SYNTHETIC FIBER MANUFACTURE

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Prepared for the Chemical Engineering Branch by SAIC

1. Market Profile:

1.1 Overview: The synthetic fiber industry is conventionally divided into two types of products, the semi-synthetics or cellulosics, which are derived from wood pulp, and the true synthetics or non-cellulosics, made from primary petrochemicals. The cellulosics include rayon, cellulose acetate and cellulose triacetate. The true synthetics include nylon, polyesters, polyolefins, and acrylics. These fiber types together account for more than 99% of total synthetic fiber production in the United States (EPA, 1982). This generic scenario addresses the production of each of these fiber types.

Other synthetic fibers are manufactured on a much smaller scale for special industrial uses, such as aramid fiber used in aerospace applications. The structures of these industries are very different from the bulk fiber business and this scenario does not provide a good guide to them. CEB engineers interested in the use of PMN chemicals in special-purpose fiber industries should refer to the monographs in the SRI Chemical Economics Handbook (SRI, 1993) or contact the submitter. The user should be aware that many of these special-purpose fiber industries are subject to very rapid change because of their limited markets. The carbon fiber industry, in particular, has suffered major setbacks in the past two years (CW, 1992).

1.2 Capacity and Employment: In most cases, the PMN submitter will state which synthetic fiber industry will be targeted as a market for the new chemical. The fiber industries in the United States have the following capacity distribution (SRI, 1993):

Production Capacity in Millions of Pounds

True Synthetics				Semisynthetics		
Acrylic	Nylon	Polyester	Polyolefin	Rayon	Acetate	Total
642	3034	3960	1956	524	672	10758

The Department of Labor identified 137 synthetic fiber plants employing a total of 78,300 workers in 1989 (DoL, 1991). A search of the Toxics Release Inventory identified 51 synthetic fiber plants (EPA, 1993a). These 51 larger plants represent the bulk of the production capacity. Most are located in the states along the Mid-Atlantic and Southeast coast, from Delaware to Georgia. All U.S. demand for synthetic fibers can be met by domestic production capacity. Export of unprocessed fibers is relatively limited. For these reasons, U.S. production and consumption data tend to match relatively closely.

2. Industry Sectors

2.1 Polyolefins: The major product of the polyolefin industry is polypropylene, a coarse fiber of high tensile strength used mainly for cord, wrapping, and heavy-duty carpeting. Polyolefin fibers are inherently difficult to dye, because there are no sites on the polymer chain to which dye molecules can be electrostatically attracted (Kirk-Othmer, 1982). Dyes may be incorporated in the polymer melt before extrusion in order to overcome this problem. U.S. consumption was 1887 million pounds in 1990. Polyolefins are produced at 84 plants owned by 70 companies. The polymer is produced by addition polymerization of propylene in the presence of a Ziegler-Natta type catalyst. There are several commercial processes for the polymerization. All but one are liquid-phase processes in which the catalyst is suspended in condensed propylene or in a hydrocarbon solvent. The polymer leaving the reactor is dried, extruded, drawn, and annealed.

PMN chemicals used in polypropylene manufacture are likely to be used as 1) dyes, 2) flame retardants, 3) lubricants, or 4) finishing agents. Dyes and flame retardants will be of the simple additive type and can be considered to be encapsulated within the fiber product. Lubricants and finishing agents are added after the extrusion step. These compounds are very unlikely to be water-soluble and water is not used in fiber drawing; therefore no water emissions are likely. The PMN chemical may volatilize during fiber drawing. EPA's Office of Air Quality Planning and Standards (EPA, 1990) has concluded that about 5 pounds of volatile organics are emitted per 1000 pounds of polypropylene manufactured.

2.2 Acrylics: Acrylic and modacrylic fibers are employed in many of the same applications for which wool is also popular. Acrylic yarns can be easily dyed in a wide range of colors and are used extensively in sweaters and afghans. The volume of acrylic yarn sold to the craft knitting trade and for carpeting has declined over the past 15 years as public taste has swung back toward natural fibers. However, the use of acrylic in commercially produced fleecewear and sweaters has risen, so that total consumption has remained constant. Consumption was 337 million pounds in 1989. The entire U.S. production of acrylic and modacrylic fibers is from 5 plants.

