EPA Office of Compliance Sector Notebook Project:

Profile of the Plastic Resin and Manmade Fiber Industries

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PLASTIC RESIN AND MANMADE FIBER INDUSTRIES
(SIC 2821, 2823, and 2824)

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AFS -   AIRS Facility Subsystem (CAA database)
AIRS -   Aerometric Information Retrieval System (CAA database)
BIFs -   Boilers and Industrial Furnaces (RCRA)
BOD -   Biochemical Oxygen Demand
CAA -   Clean Air Act
CAAA -   Clean Air Act Amendments of 1990
CERCLA -   Comprehensive Environmental Response, Compensation and Liability Act
CERCLIS -   CERCLA Information System
CFCs -   Chlorofluorocarbons
CO -   Carbon Monoxide
COD -   Chemical Oxygen Demand
CSI -   Common Sense Initiative
CWA -   Clean Water Act
D&B -   Dun and Bradstreet Marketing Index
ELP -   Environmental Leadership Program
EPA -   United States Environmental Protection Agency
EPCRA -   Emergency Planning and Community Right-to-Know Act
FIFRA -   Federal Insecticide, Fungicide, and Rodenticide Act
FINDS -   Facility Indexing System
HAPs -   Hazardous Air Pollutants (CAA)
HSDB -   Hazardous Substances Data Bank
IDEA -   Integrated Data for Enforcement Analysis
LDR -   Land Disposal Restrictions (RCRA)
LEPCs -   Local Emergency Planning Committees
MACT -   Maximum Achievable Control Technology (CAA)
MCLGs -   Maximum Contaminant Level Goals
MCLs -   Maximum Contaminant Levels
MEK -   Methyl Ethyl Ketone
MSDSs -   Material Safety Data Sheets
NAAQS -   National Ambient Air Quality Standards (CAA)
NAFTA -   North American Free Trade Agreement
NAICS -   North American Industrial Classification System
NCDB -   National Compliance Database (for TSCA, FIFRA, EPCRA)
NCP -   National Oil and Hazardous Substances Pollution Contingency Plan
NEIC -   National Enforcement Investigation Center
NESHAP -   National Emission Standards for Hazardous Air Pollutants
NO_2 -   Nitrogen Dioxide
NOV -   Notice of Violation
NO_x -   Nitrogen Oxides
NPDES -   National Pollution Discharge Elimination System (CWA)
NPL -   National Priorities List
NRC -   National Response Center
NSPS -   New Source Performance Standards (CAA)

OAR -   Office of Air and Radiation
OECA -   Office of Enforcement and Compliance Assurance
OPA -   Oil Pollution Act
OPPTS -   Office of Prevention, Pesticides, and Toxic Substances
OSHA -   Occupational Safety and Health Administration
OSW -   Office of Solid Waste
OSWER -   Office of Solid Waste and Emergency Response
OW -   Office of Water
P2 -   Pollution Prevention
PCS -   Permit Compliance System (CWA Database)
POTW -   Publicly Owned Treatments Works
RCRA -   Resource Conservation and Recovery Act
RCRIS -   RCRA Information System
SARA -   Superfund Amendments and Reauthorization Act
SDWA -   Safe Drinking Water Act
SEPs -   Supplementary Environmental Projects
SERCs -   State Emergency Response Commissions
SIC -   Standard Industrial Classification
SO_2 -   Sulfur Dioxide
SO_x -   Sulfur Oxides
SPI -   Society of Plastics Industry
TOC -   Total Organic Carbon
TRI -   Toxic Release Inventory
TRIS -   Toxic Release Inventory System
TCRIS -   Toxic Chemical Release Inventory System
TSCA -   Toxic Substances Control Act
TSS -   Total Suspended Solids
UIC -   Underground Injection Control (SDWA)
UST -   Underground Storage Tanks (RCRA)
VOCs -   Volatile Organic Compounds

I. INTRODUCTION TO THE SECTOR NOTEBOOK PROJECT

I.A. Summary of the Sector Notebook Project

Integrated environmental policies based upon comprehensive analysis of air, water and land pollution are a logical supplement to traditional single-media approaches to environmental protection. Environmental regulatory agencies are beginning to embrace comprehensive, multi-statute solutions to facility permitting, enforcement and compliance assurance, education/ outreach, research, and regulatory development issues. The central concepts driving the new policy direction are that pollutant releases to each environmental medium (air, water and land) affect each other, and that environmental strategies must actively identify and address these inter-relationships by designing policies for the "whole" facility. One way to achieve a whole facility focus is to design environmental policies for similar industrial facilities. By doing so, environmental concerns that are common to the manufacturing of similar products can be addressed in a comprehensive manner. Recognition of the need to develop the industrial "sector-based" approach within the EPA Office of Compliance led to the creation of this document.

The Sector Notebook Project was originally initiated by the Office of Compliance within the Office of Enforcement and Compliance Assurance (OECA) to provide its staff and managers with summary information for eighteen specific industrial sectors. As other EPA offices, states, the regulated community, environmental groups, and the public became interested in this project, the scope of the original project was expanded to its current form. The ability to design comprehensive, common sense environmental protection measures for specific industries is dependent on knowledge of several inter-related topics. For the purposes of this project, the key elements chosen for inclusion are: general industry information (economic and geographic); a description of industrial processes; pollution outputs; pollution prevention opportunities; Federal statutory and regulatory framework; compliance history; and a description of partnerships that have been formed between regulatory agencies, the regulated community and the public.

For any given industry, each topic listed above could alone be the subject of a lengthy volume. However, in order to produce a manageable document, this project focuses on providing summary information for each topic. This format provides the reader with a synopsis of each issue, and references where more in-depth information is available. Text within each profile was researched from a variety of sources, and was usually condensed from more detailed sources pertaining to specific topics. This approach allows for a wide coverage of activities that can be further explored based upon the citations and references listed at the end of this profile. As a check on the information included, each notebook went through an external review

process. The Office of Compliance appreciates the efforts of all those that participated in this process and enabled us to develop more complete, accurate and up-to-date summaries. Many of those who reviewed this notebook are listed as contacts in Section IX and may be sources of additional information. The individuals and groups on this list do not necessarily concur with all statements within this notebook.

I.B. Additional Information

Providing Comments

OECA's Office of Compliance plans to periodically review and update the notebooks and will make these updates available both in hard copy and electronically. If you have any comments on the existing notebook, or if you would like to provide additional information, please send a hard copy and computer disk to the EPA Office of Compliance, Sector Notebook Project, 401 M St., SW (2223-A), Washington, DC 20460. Comments can also be uploaded to the Enviroene World Wide Web for general access to all users of the system. Follow instructions in Appendix A for accessing this system. Once you have logged in, procedures for uploading text are available from the on-line Enviroene Help System.

Adapting Notebooks to Particular Needs

The scope of the industry sector described in this notebook approximates the national occurrence of facility types within the sector. In many instances, industries within specific geographic regions or states may have unique characteristics that are not fully captured in these profiles. The Office of Compliance encourages state and local environmental agencies and other groups to supplement or re-package the information included in this notebook to include more specific industrial and regulatory information that may be available. Additionally, interested states may want to supplement the "Summary of Applicable Federal Statutes and Regulations" section with state and local requirements. Compliance or technical assistance providers may also want to develop the "Pollution Prevention" section in more detail. Please contact the appropriate specialist listed on the opening page of this notebook if your office is interested in assisting us in the further development of the information or policies addressed within this volume. If you are interested in assisting in the development of new notebooks for sectors not already covered, please contact the Office of Compliance at 202-564-2395.

II. INTRODUCTION TO THE PLASTIC RESIN AND MANMADE FIBER INDUSTRIES

This section provides background information on the size, geographic distribution, employment, production, sales, and economic condition of the plastic resin and manmade fiber industries. Facilities described within this document are described in terms of their Standard Industrial Classification (SIC) codes.

II.A. History of the Plastic Resin and Manmade Fiber Industries

The Origin of Plastic Resins

Plastics today are one of the most used materials in U.S. industrial and commercial life. Table 1 lists selected plastic resins and synthetic fibers by year of development and their principal uses. The first plastics were invented in the 1800s when people experimented to produce everyday objects out of alternative materials. The first plastic was developed in 1851 when hard rubber, or ebonite, was synthesized. This was the first material that involved a distinct chemical modification of a natural material.

Table 1: Introduction of Selected Plastic Resins and Manmade Fibers

Year	Material	Example
1868	Cellulose Nitrate	Eyeglass frames
1900	Viscose Rayon	Lining in clothing, curtains
1909	Phenol-Formaldehyde	Telephone Handset
1927	Cellulose Acetate	Toothbrushes, lacquers
1927	Polyvinyl Chloride	Wall Covering, pipe, siding
1936	Acrylic	Brush Backs, display signs
1938	Polystyrene	Housewares, toys
1939	Nylon	Fibers, films, gears
1942	Low Density Polyethylene	Packaging, squeeze bottles
	Unsaturated Polyester	Boat Hulls
1952	Polyethylene terephthalate	Clothing, fiberfill
1957	Polypropylene	Safety Helmets
1964	Polyimide	Bearings
1970	Thermoplastic Polyester	Electrical/Electronic Parts
1978	Linear Low Density Polyethylene	Extruded Film
1985	Liquid Crystal Polymers	Electrical/Electronic Parts

Source: This table has been adapted from *Facts and Figures of the U.S. Plastics Industry,* (1995 Edition) prepared annually by The Society of the Plastics Industry, Inc., Washington, DC. Please refer to that document for a more complete listing of plastic resin development.

The first plastics in the U.S. were developed while John Wesley Hyatt was experimenting to produce a billiard ball from materials other than ivory. In 1870, John and his brother Isaiah took out a patent for a process producing a horn-like material using cellulose nitrate and camphor.

Another important precursor to modern plastics was the development of formaldehyde resins. Early experiments to produce white chalkboards in Germany around the turn of the 20th century led to the development of formaldehyde resins. These resins were first produced by reacting casein (milk protein) with formaldehyde.

During the 1930s, the initial commercial development of today's major thermoplastics took place. These included polyvinyl chloride, low density polyethylene, polystyrene, and polymethyl methacrylate. Demand for plastics escalated during World War II when substitutes for scarce natural materials, like rubber, were in high demand. Large-scale production for synthetic rubbers triggered extensive research into polymer chemistry and new plastic materials.

In the 1940s, polypropylene and high density polyethylene were developed, and in 1978, linear low density polyethylene was developed. Large-scale production of these materials reduced their cost substantially, which allowed these new plastics materials to compete with traditional materials like wood and metal. The introduction of alloys and blends of various polymers has made it possible to tailor properties to fit certain performance requirements that a single resin could not provide. Demand for plastics has steadily increased, and now plastics are accepted as basic materials along with the more traditional materials in designs and engineering plans (SPI, 1995).

The Origin of Manmade Fibers

In 1664, Robert Hooke first suggested that manmade yarn could be produced. He speculated, in *Micrographia,* that synthetic fibers could be patterned after the excretion of silk by silkworms.

> And I have often thought, that probably there might be a way, found out, to make an artificial glutinous composition, much resembling, if not full as good, nay better, than the Excrement, or whatever other substances it be out of which, the Silk-worm winds and draws his clew. If such a composition were found, it were certainly an easier matter to find very quick ways of drawing it into small wires for use (Linton, 1966).

During the 19th century, scientists were busy making precursor solutions of the first manmade fibers, cellulosic fibers. In 1840, F. Gottlob Keller of Germany devised a technique for making pulp for paper by squeezing powdered wood taken from a grindstone. This enabled the future production of rayon and other cellulosic items. During that same year, Louis Schwabe,

an English silk manufacturer, developed the first spinnerette through which a spinning solution could be extruded (Linton, 1966).

The first manmade fibers commercially manufactured in the U.S. were the cellulosics, led by rayon in 1910 and acetate in 1924. Cellulosic fibers are manufactured by first treating cellulose with chemicals, dissolving, and then regenerating the fibers. Cellulose is an abundant naturally occurring organic compound which makes up a large portion of the world's vegetable matter. Often referred to as artificial silk, rayon retained many of the same physical properties as cotton, such as high moisture absorption and subsequent swelling of the fibers. While cellulose acetate was first developed as a plastic in 1865, it was not successfully spun into a fiber until the 1920s. The first U.S. acetate production took place at the Cumberland, Maryland plant of British Celanese (now Hoechst Celanese).

In 1926, Du Pont Laboratories began a chemical research program that led to the advent of the synthetic, or noncellulosic, fiber industry. Unlike cellulosic fibers, synthetic fibers are wholly compounded from chemicals. The first synthetic fiber that Du Pont developed was Fiber 66. Now known as nylon-6,6, the fiber began widespread production for markets, such as nylon hosiery, in 1939. During World War II, nylon was used in producing parachutes, uniforms, and a host of other military equipment. Started primarily as a hosiery yarn, the use of nylon spread after the war into other applications like carpeting and woven fabrics.

Wrinkle-resistant and strong, the first polyester fiber, Terylene, was developed by a British scientist group called the Calico Printers Association. In 1946, Du Pont secured exclusive rights to produce this polyester fiber in the U.S. In December 1950, Du Pont announced plans to build its first plant at Kinston, North Carolina at a capacity of 36 million pounds a year and a cost of $40 million. Du Pont first unveiled the new fiber, named Dacron, at a famous press conference where it was displayed in a swimsuit that had been worn 67 days continuously without ironing. After polyester fibers were first produced commercially in the U.S. in 1953, the fibers were rapidly used to make men's suits, women's blouses, and men's shirts.

Since then, most technological advances in manmade fibers have occurred in synthetics, which now make up almost all of the U.S. production of manmade fibers. Synthetic fibers have many advantages to cellulosic fibers, such as controlled shrinkage, crease retention, and wrinkle resistance. Synthetic fibers have developed to seem more natural, softer, easier to care for, more lustrous, and more comfortable.

II.B. Introduction, Background, and Scope of the Notebook

This notebook focuses on industrial processes and environmental issues relevant to the plastic resin and manmade fiber industries. These industries were chosen for this notebook because they have certain industrial processes in common, such as polymerization and extrusion. Both the plastic resin industry and the manmade fiber industry use refined petroleum products and synthetic organic chemicals to make selected polymers, which are large molecules made up of simple repeating chemical units. Facilities then process the polymers into plastic pellets and manmade fibers. Figures 1 and 2 provide an overview of the raw material inputs, products, and end uses of plastic resin and manmade fiber.

The plastic resin industry is classified by the Office of Management and Budget (OMB) as Plastics Materials and Resins, Standard Industrial Classification (SIC) code 2821. This classification corresponds to SIC codes which were established by the OMB to track the flow of goods and services within the economy. SIC 2821 corresponds to facilities that manufacture manmade resin, plastic materials, and nonvulcanizable elastomer. Table 2 lists products that are classified under SIC 2821. The manmade fiber industry is made up of two categories: Cellulosic Manmade Fibers, SIC 2823, and Organic Fibers, Noncellulosic, SIC 2824. Cellulosic Manmade Fibers includes facilities that make cellulosic fibers, like rayon and cellulose acetate. The category, Organic Fibers, Noncellulosic, covers facilities that make other manmade fiber, including nylon and polyester. Manmade fiber products that fall under SIC Codes 2823 and 2824 are listed in Table 3.

OMB is in the process of changing the SIC code system to a system based on similar production processes called the North American Industrial Classification System (NAICS). In the NAIC system, the manufacturing of plastic resins, synthetic rubber, artificial and synthetic fibers and filaments are all classified as NAIC 3252. Resin and synthetic rubber manufacturing are further classified as NAIC 32521, and artificial and synthetic fibers and filaments manufacturing are further classified as NAIC 32522.

Only the manufacturing of plastic resin and manmade fiber is covered in this notebook. Companies that perform upstream processing, such as synthesizing reactants, and companies that perform downstream operations, such as processing plastic resins into plastic bottles or processing manmade fibers into fabric, are not covered in this notebook. For information on companies that manufacture organic chemicals (SIC 286) used in plastic resin and manmade fiber manufacture, refer to the Organic Chemicals Sector Notebook. For facilities that process resins into plastic products of different shapes, sizes, and physical properties, refer to the Rubber and Plastics Sector Notebook. Refer to the Textiles Sector Notebook for information on facilities that process manmade fibers into yarn and fabric. Note that

compounding operations, where additives are incorporated into polymers, are not covered in this notebook.

Figure 1: Plastic Resins: From raw material to finished product

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                        ┌──────────────────────┐
                        │   Oil & Natural Gas   │
                        └───────────┬──────────┘
                                    ▼
                        ┌──────────────────────┐
                        │       Monomers        │
                        └───────────┬──────────┘
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              │  Synthetic Resins    │◀──────< Additives  >
              │     SIC 2821         │        ╲──────────╱
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                                    │              ▼
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                                    │        │ Compounding │
                                    │        │   SIC 3087  │
                                    │        └─────────────┘
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Film & Sheet SIC 3081	Plastic Shapes SIC 3082	Laminated Plastics SIC 3083	Plastics Pipe SIC 3084	Plastics Bottles SIC 3085
	Plastic Foam SIC 3086	Plumbing Fixtures SIC 3088	Plastics Products, NEC SIC 3089	

Major Markets

Transportation	▶ Aerospace, Automotive, Aircraft, Marine, Railroad, Recreational
Packaging	▶ Closures, Coatings, Containers, Flexible packaging
Building/Construction	▶ Building materials, Pipe & fittings, Plumbing fixtures
Electrical/Electronic	▶ Appliance, Batteries, Business machines, Communications, Records
Furniture/Furnishings	▶ Bedding, Carpets (incl. backing), House furnishings, Rigid & flexible furniture
Consumer/Institutional	▶ Cutlery, Lawn & garden, Luggage, Medical & healthcare, Toys & sporting goods
Industrial/Machinery	▶ Engine parts, Farm & constr. equip., Mach. tools, Marine supplies, Signs & displays
Other	▶ Adhesives, Inks, Coatings
Exports	

Source: *Facts and Figures of the U.S. Plastics Industry,* (1995 Edition) prepared annually by The Society of the Plastics Industry, Inc., Washington, DC.

Figure 2: U.S. Manmade Fiber Industry: Principal raw materials, producer types, major products, and principal end uses

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                    │                             │
                    │  U.S. Manmade Fiber Industry │
                    │                             │
                    │      SIC 2823, 2824          │
                    │                             │
                    └─────────────────────────────┘
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Principal raw materials	**Producer types**	**Major products**	**Principal end uses**
Organic chemicals:	Chemical companies	Fibers and yarns:	• Apparel
• Acrylonitrile		• Acetate	• Home textiles
• Caprolactam	Oil exploration and	• Acrylic	• Carpets and rugs
• Hexamethylene-diamine (HMD)	recovery companies	• Aramid	• Industrial textiles (tires, ropes/cordage, automotive upholstery, and geotextiles)
• Adipic acid (AA)	Polymer converters	• Nylon	• Miscellaneous consumer goods (craft yarn, sewing thread, diapers, sanitary napkins, and tampons)
• Glycols (ethylene, propylene, etc.)		• Polyester	
• Dimethyl Terephthalate (DMT)		• Polyolefin	
• Terephthalic acid (TPA)		• Rayon	
Polymers:		•Spandex	
• Polyester			
• Nylon			
• Polypropylene			
Wood pulp			

Source: *Industry and Trade Summary: Manmade Fibers,* U.S. International Trade Commission, Washington, DC, 1995.

