthalates or the elements exceeded limits in the textiles below. More information and details of the studies are reported in Appendix E.

*Polyester:* Literature sources for concentrations of the specified phthalates and elements in polyester were very limited. Antimony was reported in polyester at concentrations above its ASTM soluble limit (as high as 293 ppm in a finished textile), and some authors suggest its presence is due to its use as a catalyst in the manufacture of polyester fibers (Duh, 2002; Thiele, 2004; DEPA, 2003; Greenpeace, 2013). However, we were unable to determine the exact finishes on the textiles or the source of the antimony contamination.

*Polyamide/Nylon:* Literature sources for concentrations of the specified phthalates and elements in nylon were very limited. Chromium was 0.3–2.3 ppm in 6 samples, but approximately 900 ppm in one sample, above its soluble limit of 60 ppm. It is not known if the source of the chromium in the sample was the fiber, the dye, or other finishing chemicals. The information for the raw materials and manufacturing do not indicate chromium is used in the undyed fiber.

### 6.2 References

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## **Appendices**

### **Appendix A. Authoritative Secondary Sources (Library)**

Contained in a separate document.

### **Appendix B. Authoritative Secondary Sources (Websites)**

Contained in a separate document.

### **Appendix C. Database Content**

Contained in a separate document.

### **Appendix D. Overview of Dye Association and Voluntary Chemical Limits**

Contained in a separate document.

### **Appendix E. Evidence of Specified Elements and Phthalates in Finished Textiles**

Contained in a separate document.