Acrylic fibers are produced by addition polymerization of acrylonitrile in a closed aqueous system with a water-soluble initiator. The polymer emerging from the reactor is dried. Most of the polymer (Kirk-Othmer indicates 78%) is processed by wet spinning, in which the polymer is dissolved in dimethylformamide or dimethylacetamide, then pumped through the holes of a spinneret into a bath containing a coagulant that is miscible with the solvent. In dry spinning, the dissolved polymer is pumped through a spinneret into a current of warm air. The solvent evaporates, leaving behind a thin filament of acrylic fiber. In both cases, the fiber is washed, stretched, and finished before being packaged for sale.

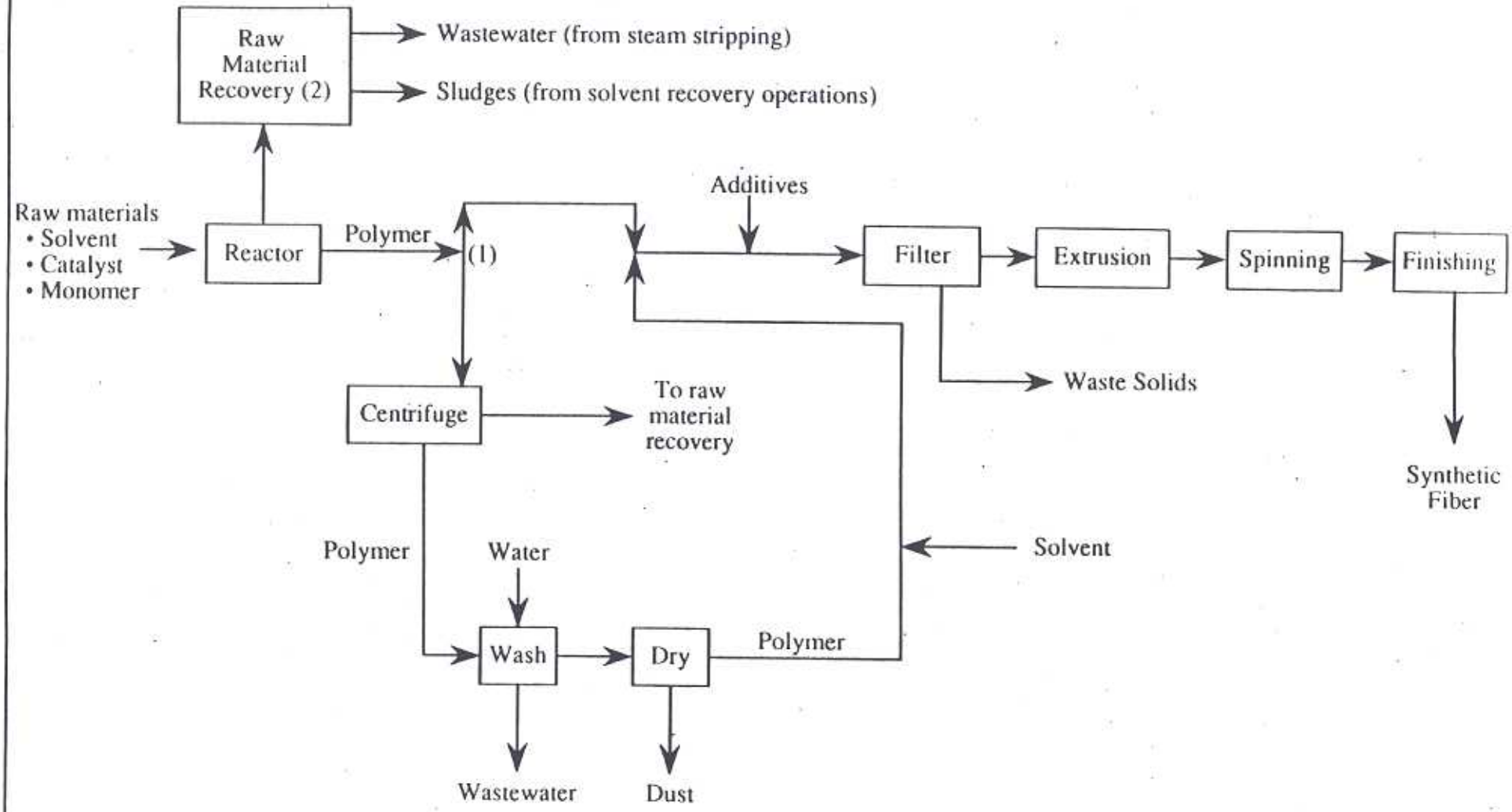
2.3 Nylon: Nylons are polyamides. Two nylons are in large-scale production: Nylon 6,6 is a condensation polymer of hexamethylene diamine and adipic acid. The two starting materials are combined in solution to form a salt. The salt is washed in a methanol bath. The salt is then polymerized in an autoclave. The polymer is washed, dried, and extruded. Nylon 6 is a polymer of caprolactam, a cyclic compound which opens during the reaction. It is also polymerized by the autoclave method.