II.C. Characterization of the Plastic Resin and Manmade Fiber Industries

II.C.1. Product Characterization

Plastic Resins

The plastic resin industry produces resins which are further treated in plastics processing facilities and sold largely to the packaging, building and construction, and consumer markets. Specific product formulations and manufacturing parameters are often kept as trade secrets since the competitiveness of many companies depends on the ability to produce resins with different physical characteristics, such as strength, toughness, and flexibility (Brydson, 1995).

Plastic resins are typically broken down into two categories: thermoplastics and thermosets. Thermoplastic resins are resins that can be heated and molded into shapes repeatedly, while thermoset resins are resins that can be heated and molded only once. Thermoplastic resins dominate plastic resin sales and production. In 1994, thermoplastics made up about 90 percent, or

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Table 2: Plastics Materials, Synthetic Resins, and Nonvulcanizable Elastomers (as listed under SIC 2821)

|		
acetal resins	ester gum	polyhexamethylenediamine adipamide resins
acetate, cellulose (plastics)	ethyl cellulose plastics	polyisbutylenes
acrylic resins	ethylene-vinyl acetate resins	polymerization plastics, except fibers
acrylonitrile-butadiene-styrene resins	fluorohydrocarbon resins	
	ion exchange resins	polypropylene resins
alcohol resins, polyvinyl	ionomer resins	polystyrene resins
alkyd resins	isobutylene polymers	polyurethane resins
allyl resins	lignin plastics	polyvinyl chloride resins
butadiene copolymers, containing less than 50 percent butadiene	melamine resins	polyvinyl halide resins
	methyl acrylate resins	polyvinyl resins
carbohydrate plastics	methyl cellulose plastics	protein plastics
casein plastics	methyl methacrylate resins molding compounds, plastics	pyroxylin
cellulose nitrate resins		resins, synthetic
cellulose propionate (plastics)	nitrocellulose plastics (pyroxylin)	rosin modified resins
coal tar resins	nylon resins	silicone fluid solution (fluid for sonar transducers)
condensation plastics	petroleum polymer resins	
coumarone-indene resins	phenol-furfural resins	silicone resins
cresol resins	phenolic resins	soybean plastics
cresol-furfural resins	phenoxy resins	styrene resins
dicyandiamine resins	phthalic alkyd resins	styrene-acrylonitrile resins
diisocyanate resins	phthalic anhydride resins	tar acid resins
elastomers, nonvulcanizable (plastics)	polyacrylonitrile resins	urea resins
	polyamide resins	vinyl resins
epichlorohydrin bisphenol	polycarbonate resins	
epichlorohydrin diphenol	polyesters	
epoxy resins	polyethylene resins	

Source: *Standard Industrial Classification Manual,* Office of Management and Budget, 1987.

Figure 3: Percentage Distribution of Plastic Resins: Sales and Captive Use, 1994
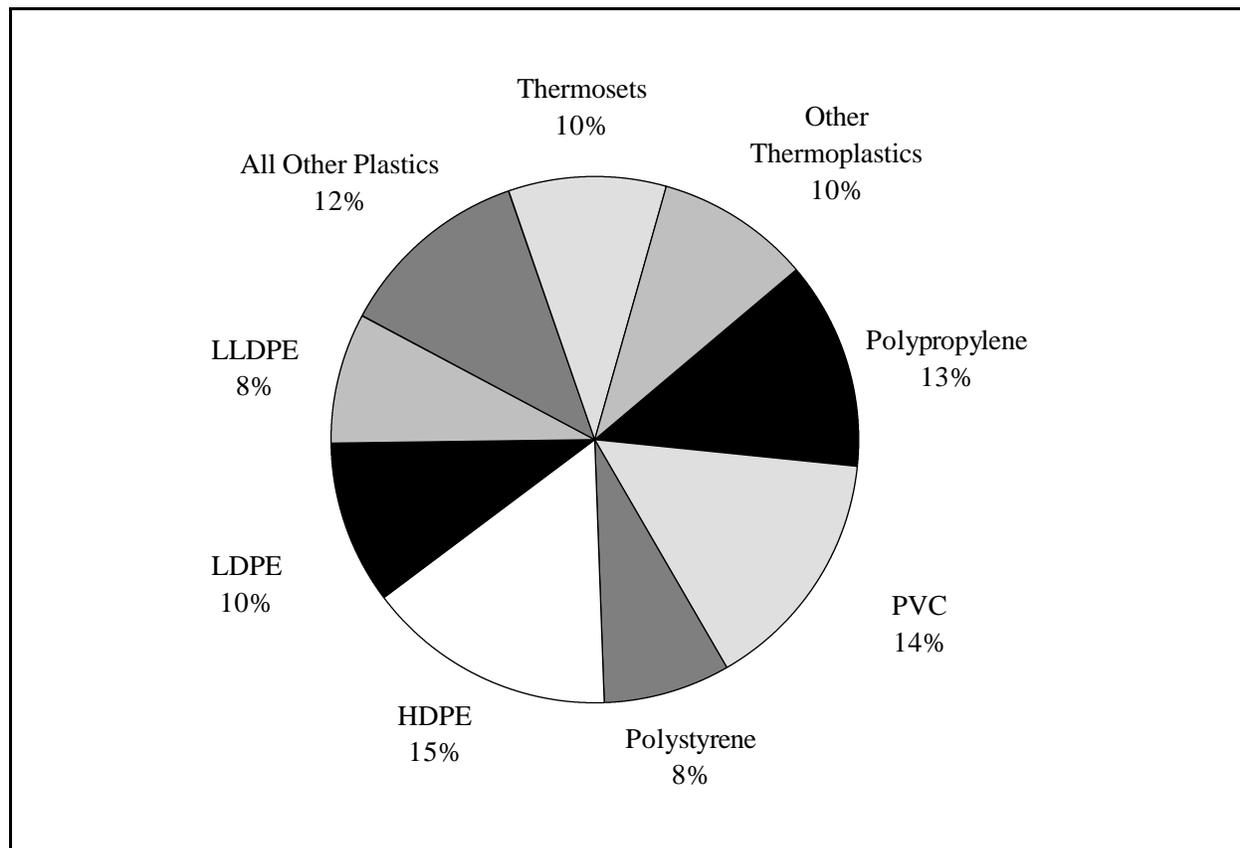
Source: SPI Committee on Resin Statistics as compiled by Association Services Group, LLC, 1995.

63.3 billion pounds, of plastic resin production by dry weight and accounted for 82 percent, or $27.2 billion dollars of the total value of shipments for plastic resin (SPI, 1995). Commercially important thermoplastics include polyethylene (all forms), polyvinyl chloride, polypropylene, and polystyrene and are shown in Figure 3. These four thermoplastics make up over 69 percent of plastic resin sales. These thermoplastics are considered general purpose, or commodity plastics since they are usually manufactured in large quantities using well established technology and are typically geared towards a small number of high volume users.

In 1994, thermosets accounted for about 10 percent, or 7.5 billion pounds, of plastic resin production by dry weight and 17 percent of the value of shipments for the plastic resin industry. The leading thermosets in sales were phenolic resins, urea resins, and unsaturated polyester resins. Specialty plastic resins, which often include thermosets, are produced on a customized basis in small production runs and typically involve significant research and development costs (Department of Commerce, 1994).

Manmade Fibers

Manmade fibers are produced primarily for use as raw materials for the textile industry. In 1993, about 34 percent of manmade fibers were sold to the carpets and rugs market, 28 percent was sold to the industrial and miscellaneous consumer products market, and 25 percent was sold to the apparel market (International Trade Commission, 1995). The increasing use of manmade fibers in a variety of markets has enabled manmade fibers to account for 57% of all fibers, natural and manmade, consumed in the U.S. Figure 4 illustrates manmade fiber consumption with respect to other fibers and shows the leading manmade fibers. The price and quality of manmade fibers are important determinants in the quality and competitiveness of apparel, home textiles, and industrial and consumer products (Department of Commerce, 1994; AFMA, 1997).

There are two main types of manmade fibers: noncellulosic (SIC 2824) and cellulosic (SIC 2823). Noncellulosic, or synthetic, fibers consist of fibers that are formed by the polymerization and subsequent fiber formation of synthetic organic chemicals and refined petroleum products.

Table 3: Manmade Fibers (as listed by SIC code)	
Cellulosics (SIC 2823)	**Noncellulosics (SIC 2824)**
Acetate fibers Cellulose acetate monofilament, yarn, staple, or tow Cellulose fibers, manmade Cigarette tow, cellulosic fiber Cuprammonium fibers Fibers, rayon Horsehair, artificial: rayon Nitrocellulose fibers Rayon primary products: fibers, straw, strips, and yarn Rayon yarn, made in chemical plants Regenerated cellulose fibers Textured yarns and fibers, cellulosic: made in chemical plants Triacetate fibers Viscose fibers, bands, strips, and yarn Yarn, cellulosic: made in chemical plants	Acrylic fibers Acrylonitrile fibers Anidex fibers Casein fibers Elastomeric fibers Fibers, manmade: except cellulosic Fluorocarbon fibers Horsehair, artificial: nylon Linear esters fibers Modacrylic fibers Nylon fibers and bristles Olefin fibers Organic fibers, synthetic: except cellulosic Polyester, fibers Polyvinyl ester fibers Polyvinylidene chloride fibers Protein fibers Saran fibers Soybean fibers (manmade textile materials) Textured fibers and yarns, noncellulosic: made in chemical plants Vinyl fibers Vinylidene chloride fibers Zein fibers
Source: *Standard Industrial Classification Manual,* Office of Management and Budget, 1987.	

In 1992, noncellulosic fibers were responsible for 88 percent, or $11.1 billion dollars, of the total value of shipments for the industry. Industry statistics from the Fiber Economics Bureau reported $10.6 billion as the value of shipments for the noncellulosic fiber industry for 1996 (ATMI, 1997b). Major noncellulosic fibers include nylons, polyesters, polyolefins, and acrylics. Polyolefins include polyethylene and polypropylene. Figure 4 shows a breakdown of U.S. fiber consumption by material.

Most cellulosic fibers are formed by the conversion of the cellulose into a soluble derivative, followed by reforming as filaments. Cellulose is an abundant naturally occurring organic compound which makes up one-third of the world's vegetable matter. In some cases, the cellulose derivative is retained in the new fiber (e.g., cellulose acetate), and sometimes the cellulose derivative is degraded and cellulose is regenerated (e.g., rayon). Lyocel is a new class of cellulosic fibers made by direct solution of cellulose (and not a derivative) in organic solvents (e.g., amine oxides) and evaporation of the solvent to form the new filaments. In 1992, the cellulosic fiber industry had a value of shipments of $1.7 billion according to the U.S. Department of Commerce. This is compared to $850 million for the 1996 value of shipments for the cellulosic fiber industry as reported by the Fiber Economics Bureau (ATMI, 1997b). Commercially important cellulosic fibers include rayon and cellulose acetate.

Figure 4: U.S. Fiber Consumption: Percentage distribution by principal fibers, 1993
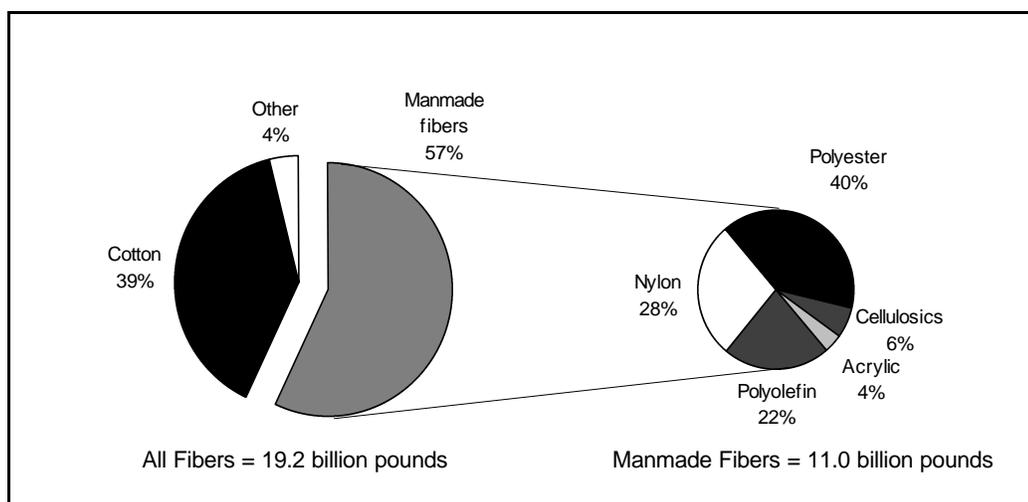
Source: *Industry and Trade Summary: Manmade Fibers,* U.S. International Trade Commission, Washington, DC, 1995.

II.C.2. Industry Characterization

Petroleum refining and synthetic organic chemical manufacturing facilities produce the raw material feedstocks used to make plastic resin and manmade fibers (except cellulosic fibers). In some cases, these facilities also make plastic resins and manmade fibers. Because of integration between the industries, the development of the petrochemical industry has contributed strongly to the growth of the plastic resin and manmade fiber industries.

Plastic Resin Industry

In 1992, the Department of Commerce reported 240 plastic resin companies and 449 establishments in 1992. The value of shipments for the industry was $31.3 billion dollars. The largest four companies accounted for 24 percent of the value of shipments, and the largest 20 companies accounted for 63 percent. Table 4 summarizes revenue and company size statistics for the industry.

Table 4: Size and Revenue for the Plastic Resin and Manmade Fiber Industries			
Item	**Plastic Resins**	**Manmade Fibers**	
	(SIC 2821)	**Cellulosic (SIC 2823)**	**Noncellulosic (SIC 2824)**
Establishments (no.)	449[c]	7[d]	71[e]
Companies (no.)[a]	240	5	42
Values of Shipments (millions of dollars)[b]	31,303.9	1,748.1	11,113.7
Total Employees (000's)	60.4	11.0	44.4

Source: *1992 Census of Manufactures, Industry Series: Plastics Materials, Synthetic Rubber, and Manmade Fibers,* US Department of Commerce, Bureau of the Census, June 1995.
Note: 1992 Census of Manufacturers data are the most recent available. Changes in the number of facilities, location, and employment figures since 1992 are not reflected in these data.

[a]Defined as a business organization consisting of one establishment or more under common ownership or control.
[b]Value of all products and services sold by establishments in the plastics and manmade fibers industries.
[c]Dun and Bradstreet information reports 1553 facilities indicating SIC 2821 as one of their top five SIC codes.
[d]Dun and Bradstreet information reports 29 facilities indicating SIC 2823 as one of their top five SIC codes.
[e]Dun and Bradstreet information reports 152 facilities indicating SIC 2824 as one of their top five SIC codes.

Employment for the industry increased from 54,700 employees in 1982 to 60,400 employees in 1992. Most employees, about 60 percent, are considered production workers. Although a small number of large, integrated companies dominate sales and production, the majority of individual establishments tend to be small. About 71 percent of establishments have

less than 100 employees. In terms of geographic distribution, four states - Texas, Illinois, Michigan, and Pennsylvania - accounted for about 40 percent of industry employment and 23 percent of establishments in 1992. Employment and geographic distribution figures appear in Table 5.

Table 5: Establishment Size and Geographic Distribution of the Plastic Resin and Manmade Fiber Industries			
Item	**Plastic Resins**	**Manmade Fibers**	
	(SIC 2821)	**Cellulosic (SIC 2823)**	**Noncellulosic (SIC 2824)**
% of establishments with less than 20 employees	24	0	4.2
% of establishments with less than 100 employees	71	14	25
Major states in which industry is concentrated, based on employment	TX, PA, MI, LA	TN, SC, VA, AL	SC, NC, VA, TN
% of industry's employment attributable to four major states	40	100	77

Source: *1992 Census of Manufactures, Industry Series: Plastics Materials, Synthetic Rubber, and Manmade Fibers,* US Department of Commerce, Bureau of the Census, June 1995.
Note: 1992 Census of Manufacturers data are the most recent available. Changes in the number of facilities, location, and employment figures since 1992 are not reflected in these data.

Manmade Fibers

The manmade fiber industry is dominated by a small number of large plants that manufacture or purchase basic organic chemicals and then synthesize them into fiber-forming polymers. These larger fiber producers often manufacture polymer for internal use and to sell to smaller firms which only process purchased polymers into fibers. The dominant firms tend to fall into one of the following categories: 1) large, multi-product chemical companies; 2) highly integrated petrochemical companies, or 3) widely diversified industrial firms with large chemicals- or materials-related segments (EPA, 1995). Few firms process fibers into end-use consumer products (International Trade Commission, 1995).

In 1992, the Department of Commerce reported 5 companies involved in cellulosic fiber manufacture and 42 companies involved in noncellulosic fiber manufacture. The value of shipments for the industry was $12.8 billion dollars in 1992. Noncellulosic fiber manufacturing accounted for 88 percent of the value of shipments for the industry. Table 4 highlights industry statistics, including value of shipments. Industry statistics reported by the

Fiber Economics Bureau indicated that the value of shipments for the manmade fiber industry was $11.5 billion in 1996, with noncellulosic fiber manufacturing accounting for 93 percent of the value of shipments for the industry (ATMI, 1997b).

The U.S. manmade fiber industry is highly concentrated. According to the U.S. International Trade Commission, nine firms accounted for roughly 70 percent of U.S. production capacity in 1994, while the remaining 30 percent was held by about 85 other firms. The number of firms and level of industry concentration varies by fiber type. In 1994, only two firms produced acrylic and three produced rayon. Although roughly 30 produced polyester and nylon and 60 produced polyolefins, seven producers accounted for about 85 percent of total U.S. nylon and polyester capacity, and three accounted for over one-half of polyolefin capacity. Recently, the number of polyolefin producers has increased to meet increasing demand and availability of low-volume production equipment.

Since the mid-1980s, the manmade fiber industry has greatly consolidated and reorganized. Facilities have tried to expand and diversify by purchasing existing plants, enlarging capacity, or starting up new capacity in other parts of the world. In an effort to improve profit margins and market share, several companies have sold their smaller fiber businesses in order to concentrate on their strongest fiber operations (International Trade Commission, 1995).

While numbers of companies and establishments remained steady from 1982 to 1992, employment for the industry dramatically decreased from 60,200 employees to 44,400 employees. Most employees, about 75 percent, are considered production workers. Roughly 25 percent of establishments have less than 100 employees. Most of the manmade fiber facilities are located in the Southeast, where the main customer, the textile mill industry, is concentrated. Three states - Tennessee, South Carolina, and Virginia - accounted for about 62 percent of industry employment in 1992. Table 5 shows employment data for the industry. Figure 5 highlights those states which have the largest number of plastic resin and manmade fiber manufacturing facilities.   Note that industry statistics from the Fiber Economics Bureau indicated that there were 42,000 employees for the manmade fiber industry in 1996. About 39,000 employees were employed by the noncellulosic fiber industry, and 3,000 employees were employed by the cellulosic fiber industry (ATMI, 1997b).

Figure 5: Geographic Distribution of Plastic Resin (SIC 2821) and Manmade Fiber (SIC 2823, 2824) Manufacturing Facilities
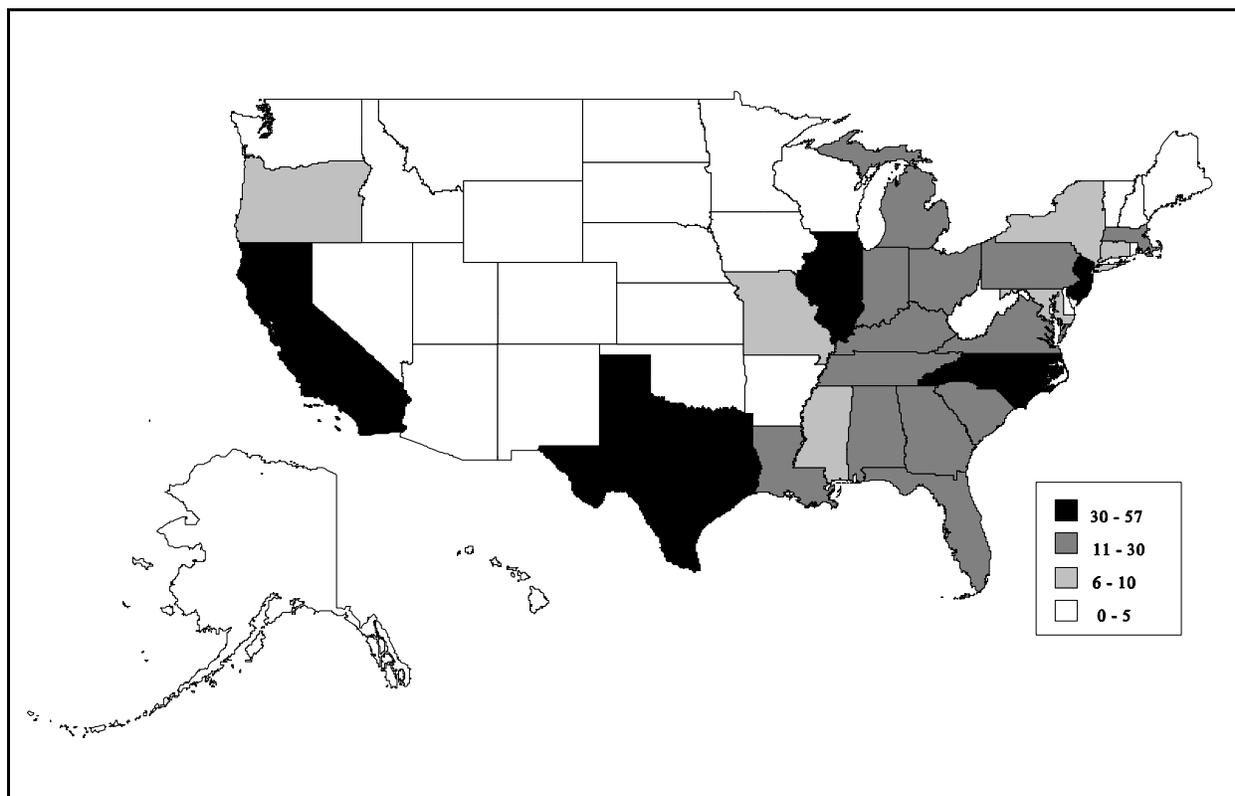
Source: *1992 Census of Manufactures, Industry Series: Plastics Materials, Synthetic Rubber, and Manmade Fibers,* US Department of Commerce, Bureau of the Census, June 1995.

Leading Companies for the Plastic Resin and Manmade Fiber Industries

Table 6 shows the top U.S. companies with plastic resin and manmade fiber operations, according to the 1997 Dun & Bradstreet's *Million Dollar Directory.* This directory compiles financial data on U.S. companies including those operating within the plastic resin and manmade fiber industries. Dun and Bradstreet's ranks U.S. companies, whether they are a parent company, subsidiary or division, by sales volume within their assigned 4-digit SIC code. Readers should note that companies are assigned a 4-digit SIC code that most closely resembles their principal industry and that sales figures include total company sales, including subsidiaries and operations not related to plastic resins and manmade fibers. Additional sources of company specific financial information include Standard & Poor's *Stock Report Services,* Moody's Manuals, and annual reports.

Table 6: Top U.S. Companies in the Plastic Resin and Manmade Fiber Industries

Plastics Resins (SIC 2821)				Manmade Fibers, Cellulosic and Noncellulosic (SIC 2823, 2824)			
Rank	Company	1996 Sales (millions of dollars)	4-digit SIC code	Rank	Company	1996 Sales (millions of dollars)	4-digit SIC code
1	Huntsman Chemical Corp. Salt Lake City, UT	1,472	2821	1	Monsanto Company Saint Louis, MO	8,962	2824
2	The Geon Company Avon Lake, OH	1,268	2821	2	Hoechst Celanese Corp. Bridgewater, NJ	7,395	2824, 2823
3	Albemarle Corp. Baton Rouge, LA	1,244	2821	3	Wellman Inc. Shrewsbury, NJ	1,109	2824
4	A Schulman, Inc. Akron, OH	1,027	2821	4	Nan-Ya Plastics Corp. Livingston, NJ	365	2824
5	Aristech Chemical Corp. Pittsburgh, PA	945	2821	5	Cookson Fibers Inc. Bristol, VA	175	2824
6	Condea Vista Company Houston, TX	882	2821	6	Du Pont EI de Nemours and Co. Camden, SC	175	2824
7	Carlisle Companies Inc. Syracuse, NY	823	2821	7	Allied Signal Inc. Chester, VA	160	2824
8	Novacor Chemicals Inc. Leominster, MA	756	2821	8	Amoco Performance Products Alpharetta, GA	124	2824
9	Amoco Fabrics and Fibers Co. Atlanta, GA	721	2821	9	BASF Corp. Anderson, SC	123	2824
10	Shintech Inc. Houston, TX	700	2821	10	Lenzing Fibers Corp. Lowland, TN	120	2823

Source: Dun & Bradstreet's *Million Dollar Directory*, 1997.

II.C.3. Economic Outlook

Plastic Resin Industry

The U.S. is a major exporter of plastics. Figure 6 shows trends in U.S. production of selected plastic resins for the past 25 years. Trade with Canada and Mexico accounted for about one-third of total U.S. plastics exports in 1992. Chronic worldwide overcapacity in plastics has continued to depress and slow growth rates. Since the industry is mature, the plastic resin industry was greatly affected by the depression in the global economy in the early 1990s. Plant closures and capacity cutbacks were partly successful in preventing further price declines during this period (Department of Commerce, 1994). From 1993 to 1998, global consumption of plastic resins is projected to increase 4 percent annually.

Figure 6: U.S. Production of Selected Resins, in millions of pounds
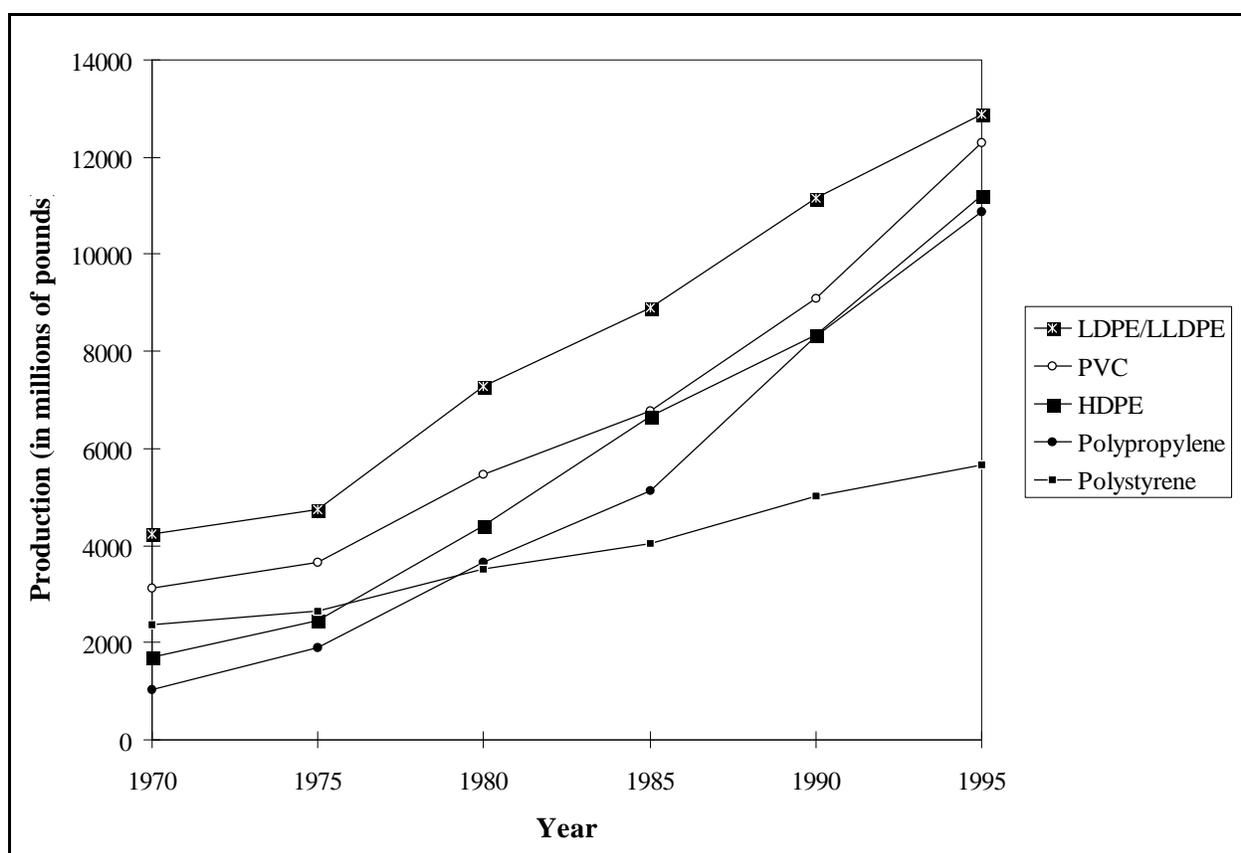
Source: U.S. Tariff Commission (for 1970 data); SPI Committee on Resin Statistics as compiled by the Association Services Group (for 1975-1995 data).

As the global economy rebounds from the recession of the early 1990s, growth is expected to be stimulated by upswings in the packaging, building, and construction markets. This growth is expected to occur primarily in countries along the Pacific Rim and in Latin America as these countries continue rapid industrialization, increased consumer spending, and substitution of other materials by plastics. Plastic resin production capacity is also increasing in these regions in response to the high demand.

The U.S. represents the largest single plastics market in the world, based on factors such as large domestic markets, readily available capital and technology, and relatively inexpensive raw material and energy costs. In the U.S., consumption and production are not experiencing high growth rates. This is, in part, the high level of substitution of traditional materials (like wood or metal) for plastics currently in place and the fact that the commodity plastics market is well-developed. As a result, major plastic resin manufacturers are merging and swapping production lines. Large multinational chemical companies are arranging licensing agreements as a way to tap into foreign markets. The plastic resin industry is also focusing on upgrading its production to higher-value-added and specialty resins tailored for niche markets. Research on plastic resins has started to focus on refining existing resins through blends and alloys and also improving catalyst technology to produce new grades of polymers. For instance, several companies are planning to produce specialty grades of polypropylene using new metallocene catalysts (McGraw-Hill, 1994).

Advances in plastic resin properties is expected to spur growth and foster the development of new end-use markets. For instance, the cost, low weight, and versatility advantages of newer plastic resins will make them more attractive in the auto assembly industries. Environmental regulations and concerns have an impact on many facets of the plastic resin industry. The demand for recycled and biodegradable plastic resins is expected to continue and drive development of more economical recycling technologies (Department of Commerce, 1994).

Manmade Fiber Industry

One-half of all fibers consumed are manmade. In 1992, global demand for manmade fibers increased by 3 percent. In the past, developed countries have dominated the manmade fiber industry. Between 1980 and 1993, the developing countries of Asia led by China, Taiwan, and Korea have accounted for most of the growth in manmade fiber production. During that period, these countries increased their aggregate share of world production from 15 to 42 percent. Developing countries are expected to continue increasing production and capability as their consumption and demand levels increase.

Figure 7: Manmade Fiber Production Data for Selected Fibers 1970-1995
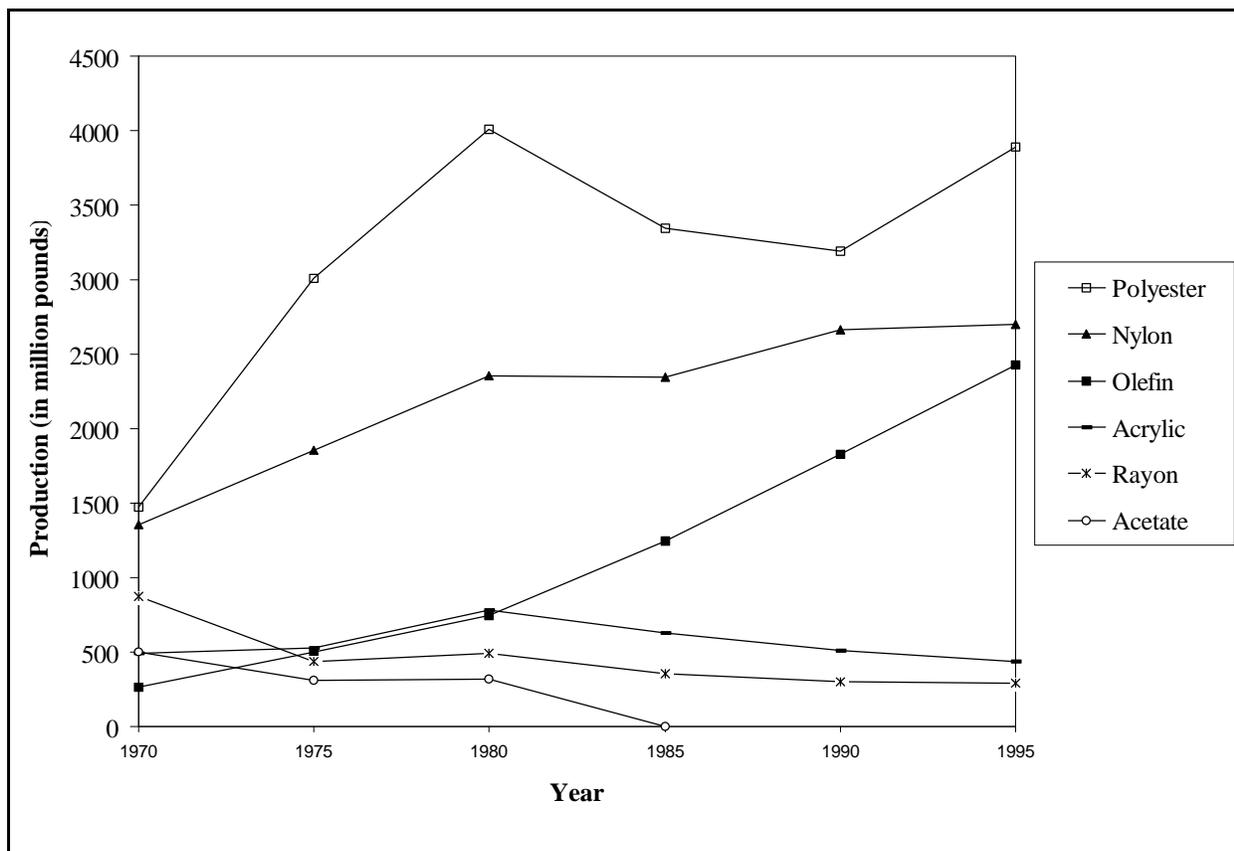
Source: Fiber Economics Bureau, Inc., 1996.

On the other hand, production in the U.S. has remained relatively stagnant. Figure 7 shows U.S. production trends from 1970 to 1995 for selected cellulosic and noncellulosic fibers. Figure 7 shows that production of polyester and nylon fibers was significantly greater than the production of cellulosic fibers, such as acetate and rayon. Note that numbers for acetate production and rayon yarn production were not available for 1985 to the present since the industries have shrunk to only a few companies. As a result, data do not appear for acetate from 1985 to 1995, and data for rayon represent rayon yarn and staple production for the period from 1970 to 1980 and rayon staple production only from 1985 to 1995.

In 1993, U.S. manmade fiber imports rose 11 percent due to increases in noncellulosic fiber imports. U.S. exports decreased 1 percent in 1993. Meanwhile, domestic shipments of noncellulosic fibers, such as nylon and polyester, increased by 2 percent. U.S. shipments of cellulosic fibers increased 14 percent to $1.8 billion primarily due to growth in rayon staple fiber demand and production. Rayon production has recently undergone extensive renovation to achieve additional environmental benefits and

become more competitive with noncellulosic fibers (U.S. Department of Commerce, 1994).

Barriers to entry into the manmade fiber industry are considerable, since production is highly capital intensive and requires significant technical expertise and economies of scale. Since the mid-1980s, the manmade fiber industry has undergone extensive consolidation and reorganization. During 1989-1993, several fiber companies sold off smaller fiber operations in order to concentrate on their strongest fiber operations, which produced higher value-added products. In addition, large companies, which traditionally produce commodity fibers, have looked to the sale of specialty fibers (e.g. heat-resistant or high-strength fibers) as a way to increase overall profits (Department of Commerce, 1994). Back-integration of the carpet industry, has resulted in the establishment of many new, small fiber producers (AFMA, 1997).

Because the manmade fiber industry is highly developed, the industry's most promising growth is expected to occur through these improvements in fiber characteristics. For instance, the *U.S. Industrial Outlook* states that microfiber yarns and fabrics have enabled manmade fibers to compete more directly with luxury fibers, such as silk and cashmere, in fashion apparel. Fabrics made with these finer fibers are usually more comfortable and softer than other fibers and can be used in a variety of finished apparel. The industry also predicts that lyocel, a new fiber which can be produced with particular environmental benefits, will contribute to cellulosic fiber growth (Department of Commerce, 1994). In addition, the industrial and technical products market is expected to continue to be dominated by manmade fibers (AFMA, 1997). Geotextiles, or manmade fibers used to reinforce civil engineering projects, biological filters, and military uses are end-uses that may create more opportunities for manmade fiber products.

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III. INDUSTRIAL PROCESS DESCRIPTION

This section describes the major industrial processes used within the plastic resin and manmade fiber industries, including the materials and equipment used, and the processes employed. The section is designed for those interested in gaining a general understanding of the industry, and for those interested in the interrelationship between the industrial process and the topics described in subsequent sections of this profile -- pollutant outputs, pollution prevention opportunities, and Federal regulations. This section does not attempt to replicate published engineering information that is available for this industry. Refer to Section IX for a list of reference documents that are available.

This section specifically contains a description of commonly used production processes, associated raw materials, the byproducts produced or released, and the materials either recycled or transferred off-site. This discussion, coupled with schematic drawings of the identified processes, provide a concise description of where wastes may be produced in the process. The first subsection, III.A., discusses polymerization processes common to the plastics resins and manmade fibers industries. The following subsection, III.B., discusses subsequent processing steps specific to manmade fiber manufacture. This section concludes with a description of the potential fate (via air, water, and soil pathways) of process-specific waste products.

III.A. Industrial Processes in the Plastic Resins and Manmade Fibers Industries

The plastic resin and manmade fiber industries both use and manufacture polymers. Polymers are large organic molecules (molecular weight $\sim 10^4$-10^7) that consist of small repeating molecules. Polymers used in the plastic resin and manmade fiber industries either occur naturally, such as cellulose, or are formed during polymerization when bond-forming reactions cause small repeating molecules to join together. Polymers are typically made from one type of simple chemical unit, or monomer. However, sometimes another compound, or comonomer, is used with the monomer to make a copolymer. Comonomers can be used to make copolymers with random chemical structures, called random copolymers, or organized chemical structures, called impact copolymers.