2.4 Polyester: The major polyester in commerce is polyethylene terephthalate. Polyester is highly resistant to chemical attack by acids, bases, oxidizing, or reducing agents and is only attacked by hot concentrated acids and bases. Polyethylene terephthalate is formed through step growth polymerization of terephthalic acid or dimethyl terephthalate with ethylene glycol at 250°-300°C in the presence of a catalyst. When dimethyl terephthalate is used, methanol is a reaction product instead of water. As the substances are polymerized, they are extruded from the polymerizing vessel in the form of a ribbon and are cut into chips. The chips are diced and conveyed to a hopper where they are fed to the melt spinning tank. Melt spinning is performed at 250°-300°C. The hot solution is forced through a spinneret and solidifies into fiber form upon contact with air. The fibers are then orientated and stretched while hot. Polyester fiber are processed into yarns and fabrics in the same manner as other fibers. (Joseph, 1966 and Needles, 1986).

2.5 Rayon: Viscose rayon is manufactured from dissolved wood pulp. The wood cellulose is reacted with sodium hydroxide to form soda cellulose. The soda cellulose is contacted with carbon disulfide to generate sodium cellulose xanthate. An alkaline solution of this material is extruded through spinnerets into a dilute sulfuric acid bath, regenerating the cellulose as a fine filaments. The data above indicates that, in 1990, the U.S. had a rayon production capacity of 524 million pounds. This included a single plant, the world's largest, which had a capacity of 220 million pounds. This facility has now closed permanently, leaving only 300 million pounds of capacity (EPA, 1993b). Much of the market for rayon has been eroded by cellulose acetate.

2.6 Cellulose acetate: Cellulose acetate is an ester formed by the acetylation of wood pulp using acetic anhydride and an acid catalyst in acetic acid (Needles, 1986). This process produces cellulose triacetate. Water is added, and the material is allowed to partially hydrolyse back to cellulose acetate. When the desired degree of acetylation has been reached, the ester is precipitated with water and dried. It is then dissolved in acetone, methanol, or methyl ethyl ketone and spun into air, where the solvent evaporates and a fiber filament is formed. Acetate fabrics accept vivid dyes and are popular for higher-priced business and fashion clothing, especially pleated items. They are less suitable for casual wear as they do not tolerate abrasion well and are best dry-cleaned. In addition, a very large amount of acetate fiber (73% of the total in 1989) is used to make cigarette filters.

Process Flow Diagram for Synthetic Fiber Production



(1) Depending on the fiber and specific plant operation, either of these two process paths will be followed (i.e. the process steps of centrifuge, wash, and dry may be skipped in certain cases.)