Polymers are central to plastic resin and manmade fiber manufacture. Many grades of different polymers are produced, each with different physical characteristics such as strength and ease of flow when melted. These different physical characteristics are achieved by changing operating parameters or by using different polymerization processes to change properties, such as polymer density and molecular weight. Polymers which have been dried and shaped into pellets are called plastic resins. These resins are further processed at plastics processing facilities which create plastic products of different

shapes, sizes, and physical properties. (Refer to the EPA Rubber and Plastics Sector Notebook for more information on plastics processing.) Polymers can also be used to make synthetic fibers, which are commonly used to make manmade textile products. Some synthetic fiber manufacturers synthesize polymers on-site, while some purchase plastic resins for use in their fiber operations. Fiber formation processes, including the use of natural polymers to make cellulosic fibers, and particular textile fiber operations will be covered later in this section.

There are several steps that are important to polymerization. First, reactants are purified prior to polymerization. During polymerization, catalysts, heat, pressure, and reaction time are all optimized to maximize polymer conversion and speed the reaction. The polymer is often then separated from the reaction mass through a series of separation and drying steps. (Exceptions to this are acrylic polymers, (AFMA, 1997b).) Finally, the polymer is extruded and pelletized for packaging and shipment. Various supporting steps are important to note because of their potential effect on the environment. These supporting steps include unloading and storage of chemicals and equipment cleaning. Note that methods used to recover raw materials and control pollution are covered in Section III.D. Although there are thousands of types of resins and fibers that may be produced during polymerization, the basic industrial processes are similar. These processes are summarized below:

> 1) preparation of reactants
> 2) polymerization
> 3) polymer recovery
> 4) polymer extrusion
> 5) supporting operations

This section briefly describes the processes involved in the manufacture of plastic resins and noncellulosic manmade fibers. These processes vary by facility. For instance, some manufacturers purchase reactants in pure form, while others may synthesize reactants on-site. Other facilities compound or incorporate additives into the finished polymers. Facilities that specialize primarily in compounding polymers are listed under SIC Code 3087 and are not covered in this notebook.

III.A.1. Preparing Reactants

Many chemicals can be used to make polymers. The most important chemicals are monomers, catalysts, and solvents. Monomers are the basic building blocks of polymers. They can be simple in structure (e.g. ethylene CH_2CH_2) or complex (e.g. ester of a dihydric alcohol and terephthalic acid - $HOCH_2CH_2OCOC_6H_4COOH$). Catalysts are chemicals used to speed up or initiate the polymerization reaction. Common catalysts include Ziegler catalysts (titanium chloride and aluminum alkyl compounds), chromium-

containing compounds, and organic peroxides. Details of commercially-used catalysts are highly guarded secrets since small differences in catalyst preparation can lead to huge differences in polymerization costs and polymer properties (Kroschwitz, 1986). Solvents are sometimes used to dissolve or dilute the monomer or reactants. The use of solvents facilitates polymer transport through the plant, increases heat dissipation in the reactor, and promotes uniform mixing in the reactor. Other chemicals used in polymerization include suspending and emulsifying agents which disperse monomer in solution.

Reactants, particularly monomers, must be sufficiently pure before they can be charged to the polymerization reactor. Trace amounts of contaminants in monomer, such as water, oxygen, and sulfur compounds in part per million quantities, can impede polymerization and decrease product yield. Most monomers and solvents can be purchased in sufficient purity for polymerization, however, sometimes reactants must be purified to remove contaminants. Facilities may use different purification methods, such as distillation or selective adsorption, to increase monomer purity. Some companies manufacture monomer and other reactants at different chemical facilities and transport them to plastic resin and manmade fiber facilities where the chemicals can be further processed to a sufficient purity level. For example, the nylon-6 monomer, E-caprolactam, is often made on-site, prepared, and charged to the polymerization reactors.

In addition to purification steps, reactants are often diluted, premixed, or otherwise treated before being sent to the reactors. The preparation and charging of reactants often varies by polymerization method. For instance, Ziegler-type catalysts are usually diluted with dry inert solvent and premixed before injection into the polymerization reactor. For suspension and emulsion polymerization, the catalyst, emulsifier, suspending agents, modifier, and activator are dissolved in water and adjusted to the proper concentration before polymerization. In some continuous processes, two agitated make-up tanks are often run in parallel so that catalysts can simultaneously be mixed and charged to the polymerization vessel from one tank while a fresh solution is prepared in the other.

III.A.2. Polymerization

Polymerization is the major process involved in the synthesis of plastic resins and manmade fibers. Two types of polymerization, addition polymerization and polycondensation, are commonly used to make plastic resins and manmade fibers. These two methods use different chemical steps to make polymers.(McKetta, 1992) In addition polymerization, monomer is polymerized using a free radical catalyst (a highly reactive molecule having one or more unpaired electrons) or a coordination catalyst (e.g. Ziegler type) to activate the monomer molecules and trigger polymerization reactions.

With polycondensation reactions, typically two or more reactants are first combined in a prepolymerizer reactor to form a monomer before polymerization. During polymerization, two reacting monomers are linked together in condensation reactions where water molecules are split off of the reacting monomers (Lewis, 1993). In polycondensation reactions, water is typically removed by vacuum to speed the reaction. Because addition polymerization processes are widely used to make plastic resins and manmade fibers, this section focuses primarily on addition polymerization processes.

Continuous versus Batch Processes

Chemical modifiers are often injected into the reactor to give polymers specific characteristics. Temperature and pressure have a profound effect on polymerization processes and may be varied in order to control conversion, reaction rate and end properties of the polymer produced. Addition polymerization is a highly exothermic reaction, and reactor conditions are tightly monitored to control heat production and reaction stability. Continuous processes are typically used for large-volume, or commodity, polymerizations, while batch or semibatch processes are used for low-volume, or specialty, polymerizations. In continuous processes, the feed is continuously charged into the reactor and effluent is continuously removed. In batch processes, all reagents are added to the reactor and remain in the reactor for the same amount of time. In semibatch processes, some reactants are added at intervals while some byproducts are removed (Kroschwitz, 1986).

Types of Reactors

Two main reactor types are used in polymerization: stirred tank reactors and linear-flow reactors. Stirred-tank reactors (or autoclaves) are usually made of stainless steel and range in size from 1,400-2,800 ft^3 (40-80 m^3), although some reactors as large as 7,000 ft^3 (200 m^3) are in commercial use. The reactors usually consist of a jacketed cylindrical vessel with an agitator and have highly polished stainless steel linings which are noncorrosive and minimize polymer deposits left on walls (Kroschwitz, 1986). Stirred-tank reactors also have thick walls to withstand high pressures and support low heat transfer capacity. Temperature is controlled by heat transfer to the jacket, internal cooling coils, water cooled impellers, external reflux condensers, and external heat exchangers. Typical temperatures range from 160- 570°F (70-300°C), and conversion rates ranges from a low of 2 percent to 85 percent (McKetta, 1992). Due to their versatility, stirred-tank reactors operated for batch processing are used to produce a large portion of polymers in the United States. Often two or more reactors of similar size are used in series to increase monomer to polymer conversion rates, to make maximum

use of catalyst productivities, and to reduce separation costs of removing monomer from the diluent. The first reactor is sometimes referred to as the prepolymerizer since monomer conversion rates are low (McKetta, 1992).

Continuous processes are typically operated in gas-phase fluid-bed reactors or linear-flow reactors. Gas-phase fluid-bed reactors are widely used in polymerizing ethylene and propylene by way of coordination catalysts. The reactor is a vertical cylinder containing a bed of solid polymer powder maintained in a fluidized state by passing a stream of reaction gas up from the base of the reactor. Catalyst and monomer are added through the sides of the reactor. The reaction gas is withdrawn from the top of the reactor and heat of reaction is removed with a compressor and cooler before being recirculated back up through the polymer powder. The solid polymer powder is removed periodically as it builds up in the base of the reactor by opening a discharge valve that blows the product powder into a disengaging system. (SRI, 1995) Figure 8 shows a simplified diagram of a gas-phase fluid-bed reactor.

**Figure 8: Gas-Phase Fluid-Bed Reactor for Production of Polyethylene**
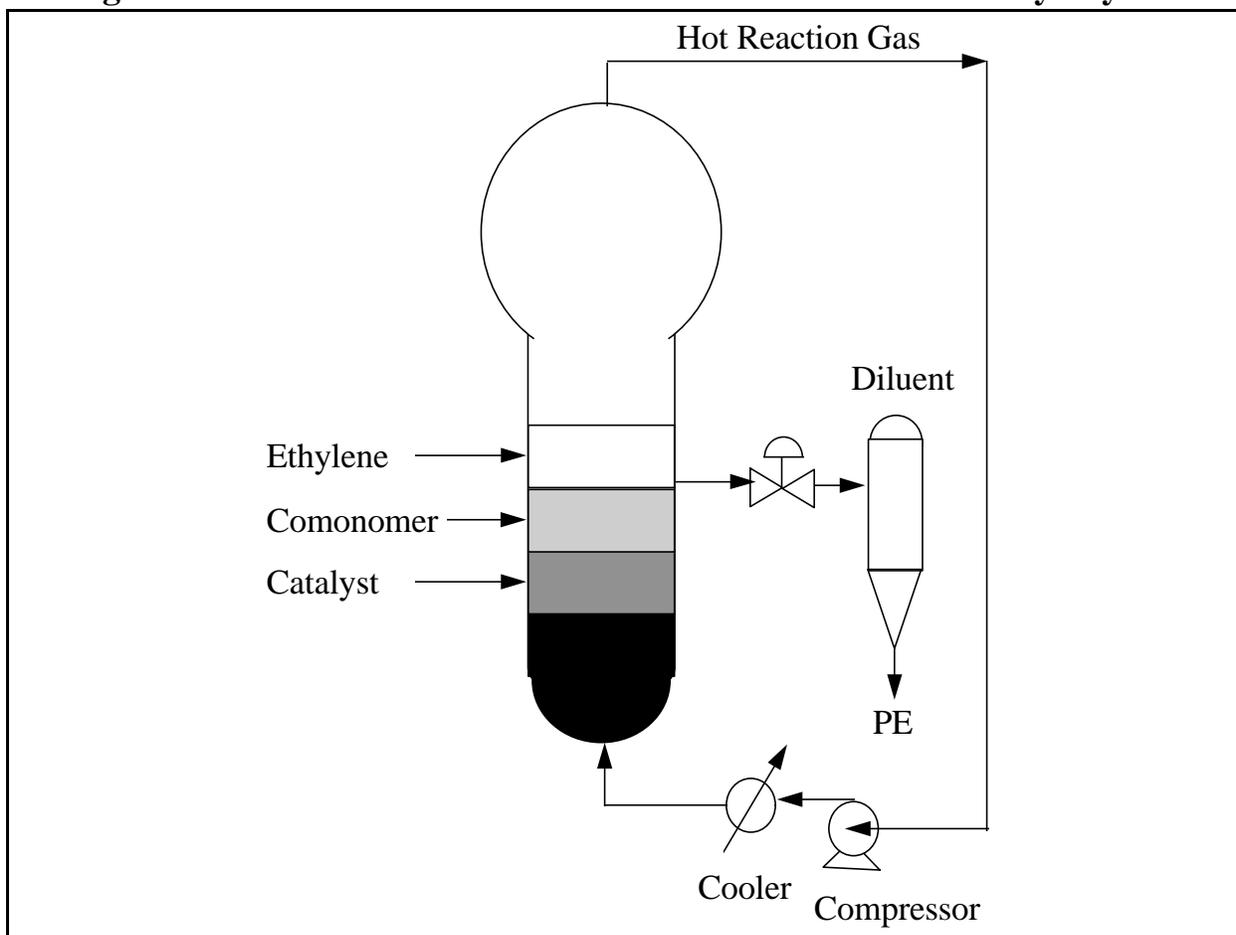
Source: SRI International 1995.

Linear-flow reactors are tubular and jacketed with a heat transfer fluid, like Dowtherm® or water (Kroschwitz, 1986). The tubes may be several hundred meters in length, but are often coiled in helix-like structures as a way to save space and avoid buildup of polymer in elbows. Typical residence time in the reactors varies from 30 to 60 seconds. The reactors have three different zones used for preheating, polymerization, and cooling.

Loop reactors are the most common linear-flow reactors. Loop reactors have long straight lengths of tubing interjected with short bends and are typically 490-540 ft (150-165 m) long. The reaction slurry is circulated around the loop at speeds of 10-30 ft/s (3.3-10 m/s) by axial flow pumps. The residence time of the reactants in the loop reactors ranges from 45 to 60 seconds, and polymerization temperatures range from 390-480°F (200-250°C). A schematic diagram of a typical loop reactor is shown in Figure 9. Polymer slurries containing 20-70 percent solid polymer particles are collected in settling legs located at the base of the reactor. When two loop reactors are used in series, a portion of the slurry in the first loop is continuously withdrawn and pumped into the second reactor, from which polymer is removed as a slurry. Emissions and wastes generated during polymerization include VOC emissions from leaks and spills, solid wastes from off-specification polymer, and spent solvent from incomplete polymerization (Kroschwitz, 1986).

Figure 9: Typical Loop Reactor for Production of Polyethylene
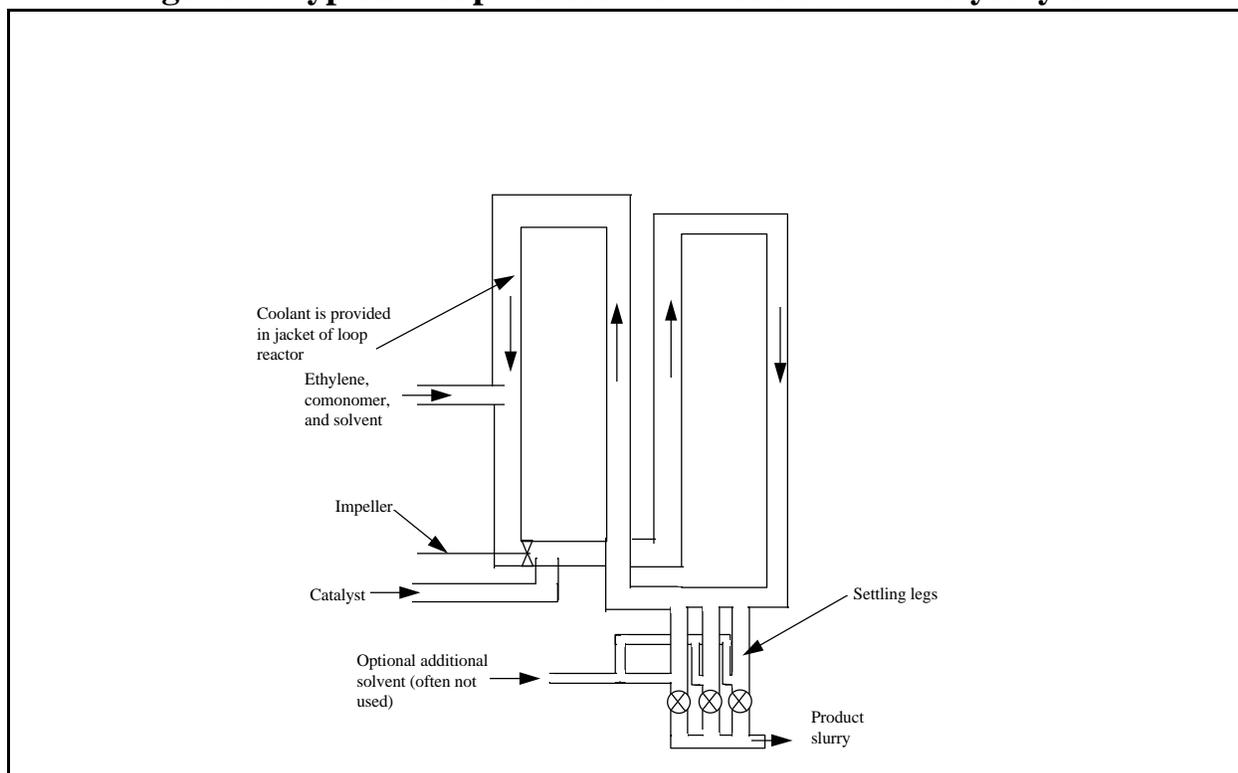
Methods of Polymerization

The specific polymerization method used is key to polymer manufacturing. Different polymerization conditions and processes are used to synthesize different polymers and to create different grades of a given polymer (McKetta, 1992). Addition polymerization methods are covered primarily in this section. Five general methods are used commercially for polymerization: bulk, solution, suspension, emulsion, and polycondensation. Table 7 lists typical polymerization method and reactants for leading commercial plastic resins. Note that distinctions between these methods are not well-defined and that some companies use a combination of polymerization methods. In addition, details of specific processes are often protected by manufacturers since small process variations can result in significant reductions in operating costs and unique changes in polymer characteristics.

Source: *Encyclopedia of Chemical Processing and Design.* Volume 39. J.J. McKetta (ed.), Marcel Dekker, Inc., New York, 1992.

Table 7: General Polymerization Parameters for Selected Polymers

Polymer	Polymerization Method	Monomer	Catalyst	Solvent	Other Possible Reactants
HDPE	solution, suspension	ethylene	Ziegler-type catalysts	isobutane, hexane	
LDPE	bulk, suspension	ethylene	organic peroxides, peroxyesters	hydrocarbons	
LLDPE	solution	ethylene	Ziegler-type or Phillips chromium oxide catalysts	octene, butene, or hexene	
Polypropylene	bulk, solution, suspension	propylene	Ziegler-Natta catalysts	hexane, heptane, or liquid propylene	
Polystyrene	bulk, suspension, solution	styrene	heat, organic peroxides	styrene, ethylbenzene	
PVC	suspension	vinyl chloride	azo compounds, organic peroxides	water	polyvinyl alcohols (suspending agent)
Acrylic/ Modacrylic	solution, suspension, emulsion	acrylonitrile	organic peroxides, azo compounds, inorganic redox initiators	dimethylacetamide or aqueous inorganic salt solutions	
Nylon-6	bulk; polycondensation	ε-caprolactam	water	---	acetic acid (molecular weight regulator)
Nylon-6,6	bulk; polycondensation	hexamethylene diammonium adipate			adipic acid (viscosity stabilizer), polyphosphoric acid (reaction accelerator)
Polyester (Polyethylene terephthalate)	bulk; polycondensation	terephthalic acid and ethylene glycol	antimony oxides and derivatives	---	

Bulk Polymerization

> In bulk polymerization, primarily monomer and a catalyst are used to make polymer. Two reactor vessels are often used to complete polymer conversion and recycle unreacted monomer. Because few solvents or other chemicals are used, bulk processes typically produce purer polymers and generate less pollutants than those produced by other processes. Separation procedures of polymer and reactants are also simplified, reducing expensive solvent recovery equipment costs. Figure 10 shows a flow chart for a high density polyethylene process with simplified separation steps. In the figure, high density polyethylene is separated from the monomer in the flash drum and goes through a series of recovery and finishing steps. The monomer is recovered using a stripper and a dehydrator. Increased conversion rates and decreased recovery costs have made bulk processes increasingly favored in the industry (McKetta, 1992). Note that bulk processes used for polycondensation reactions are discussed later in this section.

## Figure 10: High-Density Polyethylene Process Flow Diagram
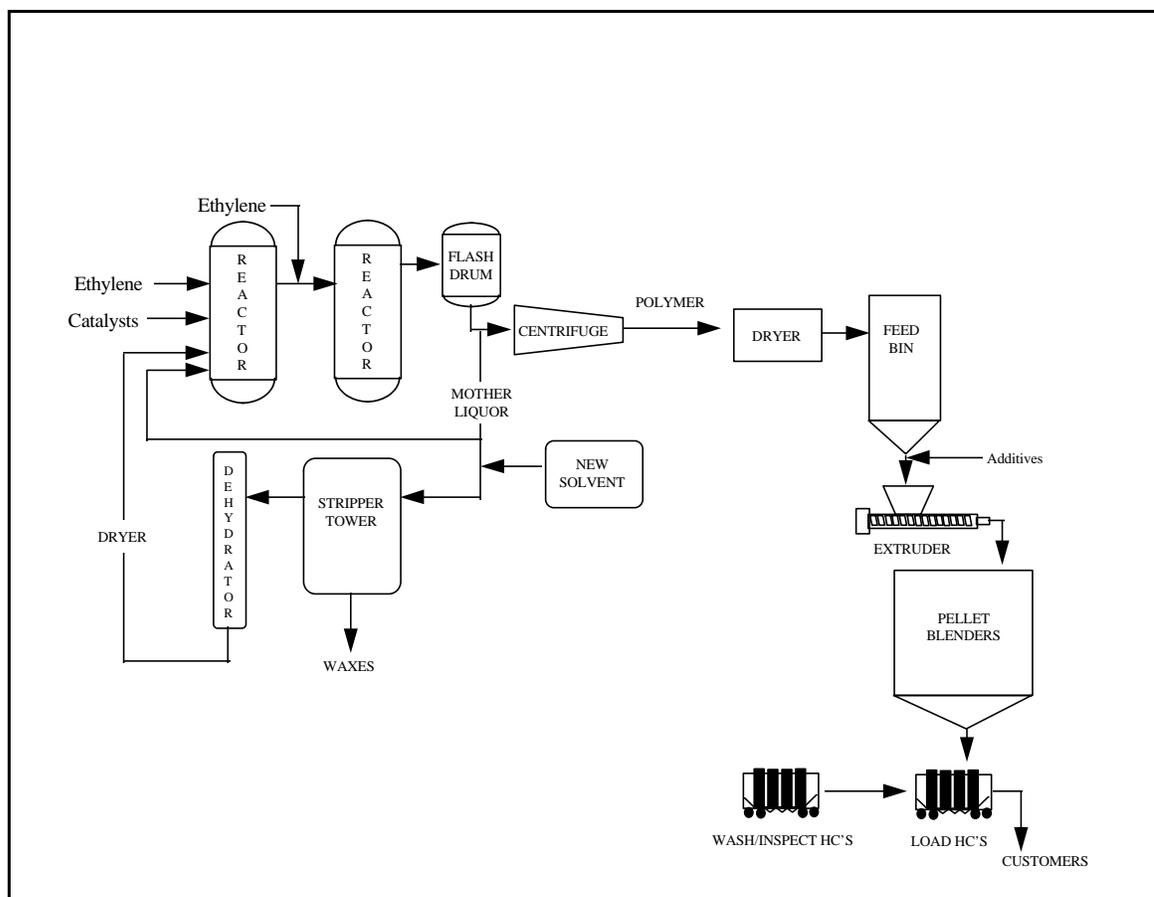
Source: Exxon Chemical Company's *Mont Belvieu Plastics Plant Brochure.*

Bulk processes can be divided into two types based on whether or not the monomer and polymer are soluble in each other. If the monomer and polymer are not soluble in each other, polymer slurries are formed which consist of solid polymer particles mixed with either liquid or gaseous monomer. Polyester and nylon are among many polymers produced in continuous-flow bulk polymerization systems.

Gas-phase polymerization is a type of bulk polymerization primarily used to synthesize polyethylene and polypropylene. Gaseous monomer and comonomer are fed continuously into a reactor that is filled with fluidized polymer particles. Figure 11 shows a photo of two fluid reactors used for making polypropylene. In the Unipol process, up flowing monomer reacts with granular polymer particles suspended in a vertical cylindrical reactor. The bed is typically 40-50 ft (12-15 m) high and 15-16 ft (4.5-5 m) in diameter. Pressures range from 265 to 310 psi (18-21 atm), and temperatures range from 176 to 212°F (80-100°C). A distributor plate is attached to the bottom of the reactor to maintain uniform flow of monomer and even distribution of polymer and catalyst throughout the bed. Monomer gas is cooled and partially condensed in an external cooler to remove reaction heat. Only 2 percent of monomer reacts per pass, so large volumes of gas are recycled. Large polymer particles collect in the bottom of the reactor where they are semicontinuously removed (McKetta, 1992).

Figure 11: Fluid Reactors Used for Making Polypropylene
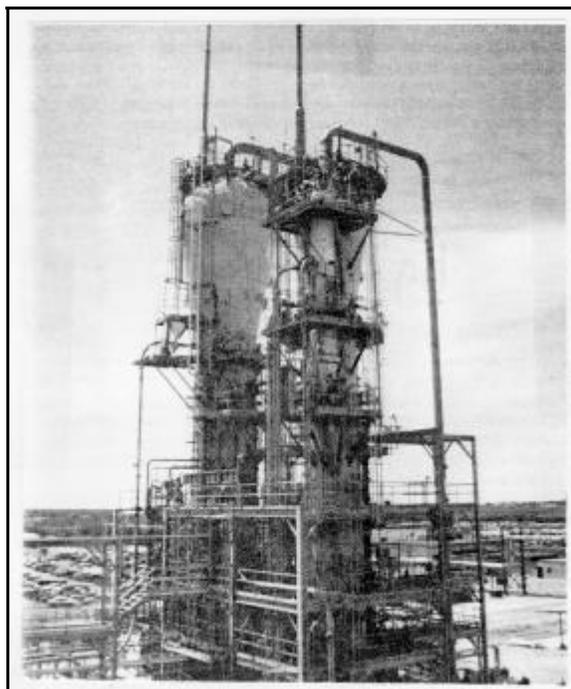
Source: *Principals of Polymer Systems, 4th Edition,* Ferdinand Rodriguez, Taylor and Francis, Washington, DC, 1996. Reproduced with permission. All rights reserved.
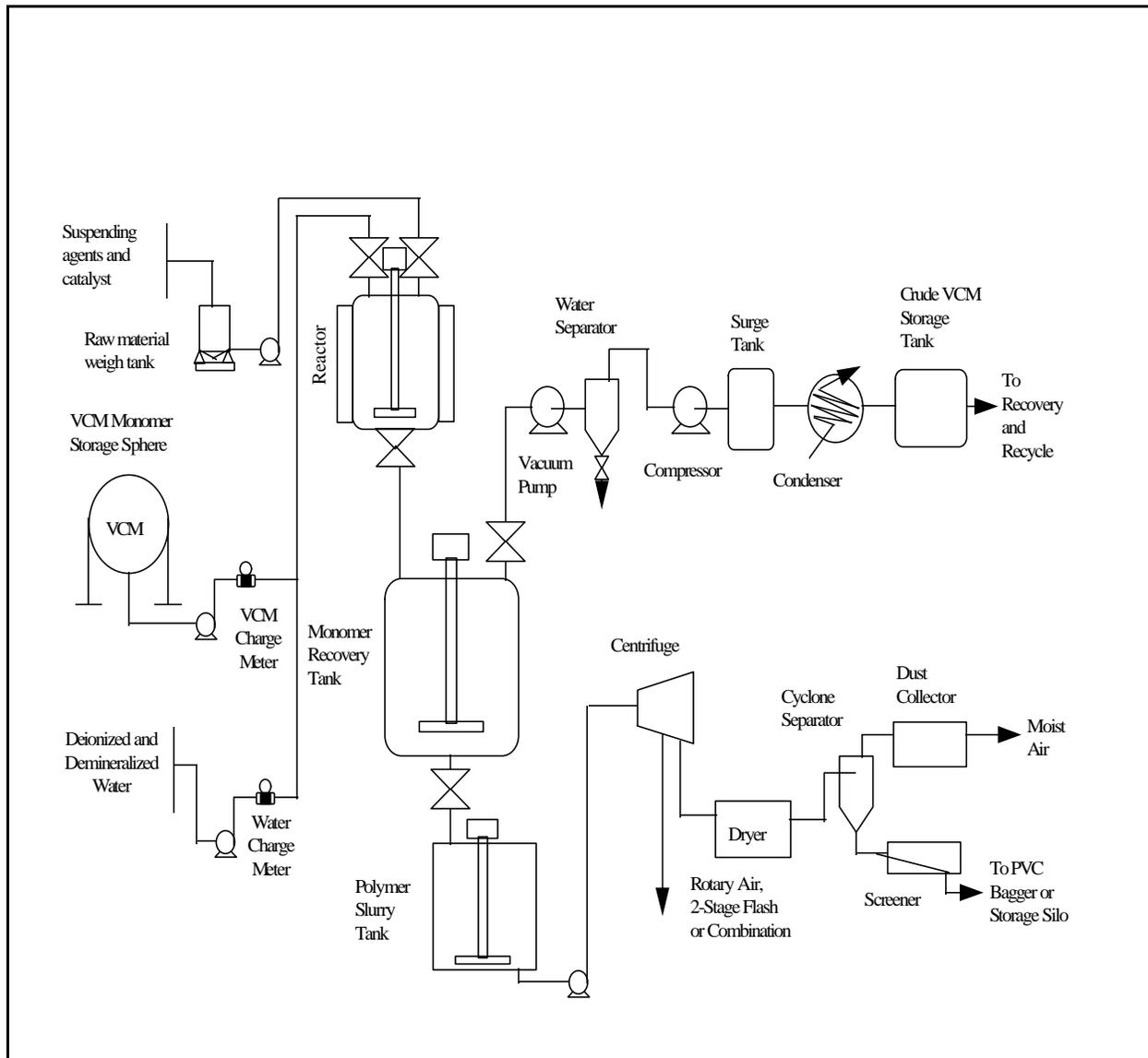
Solution Polymerization

Solution polymerization is commonly used to make plastic resins and textile fibers. In solution polymerization, a solvent is mixed with monomer in the reactor. Use of solvents reduces reaction mass viscosity, improves heat transfer rates, and increases mixing efficiency during polymerization. Choice of solvent can have a large effect on polymer properties and the rate of polymerization. Because solution polymerization requires additional processing and recovery steps, companies typically try to optimize solvent to monomer ratios to reduce polymerization costs and emissions (Kroschwitz, 1986). Reactors are often operated in series for continuous operations.

In solution polymerization, the polymer may be soluble or insoluble in the solvent. When the polymer is insoluble in the solvent, a slurry is formed of solid polymer particles dispersed in solvent. Slurry processes can be divided into two categories, light slurry and heavy slurry, based on the molecular weight of the solvent. Slurry processes are commonly used in the continuous production of high-density polyethylene, linear low-density polyethylene, and polypropylene. Polymers are typically formed at temperatures of 320-480°F (160-250°C), with a dissolved polymer content of usually 10-15 percent. Loop reactors are often used, although some companies use a series of stirred autoclaves as polymerization vessels. Typical solvents used include isobutane (light slurry) and hexane (heavy slurry). Typical slurry composition by weight is 30 percent particulates, 68 percent solvent, and 2 percent monomers. Reaction pressure is about 650 psi (44 atm) and reaction temperature is about 225°F (107°C). Typical polymer concentrations are 50-70 percent (McKetta, 1992).

Suspension Polymerization

In suspension polymerization, agitation and suspending agents are used to suspend monomer and polymer particles in water. The suspending agents also maximize heat transfer, maintain uniform mixing, and prevent polymer clumping in the suspension. Catalysts are added to initiate the reaction and typically include azo compounds, organic peroxides, or peroxydic carbonates. In suspension processes, polymerization is initiated in the monomer droplets and proceeds as miniature bulk reactions. The polymer droplets, usually 0.006-0.20 in (0.15-5 mm) in diameter, settle out of solution as soon as agitation is stopped. Figure 12 shows the typical flow diagram for the suspension polymerization of polyvinyl chloride (PVC). Note that monomers and polymers produced by suspension and emulsion processes undergo additional recovery steps than those produced by bulk or solution processes. For example, Figure 12 shows that the polymer slurry is centrifuged and separated following polymerization. Monomer undergoes additional recovery and drying steps to remove water from the monomer.

Figure 12: Typical Process Flow Diagram for Suspension Polymerization of PVC

Source: *Encyclopedia of Chemical Processing and Design,* Volume 40, J.J. McKetta (ed.), Marcel Dekker, Inc., New York, 1992.

Industrial suspension processes generally use batch reactors. Suspension polymerization processes are used for about 90 % of all PVC produced. Stirred-tank reactors for PVC production range in size from 1,000-50,000 gallons, and reaction temperatures typically range from 110-160°F (45-70°C). Note that polymers produced by suspension processes must undergo additional monomer and polymer recovery steps than those produced by bulk and solution processes (Kroschwitz, 1986).

Emulsion Polymerization

Emulsion polymerization is similar in method to suspension polymerization but uses smaller monomer and polymer particles. Emulsion polymerization uses emulsifiers and additives to suspend monomer and polymer particles in water. In emulsion polymerization, surfactant accumulates around monomer particles, forming micelles that act as tiny polymerization vessels. Polymers form as more monomers react. Agitation optimizes reaction rate by dispersing monomer, catalyst, and polymer and by transporting heat to the reactor surface. Emulsion processes typically produce moderately viscous reaction masses. About 10% of PVC and some polystyrene are produced by emulsion processes. Emulsion polymerization methods typically produce polymers that are smaller and more difficult to process than those produced by suspension polymerization methods. Polymers produced by emulsion processes are also characterized by high polymer viscosity, high heat transfer rates, and more difficult transport and agitation of the polymer slurry. For those reasons, emulsion processes are frequently replaced with suspension polymerization methods (Kroschwitz, 1986).

Polycondensation

Polycondensation reactions are used to make polymers, such as polyesters, polyamides (or nylons), polyurethanes, phenolics, urea resins, and epoxies. Polycondensation is an equilibrium reaction that depends on temperature, pressure, and the efficient removal of reactants and the catalyst (Kroschwitz, 1986). Typically, two or more reactants are first combined to form a monomer. The monomer is then charged to a polymerizer where monomers link together in condensation reactions. Condensation reactions occur when two molecules are linked together from the splitting of water molecules from the reacting molecules. Reaction temperatures range from 446 to 545°F (230 to 285°C) for nylon-6,6 and polyester. These reactions are endothermic, unlike addition polymerization reactions, and therefore, require the addition of heat to complete polymerization (ATMI, 1997b).

For nylon-6,6, polycondensation of nylon salt is carried out continuously for commodity nylon production and batchwise for special grade nylon production. The reaction typically takes place in several stages. The first stage takes place in a tank or tubes under pressure greater than 250 psig.

Water vapor is removed through a throttle valve or in a subsequent separator. The last stage of the polycondensation occurs under atmospheric or subatmospheric pressure to further facilitate water removal. Additives are often introduced during polycondensation to impart desirable properties to resins and chips. Viscosity stabilizers, such as acetic acid, are sometimes used to limit the degree of polymerization. Reaction accelerators, such as phosphoric acid, sometimes used to speed the reaction (McKetta, 1992).

III.A.3. Polymer Recovery

Once polymerization is completed, a reaction mixture is produced which consists of polymer, monomer, and trace amounts of catalyst. Because reaction mixture consistency varies according to which polymerization method is used, different polymer separation and recovery steps are required of different polymerization methods. To recover the polymer, the reaction mixture typically goes through a series of three separation and purification steps: 1) unreacted monomer is separated from the polymer; 2) liquids and solids are separated; and 3) residual water or solvents trapped in the polymer are purged by drying the polymer.

The first step in polymer recovery is flashing, in which solvents and unreacted monomers are volatilized from the reaction mixture and drawn off for recovery. Flashing is achieved by lowering the pressure in a staged separation system, which causes monomers and solvents with low boiling points to evaporate. A large portion of monomer and solvent is removed during this step. Remaining monomer in the polymer can be removed in a low-pressure degasser, as in bulk polymerization processes, or by gravity, as in gas-phase processes. In some cases, combinations of heating, flashing, thin-film evaporation, and vacuum stripping are used to separate residual solvent from the polymer.

For reaction mixtures that contain heavy solvents or liquids, further steps are used to separate the polymer from the reaction mixture. Typically, the mixture is centrifuged or filtered to separate the solid polymer granules from the liquids. The polymer is then washed and stripped of residual solvent and monomers.

Most polymer recovery operations include a drying step. Polymers are usually solvent or water-wet and are dried after being centrifuged. Drying removes water and residual solvents from the polymers. Flash drier-fluidized bed systems with gas recycle are commonly used for polypropylene and high-density polyethylene. Combination dryers, such as single and multistage fluidized-bed systems, are also used. In the flash dryer-fluidized bed system, the flash dryer removes surface water in a matter of seconds, while the fluidized bed completes moisture removal by holding the polymer at drying temperatures for about 30 minutes. In rotary dryers, a hot gas passes over the

polymer particles, transferring heat and vaporizing solvent and water molecules. Rotary dryers and two-stage flash dryer-fluidized-bed systems have also been used to dry the wet PVC cakes resulting from polymerization. Polyester is often dried by hot, dry air or inert gas in tumble, column, or fluidized-bed dryers at about 180°C. Wastes generated from drying operations include primarily VOC emissions (Kroschwitz, 1986).

III.A.4. Polymer Extrusion

Most polymers undergo further processing steps to form plastic pellets. The polymer is usually extruded and pelletized before being packaged and incorporated with additives to prevent product deterioration. After polymer recovery, the polymer is fed to a screw extruder which melts the polymer. The molten polymer is then fed to a pelletizer, which may be capable of producing up to 5000 pounds of pellets per hour. The pelletizer extrudes molten polymer out of small orifices, forming continuous strands 0.08-0.16 in (2-4 mm) in diameter. These strands are cooled and then cut using either a fixed or rotating knife. The pellets are then dried to remove any dissolved monomer that would exude from the pellets during storage. Additives are often added directly to the extruder, to a blender prior to the extrusion step, or later in a highly concentrated master batch. Often antioxidants are added to prevent deterioration of product properties during storage, shipment, and product fabrication. Other additives may be added to increase ultraviolet light stability, reduce the tendency for static electrical charges, or add color and pigment (McKetta, 1992).

III.A.5. Supporting Operations

Various supporting steps to the manufacture of plastic resins and manmade fibers are important to note because of their effect on the environment. Supporting steps include the unloading and storage of chemicals and equipment cleaning. Some of these supporting processes are discussed below. Note that supporting operations, such as raw material recovery and pollution control, are mentioned in Section III.C.

Equipment Cleaning

Cleaning of equipment, such as reactors and storage vessels, is performed periodically as routine maintenance on the plant. Polymerization reactors are cleaned often to remove buildup of polymer on heat transfer surfaces which can result in contamination between batch runs of different polymers or different grades of polymers. Reactor cleaning is particularly important for suspension and emulsion polymerization processes since the reaction mass is very viscous. Deposits on reactors may consist of polymer gels or coagulum. Spray rinse valves are often installed in the reactor top to facilitate washing while the reactor is emptied. High pressure water-jet

streams and hydraulic reactor cleaners are also used to remove hard deposits. Solvents and manual scraping are also sometimes used (Kroschwitz, 1986).

Cleaning of loading vehicles and storage vessels is performed both before and after loading. Before plastic pellets can be loaded into rail hopper cars or bulk trucks, the vehicles are cleaned to remove residual trapped and clinging pellets as well as other contaminants that may be present. Pellets are removed first using suctioning and then using wash water. The rinse water is collected into the facility drainage and containment system where residual pellets are recaptured via a series of dams, skimmers, and surface booms. Wastes from equipment cleaning also include wastewater contaminated with dilute concentrations of organics, acids, and salts (EPA, 1992).