(2) Catalysts are rarely recovered and are typically discharged in wastewater.

An individual plant may have fewer or greater steps than shown, due to the many variations in products, systhesis, and unit operations.

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3. Environmental Releases and Exposures:

3.1 Number of sites/workers: Use the entries for the appropriate industry sector in the table below; these are derived from the list of plants in the Chemical Economics Handbook.

Fiber	Number of sites	Production per site (x 10^6 lb/yr)
Polyolefins	84	23
Acrylics	5	129
Nylon	12	187
Polyester	11	250
Rayon	3	100
Acetate	3	225

These plants are large operations, averaging 670 total workers per site. Assume 15-30 exposed workers per site. All plants can be assumed to operate 3 shifts, 250 days/year.

3.2 Water releases: Assume no water releases if the PMN chemical is incorporated into the fiber by chemical reaction or encapsulation. If the new chemical is applied after fiber formation and the fiber is later washed in preparation for spinning, then it may be dissolved in the washer. The OCPSF Development Document for Effluent Limitation Guidelines provides wastewater generation rates for each of the fiber classes listed in the table below. Water releases may be estimated using the wastewater generation rate and solubility of the PMN chemical.

Fiber Class	Wastewater, Liters/site-day
Acrylic	6,650,000
Cellulose Acetate	17,850,000
Nylon	120,000
Polyester	300,000
Polypropylene	4,100,000
Rayon	17,250,000

3.3 Air releases: There will be no releases if the vapor pressure of the PMN chemical is low (<0.001 mmHg). A review of recent new chemical submittals suggests that few PMN chemicals related to this industry will be volatile. If the PMN chemical is coated onto the fiber after the generation of polymer and has a significant vapor pressure, all of it will eventually be released to the atmosphere. The main source of air emissions from the synthetic fibers manufacturing industry is volatilization of the process solvent. If the PMN chemical forms part of the solvent mixture, its volatilization rate can be estimated from the known volatilization rate of the main component:

$$\frac{Q_i}{Q_s} = \frac{M_i P_i x_i}{M_s P_s}$$

where

Q_i	=	Volatilization rate of PMN chemical, $kg.day^{-1}$
Q_s	=	Volatilization rate of solvent, $kg.day^{-1}$
M_i	=	Molecular weight of PMN chemical
M_s	=	Molecular weight of solvent
P_i	=	Vapor pressure of PMN chemical, mmHg
P_s	=	Vapor pressure of solvent, mmHg
x_i	=	Mole fraction of PMN chemical in the solvent mixture

This equation assumes that the volatilization rate of a chemical is proportional to MP. This is true for the CEB model of releases from transfer operations. For the CEB open surface volatilization model, the rates are proportional to $M^{0.835}(1/29+1/M)^{0.25}P$. The above equation is a conservative approximation for the open surface case. The emission rates of the volatile solvents from each industry sector have been tabulated by EPA's Office of Air Quality Planning and Standards (EPA, 1990):

Process	Releases per 1000 kg fiber, kg	Chemical	Vapor pressure, mmHg	Molecular weight
Rayon, viscose process	251	Carbon disulfide	297	76.1
Cellulose acetate, filter tow	112	Acetone	180	58.1
Cellulose acetate and triacetate, yarn	199	Acetone	180	58.1
Acrylic	40	Dimethylformamide	4	73.1
Modacrylic	125	Dimethylformamide	4	73.1

3.4 Landfill/incineration: This should be limited to container residue. Since fiber production plants are large, centralized facilities, PMN chemicals may be delivered by bulk road or rail tanker. In this case, the tank cars may be dedicated and container residue cleaned out periodically at the PMN chemical supplier's site.