Unloading and Storage of Reactants

Unloading and storing reactants is an important step in polymerization. These operations are closely monitored to avoid contamination of reactants, runaway or accidental polymerization, and fugitive emissions. To reduce fugitive emissions, gaseous compounds are often unloaded from tank cars by pressurizing the tank car with vapors from the storage tank. Compressor valves are then reversed to remove and transfer vapor from tank cars to storage tanks.

Chemicals are typically stored in large stainless steel storage tanks equipped with both external and internal covers. Tank design is mostly concerned with safety, since materials may be flammable, toxic, or autocatalytically polymerized. Autocatalytic polymerization occurs when monomer starts polymerizing spontaneously in the storage tank. Monomers are typically stored in pressure vessels equipped with excess flow valves on the outlet connection. These valves safeguard against complete discharge in the event of pipe rupture. In addition, monomer storage tanks are often equipped with systems to avoid unwanted polymerization including systems to inject inhibitor into reactors to stop polymerization and insulation and coiling coils to prevent polymerization.

Liquids with high boiling points are stored in vented atmospheric tanks. Solvents are usually stored under a blanket of nitrogen gas to minimize air contamination. Some catalysts, such as the Ziegler-type, are so explosive when in contact with water and air that they are diluted with hydrocarbons for easier handling (Kroschwitz, 1986). For these safety reasons, tanks are usually located outdoors and away from production facilities. Because of stringent dust and moisture standards for polymerization, unloading and storage systems may have elaborate air conditioning and ventilation systems. Emissions generated from storage operations include air emissions of VOCs (EPA, 1993).

Conveyance

Charging reactants to reactors is one of the most important conveyance steps in plastic resin and manmade fiber production. Charging reactants and polymer must be controlled carefully to avoid producing off-spec product and causing polymer buildup in the pipes. Polymerization feed is automatically measured and charged into the reactors. Measuring and charging reactants varies depending on whether the process is batch or continuous and what accuracy of formulation is required. Batch methods use weigh tanks, volumetric charge tanks, and flow meters to feed the polymerization vessels. For continuous processes, reactants are fed continuously at a specific rate into the reactor. Reactor heat-up, purge, evacuation, charge, and discharge are all controlled by automatic control systems equipped with temperature and pressure overrides.

Conveying systems are also used to move plastic pellets between plant operations. An example of a pneumatic conveying system in a pellet blending operation is shown in Figure 13. Pellets are conveyed using pneumatic or mechanical systems to move pellets between the pelletizers and drying systems and between storage silos and shipping containers. In pneumatic systems, high-pressurized air can be used to transport pellets through the plant. Mechanical systems are generally used to transport pellets across short distances using rigid driven screws to force pellets through a conduit. Pellet spills can occur during each conveyance and can be avoided by controlling the rate of pellet entry and delivery from the conveying system. Wastes generated during conveying operations may include VOC emissions from leaks and spills (EPA, 1992).

Pellet Storage

Plastic pellets must be stored carefully to avoid product contamination or accidental spills. EPA has identified preventive measures to minimize pellet loss and entry into water streams which apply to plastic resin and manmade fiber plants and downstream processing plants. After polymer finishing, the plastic pellets are transferred to intermediate storage vessels consisting of 30,000 to 100,000 pound silos. The pellets are then transferred to silo lots where they are sampled, bagged for shipment, and transferred to downstream processes for hot-melt mixing and incorporation of additives. Pellets are packaged in containers ranging from 50 pound bags to 100,000 pound railway hopper cars. Wastes from pellet storage include solid wastes or wastewater containing plastic pellets (EPA, 1992; SPI, 1994).

Figure 13: Typical Pneumatic Conveying System in a Pellet Blending Operation

Storage Silo   Storage Silo

Manual Feed
from Bags   Bagging
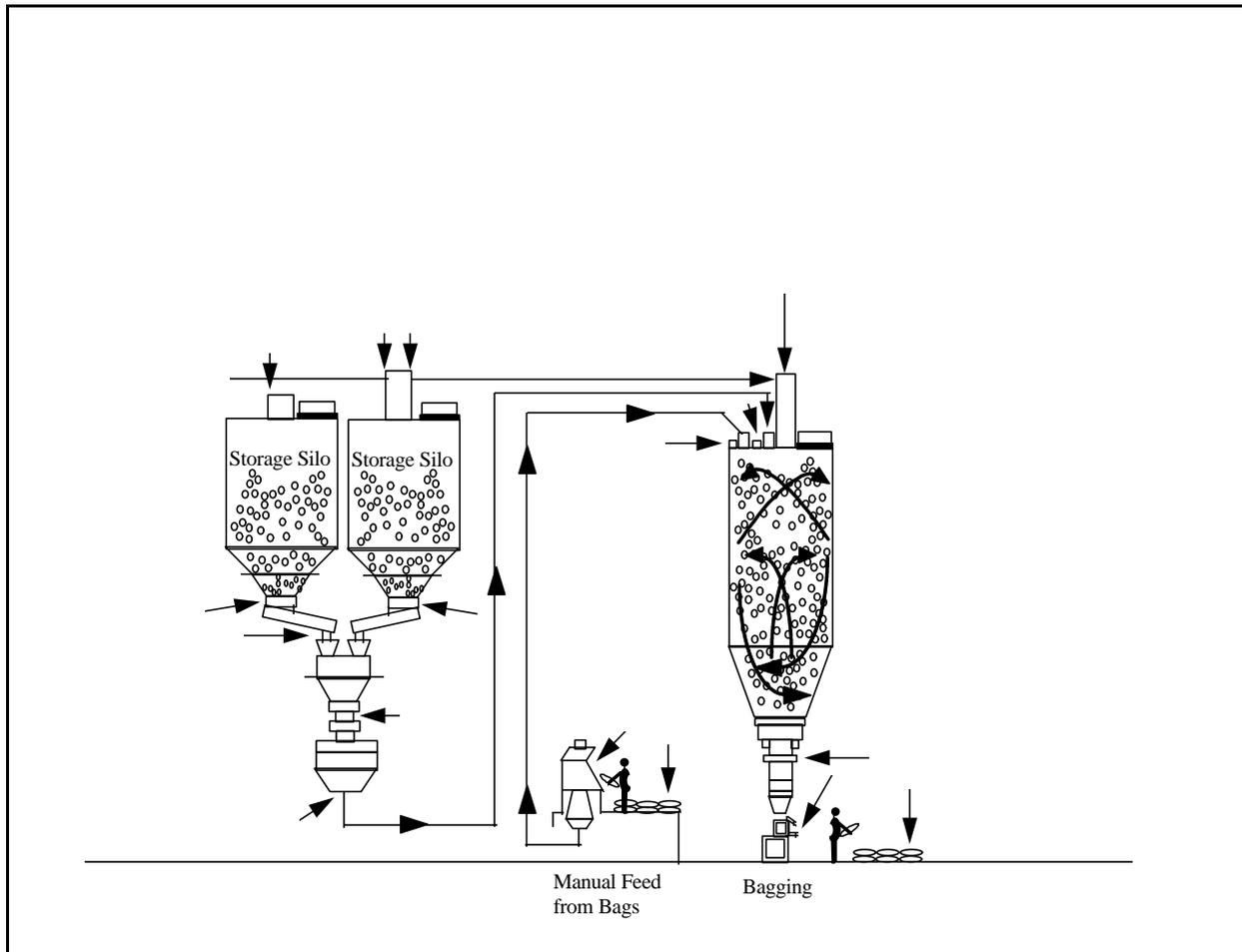
Source: U.S. EPA, *Plastic Pellets in the Aquatic Environment: Sources and Recommendations*, Office of Water, December 1992.

III.B. Industrial Processes Specific to the Manmade Fiber Industry

The manufacture of manmade fibers is closely linked with the synthesis of plastic resins. Fibers are the fundamental unit of textiles and fabrics and can be defined as a unit of matter having a length at least 100 times its width or diameter (Rodriguez, 1996). Fiber spinning processes may be similar for some noncellulosic fibers and cellulosic fibers. Manmade fibers can be produced from polymers that have been continuously or batch polymerized, or by dissolving cellulosic materials. The polymer or cellulosic solution is then forced through tiny holes of spinnerets (which function much like bathroom shower heads) and extruded into fibers (International Trade Commission, 1995). In manmade fiber plants, polymerization of the fiber polymer can occur at the same facility that produces the fiber, with continuous polymerization equipment linked directly to a fiber spinning unit (EPA, 1995). Subsequent processing steps typically include drawing, crimping, texturizing, and twisting. The following sections will discuss polymerization, primary methods of spinning, and fiber processing steps.

III.B.1. Polymerization

Many of the leading commercial manmade fibers, such as polyethylene terephthalate (PET) and polypropylene, use polymers similar to those derived from commodity plastic resins. Other manmade fibers are manufactured from polymers formed using similar polymerization methods as those mentioned in the preceding section. For instance, nylon and polyester are polymerized using polycondensation or melt polymerization methods. Recall that some manmade fibers are manufactured using natural polymers, such as cellulosic fibers, and do not undergo polymerization.

In some plants, polymerization equipment is hooked up directly to fiber spinning equipment. For continuous manufacture of polyester fiber, terephthalic acid and ethylene glycol are first passed through primary and secondary esterifiers to form the monomer. The melt is then passed to low and high polymerizers to achieve higher conversion rates. The high polymerizer is usually equipped with a high vacuum and high walls to allow excess ethylene glycol to escape, promoting chain extension. The polymer is then fed to several banks of direct fiber melt spinning heads or a solid polymer chipping system (Kroschwitz, 1986). Wastes generated during polymerization may include VOC emissions from leaks, spills, and vents; solid wastes from off-specification polymer; and spent solvent from incomplete polymerization (AFMA, 1997).

III.B.2. Spinning

Spinning, in terms of manmade fibers, refers to the overall process of polymer extrusion and fiber formation. Fibers are formed by forcing a viscous fluid or polymer solution through the small orifices of a spinneret and immediately solidifying or precipitating the resulting filaments. Facilities typically produce fibers of different thickness or denier, where denier is defined as the weight in grams of 9,000 meters (9,846 yards) of filament yarn. Fiber denier can range from less than one to 3,600 denier (McKetta, 1992).

The three primary methods of spinning are melt, dry solvent, and wet solvent, which are shown in Figure 14. A fourth and less commonly used method is reaction spinning. Table 8 lists the different types of spinning methods with the fiber types and typical reactants used for each method. The spinning process used for a particular polymer is determined by the polymer's melting point, melt stability, and solubility in organic and/or inorganic (salt) solvents, as well as the end use of the fibers (AFMA, 1997; EPA, 1993). Spinning processes involve spinning units which are made up of meter pumps, filter packs, spinnerets, and quench cells. Meter pumps are used to transport polymer through the spinning units at a constant rate. The polymer is passed through a filter and a spinneret. Note that fibers may be colored by including pigments prior to extrusion (AFMA, 1997).

The spinnerets are plates containing holes, of varying diameters and shapes, through which molten or dissolved polymer is extruded. Pressures can reach as high as 2900 psi (20 MPa). The spinnerets are usually made of stainless steel or nickel alloy for melt and dry spinning processes, although for more corrosive wet spinning processes they are usually made of glass or a platinum alloy. The spinneret may be a recessed flat plate (melt spinning) or a protruding thimble shape (dry and wet spinning). The spinnerets for molten polymers are relatively thick 0.1-0.4 in (3-10 mm) and have hole diameters of 0.007-0.030 in (175-750 μm). For solution polymers, the spinnerets are slightly thinner with smaller hole diameters.

The number of holes in a spinneret ranges from a few to several thousand. These holes may be divided into groups to produce, for instance, two 30-filament yarns from a 60-hole spinneret. The exit hole is usually circular, however fibers may have lobed, dumbbell-, or dogbone-like cross-sections (dry-spun fibers) or round, lobed, serrated, or bean-shaped cross-sections (wet-spun fibers). Wastes generated during spinning operations include VOC emissions and wastewater contaminated with solvents.

Figure 14: General Process Diagram for Melt, Dry, and Wet Spun Synthetic Fibers
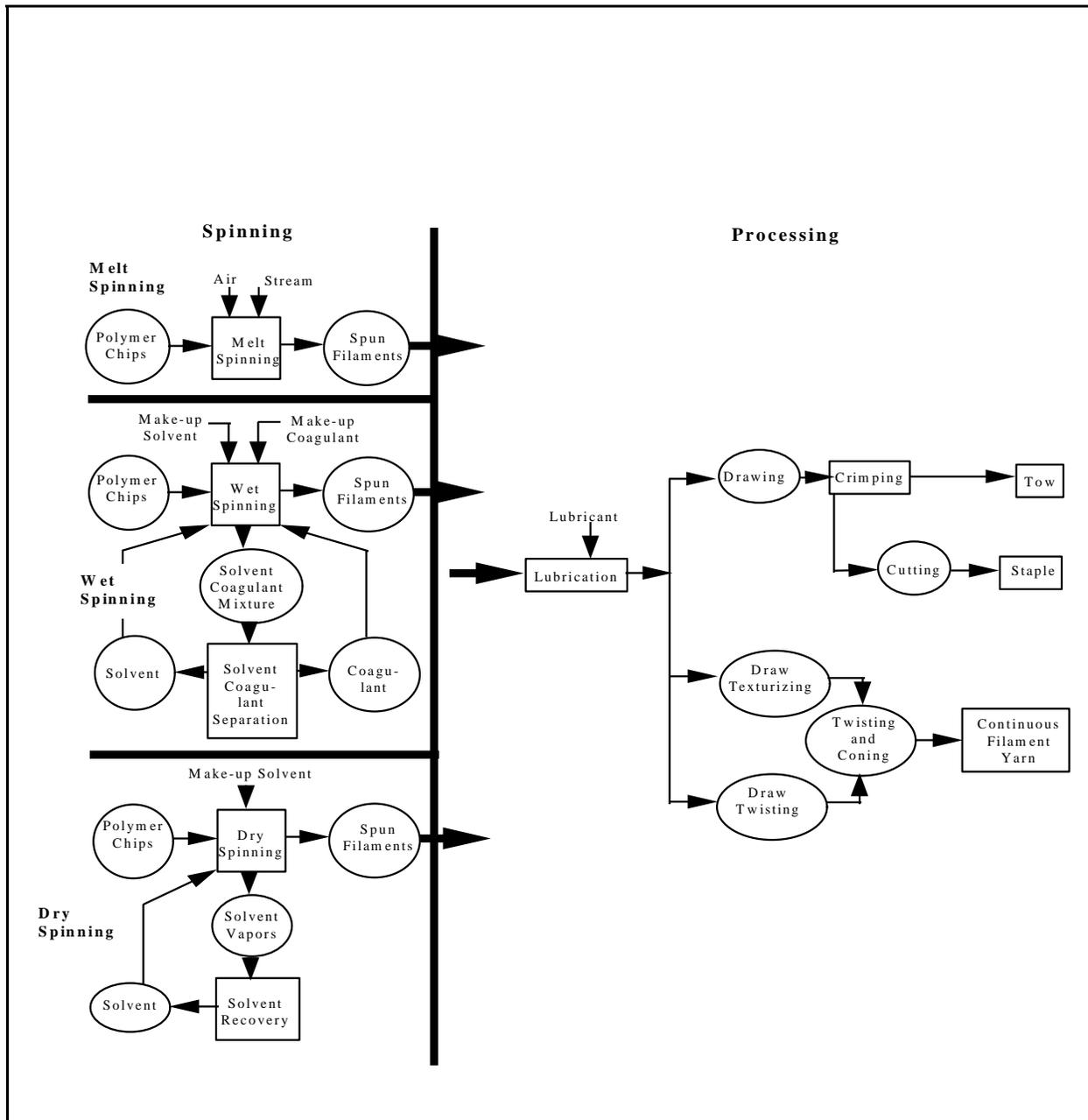
Source: U.S. EPA, *AP-42,* Office of Air and Radiation, 1993.

Table 8: Typical Fiber Spinning Parameters for Selected Fibers		
Spinning Method	**Fiber Type**	**Solvents or Other Reactants**
Melt Spinning	nylon-6 nylon-6,6 polyester polyolefin	N/A

Solvent Spinning
    Dry solvent spinning
	acrylic/modacrylic
	cellulose acetate/
	   cellulose triacetate
	spandex
		dimethylacetamide
		acetone or chlorinated hydrocarbon
		
		di-isocyanate, ethylenediamine, monoamine
		(stabilizer)

Wet solvent spinning	acrylic/modacrylic	dimethylacetamide
Reaction Spinning	spandex rayon (viscose process)	di-isocyanate, ethylenediamine, toluene sodium hydroxide, carbon disulfide, sulfuric acid
Source: U.S. EPA, *AP-42,* Office of Air and Radiation, 1993; AFMA, 1997.		

Types of Spinning

Melt Spinning

Melt spinning processes use heat to melt polymer which can then be extruded through the spinneret. Spinning assemblies are fed by either electrically-heated screw extruders, which convert powdered or chipped polymer into a polymer melt, or directly from a continuous melt polymerization process. Many nylon and polyester plants use continuous melt polymerization and send molten polymer from polymerization units directly to the spinning units. During polymerization or extrusion, various additives may be incorporated to impart special properties to the fibers, such as heat stability, anti-static, and eased dyeing.

Polymer chips or polymer melt is then passed through metering gear pumps, which feed the molten polymer to a filter system at pressures of 500-1000 psi (7,400-14,700 atm). The filter system screens out large solid or gel particles through a series of metal gauzes interspersed in layers of graded sand (EPA, 1993). The filter may also screen out catalyst residues or precipitated additives (McKetta, 1992). The filter may be enclosed in a Dowtherm-heated manifold to maintain uniform temperature. After passing through the filter, the molten polymer is fed to the spinneret (Kroschwitz, 1986). A narrow zone below the spinneret may be filled with inert gas to prevent deposits of degradation products around the holes for oxidation-sensitive polymers. Extruded filaments are quenched by a cool, filtered airstream which solidifies the filaments.

Dry Spinning

Dry spinning is typically used for easily dissolved polymers such as cellulose acetate, acrylics, and modacrylics. In dry spinning processes, the polymer is first dissolved in an organic solvent. The solution (or spinning dope) is then blended with additives, filtered, and charged to a spin cell. The spin cell contains a feed vessel, a heat exchanger, a spinneret, and a quench cell. The spin cell may be 5-10 m (5.5-11 yards) long and 13-23 cm (5.1-9.1 in) in diameter (Grayson, 1984). The solution is heated to a temperature above the solvent boiling point and is then extruded through the spinneret into a zone of heated gas. The solvent evaporates into the gas stream, leaving solidified filaments. The heated gas stream is typically air although inert gas, such as nitrogen and super-heated solvents, can also be used. Fibers are then passed through baths to wash residual solvent from the fibers. To reduce costs and pollution, the wash water from these baths is typically recycled. These baths may be followed by activated carbon systems used to adsorb solvent from process air (AFMA, 1997). Fibers produced by dry spinning contain less void space than those produced by melt spinning and therefore have higher densities and lower dyeability than those produced by other methods (Kroschwitz, 1986). Of the three primary spinning methods, dry spinning operations have the largest potential VOC emissions `to the air (EPA, 1993).

Wet Spinning

Wet spinning processes also use solvents, such as dimethylacetamide or aqueous inorganic salt solutions, to prepare spinning dope (AFMA, 1997). In wet spinning, the polymer is dissolved in solvent in a solution vessel and is forced through a spinneret which is submerged in a coagulation bath. As the polymer solution emerges in the coagulating bath, the polymer is either precipitated or chemically regenerated. In precipitation, the fiber is formed when solvent diffuses out of the thread and coagulant diffuses into the thread. For some processes, a chemical reaction occurs during precipitation which generates fibers. Coagulated filaments pass over a guide to godets or drive rollers. Windup speeds are about 150 m/min. The yarn is then passed through additional baths for washing and residual solvent removal (Kroschwitz, 1986).

Reaction Spinning

Reaction spinning methods are typically used to make spandex and rayon. The process begins with the preparation of a viscous spinning solution containing a dissolved low molecular weight polymer, such as polyester, in a suitable solvent and a reactant, such as di-isocyanate. The spinning solution is then forced through spinnerets into a solution containing a diamine (similar to wet spinning) or is combined with a third reactant and then dry spun. The primary distinguishing characteristic of reaction spinning processes is that the

final cross-linking between the polymer molecule chains in the filament occurs after the fibers have been spun. The fiber is then transported from the bath to an oven, where solvent is evaporated (EPA, 1993).

In the U.S., most rayon is made by the viscose process. This process is worth noting because it is typically associated with a large volume of air emissions. Shown in Figure 15, the viscose process converts cellulose from one form (dissolved pulp) to another (rayon). Although the manufacturing process further purifies the cellulose, alters the physical form of the fiber, and modifies the molecular orientation within the fiber and its degree of polymerization, the product is essentially the same chemical as the raw material. Since the product retains the same chemical structure, all other chemicals used in the process and all byproducts formed in the process must be removed.

Figure 15: Typical Process Flowchart for Synthesis of Rayon Fibers Using the Viscose Process
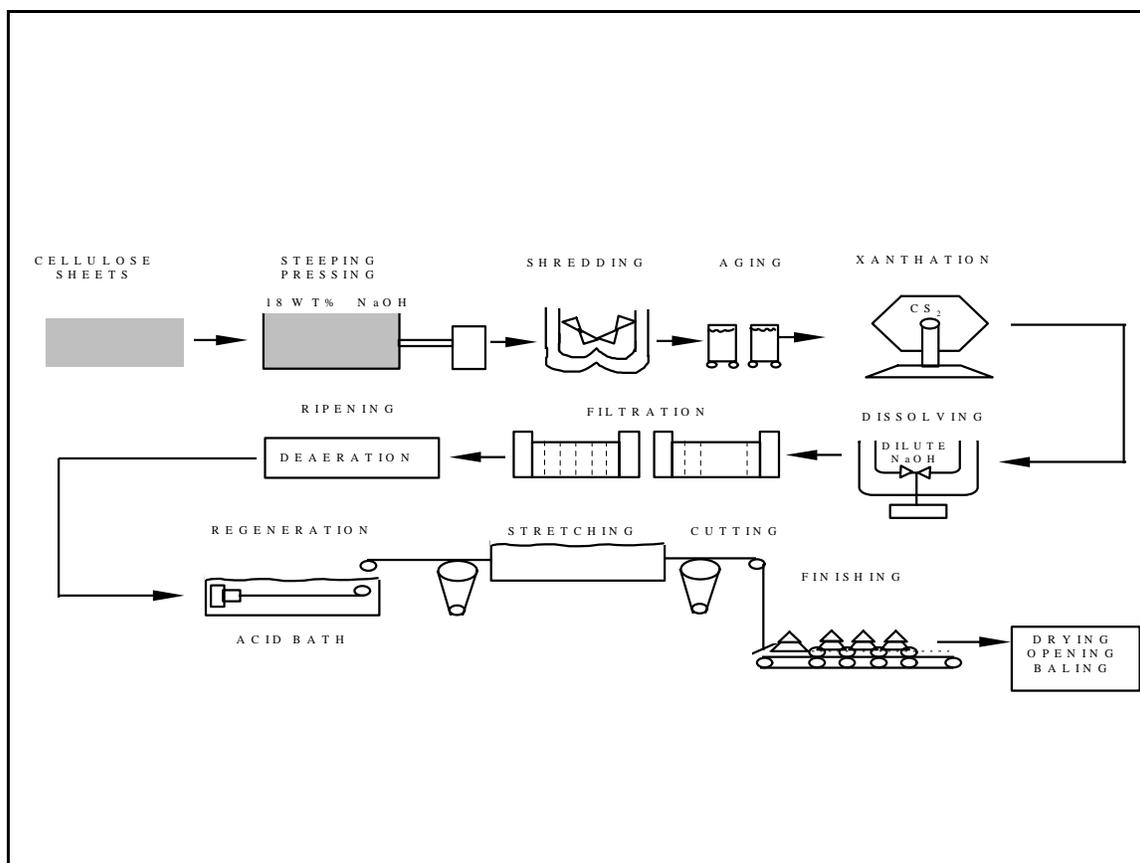
Source: U.S. EPA, *AP-42,* Office of Air and Radiation, 1993.

The series of chemical reactions in the viscose process used to make rayon consists of the following stages. First, purified cellulose pulp is steeped in a solution of sodium hydroxide and water, producing an alkali cellulose slurry. The excess sodium hydroxide solution is removed from the slurry, producing alkali cellulose crumb. The crumb is shredded and fed into silos for aging, a process which controls the degree of polymerization of the cellulose molecules. After aging, the alkali cellulose is reacted in large reactors with carbon disulfide, producing sodium cellulose xanthate, which is then dissolved in dilute aqueous sodium hydroxide. That solution is known as viscose.

The viscose solution is then aged (ripened), during which a series of chemical reactions takes place. The most important of these reactions is the splitting off of carbon disulfide and the regeneration of cellulose. These include the redistribution of the carbon disulfide on the cellulose molecules and the formation of small amounts of sulfur byproducts. The viscose is filtered several times and deaerated prior to spinning. The viscose is then extruded through spinnerettes, typically containing thousands of very small holes, into a spinning bath of dilute sulfuric acid, sodium sulfate, zinc sulfate, various spinning aids, and water. The cellulose xanthate, in the viscose, reacts with the acidic spinning bath, forming an unstable xantheic acid derivative which loses carbon disulfide to yield regenerated cellulose. The carbon disulfide is released from the xanthate, and the sulfur byproducts created during aging react to form hydrogen sulfide.

After spinning the fibers are collected together, stretched to orient the cellulose molecules along the axis of the fibers, processed to remove the residual chemicals from the cellulose, finished, dried, and packaged. The fibers may be cut after stretching but prior to further processing, producing rayon staple (cut) fiber, or they may be processed without cutting, producing rayon filament or tow (AFMA, 1997; EPA, 1993).

III.B.3. Fiber Processing

In most cases, the extruded product from melt, dry, wet, or reaction spinning is further processed to impart particular qualities to the fibers and facilitate downstream processing. Fibers can be processed as filament yarn or as staple. Figure 14 illustrates general fiber processing steps.

After fibers have been formed, spin finish is usually applied by collecting the extruded filaments on a grooved ceramic guide or rotating roller coated with spin finish. The spin finish, which includes lubricants and finishing oils, facilitates further processing steps by reducing friction and static, and improving further mechanical processing (AFMA, 1997). Mineral oils have historically been used as lubricants, and organic compounds have been used to reduce static. Spin finishes vary according to fiber type and are critical to

the processing of fibers into yarns and fabrics. Insufficient lubrication of fibers can lead to strains in the fabric which may produce uneven dyeing, decreased strength, or unpleasing aesthetic qualities (Grayson, 1984).

Filament Yarn

After finish is applied, a thread guide converges the individual filaments to produce a continuous filament yarn that contains between 15 and 1000 filaments (AFMA, 1997). The spun yarn is then either immediately wound onto bobbins and collected in cans or is further treated to impart special fiber qualities (EPA, 1993). Filaments are typically drawn to align and orient the polymer molecules and strengthen the filament. In melt spinning operations, companies have moved towards high-speed spinning processes which combine spinning and drawing operations. Filaments may be forwarded at speeds of 300 to 6,000 m/min for subsequent processing. For polyester, the different commercial melt-spinning processes are classified according to the degree of molecular orientation in the fiber. For instance, polyester spinning processes operating at speeds of 500 to 1,500 m/min give low oriented spun yarn (LOY), while processes operating at between 4,000 and 6,000 m/min give partially oriented yarn (POY) (Kroschwitz, 1986).

Thermoplastic fibers can be further modified by thermomechanical annealing treatments, including texturing. Texturing uses curling, crimping, and tangling apparatuses to give straight, rod-like filament fibers the appearance, structure, and feel of natural fibers (EPA, 1995). Filaments may be mechanically distorted by compressing the fibers in a stuffing box or between rolls or by false twisting, where twisting is followed by heat setting and releasing or reversing the twist. Textured yarns are either fine denier (15-200 denier) for woven, knitted stretch and textured fabrics for apparel or heavy (1,000-3,600 denier) for carpet (McKetta, 1992). Recall that denier is the weight in grams of 9,000 meters (9,846 yards) of yarn.

Staple

Many manmade fiber operations produce staple, or yarn that is cut into specific lengths, for use by textile manufacturers. To make staple, a tow is formed by collecting thousands of continuous filaments into large rope-like bundles. These bundles are combined from all the spinning positions and thrown into a large "creel can" at speeds of 1,000 to 2,000 m/min. This bundle of filaments is 50,000 to 250,000 total denier, with as-spun denier ranging from 2.5 to 9.0 (Dekker, 1992). The bundles are then spread out into a flat band winding over the feed rolls and draw rolls of the draw machine. After drawing, the fiber may be heat set and crimped to change the tensile properties. The tow can be shipped for further processing, or it can be converted into staple-length fiber by simply cutting it into specified lengths, usually an inch to several inches long. When manmade fibers are produced

for blending with natural fibers, they are cut into similar lengths as the natural fibers, typically 1.5-5.0 in (3.8-12.5 cm) (Kroschwitz, 1986). A baling unit following the cutting machine collects and bales the cut fiber (Kent, 1992).

Wastes generated during fiber processing operations arise from the spin finish application and drying steps (Wellman, 1997). During processing, fiber finishes can be sources of volatile and hazardous air pollutants that may be emitted into the air and into wastewater (AFMA, 1997).

III.B.4. Supporting Operations

Solvent Recovery

Solvents used in spinning processes are typically recovered by distillation. Other recovery systems include gas adsorption and condensation and are specific to either fiber type or spinning method. Dry spinning processes typically use condenser or scrubbers for recovering solvent from the spin cell. Distillation columns are used to recover solvent from the condenser, scrubber, and wash water. Efficient solvent recovery is particularly important in dry spinning since solvent is used at three to five times the quantity of polymer. Wet spinning processes typically use distillation to recover solvent from the spinning bath, drawing, and washing operations. Scrubbers and condensers are used to recover solvent emissions from the spinning cells and the dryers. Carbon adsorption is used to recover emissions from storage tank vents and from mixing and filtering operations (EPA, 1993). Refer to Section III.A. for a more detailed discussion of pollution control equipment.

III.C. Raw Material Inputs and Pollution Outputs in the Production Line

Raw material inputs to plastic resin and manmade fibers industries primarily consist of synthetic organic chemicals, such as ethylene glycol and acrylonitrile, and refined petroleum products, such as ethylene. The majority of these chemicals are used either as monomers or as monomer precursors. Other uses are as solvents, catalysts, and additives. Because chemical processes rarely convert 100 percent of raw materials to desired products, byproducts and unreacted monomer may constitute a large part of facilities' wastestreams. Pollutant outputs generally include VOCs, off-spec or contaminated polymer, and wastewater from equipment cleaning. Typical wastestreams associated with processes involved in plastic resin and manmade fiber manufacture are listed in Table 9. Wastestreams vary depending on what polymer is being synthesized, what fiber spinning method is used, and whether a batch or continuous process is used. Small-scale batch facilities that make polymers to order often have complex and variable wastestreams (New Jersey Hazardous Waste Facilities Siting Commission, 1987).

Air Emissions

Over 70 percent of TRI releases for plastic resin and manmade fiber plants are in the form of air emissions. Commonly released chemicals include carbon disulfide, methanol and other volatile solvents and monomers. Typical chemicals released are listed in the following section on TRI releases and transfers. Air emissions from plastic resin and manmade fiber plants arise from point sources and fugitive emission sources, such as valves, pumps, tanks, compressors, etc. Point sources of air emissions may include monomer storage and feed dissolver tanks and reactors.

While individual leaks are typically small, the sum of all fugitive leaks at a plant can be one of its largest emission sources. Fugitive emissions can be emitted continuously or intermittently. Continuous air emissions may be emitted from monomer recovery systems, dryer stacks and miscellaneous solid handling vents, centrifuge vents, and blending operations. Fugitive emissions can also result from volatilization of monomers, solvents, and other volatile organic compounds during polymerization; sublimation of solids during resin production; wastewater treatment; and volatilization of solvents during storage and handling of resins. These emissions are largely controlled by solvent and monomer recovery systems. Potential VOC emission release points for a typical polymerization method are shown in Figure 16. In the figure, volatile organic compounds emitted from particular operations are shown as dashed lines, and solid wastes and water wastes are shown by bolded arrows.

Table 9: Summary of Potential Releases Emitted During Plastic Resin and Manmade Fiber Manufacturing			
Process	**Air Emissions**	**Process Wastewater**	**Residual Wastes**
Preparing Reactants	volatilized monomer, solvents	little or no wastewater produced	raw material drum residuals
Polymerization	volatilized monomer, solvents, reaction byproducts	little or no wastewater produced	off-specification or contaminated polymer, reaction byproducts, spent equipment oil, spent solvent, catalyst manufacture waste, gas purification catalyst waste
Polymer Recovery	volatilized solvents and unreacted monomer	little or no wastewater produced	little or no residual waste produced
Polymer Extrusion	volatilized solvents and unreacted monomer	extruder quench water	off-specification or contaminated polymer
Equipment Cleaning	volatilized solvents and unreacted monomer	reactor and floor wash water contaminated with organics, acids, and salts; equipment rinse water	little or no residual waste produced
Unloading and Storage of Reactants	volatilized monomer and solvents	Rinse water from cleaning out transport vehicles containing solvents, monomers, and other reactants	little or no residual waste produced
Conveyance and Pellet Storage	volatilized residual monomer or solvents from plastic pellets	little or no wastewater produced	plastic pellets from leaks or spills
Spinning	volatilized residual monomer solvents, additives, other organics, volatilized finishes	water contaminated with residual monomer solvents, additives, other organics, finishes	off-spec polymer, off-spec fiber, and residual finishes
Fiber Processing	volatilized residual monomer solvents, additives, other organics, volatilized finishes	water contaminated with residual monomer, solvents, additives, other organics	residual monomer and solvents; off-spec fibers
Pollution Control Systems	volatilized solvents and unreacted monomer	water contaminated with residual solvents and unreacted monomer; air stripper water	little or no residual waste produced

Source: U.S. EPA, *AP-42,* Office of Air and Radiation, 1993; U.S. EPA, *Best Management Practices for Pollution Prevention in the Textile Industry,* Office of Research and Development, 1995; *SOCMA Pollution Prevention Study,* Prepared for SOCMA, Washington, DC, 1993; Randall, P.M., "Pollution Prevention Strategies for Minimizing of Industrial Wastes in the Vinyl Chloride Monomer - Polyvinyl Chloride Industry," in *Environmental Progress*, volume 13, no. 4, November 1994; AFMA, 1997; Wellman, 1997.

Figure 16: Potential Emissions from Plastic Resin Manufacturing Operations
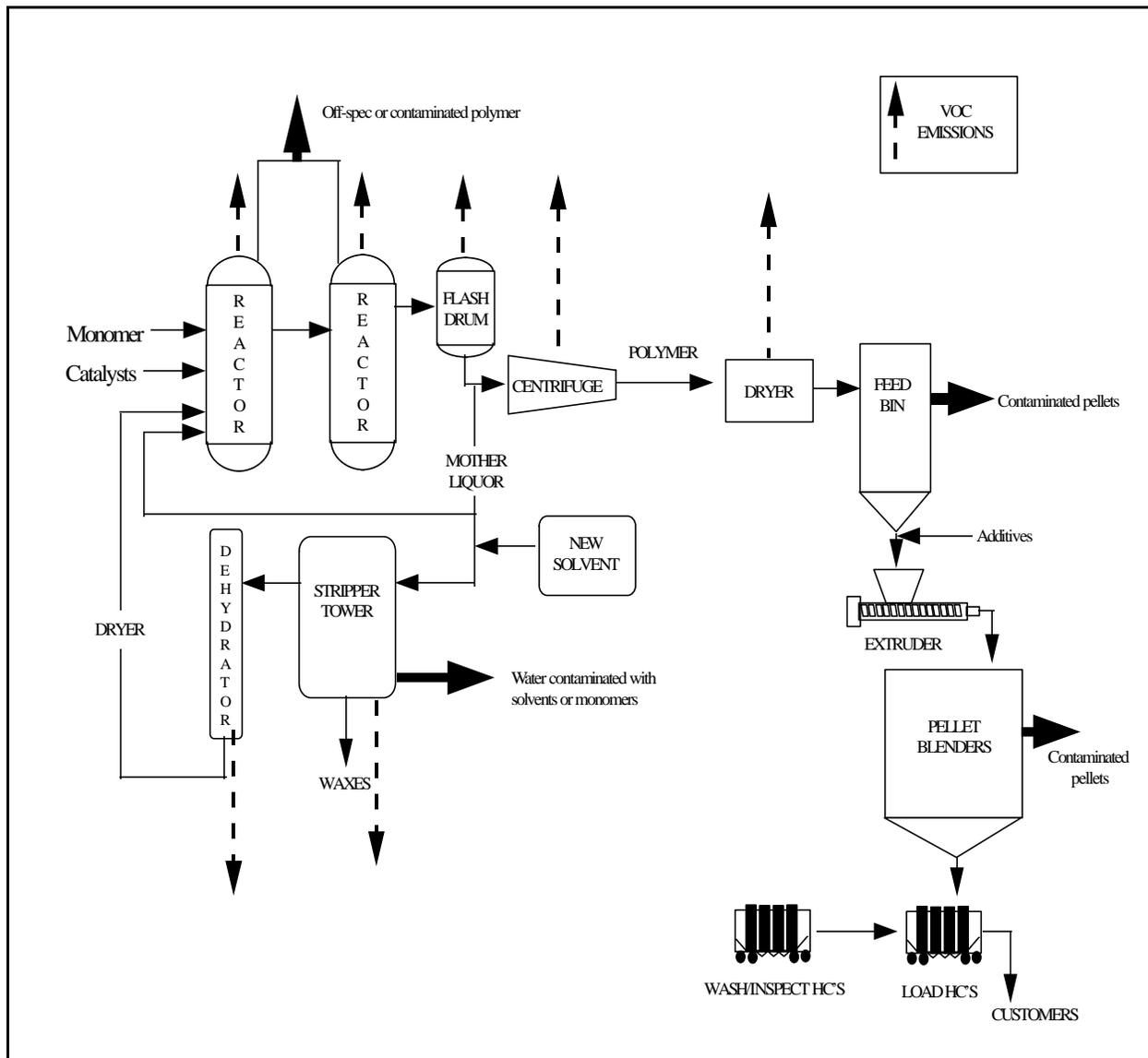
Adapted from *Exxon Chemical Company's Mont Belvieu Plastics Plant Brochure*; Synthetic Organic Chemical Manufacturers Association, *SOCMA Pollution Prevention Study,* Prepared for SOCMA, Washington, DC, 1993; Randall, P.M., "Pollution Prevention Strategies for Minimizing of Industrial Wastes in the Vinyl Chloride Monomer - Polyvinyl Chloride Industry," in *Environmental Progress*, volume 13, no. 4, November 1994; U.S. EPA, *AP-42,* Office of Air and Radiation, 1993.