3.5 Inhalation: Many synthetic fibers are manufactured using toxic solvents. Preventive measures must be taken in the plant to reduce concentrations of these chemicals below the OSHA Permitted Exposure Limits. The same ventilation and exposure control methods will serve to limit the concentration of a volatile PMN chemical in the air. Therefore, the "analogous chemical" method may be used to estimate the air concentration of the PMN corresponding to the OSHA PEL for the solvent, and consequently, the rate of inhalation exposure to the PMN chemical. The following three equations are used in the "analogous chemical" method of determining inhalation exposure:

1) $C_{v,s} = C_{v,k} (P_s x_s / P_k x_k)$ (Equation 4-4, CEB Manual)

where:
$C_{v,s}$ = Estimated airborne concentration of the PMN chemical, ppm
$C_{v,k}$ = OSHA PEL for known chemical, ppm (see table below)
P_s = Vapor pressure of PMN chemical, torr
P_k = Vapor pressure of known chemical, torr
x_s = Mole fraction of PMN chemical in mixture
x_k = Mole fraction of regulated chemical in mixture

2) $C_{m,s} = C_{v,s}\ M/V$ (Equation 4-5, CEB Manual)

where: $C_{m,s}$ = Airborne concentration of PMN, mg/m^3
$C_{v,s}$ = Airborne concentration from above, ppm
M = MW of PMN chemical
V = 24.45 l/mole

3) $I = C_{m,s}bh$

$C_{m,s}$ = Airborne concentration of PMN, from above
b = Average inhalation rate of 1.25 m^3/hr
h = 8 hours, based on OSHA PEL 8-hr TWA

The relevant OSHA PELs are listed in the table below. Nylon production does not involve the use of any chemicals which are regulated as inhalation hazards.

Fiber Class	Regulated Chemical	Molecular Weight	OSHA PEL (ppm)
Polyolefins	Hexane	86.17	50
Acrylics	Acrylonitrile	53.06	1
Nylon	N/A		N/A
Polyester	Methanol	32.04	200
Rayon	Carbon disulfide	76.14	1
Acetate	Acetone	58.08	1,000

3.6 Dermal contact: Use standard CEB assumptions.

REFERENCES

(CW, 1992) "Defense Cuts Shoot Down Performance Fibers", in Chemical Week, January 22, 1992.

(DoL, 1991) Employment and Wages Annual Averages, 1990, U.S. Department of Labor, Bureau of Labor Statistics, November 1991.

(EPA, 1980) Background Data on the Plastics Industry for the Development of OCPSF Effluent Limitations Guidelines. U.S. EPA, Office of Water, 1980.

(EPA, 1982) Synthetic Fiber Production Facilities - Background Information for Proposed Standards. U.S. EPA, Office of Air, Noise, and Radiation, October 1982.

(EPA, 1987) Development Document for Effluent Limitations Guidelines, New Source Performance Standards, and Pretreatment Standards for the Organic Chemicals, Plastics and Synthetic Fibers Point Source Category. U.S. EPA, Office of Water Regulations and Standards, October 1987.

(EPA, 1990) Compilation of Air Pollutant Emission Factors, Chapter 5.19 - Synthetic Fiber Production. U.S. EPA, Office of Air Quality Planning and Standards, September 1990.

(EPA, 1993a) Toxics Release Inventory, Reporting Year 1991. This was accessed directly from the database at the EPA's National Computer Center.

(EPA, 1993b) Record of Decision for Avtex Fibers, Front Royal, Virginia. EPA, Office of Solid Waste and Emergency Response. This file remains open while cleanup activities continue at this Superfund site.

(Joseph, 1966) M.L. Joseph, Introductory Textile Science, Holt, Rinehart, Winston, 1966.

(Kirk-Othmer, 1982) Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition. Articles on "Acrylic Fibers", "Polyamides", and "Polyolefins". John Wiley, 1982.

(Needles, 1986) H.L. Needles, Textile Fibers, Dyes, Finishes, and Processes, Noyes, 1986.

(NIOSH, 1990) Pocket Guide to Chemical Hazards. National Institute for Occupational Safety and Health, June 1990.

(SRI, 1993) Chemical Economics Handbook, SRI International. Monographs on chemical industries, updated frequently.