Sources of intermittent air emissions typically include unloading and charging operations, reactors, safety valves, stripping towers, pumps, flanges, filters, strainers, and seals (Randall, 1994). Fugitive emissions can be reduced through a number of techniques, including installing leak resistant equipment such as sealless pumps and bellows valves, reducing the number of tanks and other potential sources, and in the case of light liquid or vapor systems, implementing an ongoing leak detection and repair program (Wellman, 1997).

In addition to pollutants emitted during polymerization, fiber finishes are sources of volatile and hazardous air pollutants emitted from manmade fiber processing operations. Because melt spinning does not require the use of solvents, melt spinning emits significantly less VOCs than dry or wet spinning processes. Dry spinning typically emits the largest amounts of VOC per pound of fiber produced of the three main spinning methods. Dry spinning can emit from 5 to 150 kg total non-methane organic carbons (TNMOC) per Mg of product, while melt spinning can emit less than 5 kg TNMOC per Mg product. Wet spun fibers typically emit 5 to 20 kg TNMOC per MG product. Air pollutant emissions include volatilized residual monomer, fiber lubricants, organic solvents, additives, and other organic compounds used in fiber processing (EPA, 1993).

Unrecovered solvent accounts for some of the VOC emissions from fiber spinning processes, particularly for acetate production. Typically, 94 to 98 percent of the solvents used in fiber spinning processes is recovered. The largest amounts of unrecovered solvent are emitted from the fiber spinning and drying steps. Other emission sources include dope preparation (dissolving the polymer, blending the spinning solution, and filtering the dope), fiber processing (drawing, washing, crimping), and solvent recovery. Figure 17 illustrates the potential release points of VOCs in a typical fiber spinning operation (EPA, 1993). Other pollutants emitted during manufacturing include air pollutants emitted during combustion. Criteria air pollutants, such as SO_x, NO_x, CO, and CO_2, are emitted from combustion equipment used to heat reactors, dryers, and other process equipment.

Figure 17: VOC Emissions from Fiber Processing Operations
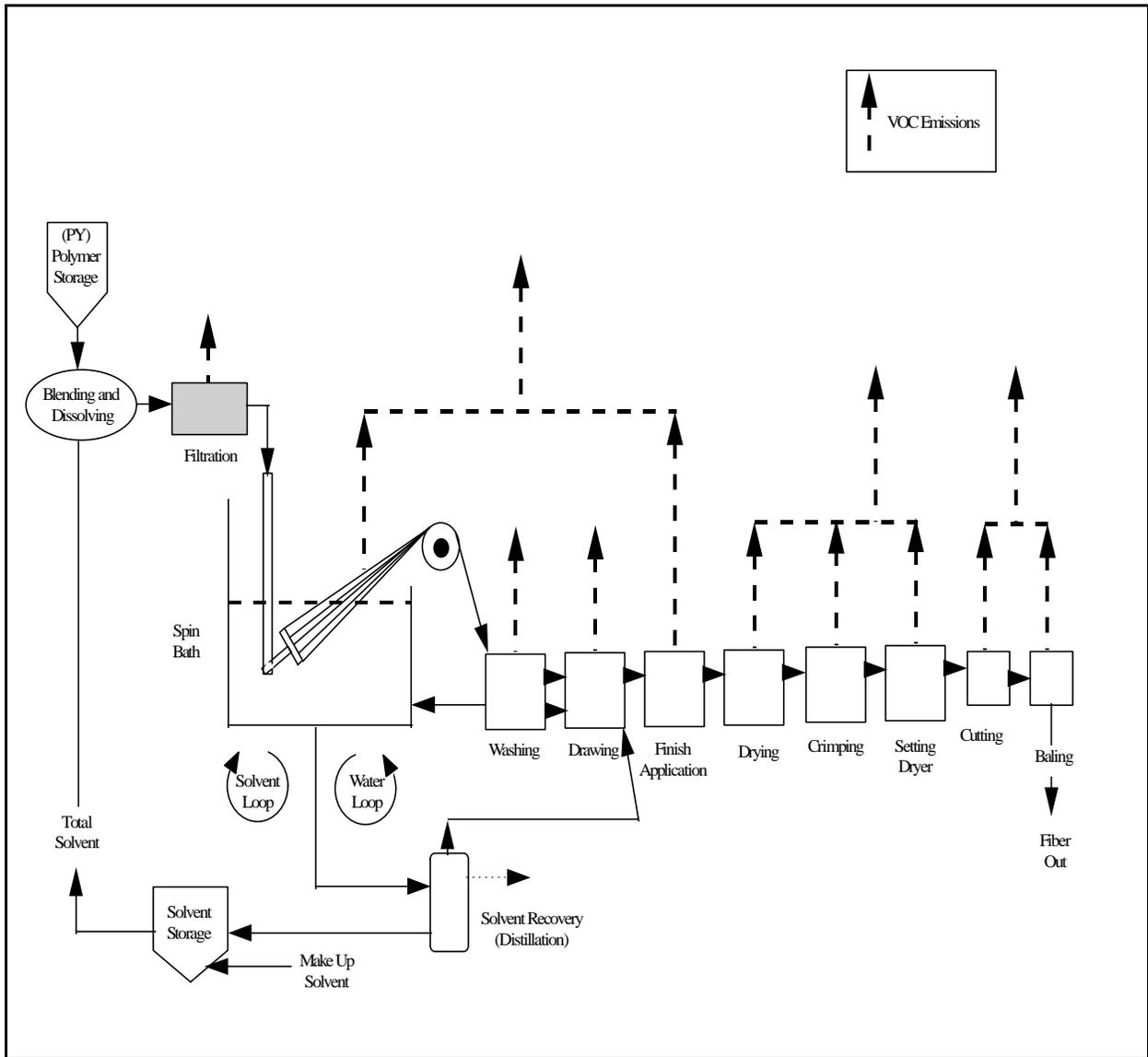
Source: U.S. EPA, *AP-42,* Office of Air and Radiation, 1993.

Wastewater

Plastic resin and manmade fiber facilities generate relatively large amounts of wastewater from processes, cooling operations, utilities and maintenance, and air pollution control systems. Unless solvents are used in polymerization processes, wastewater contaminants are usually restricted to off-spec polymer, polymer, and raw materials (EPA, 1987). Wastewater streams from polymerization operations typically contain dilute concentrations of organics, acids, and salts. Process wastewater may be generated from water that comes into direct contact with raw materials, intermediate products, finished products, byproducts, or waste product. Process wastewater may also be generated from indirect contact process water discharged from vacuum jets and steam ejectors. Cooling water makes up a large portion of water used in the industries and can either be generated from water that contains contaminants or from water used in noncontact processes, such as water treatment wastes and boiler blowdown (EPA, 1987).

Effluent containing contaminants may also be discharged from batch operations during equipment cleaning. Wastes generated from cleaning operations include vessel wash waters, floor wash waters, equipment draining, sump draining, and air stripper water effluent. These discharges can be minimized by initiating water conservation programs and by cleaning reactors using high-pressure water or process solvents which can be recycled into the reactor (SOCMA, 1993).

Wastewater is also generated during monomer and polymer recovery processes, such as centrifuging, monomer stripping, and slurry tanks. Process sources generate liquid wastes with relatively high concentrations of contaminants, including equipment oil, spent solvent, and raw material drum residuals. Leaks and spills also generate waste and often occur at pumps, flanges, valves, and agitator seals. Loading/unloading operations and bag filling operations also are common sources of leaks and spills (Randall, 1994).

In addition to pollutants emitted during polymerization, fiber finishes are sources of volatile and hazardous pollutants found in manmade fiber plant wastewater. Spin finishes may increase biological oxygen demand (BOD) and chemical oxygen demand (COD) and some may be toxic to aquatic life (EPA, 1995).

Residual Wastes

Residual wastes make up a significant portion of wastes from plastic resin and manmade fiber facilities. Unless solvents are used in polymerization processes, residual wastes are usually restricted to off-spec polymer, polymer, and raw material chemicals (EPA, 1987). Typical contaminants include contaminated polymer, catalyst manufacture waste, gas purification catalyst

waste, reaction by-products, waste oil, and general plant wastes (Clements and Thompson, 1993). Although properly run and maintained plants with new technology may be capable of obtaining 95 percent or higher polymer yields, off-spec and contaminated polymer is still generated and makes up a sizeable portion of the wastestream. Unreacted or improperly reacted polymer synthesis or regeneration residues may include monomers, oligomers, metals, degradation products, solvents, and coagulants (EPA, 1995). Other sources of residual waste include cleanup absorbents, spent activated carbon, laboratory wastes, and air pollution control residues (SOCMA, 1993). Process-related residual waste can be reduced by implementing better inventory control practices, personnel training, and enhanced process control systems. Process changes and raw material substitutions can also be used to reduce residual waste pollution.

III.D. Pollution Control Systems

Recovery of raw materials, such as solvents and monomers, is widely practiced in the industries and is highly integrated into industrial processes as a means to reduce costs associated with raw materials and subsequent treatment of waste. During the polymer separation step, often solvent and monomers are flashed from the reaction mixture. The flashed monomer and solvent are then condensed into liquids using a compressor and separated using vacuum distillation. Monomer and comonomer are passed through a series of distillation columns to increase purity. These chemicals may then be sent to either a monomer recovery unit or an incinerator to be burned as fuel or to reduce air emissions through thermal destruction. Wastewater can be generated during monomer and polymer recovery processes, such as centrifuging, monomer stripping, and slurry tanks (AFMA, 1997; EPA, 1987). Selected equipment and methods used by the industries to recover raw materials and reduce air and water pollution are described below.

Air Pollution Control Systems

Condensers. Condensers are widely used in the plastic resin and manmade fiber industries to recover monomers and solvents from process operations (a process condenser) and as air pollution control devices to remove VOCs from vented gases. Process condensers differ from condensers used as air pollution control devices as the primary purpose of a process condenser is to recover material as an integral part of a unit operation. The process condenser is the first condenser located after the process equipment and supports a vapor-to-liquid phase change for the vapors produced in the process equipment. Examples of process condensers include distillation condensers, reflux condensers, process condensers in line before the vacuum source, and process condensers used in stripping or flashing operations (EPA, 1978). Vents on condensers can be sources of VOC emissions.

Adsorption. Adsorption is another method for removing VOCs from individual process wastestreams through organic vapor recovery. This method can be used to filter out and recover solvents by passing process streams through a packed column of activated carbon or any other porous surface which has a microcrystalline structure. As the gas stream passes through the column, the VOCs adsorb to the column surface. Eventually, the adsorption material in the column becomes clogged with adsorbed contaminants and must be either regenerated or disposed (Masters, 1991; EPA, 1987; CMA, 1989).

Scrubbers. Scrubbers or gas absorbers are used to remove one or more constituents from a gas stream by treatment with a liquid. When using a scrubber as an air pollution control device, the solubility of the constituents in the gas stream in the absorbing liquid must be determined. The main types of scrubbers are the packed tower, plate or tray tower, venturi scrubber, and spray tower (EPA, 1978).

Combustion or Incineration. Another method for controlling VOC emissions is combustion or incineration. Although combustion systems can achieve high removal efficiencies, these systems are typically more expensive to install, operate, and maintain and have secondary emissions associated with their operation. Additionally, scrubbers may be required to control inorganic gases produced as byproducts of combustion (EPA, 1978).

Water Pollution Control Systems

Distillation. Distillation is used to separate liquids for recovery. Two widely used types of distillation are batch and continuous (or fractionation). Batch distillation is used when components' vapor pressures vary widely. In batch distillation, solvent waste is first placed inside a container where heat is applied and condensed overhead vapor is removed simultaneously. Continuous distillation is commonly used to separate multiple fluids from a wastestream and uses a column that contains multiple trays or packing materials to provide high vapor-liquid surface area. Vapors that rise to the top of the heated column are condensed and removed, while a portion is returned to the column for further fractionation. Lower boiling solvents progressively enter the vapor, leaving a liquid with less volatile contaminants at the bottom of the column (CMA, 1989).

Gas Stripping (Air and Steam). Stripping can be used to remove relatively volatile components that are dissolved or emulsified in wastewater. This is achieved through the passage of air, steam, or other gas through the liquid. The stripped volatiles are usually processed by further recovery or incineration. In air stripping processes, a liquid containing dissolved gases

is brought into contact with air in a stripping tower, causing an exchange of gases between the air and the solution. If the concentrations of gases are low, the gases can be emitted directly to the air. If the concentrations are high, these gases are passed to air pollution control devices.

In steam stripping processes, volatile components are distilled by fractionation from a wastewater stream. Steam stripping towers operate by passing preheated wastewater downward through the distillation column. Superheated steam and organic vapors flow countercurrent to the wastewater stream, rising up from the bottom of the column. Contact between the two streams progressively reduces the concentrations of VOCs in the wastewater as it approaches the bottom of the column. Reflux condensing may be used to alter the composition of the vapor stream taken from the stripping column (EPA, 1987).

III.E. Management of Chemicals in the Production Process

The Pollution Prevention Act of 1990 (PPA) requires facilities to report information about the management of Toxics Release Inventory (TRI) chemicals in waste and efforts made to eliminate or reduce those quantities. These data have been collected annually in Section 8 of the TRI reporting Form R beginning with the 1991 reporting year. The data summarized below cover the years from 1994 through 1997 and are meant to provide a basic understanding of the quantities of waste handled by the industries, the methods typically used to manage this waste, and recent trends in these methods. TRI waste management data can be used to assess trends in source reduction within individual industries and facilities, and for specific TRI chemicals. This information could then be used as a tool in identifying opportunities for pollution prevention compliance assistance activities.

While the quantities reported for 1994 and 1995 are estimates of quantities already managed, the quantities reported for 1996 and 1997 are projections only. The PPA requires these projections to encourage facilities to consider future waste generation and source reduction of those quantities as well as movement up the waste management hierarchy. Future-year estimates are not commitments that facilities reporting under TRI are required to meet.

Table 10 shows that the TRI reporting plastic resin manufacturing facilities managed about 1.4 billion pounds of production related wastes (total quantity of TRI chemicals in the waste from routine production operations in column B) in 1995. The yearly data in column B indicate that plastic resin manufacturing facilities substantially lowered the amount of production-related waste managed between 1994 and 1995. Projections for production-related waste management indicate slight increases between 1995 and 1996 followed by a slight decrease in 1997. Values in column C are intended to reveal the percentage of TRI chemicals that are either transferred off-site or

released to the environment. Column C is calculated by dividing the total TRI transfers and releases (reported in Sections 5 and 6 of the TRI Form R) by the total quantity of production-related waste (reported in Section 8). The percentage of TRI chemicals transferred off-site or released to the environment by the plastic resin industry increased more than three fold between 1994 and 1995.

The data indicate that about 82 percent of the TRI wastes are managed onsite through recycling, energy recovery, or treatment (columns D, E, and F, respectively) in 1995. About 13 percent of the wastes were managed off-site. The remaining portion of TRI chemical wastes (about 5 percent), shown in column J, were released to the environment through direct discharges to air, land, water, and underground injection, or were disposed off-site. The overall proportions of wastes managed onsite (columns G, H, and I) and off-site (columns D, E, and F) are expected to remain relatively constant between 1995 and 1997. Note that between 1994 and 1995 the proportion of waste treated on-site decreased by 12.5 percent and the proportion of waste recycled on-site increased by almost 16 percent.

Table 10: Source Reduction and Recycling Activity for the Plastic Resin Industry (SIC 2821) as Reported Within TRI

A	B	C	On-Site			Off-Site			J
	Quantity of Production-Related Waste (10^6 lbs.)[a]	% Released and Transferred[b]	D	E	F	G	H	I	% Released and Transferred[b]
Year			% Recycled	% Energy Recovery	% Treated	% Recycled	% Energy Recovery	% Treated	
1994	4,116	5.1	23.5	11.8	43.2	1.7	7.4	3.7	8.8
1995	1,363	18.8	39.3	11.9	30.6	6.2	4.4	2.6	5.1
1996[p]	1,448	N/A	36.1	15.8	27.7	7.3	3.8	2.1	7.2
1997[p]	1,432	N/A	37.0	15.2	28.3	7.4	3.6	2.0	6.5

Source: *U.S. EPA, Toxic Release Inventory Database, 1995.*
[a] Within this industry sector, non-production related waste < 1% of production related wastes for 1995.
[b] Total TRI transfers and releases as reported in Section 5 and 6 of Form R as a percentage of production related wastes.
[c] Percentage of production related waste released to the environment and transferred off-site for disposal.
[p] Represents projected wastes for 1996 and 1997.

Table 11 shows that the TRI reporting manmade fiber manufacturing facilities managed about 689 million pounds of production related wastes (total quantity of TRI chemicals in the waste from routine production operations in column B) in 1995. The yearly data in column B indicate that fiber manufacturing facilities project yearly increases in production-related waste between 1994 and 1997. Values in column C are intended to reveal the percentage of TRI chemicals that are either transferred off-site or released to the environment. Column C is calculated by dividing the total TRI transfers and releases (reported in Sections 5 and 6 of the TRI Form R) by the total quantity of production-related waste (reported in Section 8). The percentage of TRI chemicals transferred off-site or released to the environment by the manmade fiber industry decreased slightly between 1994 and 1995.

The data indicate that about 79 percent of the TRI wastes are managed onsite through recycling, energy recovery, or treatment (columns D, E, and F, respectively) in 1995. About 7 percent of the wastes were managed off-site. The remaining portion of TRI chemical wastes (about 14 percent), shown in column J, were released to the environment through direct discharges to air, land, water, and underground injection, or were disposed off-site. The overall proportions of wastes managed onsite (columns G, H, and I) are expected to increase by 7.3 percent between 1995 and 1997. The overall proportions of wastes managed off-site (columns D, E, and F) are expected to decrease by 1.9 percent between 1995 and 1997. Note that between 1995 and 1997 the proportion of waste treated on-site is expected to decrease by 12.3 percent and the proportion of waste recycled on-site is expected to increase by about 20 percent.

Table 11: Source Reduction and Recycling Activity for the Manmade Fiber Industry (SIC 2823, 2824) as Reported Within TRI									
A	B	C	On-Site			Off-Site			J
Year	Quantity of Production-Related Waste (10^6 lbs.)[a]	% Released and Transferred[b]	D	E	F	G	H	I	% Released and Transferred[b]
			% Recycled	% Energy Recovery	% Treated	% Recycled	% Energy Recovery	% Treated	
1994	634	21.0	23.0	0.70	55.5	7.6	0.50	0.13	12.9
1995	689	20.8	30.5	0.75	48.0	6.2	0.23	0.29	14.2
1996[p]	814	N/A	43.5	0.65	39.7	4.8	0.13	0.29	10.9
1997[p]	908	N/A	50.3	0.56	35.7	4.3	0.13	0.40	8.6

Source: *U.S. EPA, Toxic Release Inventory Database, 1995.*

[a] Within this industry sector, non-production related waste < 1% of production related wastes for 1995.
[b] Total TRI transfers and releases as reported in Section 5 and 6 of Form R as a percentage of production related wastes.
[c] Percentage of production related waste released to the environment and transferred off-site for disposal.
[p] Represents projected wastes for 1996 and 1997.

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